

Plasmonic Nanostructures: A Microscopic Perspective

vorgelegt von
M.Sc.

Robert Salzwedel

ORCID: 0000-0002-7614-9210

an der Fakultät II – Mathematik und Naturwissenschaften
der Technischen Universität Berlin
zur Erlangung des akademischen Grades

Doktor der Naturwissenschaften

- Dr. rer. nat. -

genehmigte Dissertation

Promotionsausschuss:

Vorsitzender: Prof. Dr. Stefan Eisebitt

Gutachter: Prof. Dr. Andreas Knorr

Gutachter: Prof. Dr. N. Asger Mortensen

Tag der wissenschaftlichen Aussprache: 29. September 2023

Berlin 2024

Publications

Publications in Peer-Reviewed Journals

- **Robert Salzwedel**, Lara Greten, Stefan Schmidt, Stephen Hughes, Andreas Knorr, and Malte Selig. “*Spatial Exciton Localization at Interfaces of Metal Nanoparticles and Atomically Thin Semiconductors*” [Physical Review B](#) **109**, 035309 (2024).
- Lara Greten, **Robert Salzwedel**, Manuel Katzer, Henry Mittenzwey, Dominik Christiansen, Andreas Knorr, and Malte Selig. “*Dipolar Coupling at Interfaces of Ultrathin Semiconductors, Semimetals, Plasmonic Nanoparticles and Molecules*” [physica status solidi \(a\)](#) **221**, 2300102 (2024).
- Dominik Hoeing, **Robert Salzwedel**, Lena Worbs, Yulong Zhuang, Amit K. Samanta, Jannik Lübke, Armando D. Estillore, Karol Dlugolecki, Christopher Passow, Benjamin Erk, Nagitha Ekanayake, Daniel Ramm, Jonathan Correa, Christina C. Papadopoulou, Atia Tul Noor, Florian Schulz, Malte Selig, Andreas Knorr, Kartik Ayyer, Jochen Küpper, and Holger Lange. “*Time-Resolved Single-Particle X-ray Scattering Reveals Electron-Density Gradients As Coherent Plasmonic-Nanoparticle-Oscillation Source*”, [Nano Letters](#) **23**, 5943 – 5950 (2023).
- **Robert Salzwedel**, Andreas Knorr, Dominik Hoeing, Holger Lange, and Malte Selig. “*Theory of radial oscillations in metal nanoparticles driven by optically induced electron density gradients*” [The Journal of Chemical Physics](#), **158**, 064107 (2023).
- Chelsea Carlson, **Robert Salzwedel**, Malte Selig, Andreas Knorr, and Stephen Hughes. “*Strong coupling regime and hybrid quasinormal modes from a single plasmonic resonator coupled to a transition metal dichalcogenide monolayer*”, [Physical Review B](#), **104**, 125424 (2021).

Accepted Manuscripts

- Lara Greten, **Robert Salzwedel**, Tobias Göde, David Greten, Stephanie Reich, Stephen Hughes, Malte Selig, and Andreas Knorr. “*Strong Coupling of Two-Dimensional Excitons and Plasmonic Photonic Crystals: Microscopic Theory Reveals Triplet Spectra*” Invited Paper to [ACS Photonics](#), Special Issue “[Frontiers and Applications of Plasmonics and Nanophotonics VSI](#).” (Accepted February 2024)

Conference Contributions

- Poster Presentation: “*Exciton-Plasmon Hybridization at Interfaces of Metal Nanoparticles and 2D Semiconductors*”, Nonlinear Optics and Plasmonics, Lecce, September 2023
- Contributed Talk: “*Theory of Radial Oscillations in Metal Nanoparticles*”, Berlin School of Optical Sciences and Quantum Technologies, Monthly Seminar, Berlin, July 2023
- Invited Talk: “*Theory of Exciton-Plasmon Hybridization*”, Group Seminar Stephanie Reich, FU Berlin, June 2023
- Poster Presentation: “*Exciton-Plasmon Localization and Hybridization at Interfaces of Metal Nanoparticles and 2D Semiconductors*”, Surface Plasmon Photonics (SPP10), Houston, May 2023
- Contributed Talk: “*Theory of Exciton localization in TMDCs using Metal Nanoparticles*”, Spring Meeting of German Physical Society (DPG), Dresden, March 2023
- Poster Presentation: “*Radial Oscillations of Metal Nanoparticles*”, Annual Retreat of Berlin School of Optical Sciences and Quantum Technologies (BOS.QT), Gut Gremmelin, October 2022
- Contributed Talk: “*Theory of Radial Oscillations in Metal Nanoparticles Driven by Optically Induced Electron Density Gradients*”, Spring Meeting of German Physical Society (DPG), Regensburg, September 2022
- Invited Talk: “*Radial Oscillations of Metallic Nanoparticles*”, Group Seminar Stephen Hughes, Kingston, April 2022
- Contributed Talk: “*Theory of Radial Oscillations in Metal Nanoparticles Driven by Optically Induced Electron Density Gradients*”, International Conference on Physics of Light-Matter Coupling in Nanostructures (PLMCN 2022), Varadero, Cuba, April 2022
- Invited Talk: “*Excitations in Quantum Nanostructures*”, Group Seminar Christiane Koch, FU Berlin, December 2021
- Poster Presentation: “*Theory of Coherent Phonon Mode Excitation in Metal Nanoparticles*”, Optics of Excitons in Confined Systems (OECS 2021), Dortmund (virtually), August 2021
- Poster Presentation: “*Theory of Coherent Phonon Mode Excitation in Metal Nanoparticles*”, Spring Meeting of German Physical Society (DPG), virtually, March 2021

Conference Organization

- 1st BOS.QT Day, Annual One-Day Conference of Berlin School of Optical Sciences and Quantum Technologies, jointly with Gabriela Luna Amador, Magnus Haus, Berlin, April 2023

Abstract

The fields of plasmonics and two-dimensional semiconductors represent some of the most rapidly advancing areas in current solid-state research, driven by the immense potential of these materials for numerous technological applications. This work is situated at the intersection of these two dynamic fields. It focuses on the development of the microscopic framework to describe the electron dynamics in metal nanostructures and the theoretical understanding of exciton dynamics in hybrid metal-semiconductor nanostructures.

The methodological umbrella is provided by the Heisenberg equations of motion. It is employed to derive a spatio-temporal, momentum-resolved phase space description of the electron dynamics in metal nanostructures as well as a momentum-resolved description of excitons in hybrid systems consisting of transition metal dichalcogenide (TMDC) monolayers and metal nanostructures.

The first part of this thesis focuses on studying a system comprising a metal nanoparticle and a TMDC monolayer using self-consistent Maxwell-Bloch theory. The combined system yields an effective eigenvalue equation governing the center-of-mass motion of dressed excitons in a plasmon-induced potential. Bound states with negative eigenenergies are found in the dynamical equation of the exciton-plasmon hybrid, indicating exciton localization in the plasmon-induced potential. The coupling regime is quantified by computing the scattered light in the near-field, revealing strong exciton-plasmon coupling with an avoided crossing behavior and an effective Rabi splitting of tens of meV.

The key achievement of this work lies in the successful development of a comprehensive microscopic approach for studying spatio-temporal, momentum-resolved electron and phonon dynamics in metals in a Wigner phase space representation. This approach accurately reproduces macroscopic equations in both local and non-local formulations and incorporates geometrical effects and multi-band processes, enabling a description of interband transitions based on microscopic parameters. To investigate the potential of actively tuning the optical response of metal nanoparticles using strong THz fields, we develop a fully numerical method combining the three-dimensional momentum-resolved microscopic Boltzmann scattering equations for the electronic Wigner function with a three-dimensional finite-difference time-domain solver. This approach allows for a spatio-temporal treatment of microscopic dynamics, including non-equilibrium, non-perturbative, and nonlocal phenomena, as well as interband transitions. The same scenario is described using an analytical model, revealing that the additional THz pulse effectively renormalizes the electronic ground state of the system through pressure renormalization of the electron gas within the nanoparticle. This leads to a blue shift of the plasmon resonance, which is also observed in experiments.

Finally, the framework is applied to study the onset of radial oscillations in spherical nanoparticles. This microscopic approach incorporates direct electron-coherent phonon interaction, which reveals an additional driving source for nanoparticle oscillations. In particular, we identify spatial electron density gradients as the dominant driving source for the onset of radial oscillations on short time scales beyond thermal contributions, providing a compelling explanation for recent experimental findings.

Deutsche Zusammenfassung

Die Bereiche Plasmonik und zweidimensionale Halbleiter gehören zu den am schnellsten wachsenden Gebieten der heutigen Festkörperforschung. Dies wird durch das enorme Potential dieser Materialien für zahlreiche technologische Anwendungen angetrieben. Diese Arbeit ist an der Schnittstelle dieser beiden dynamischen Gebiete angesiedelt. Ihr Fokus liegt auf der Entwicklung einer mikroskopischen Beschreibung der Elektronendynamik in metallischen Nanostrukturen und einem theoretischen Verständnis der Exzitonendynamik in hybriden Metall-Halbleiter-Nanostrukturen.

Den methodischen Rahmen bilden die Heisenbergschen Bewegungsgleichungen. Diese werden verwendet, um eine raum-, zeit- und impuls aufgelöste Phasenraumbeschreibung der Elektronendynamik in metallischen Nanostrukturen sowie eine impuls aufgelöste Beschreibung von Exzitonen in Hybridsystemen aus Übergangsmetall-dichalkogenid-Monolagen (TMDC-Monolagen) und metallischen Nanostrukturen abzuleiten.

Der erste Teil dieser Arbeit widmet sich der Untersuchung eines Systems bestehend aus einem Metallnanopartikel und einer TMDC-Monolage, das mithilfe einer selbstkonsistenten Maxwell-Bloch Theorie beschrieben wird. Das kombinierte System liefert eine effektive Eigenwertgleichung, welche die Bewegung des Massenschwerpunktes von *dressed excitons* in einem plasmoninduzierten Potential beschreibt. In der dynamischen Gleichung für die hybriden Exziton-Plasmon-Teilchen finden sich gebundene Zustände mit negativen Eigenenergien, was auf eine Lokalisierung der Exzitonen im plasmoninduzierten Potential und eine starke Kopplung zwischen Exzitonen und Plasmonen hinweist. Die Stärke der Kopplung wird durch die Berechnung des gestreuten Lichts im Nahfeld quantifiziert und zeigt eine starke Exziton-Plasmon-Kopplung, die sich in der Vermeidung des Kreuzens von Systemresonanzen und einem effektiven Rabi-Splitting von einigen zehn Millielektronenvolt manifestiert.

Die wichtigste Errungenschaft dieser Arbeit ist die erfolgreiche Entwicklung eines umfassenden mikroskopischen Modells zur Untersuchung der raum-, zeit- und impuls aufgelösten Elektronen- und Phononendynamik in Metallen in einer Wigner-Phasenraumdarstellung. Dieser Ansatz reproduziert bekannte makroskopische Gleichungen sowohl in lokalen als auch in nichtlokalen Formulierungen und erlaubt die Einbeziehung von geometrischen Effekten und Multibandprozessen, sodass eine Beschreibung von Interbandübergängen auf der Basis mikroskopischer Parameter möglich ist. Um die Möglichkeit der Beeinflussung der optischen Resonanzposition von metallischen Nanopartikeln durch starke THz-Felder zu untersuchen, entwickeln wir ein vollständig numerisches Verfahren. Dieses kombiniert die dreidimensionalen, impuls aufgelösten mikroskopischen Boltzmann-Streuungsgleichungen für die elektrische Wigner-Funktion mit einer dreidimensionalen *Finite-Difference Time-Domain* Methode. Dieser Ansatz liefert eine räumlich und zeitlich aufgelöste Beschreibung der mikroskopischen Dynamik von nichtlokalen Nichtgleichgewichtsphänomenen, die nicht störungstheoretisch behandelt werden können, und erlaubt die Einbeziehung von Interbandübergängen. Das gleiche Szenario wird durch ein analytisches Modell beschrieben, das zeigt, dass der zusätzliche THz-Puls den elektronischen Grundzustand des Systems durch Druckrenormierung des Elektronengases innerhalb des

Nanopartikels renormiert, was zu einer Blauverschiebung der Plasmonenresonanz führt, die auch experimentell beobachtet wird.

Schließlich wenden wir unseren mikroskopischen Ansatz an, um den Beginn von radialen Atmungsmoden in metallischen Nanokugeln zu untersuchen. Damit kann die Wechselwirkung zwischen Elektronen und kohärenten Phononen untersucht und in die theoretische Beschreibung des Oszillationsbeginns integriert werden. Hierbei identifizieren wir räumliche Gradienten in der Elektronendichte als die dominante Antriebsquelle für radiale Oszillationen, insbesondere auf kurzen Zeitskalen, jenseits thermischer Beiträge, was eine überzeugende Erklärung für jüngste experimentelle Ergebnisse liefert.

Table of Contents

Abstract	i
Deutsche Zusammenfassung	iii
Table of Contents	v
1. Introduction	1
2. Theoretical Framework	5
2.1. Second Quantization	5
2.1.1. Cluster Expansion	8
2.1.2. Formal Integration and Markov Approximation	8
2.2. Atomically Thin Semiconductors	9
2.3. Electrodynamics of Metals	13
2.3.1. Local Response Approximation - Drude Model	14
2.3.2. Microscopic Material Models	15
2.3.3. Thermalization in Metals and Semiconductors	17
2.3.4. Nonlocal Hydrodynamic Model	18
2.3.5. Surface Response Formalism	19
2.3.6. Interband Transitions	20
2.4. Plasmonics - Geometrical Effects	21
2.4.1. Localized Surface Plasmons (LSP)	22
2.4.2. Mie Scattering	23
2.4.3. Nonlocal Mie Theory	25
2.4.4. Self-Consistent Electric Field Approach	26
2.4.5. Surface Plasmon Polaritons (SPPs)	27
3. Plasmon-Induced Exciton Localization and Hybridization in 2D Materials	31
3.1. Hamiltonian	33
3.1.1. Free TMDC Hamiltonian	33
3.1.2. Carrier-Light Interaction	34
3.1.3. Carrier-Carrier Interaction	35
3.2. Macroscopic TMDC Polarization	37
3.3. Semiconductor Bloch Equations	38
3.3.1. Electron Picture	38
3.3.2. Wannier Equation	40
3.3.3. Exciton Picture	41
3.4. Self-Consistent Maxwell-Bloch Approach	43
3.4.1. Optical Response of Nanoparticle Plasmons	44
3.4.2. Green's Function Approach to Electromagnetic Interaction	44
3.4.3. Optical Response of the Coupled Nanostructure	45

3.5. Plexcitonic States	48
3.5.1. Plexcitonic Eigenvalues	49
3.5.2. Plexcitonic Eigenvectors and Probability Density	52
3.6. Exciton Localization	53
3.7. Strong Coupling	56
3.8. Conclusions	59
3.9. Perspectives	59
3.9.1. Propagating Surface Polaritons	60
3.9.2. Spatio-Temporal Description in Wigner Function Framework	61
4. Spatio-Temporal Description of Microscopic Scattering Equations	63
4.1. Hamiltonian	64
4.2. Wigner Function	66
4.3. Bloch Equations for Electronic Wigner Function	67
4.3.1. Free Electronic Motion	68
4.3.2. Electron-Light Interaction	68
4.3.3. Electron-Electron Interaction	69
4.3.4. Electron-Phonon Interaction	73
4.4. Phonon Scattering Equations	75
4.5. Derivation of Macroscopic Quantities from Microscopic Equations	76
4.5.1. Microscopic Drude Model	77
4.5.2. Microscopic Hydrodynamic Drude Model	78
4.6. Geometrical Effects at the Microscopic Level: Hartree Mean-Field Contribution	80
4.6.1. Coulomb Potential on the Microscopic Level	80
4.6.2. Hartree Mean-Field and Oscillator Equation	81
4.7. Interband Transitions in Metals: A Microscopic Optical Response Model	82
4.7.1. Microscopic Dynamics	83
4.7.2. Macroscopic Observables – Translationally Invariant Systems	84
4.7.3. Self-Consistent Optical Response of Metal Nanoparticles	86
4.8. Conclusions	87
4.9. Perspectives	89
5. Active Control of Plasmon Resonance	91
5.1. Experimental Motivation	93
5.2. Numerical Framework	94
5.3. Finite-Difference Time-Domain Solver	95
5.3.1. Full 3D FDTD Implementation	96
5.3.2. Material Modeling	98
5.3.3. Boundary Conditions	101
5.3.4. Excitation Mechanisms	107
5.3.5. Observables – Post-Processing	110
5.3.6. Work Flow	115
5.4. Coupled Kinetic Maxwell-Boltzmann Engine	115
5.5. Analytical Non-Perturbative Approach	117
5.5.1. Hydrodynamic Equations	118
5.5.2. THz Field in Nonlocal Mie Theory	120
5.6. Conclusions	125

5.7. Perspectives	126
6. Radial Oscillations of Metal Nanoparticles	129
6.1. Experimental Motivation	131
6.2. Prerequisites	132
6.2.1. Current Theoretical Description	133
6.2.2. Two-Temperature Model	134
6.2.3. Coherent and Incoherent Phonons	135
6.2.4. Thermal Expansion	136
6.3. Coherent Phonon Dynamics	136
6.4. Mesoscopic Electron Dynamics in the Hydrodynamic Limit	140
6.4.1. Intraband Case	141
6.4.2. Interband Case	145
6.4.3. Qualitative Comparison	147
6.5. Vibrational Eigenmodes - Lamb Modes	147
6.5.1. Thermal Expansion	149
6.5.2. Electric Field Overlap	149
6.6. Numerical Results	151
6.6.1. Temporal Density Behavior	151
6.6.2. Oscillation Onset	152
6.6.3. Comparison to Current Theory	153
6.6.4. Comparison to Experimental Results	155
6.7. Conclusions and Perspectives	156
7. Conclusions and Perspectives	159
A. Parameters	161
B. Fourier Transformation	163
C. Light-Matter Interaction Hamiltonian in r-E coupling	165
C.1. Interband Light-Matter Interaction	166
C.2. Intraband Light-Matter Interaction	166
D. Exciton-Plasmon Hybridization	169
D.1. Complex Contour Integration	169
D.2. Numerical Solution of the Plexcitonic Equation	171
E. Screened Coulomb Potential in Multilayer Systems	173
E.1. Coulomb Potential for 5-Layer System	173
E.2. Extension to N-layer System	174
F. Microscopic Spatio-Temporal Electron Description	177
F.1. Microscopic Dynamics in Single-Band Description	177
F.1.1. Free Electronic Motion	177
F.1.2. Electron-Light Interaction	178
F.1.3. Electron-Phonon Interaction	178

G. Hartree Mean-Field on Microscopic Level	181
G.1. Hartree Mean-Field with Spherical Boundary Conditions	181
G.2. Implication on Equations of Motion	187
H. Finite-Difference Time-Domain (FDTD) Method	189
H.1. Freely Propagating Maxwell's equation	189
H.2. Perfectly Matched Layers	190
H.2.1. Analytical Expressions	190
H.3. Update Equations for Perfectly Matched Layers	193
H.3.1. D-Fields	193
H.3.2. E-Fields	193
H.3.3. H-Fields	194
H.4. Update Equations for Periodic Boundary conditions	194
H.4.1. D-Fields	194
H.4.2. H-Fields	195
H.5. Total Field-Scattered Field (TFSF)	196
H.6. Monitors	197
I. Radial Oscillations	199
I.1. Phenomenological Models	199
I.2. Microscopic Dynamics of Coherent Phonon Modes	201
I.2.1. Coherent Phonon Damping	201
I.3. Momentum Closure of the Microscopic Equations	205
I.4. Microscopic Temperature Equation	206
I.5. Lamb modes - Eigenmodes of a Traction-Free Sphere	207
I.5.1. Boundary Conditions	209
I.5.2. Overlap Integrals	209
I.6. Pump Fluence	210
Bibliography	213
Acknowledgments	251

List of Figures

1.1. Images of Nanostructures.	2
2.1. The Crystal Structure of TMDC Monolayers	10
2.2. First TMDC Brillouin Zone	10
2.3. MoS ₂ Band Structure	11
2.4. Exciton Formation Below the Free-Particle Band Gap	12
2.5. Conceptual Idea of Drude Theory	15
2.6. Visualization of the Implicit Equation for the Plasma Frequency	16
2.7. Example for a Classical Boltzmann Scattering Process	18
2.8. Gold Permittivity	22
2.9. Resonance Shift of Gold Spheroid under Changing Aspect Ratio	25
2.10. Extinction Cross Section from Nonlocal Polarizability	26
2.11. Dispersion Relation of Surface Plasmon Polaritons (SPPs)	28
3.1. Considered Coupled Nanostructure TMDC and AuNP Absorption Spectra	32
3.2. Effective Parabolic Eight Band Model for the TMDC Band Structure. . .	34
3.3. Illustration of Coulomb-Mediated Electron-Electron Scattering Process. .	35
3.4. Schematic of the Four-Layer System	36
3.5. Calculated TMDC Absorption Spectra for Typical Materials	43
3.6. Parabolic U and Conical V Excitonic Dispersion	49
3.7. Excitonic Density of States (DOS)	51
3.8. Plexcitonic Eigenvalue Spectrum	52
3.9. In-Plane Probability Density in Real Space	53
3.10. Out-of-Plane Probability Density in Real Space	54
3.11. Full TMDC polarization in Real Space	55
3.12. Circular Components of Macroscopic TMDC Polarization in Real Space .	56
3.13. Peak Splitting	58
3.14. Avoided Crossing	59
3.15. Parameter Dependencies of Rabi Splitting	60
4.1. Electron and Phonon Band Structures of Gold	65
4.2. Illustration of Hartree Mean-Field	82
4.3. Microscopic Model Fitting to Johnson and Christy Data	86
4.4. Fitting Total Susceptibility Function to UV-Vis Spectrum of AuNP Solution	88
5.1. Active Modulation Mechanisms for Tuning Plasmon Resonance	91
5.2. THz Shift – Experiment Setup and Preliminary Results	93
5.3. Illustration of Coupled Kinetic Maxwell-Boltzmann Solver	94
5.4. Illustration of a Yee Cell	97
5.5. Benchmarking the 3D FDTD Code: Reflection and Transmission Spectra .	102
5.6. Finite-Difference Time-Domain (FDTD) Method – Standard Iteration . .	103
5.7. Fourier Decomposition of an Optical Pulse	108

5.8. 2D Illustration of the Total-Field Scattered-Field (TFSF) Method	109
5.9. Results for One-Point Green's Function Calculation	112
5.10. Computational Domain and Field Monitors for the FDTD Simulation . . .	113
5.11. Benchmark of Scattering Cross Section Using FDTD Calculation	114
5.12. Standard FDTD Iteration	115
5.13. Time Evolution of the Electron Distribution after Optical Excitation . . .	117
5.14. Impact of Non-Perturbative THz Field on Metal Nanoparticle Polarizability	124
5.15. Impact of Non-Perturbative THz Field on Extinction Cross Section	126
6.1. Schematic of Relaxation Dynamics in Plasmonic Nanoparticles	130
6.2. Transient Small-Angle X-ray Scattering in a Single-Particle Imaging Scheme	132
6.3. Hartland's Data: Transient Absorption and Classical Theory	134
6.4. Direct Coupling Mechanism from Microscopic Theory	137
6.5. Electric Field of a Spherical Metal Nanoparticle	150
6.6. Temporal Behavior of the Electron Density	151
6.7. Electron Density Gradient Contributions to Radial Breathing Oscillations	153
6.8. Onset of Radial Breathing Mode Oscillations	154
6.9. Phase Shift: Oscillation Onset Depending on the Coupling Model.	155
6.10. Experiment-Theory Comparison for Oscillation Onset	156
D.1. Contour Integral: Different Contour Closures.	170
E.1. Geometry Illustration of the 5-Layer System.	174
E.2. Sketch of N-Layer System	175

1. Introduction

“I am among those who think that science has great beauty.”

– Marie Curie

Throughout history, humans have been eager to explore the capabilities of materials to harness them for various purposes. From ancient times, when early humans crafted basic tools from available materials, to milestones such as the invention of the wheel and the industrial revolution, our ability to build tools has been the catalyst for transformative technological developments.

Behind these monumental achievements lies the essential role of basic research, which curiously explores and pushes the boundaries of what was previously known. It is this relentless pursuit of understanding that has paved the way for groundbreaking innovations shaping the course of human history. One example in the context of this work is Mie’s early research on the color of colloidal gold solutions [1], which laid the foundation for modern scattering theory. Another example is the fundamental understanding of quantum mechanics during the first quantum revolution, which led decades later to the development of first-generation quantum technologies such as transistors, lasers, and MRIs – innovations that were unimaginable at the time when their foundations were being studied, illustrating the beauty of scientific exploration.

In the last decades, our fabrication capabilities have reached the physical size limits, allowing us to design and produce materials at the nanoscale with the ability to harness quantum mechanical phenomena, marking yet another significant milestone in what is now known as the second quantum revolution [2]. As we venture into this technologically advanced field, it is essential to emphasize the importance of responsible progress [3]. At a time when the costs of technological progress are evident, it is increasingly important to carefully consider the implications of our innovations.

Novel nanoscale devices hold enormous promises, in particular by making devices more cost and energy efficient, while at the same time improving their performance. In this thesis, we explore two different nanoscale material systems, of which we show pictures in Fig. 1.1: First, we study 2D semiconductors, where the physics is dominated by excitons. Then, we move on to investigate metals at the nanoscale, with a special focus on localized surface plasmons (LSPs).

Extensive research on 2D materials has been made possible by the development of exfoliation techniques. Initially demonstrated with graphene [6, 7], these techniques quickly expanded to include other van der Waals materials [8], making 2D materials readily available for scientific study. In this work, our focus will be on transition metal dichalcogenides (TMDCs), a class of materials that exhibit remarkable optical properties: In the monolayer limit, TMDCs are direct band gap semiconductors with high absorption rates of up to 10 % [8, 9]. Additionally, they exhibit valley-selective dichroism [10, 11] and a spin-split band structure [11–13], promising their application in spintronic devices from nonmagnetic materials [5, 14–16]. The reduced dimensionality of these atomically thin materials enhances the Coulomb interaction, leading to the formation of tightly bound

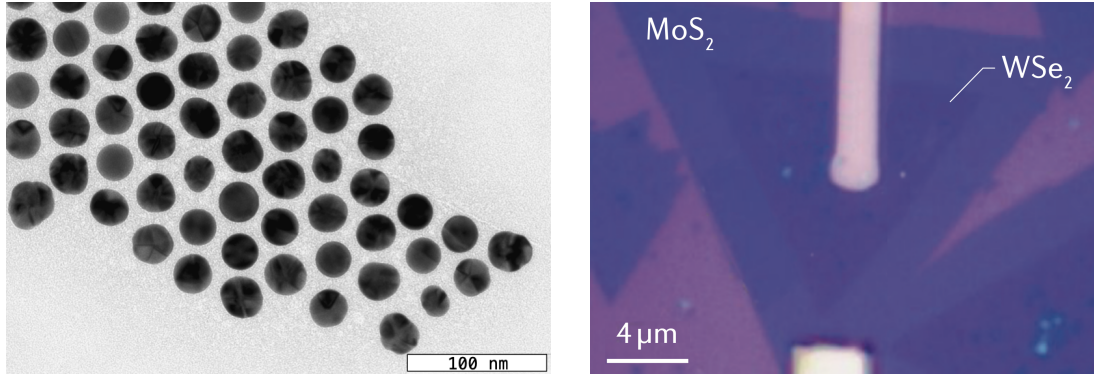


Figure 1.1.: **Images of Nanostructures.** (Left) Transmission Electron Microscope images of self-assembled gold nanoparticle arrays, reprinted with permission from Ref. [4], © ACS 2023. (Right) Optical microscope image of a MoS₂/WSe₂ heterostructure, reprinted with permission from Ref. [5], © Springer Nature 2017.

electron-hole pairs known as excitons [17–19]. The large excitonic binding energies up to several hundreds of meV in TMDCs provide an excellent platform for studying exciton physics [20, 21].

These properties, along with their high sensitivity to the surrounding environment [22–26], make them ideal for functionalization [27] with external nanoparticles, such as molecules [25, 28–30], metal nanoparticles [31–33], or quantum dots [34] to locally tailor their optical properties. Furthermore, recent research has taken advantage of the van der Waals properties of these materials to create heterostructures [35–37], resulting in the formation of interlayer excitons. Moreover, Moiré effects resulting from different twist angles or lattice periodicities have been investigated [38–43]. These advancements enable researchers to combine individual materials into unique configurations, using what is often referred to as “atomic-scale Lego” [35], allowing for the effective design of hybrid devices with tailored properties.

A promising technological application of TMDCs [44] is their use as single-photon emitters [45, 46] through deterministic creation of defects within the structure [46], strain-induced localization that attracts carriers [47, 48], and Moiré potentials [49, 50] that allow localization of carriers within the TMDC monolayer.

The second material system considered in this thesis are metal nanostructures that support plasmonic excitations [51–55]. This research field lies at the interface of material science and classical electromagnetism. Over the years, it has evolved from its initial focus on sub-wavelength field confinement and local field enhancement [56–60], as well as guiding [61] into a transdisciplinary research field, spanning chemistry [62], optics [63, 64], material science [65, 66], and energy harvesting [67, 68], holding great promise for significant applications [69, 70].

In contrast to the field of 2D semiconductors, plasmonics, as a more mature research area, is on the verge of finding practical applications on an industrial scale [71, 72]. Notable applications include plasmon-enabled catalysis, i.e., facilitating CO₂ reduction and hydrogen production [73–75], and metamaterials [65] for advanced antenna design [76–78], active light guiding [79, 80], and plasmonic lenses [81, 82]. Additionally, plasmonics finds applications in modulators [83, 84], photothermal cancer therapy [85, 86], biochemical sensing [62, 87, 88], and energy harvesting [89, 90].

In addition, exciting potential avenues for new applications are emerging, such as using plasmonics to enhance nonlinearities [91–95], explore hot-electron physics [71, 96], utilize Purcell enhancements [97–99], and implement active plasmonic systems [100–104].

Historically, a major driving force behind the field of plasmonics has been its ability to enhance Raman spectroscopy, enabling single-molecule detection [105–107]. Over time, this field has grown, particularly in the coupling of plasmonic systems with other (excitonic) systems to enhance light-matter interactions up to the strong coupling regime [108–118].

From a theoretical perspective, plasmons are classically understood as collective excitations of conduction electrons [119]. From a quantum mechanical point of view, they are interpreted as collective excitations around the Fermi energy, mediated by the Coulomb interaction, resulting in significantly higher energies compared to individual electron-hole excitations. Initial calculations were performed in Refs. [120–123]. Today, theoretical descriptions of plasmons range from basic methods in quasi-static Mie scattering theory [124, 125] to more advanced approaches such as quasi-normal modes [126–130] or full numerical implementations of classical electrodynamics, such as finite-difference time-domain [131], finite element [132], and boundary element methods [133].

Two of the most extensively studied plasmonic excitations are surface plasmon polaritons (SPPs), which are found in an increasing number of systems [134, 135], and localized surface plasmons (LSPs) [51, 136]. Recently, there has been significant interest in gap plasmons in micro- or picocavities [137–139].

As the size of nanoparticles and nanogaps has continuously decreased to the nanoscale and below [140], it has become possible and crucial to include quantum properties in the description of these systems. This development has led to the emergence of the field of quantum (nano)plasmonics [141–144]: Two dominant models have been established to incorporate quantum corrections into the classical description of plasmonic structures. The first model is the hydrodynamic approach [145–152], which exploits the hydrodynamic nature of the electron gas to incorporate nonlocal effects into the description. The second model is the surface response formalism based on Feibelman parameters [153–156], providing an alternative approach by considering the surface electronic response to incorporate quantum effects into plasmonic phenomena.

Having introduced the two relevant systems in this thesis, it is essential to highlight the significant research efforts dedicated to coupled systems, allowing for exciton-plasmon hybridization [157–161]. Exploring various coupling regimes of electromagnetic modes to quantum emitters has provided unprecedented control over quantum states [113, 129, 162].

The research presented in this thesis lies at the intersection of the two vibrant research areas we just introduced: 2D materials and plasmonics. Our primary focus is on the theoretical understanding of light-matter interactions and carrier dynamics within these structures. In particular, we aim to explore the potential synergy of combining these two materials to tailor their distinct properties. In addition, we seek to extend existing microscopic theories for metal structures to enable a deeper understanding of their microscopic dynamics.

Structure and Scope of This Thesis

The thesis begins with a brief introduction of the fundamental concepts and material properties, as well as their theoretical treatment in Ch. 2.

The main part, which presents our results, is divided into four separate chapters, Chs. 3-6. The common theoretical framework used to describe the microscopic dynamics is the Heisenberg equations of motion, which are applied in various scenarios. Each chapter briefly introduces the specific context relevant to the situation being studied and concludes with perspectives for further exploration. The overall conceptual idea is to explore theoretical techniques that have been successfully applied in the semiconductor community and apply them to metals to gain a deeper understanding of their dynamics from a microscopic, momentum-resolved perspective.

In Ch. 3, we stay in the realm of semiconductors and study a system consisting of a TMDC monolayer and a metal nanoparticle. In this system, we treat the TMDC in the framework of the semiconductor Bloch equations and derive an equation of motion for the excitons under the influence of the metal nanoparticle. The resulting eigenvalue equation analytically captures the interaction of excitons and metal nanoparticles and is discussed in detail, providing interpretations of the associated eigenstates. In addition, the equation is used to explore different coupling regimes and to obtain macroscopic variables that could be measured experimentally.

In Ch. 4, we change the material system and apply the second quantization framework to the electron dynamics in metals. For comparison with the hydrodynamic description at the macroscopic level, we derive a spatio-temporal description using the Wigner phase space representation. From this, fundamental dynamical equations are derived, which will be employed throughout the thesis. These equations are used to study two situations explicitly, namely the inclusion of geometry in the microscopic equations, and the description of interband processes using a two-band model.

In Ch. 5, we use this microscopic framework to study the possibility of active tuning of the localized surface plasmon resonance using strong THz pulses, inspired by preliminary experimental results. This is done using two different approaches: The first one is a fully numerical solver that combines a self-written three-dimensional finite-difference time-domain solver with a three-dimensional momentum-resolved microscopic Boltzmann scattering solver using the equations developed in Ch. 4. At the time of writing, this project remains a work in progress, but promises valuable insights into the complex dynamics in nanostructures. In a second approach, the same experimental situation is modeled fully analytically by treating the THz field non-perturbatively as a distortion of the electronic ground state. The effect of the THz field on the optical response of the nanoparticle is discussed qualitatively.

In Ch. 6, we once again use the microscopic framework and extend it to include coherent phonons, which are the observable of interest in this chapter, as we study transient nanoparticle oscillations after optical excitation. This allows to include a direct interaction channel of excited electrons and coherent phonons in the theoretical description, allowing to investigate the opportunity of a more immediate oscillation onset. We compare our microscopic framework with previous models based on thermal expansion and recent experimental results that were able to observe the onset process of these oscillations. This comparison underscores the need for an additional, more direct interaction contribution.

The final chapter, Ch. 7, summarizes the main concepts and findings of this thesis and presents perspectives for future research.

2. Theoretical Framework

“When I started to think about it, I felt that the main problem was to explain how the electrons could sneak by all the ions in a metal. . . . I found to my delight that the wave differed from a plane wave of free electron only by a periodic modulation. This was so simple that I didn’t think it could be much of a discovery, but when I showed it to Heisenberg, he said right away, ‘That’s it.’”

– Felix Bloch

We must be clear that when it comes to atoms, language can be used only as in poetry. In this chapter, we aim to provide a concise yet comprehensive overview of the current theoretical descriptions relevant to this thesis. Our objective is to contextualize our research by introducing the material systems we will investigate and the approaches commonly employed in their treatment. This foundation will be essential for understanding the subsequent chapters of this thesis, where we will present our contributions and findings.

We begin in Sec. 2.1 with a brief introduction to the second quantization framework that will be used throughout this thesis to describe microscopic carrier dynamics, in particular electrons and excitons. Moving forward, in Sec. 2.2 we introduce transition metal dichalcogenides, one of the material platforms we will investigate in this thesis.

In Sec. 2.3, we begin to introduce metals, which are the second material platform in this thesis, and how they are currently described in the literature for bulk systems within the framework of classical electrodynamics. Additionally, we discuss how geometrical effects are described in metal nanostructures in Sec. 2.4.

2.1. Second Quantization

In quantum mechanics, the dynamics of a system are generally governed by the *Schrödinger equation*

$$i\hbar\partial_t\Psi(\mathbf{r},t) = H\Psi(\mathbf{r},t), \quad (2.1)$$

postulated by Erwin Schrödinger in 1926 [163]. The equation describes the time evolution of a wave function describing a quantum-mechanical state. Quantities that can be accessed experimentally are named observables and appear as expectation values of Hermitian operators in the formalism of quantum mechanics. It often proves useful to switch to a picture that addresses the time evolution through time-dependent operators. This is done using the *Heisenberg equation* [164]

$$i\hbar\frac{\partial}{\partial t}\mathcal{O}(t) = [\mathcal{O}(t), \hat{H}(t)]_- , \quad (2.2)$$

that is equivalent to the Schrödinger equation. It will be the equation used to describe the microscopic dynamics in this thesis.

For many-body systems made up from numerous particles, we will employ the formalism of second quantization. In the following, we will discuss this formalism for fermionic systems, as we are mostly interested in the dynamics of electrons. However, an analogous formulation is available for bosons [165–167]. Compared to the first quantization approach, the formalism of second quantization changes from explicit N-particle wave functions to an occupation number representation. The main advantage of this method is that the indistinguishability of identical quantum particles is naturally contained in the formalism. Thus, an N-particle quantization would require an (anti-)symmetrization over all constituents. Hence, a description using the occupation number representation comes in more naturally.

We start by defining the Fock space as a direct sum of individual Hilbert spaces of fixed particle number N,

$$\mathcal{H}_{\text{Fock}} \equiv \mathcal{H}_0 \oplus \mathcal{H}_1 \oplus \mathcal{H}_2 \dots . \quad (2.3)$$

A state in the Fock space is then given by

$$|n_1, n_2, n_3, \dots\rangle, \quad (2.4)$$

where n_j gives the occupation number of state j . Those states can be created from the vacuum using creation operators $a_i^\dagger$. For fermions, an arbitrary state can be expressed as

$$|n_1, n_2, n_3, \dots\rangle = (a_1^\dagger)^{n_1} (a_2^\dagger)^{n_2} (a_3^\dagger)^{n_3} \dots |\text{vac}\rangle, \quad (2.5)$$

where $|\text{vac}\rangle$ is the unoccupied vacuum state. The operator $a_j^\dagger$ creates a particle in the state n_j . There are also annihilation operators a_j that annihilate particles in the respective state. To preserve the fundamental fermionic antisymmetry upon particle exchange, we require the fermions to anticommute,

$$\left[a_i, a_j^\dagger \right]_+ \equiv a_i a_j^\dagger + a_j^\dagger a_i = \delta_{ij}, \quad \left[a_i^{(\dagger)}, a_j^{(\dagger)} \right]_+ = 0. \quad (2.6)$$

In order to perform our calculations in second quantization, it is crucial to find a way to include operator quantities in the second quantization formalism. This can be achieved by canonical transformation. For one-particle operators, this can generally be done by

$$\hat{O}_1^{(1)}(\mathbf{r}, t) \rightarrow \hat{O}_1^{(2)} = \int d^3\mathbf{r} \, \Psi^\dagger(\mathbf{r}, t) \hat{O}_1^{(1)} \Psi(\mathbf{r}, t), \quad (2.7)$$

where $\Psi(\mathbf{r}, t)$ are the field operators which also obey anticommutation relations

$$\left[\Psi(\mathbf{r}, t), \Psi^\dagger(\mathbf{r}', t) \right]_+ = \delta(\mathbf{r} - \mathbf{r}'), \quad \left[\Psi^{(\dagger)}(\mathbf{r}, t), \Psi^{(\dagger)}(\mathbf{r}', t) \right]_+ = 0. \quad (2.8)$$

At this stage, one can perform a mode expansion and expand the field operators into a complete set of spatial modes, denoted by

$$\Psi^\dagger(\mathbf{r}, t) = \sum_{\mathbf{k}\lambda} \phi_{\mathbf{k}\lambda}^*(\mathbf{r}) a_{\mathbf{k}\lambda}^\dagger(t) \quad \text{and} \quad \Psi(\mathbf{r}, t) = \sum_{\mathbf{k}\lambda} \phi_{\mathbf{k}\lambda}(\mathbf{r}) a_{\mathbf{k}\lambda}(t). \quad (2.9)$$

Here, we adopt the typical notation used in solid-state physics, which employs the momentum $\mathbf{k}$ and band λ as quantum numbers. From this, it is straightforward to identify the definition of one-particle operators in second quantization [167],

$$\hat{O}_1^{(2)} = \sum_{\mathbf{k}\mathbf{k}'\lambda\lambda'} \left(\int d^3\mathbf{r} \phi_{\mathbf{k}\lambda}^*(\mathbf{r}) \hat{O}_1^{(1)} \phi_{\mathbf{k}'\lambda'}(\mathbf{r}) \right) a_{\mathbf{k}\lambda}^\dagger(t) a_{\mathbf{k}'\lambda'}(t). \quad (2.10)$$

This can also be written using the Dirac notation,

$$\hat{O}_1^{(2)} = \sum_{\mathbf{k}\mathbf{k}'\lambda\lambda'} O_{\mathbf{k}\mathbf{k}'}^{\lambda\lambda'} a_{\mathbf{k}\lambda}^\dagger a_{\mathbf{k}'\lambda'}, \quad O_{\mathbf{k}\mathbf{k}'}^{\lambda\lambda'} = \langle \mathbf{k}\lambda | \hat{O}_1^{(1)}(\mathbf{r}) | \mathbf{k}'\lambda' \rangle. \quad (2.11)$$

In a similar derivation, one can find the same for two-particle operators [167],

$$\hat{O}_2^{(2)} = \sum_{\substack{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3\mathbf{k}_4 \\ \lambda_1\lambda_2\lambda_3\lambda_4}} \mathcal{O}_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3\mathbf{k}_4}^{\lambda_1\lambda_2\lambda_3\lambda_4} a_{\mathbf{k}_1\lambda_1}^\dagger a_{\mathbf{k}_2\lambda_2}^\dagger a_{\mathbf{k}_3\lambda_3} a_{\mathbf{k}_4\lambda_4}, \quad (2.12)$$

$$\mathcal{O}_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3\mathbf{k}_4}^{\lambda_1\lambda_2\lambda_3\lambda_4} = \langle \mathbf{k}_1\lambda_1, \mathbf{k}_2\lambda_2 | \hat{O}_2^{(1)}(\mathbf{r}, \mathbf{r}') | \mathbf{k}_3\lambda_3, \mathbf{k}_4\lambda_4 \rangle. \quad (2.13)$$

At this stage, one usually uses the periodicity of the lattice to employ the Bloch theorem. It states that for periodic potentials, solutions of the stationary Schrödinger equation are of the form [168]

$$\phi_{\mathbf{k}\lambda}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}\lambda}(\mathbf{r}). \quad (2.14)$$

The functions $u_{\mathbf{k}\lambda}(\mathbf{r})$ also carry the lattice periodicity $u_{\mathbf{k}\lambda}(\mathbf{r}) = u_{\mathbf{k}\lambda}(\mathbf{r} + \mathbf{R})$. This effectively allows reducing the theoretical description to the first Brillouin zone. Dynamical equations for any observables of choice, $\mathcal{O}$, are obtained via the *Heisenberg equation of motion framework*, here denoted via the Ehrenfest theorem [169],

$$i\hbar\partial_t \langle \mathcal{O}(t) \rangle = \langle [\mathcal{O}(t), H]_- \rangle. \quad (2.15)$$

For the scope of this thesis, we will be interested in the dynamical evolution of operators of the general form

$$\sigma_{\mathbf{k}\mathbf{k}'}^{\lambda\lambda'} \equiv \langle a_{\mathbf{k}\lambda}^\dagger a_{\mathbf{k}'\lambda'} \rangle = \langle \lambda_{\mathbf{k}}^\dagger \lambda_{\mathbf{k}'}' \rangle. \quad (2.16)$$

This operator creates an electron with momentum $\mathbf{k}$ in band λ while annihilating one with momentum $\mathbf{k}'$ in band λ' . Here, we mostly restrict to a two-band model. As we will see throughout this thesis, these observables will be used to describe band occupations $f_{\mathbf{k}}^\lambda \equiv \sigma_{\mathbf{k},\mathbf{k}}^{\lambda\lambda}$, intraband transitions $f_{\mathbf{k}-\mathbf{q},\mathbf{k}}^\lambda \equiv \sigma_{\mathbf{k}-\mathbf{q},\mathbf{k}}^{\lambda\lambda}$, and interband polarizations $p_{\mathbf{k}} \equiv \sigma_{\mathbf{k},\mathbf{k}}^{vc}$, with v for valence and c for conduction band. In the second equality in Eq. (2.16), we used the abbreviated notation that we will use for fermionic particles in this thesis, where we absorb the band index into the annihilation (creation) operator $\lambda_{\mathbf{k}}^{(\dagger)}$ itself. From this, it is possible to derive the usual *semiconductor Bloch equations* for the band occupations and interband polarizations [170–174].

2.1.1. Cluster Expansion

If one calculates the dynamical equations for a two-operator quantity $\sigma_{\mathbf{k}\mathbf{k}'}^{\lambda\lambda'}$, cf. Eq. (2.12), while including a two-particle Hamiltonian, it becomes apparent that the equation of motion does not close, but couples to four-operator expectation values describing correlations between electrons. An example of this kind of interaction will be found later by the Coulomb interaction or the electron-phonon coupling. This can be solved in principle by deriving an equation for the four-operator quantity, which couples to a six-operator quantity, which couples to eight-operator quantities, and so on. This is what is usually called a *hierarchy problem* and is often encountered in many-body physics. To obtain a solution, the hierarchy must be truncated at some level. In the context of this work, we use a correlation expansion based on the idea that correlations, i.e., higher-order expectation values, are of decreasing importance as the number of involved charge carriers increases [175].

To address the hierarchy problem, we use a cluster expansion method [171]. In this approach, the expectation value is approximated by “a functional structure” [171] that includes all clusters up to a certain predetermined level, while excluding all remaining clusters of higher rank. In particular, this allows for systematic improvements in the accuracy of the approximations by progressively including more clusters. Since the explicit formulas for bosons and fermions are different, we use the generic prescription outlined in Ref. [171]. We begin with the trivial case of the singlet state, which corresponds directly to the singlet itself,

$$\langle 1 \rangle = \langle 1 \rangle_S. \quad (2.17)$$

The first real correlation is found for the doublet

$$\langle 2 \rangle = \langle 2 \rangle_S + \langle 2 \rangle_C. \quad (2.18)$$

In this approach, the first term represents the factorization into singlet states, while the second term accounts for the correlations within the doublet state. The factorization into singlet states while neglecting correlations at this level for fermions is commonly known as the Hartree-Fock approximation. This formulation can be extended to N-particle situations, but for the purpose of this introduction we limit ourselves to this level of approximation. For a more complete understanding, readers are encouraged to refer to the detailed discussion in Ref. [171].

2.1.2. Formal Integration and Markov Approximation

When incorporating contributions from correlated quantities in Eq. (2.18), as successfully done in our group [176–180], one usually derives a dynamical equation for these correlated quantities using the Heisenberg equation of motion. This results in an equation that is formally equivalent to,

$$\dot{y}(t) + iE(t)y(t) = Q(t) \quad (2.19)$$

which is an inhomogeneous first-order ordinary differential equation in time. According to Ref. [181], equations of this form can be solved using the integrating factor,

$$\mu = \exp \left\{ i \int_{t_0}^t E(t') \, dt' \right\}, \quad (2.20)$$

which allows obtaining the general solution,

$$y(t) = y(t_0) + \exp\left\{-i \int_{t_0}^t E(t') dt'\right\} \int_{t_0}^t Q(t') \exp\left\{i \int_{t_0}^{t'} E(t'') dt''\right\}. \quad (2.21)$$

For our specific use cases, the function $\mathbf{E}(t)$ is usually a band structure contribution and, therefore, time-independent. Utilizing this fact and making the additional assumption that $y(t \rightarrow -\infty) = 0$, the general solution can be simplified to

$$y(t) = \int_{-\infty}^t Q(t') \exp\{-iE(t - t')\} dt', \quad (2.22)$$

or, after performing the coordinate transformation $s = t - t'$,

$$y(t) = \int_0^\infty Q(t - s) \exp\{-iEs\} ds. \quad (2.23)$$

From this, one usually performs the *Markov approximation*, which can be expressed as $Q(t - s) \approx \tilde{Q}(t)e^{-i\Delta Es}$. This effectively assumes that $\tilde{Q}(t)$ varies slowly relative to the fast optical oscillation in the exponent, which is reasonable since the oscillatory contribution has already been separated.

Therefore, this effectively means that the remaining memory kernel t' of the quantity $\tilde{Q}(t)$ can be neglected, since $\tilde{Q}(t)$ varies much slower compared to the optical frequency. This results in

$$y(t) = \tilde{Q}(t) \int_0^\infty \exp\{-i(E + \Delta E)s\} ds = -i\tilde{Q}(t)\zeta(-E - \Delta E), \quad (2.24)$$

where we use the definition of the Heitler Zeta function [182, 183],

$$\zeta(x) = -i \int_0^\infty \exp\{ixt\} = \mathcal{P}\left(\frac{1}{x}\right) - i\pi\delta(x). \quad (2.25)$$

Using this result and the definition of the ζ -function in the equations of motion, it will usually be found that the correlation contributions account for dephasing effects via the δ -function part, and renormalization of the mean-field effects via the principal-value part. This will be used to evaluate the impact of correlation originating from electron-phonon and electron-electron interactions in Sec. 4.3.

2.2. Atomically Thin Semiconductors

Transition metal dichalcogenides (MX_2) are compounds composed of one transition metal atom (M) and two chalcogenide atoms (X) arranged in a trigonal prism crystal structure. The crystal structure consists of six chalcogenide atoms surrounding a transition metal atom, all with equal bond lengths. This arrangement is shown in Figure 2.1a. In a monolayer of MX_2 , these single prisms are stacked to form a hexagonal lattice with alternating transition metal and chalcogenide atoms, as shown in Fig. 2.1b.

The hexagonal lattice reveals strong covalent bonds within the monolayer. Multiple layers can stack on top of each other via weaker van der Waals forces in a variety of ways; the interested reader is referred to Refs. [184, 185]. For a mathematical description, we

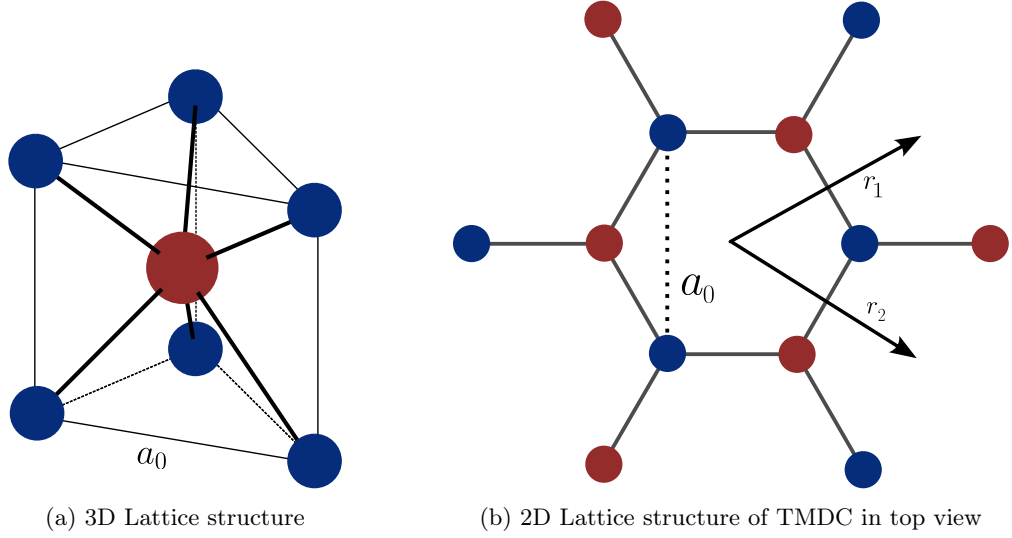


Figure 2.1.: **The Crystal Structure of TMDC Monolayers.** (a) shows the trigonal prism structure of TMDCs. (b) shows the hexagonal lattice structure of 2D TMDCs. The lattice constant a_0 is the distance of two similar atoms.

begin by defining the lattice vectors that connect adjacent unit cell centers and are needed to describe the translational invariance of the crystal. Using the lattice constant a_0 , cf. Fig. 2.1, the lattice vectors are given by

$$\mathbf{r}_1 = \frac{a_0}{2} (\sqrt{3} \mathbf{e}_x + \mathbf{e}_y), \quad (2.26a)$$

$$\mathbf{r}_2 = \frac{a_0}{2} (\sqrt{3} \mathbf{e}_x - \mathbf{e}_y). \quad (2.26b)$$

Typical values for the lattice constant a_0 are around 0.3 nm [186]. Compared to other two-dimensional materials, e.g., graphene, the inversion symmetry in TMDC monolayers is broken as a result of the three-atomic basis, cf. Fig. 2.1. However, the lattice structure remains symmetric under discrete rotations by multiples of $2\pi/3$, and discrete translations within the x - y plane.

Most of our calculations will be performed in reciprocal space, which provides a convenient framework due to the periodicity of crystal structures. A comprehensive introduction to reciprocal space can be found in Ref. [166]. In the reciprocal lattice, the lattice vectors are defined using the general form:

$$\mathbf{g}_i \cdot \mathbf{r}_j = 2\pi \delta_{ij}.$$

In combination with the vectors in Eq. (2.26), the

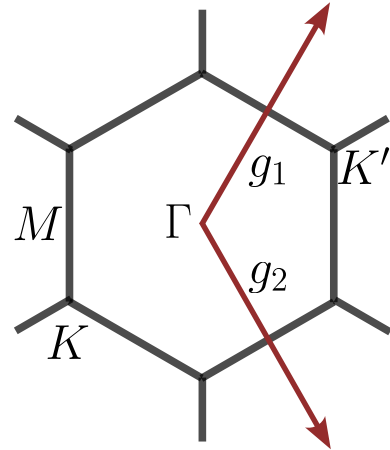


Figure 2.2.: **First TMDC Brillouin Zone.** Brillouin zone in reciprocal space with the high symmetry points Γ , M , and K/K' .

condition for the reciprocal lattice vectors can be expressed in the following way

$$\mathbf{g}_1 = \frac{2\pi}{a_0} \left(\frac{1}{\sqrt{3}} \mathbf{e}_x + \mathbf{e}_y \right),$$

$$\mathbf{g}_2 = \frac{2\pi}{a_0} \left(\frac{1}{\sqrt{3}} \mathbf{e}_x - \mathbf{e}_y \right).$$

In the hexagonal reciprocal space defined by these basis vectors, a set of high symmetry points can be identified, as shown in Fig. 2.2. The Γ point, located at the center of the Brillouin zone, remains invariant under any rotation [187]. Due to the broken inversion symmetry caused by the alternating transition metal and chalcogenide atoms in the unit cell of the TMDCs, there are two distinct K points, called K and K' points, respectively. These K and K' points are located at alternating vertices in the Brillouin zone [168]. This phenomenon gives rise to several intriguing physical effects, such as circular dichroism and spin-valley locking. In addition, the M points are located at the centers of the edges.

In the monolayer limit, the band structure of TMDCs can be obtained by *ab initio* calculations using density functional theory [188]. Fig. 2.3 shows a typical band structure of TMDCs for the case of MoS_2 .

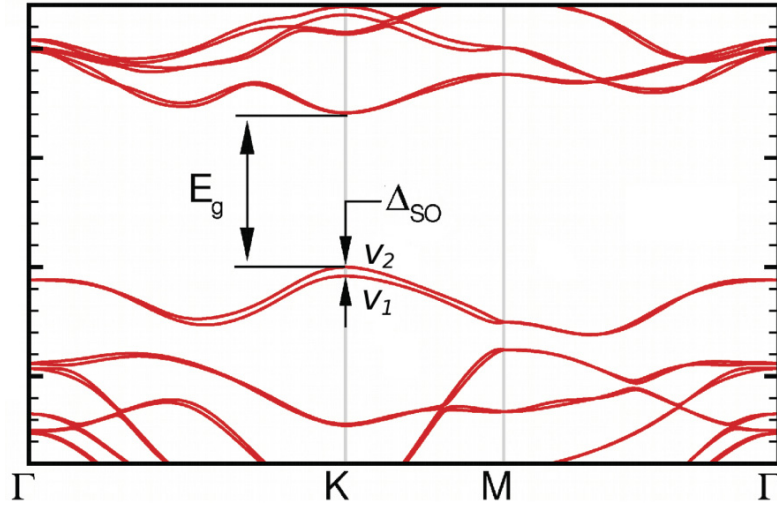


Figure 2.3: MoS₂ Band Structure. The band structure of monolayer MoS₂ exhibits a significant spin-splitting of the valence and conduction bands at the K/K' points, attributed to strong spin-orbit coupling. This spin-splitting is evident in the absorption spectrum. Reprinted figure with permission from Ref. [188]. Copyright (2012) by the American Physical Society.

Even if the exact form of the band structure is specific to MoS₂, we will use it to explain features that are common among all TMDC monolayers. The characteristic feature of TMDCs that has sparked a surge in scientific interest in these materials over the past decade is that they exhibit a direct band gap in the monolayer limit [8], which results in a significant photoluminescence enhancement of TMDC layers compared to the multilayer case. Due to their shape, the band gap extrema are often referred to as valleys and approximated to be parabolic around the respective K/K' point. This will be done once we start our analytical calculations in Sec. 3.1.1. In addition to the direct band gap, the optical transitions are valley selective as σ_+ - or σ_- -polarized light can only induce optical

transitions at the K or K' valley respectively [10], a fact that results from the band gap being located at the vertices rather than the center of the Brillouin zone. As can be seen in Fig. 2.3, the valence band is split in two at the K/K' points. This split is due to strong spin-orbit coupling in the TMDC layer, originating from d orbitals [11] that constitute the band structure close to the K/K' points. As the valence and conduction band are made up by different d -orbitals, the spin-splitting effect is much weaker but exists in the conduction band as well [12, 189]. The splitting in the valence band typically reaches several hundred meV, while in the conduction band, it reaches multiple tens of meV [12].

Following the absorption of a photon in the TMDC, an electron is promoted to the conduction band, leaving behind a hole in the valence band. Those charges interact via attractive Coulomb interaction and form a bound electron-hole pair, a so-called *exciton*. Due to their two-dimensional nature, the field lines can effectively propagate outside the material, resulting in a net reduction of the dielectric screening, which leads to large exciton binding energies on the order of 0.5 meV [17, 190, 191]. Due to their substantial oscillator strength, TMDCs can achieve absorption rates of up to 10 % in the visible regime [8, 9], which is even more remarkable considering their two-dimensional nature."

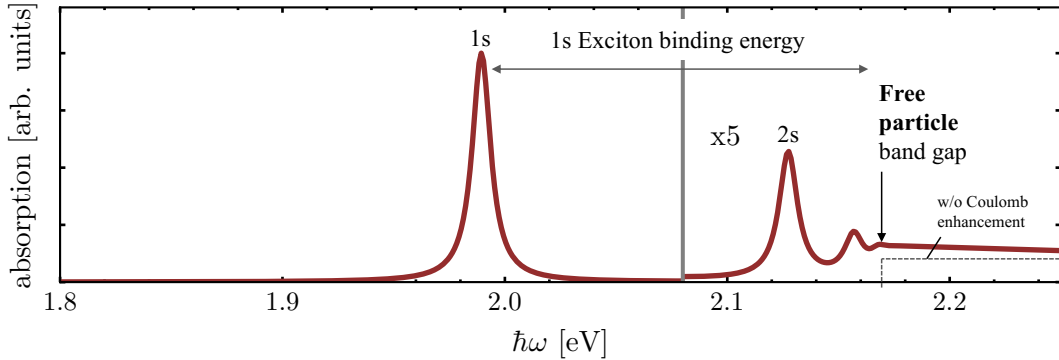


Figure 2.4.: **Exciton Formation Below the Free-Particle Band Gap.** The figure illustrates exciton formation below the free-particle band gap, showing a strong $1s$ peak along with weaker higher-order excitonic resonances. Accordingly, the optical band gap is decreased to the energy level of the $1s$ exciton resonance. Above the free-particle band gap, the spectrum appears continuous. For the calculated spectrum, values for MoSe_2 are used. The figure is inspired by Ref. [18].

As can be seen in Fig. 2.4, the optical spectra of TMDC monolayers reveal strong and spectrally well separated excitonic resonances, making them an ideal candidate to study excitonic effects. In general, there are two types of excitons, Wannier-Mott excitons and Frenkel excitons, depending on the exciton Bohr radius. In TMDC monolayers, their Bohr radius is on the order of a few nanometers to several lattice periods [18], which corresponds to the intermediate range. Strictly speaking, an intermediate description would need to be considered. However, experimental observations have indicated that a Wannier-Mott description is sufficient to explain results quantitatively [18].

2.3. Electrodynamics of Metals

In most cases, the interaction of metals with electromagnetic fields can be understood in terms of classical electrodynamics. The theoretical description is therefore firmly rooted in the well-known Maxwell equations [192, 193],

$$\nabla \cdot \mathbf{D}(\mathbf{r}, t) = \rho(\mathbf{r}, t), \quad (2.27a)$$

$$\nabla \cdot \mathbf{B}(\mathbf{r}, t) = 0, \quad (2.27b)$$

$$\nabla \times \mathbf{E}(\mathbf{r}, t) = -\partial_t \mathbf{B}(\mathbf{r}, t), \quad (2.27c)$$

$$\nabla \times \mathbf{H}(\mathbf{r}, t) = \mathbf{j}(\mathbf{r}, t) + \partial_t \mathbf{D}(\mathbf{r}, t). \quad (2.27d)$$

Here, $\mathbf{D}$ is the electric displacement, ρ the free electric charge density, $\mathbf{B}$ the magnetic flux density or magnetic induction, often also ambiguously referred to as the magnetic field, the electric field $\mathbf{E}$ and the magnetic field $\mathbf{H}$ and the electric current density $\mathbf{j}$ of free charges. These essential equations are widely utilized in various numerical implementations [194], such as finite-element methods [132] (e.g., COMSOL [195]), the finite-difference time-domain method [131] (e.g., ANSYS Lumerical [196]), surface integral methods, namely the SIE method [197] or the boundary element method (BEM) [133], the discontinuous Galerkin time domain (DGTD) method [198, 199], or volume integral methods [200].

For the case of non-magnetic, homogeneous, linear media that will be important throughout this thesis, these equations are linked through [201]

$$\mathbf{D}(\mathbf{r}, t) = \varepsilon_0 \int \int \varepsilon(\mathbf{r}, \mathbf{r}', t - t') \mathbf{E}(\mathbf{r}', t') d^3\mathbf{r}' dt', \quad (2.28a)$$

$$\mathbf{B}(\mathbf{r}, t) = \mu_0 \mathbf{H}(\mathbf{r}, t), \quad (2.28b)$$

$$\mathbf{P}(\mathbf{r}, t) = \varepsilon_0 \int \int \chi(\mathbf{r}, \mathbf{r}', t - t') \mathbf{E}(\mathbf{r}', t') d^3\mathbf{r}' dt', \quad (2.28c)$$

with the vacuum permittivity, ε_0 , the vacuum permeability μ_0 and the relative permittivity $\varepsilon(\mathbf{r}, \mathbf{r}', t - t')$ which is 1 for vacuum. Here, we chose the formulation in terms of the polarization, as this will be the predominant observable throughout this thesis. However, in agreement with the Maxwell's equations, one could also reformulate these equations in terms of the electric current density $\mathbf{j}(\mathbf{r}, t)$ using the conductivity $\sigma(\mathbf{r}, \mathbf{r}', t - t')$ [202],

$$\mathbf{j}(\mathbf{r}, t) = \int \int \sigma(\mathbf{r}, \mathbf{r}', t - t') \mathbf{E}(\mathbf{r}', t') d^3\mathbf{r}' dt'. \quad (2.29)$$

As the current density is the time derivative of the polarization $\partial_t \mathbf{P} = \mathbf{j}(\mathbf{r}, t)$, one can generally connect conductivity, permittivity, and susceptibility via

$$\chi(\mathbf{r}, \mathbf{r}'; \omega) = \frac{i\sigma(\mathbf{r}, \mathbf{r}'; \omega)}{\omega \varepsilon_0}, \quad \varepsilon(\mathbf{r}, \mathbf{r}'; \omega) = \varepsilon_\infty(\mathbf{r}, \mathbf{r}') + \frac{i\sigma(\mathbf{r}, \mathbf{r}'; \omega)}{\omega \varepsilon_0}. \quad (2.30)$$

The convolution in Eqs. (2.28) can be expressed as a product in Fourier space that reads

$$\mathbf{D}_Q(\omega) = \varepsilon_0 \varepsilon_Q(\omega) \mathbf{E}_Q(\omega), \quad (2.31a)$$

$$\mathbf{B}_Q(\omega) = \mu_0 \mathbf{H}_Q(\omega), \quad (2.31b)$$

$$\mathbf{P}_Q(\omega) = \chi_Q(\omega) \mathbf{E}_Q(\omega). \quad (2.31c)$$

In these equations, the material properties are encoded in terms of conductivity, permittivity, or susceptibility, which can be used interchangeably, as shown in Eq. (2.30).

Most commonly, these equations use phenomenological material models to describe the response of the system qualitatively and quantitatively. For metals, there is a large zoo of material models due to the lack of characteristic high-symmetry points in their band structure that can be easily approximated (unlike direct band gap semiconductors). In order to improve these phenomenological models, all these equations should be further advanced to the microscopic level, which will be the central focus in Ch. 4).

In the following subsections, we provide an overview of the material systems considered in this work and their respective descriptions in the existing literature. We focus on a description in terms of permittivity.

2.3.1. Local Response Approximation - Drude Model

A very useful approximation to handle the convolution in Eq. (2.28) is the Local Response Approximation (LRA), which can be expressed as follows

$$\varepsilon(\mathbf{r}, \mathbf{r}'; \omega) = \varepsilon(\mathbf{r}; \omega) \delta(\mathbf{r} - \mathbf{r}'). \quad (2.32)$$

This way, the optical response of the system is fully described locally using a permittivity function that depends entirely on the location and disregards effects of the surroundings, i.e., nonlocal effects. This is a strong approximation, but at the same time has been a very successful theory to describe experimental observations over the years.

This approach is commonly combined with the piecewise-constant approximation (PCA), where a constant, spatially invariant, and frequency-dependent permittivity is assumed for each region [51, 203],

$$\varepsilon(\mathbf{r}; \omega) \approx \begin{cases} \varepsilon(\omega) & , \quad \mathbf{r} \in \text{material} \\ 1 & , \quad \mathbf{r} \in \text{surrounding} \end{cases}. \quad (2.33)$$

The formulation presented above is advantageous as it allows for a clear separation of bulk material properties from geometrical effects, enabling the treatment of these aspects on different levels. This separation is especially useful for numerical implementations. Typically, the first step is to derive the permittivity $\varepsilon(\omega)$, which characterizes the optical response of the bulk material. Then the geometrical information is added in a separate step.

This separation is particularly useful for numerical implementations as this usually works by first deriving the permittivity $\varepsilon(\omega)$, which characterizes the optical response of the bulk material, and then separately adding geometrical information in a second step.

In the following sections, we will discuss typical models used to describe the bulk properties of metals. We will focus mainly on the optical to infrared frequency range, as this is the spectral range relevant to the scope of this work. Within this range, the Drude model [119] is one of the most commonly used models. This phenomenological model, historically the first to explain Ohm's law [119], can effectively capture the optical response of metal systems in the region where intraband effects dominate and interband effects can be neglected. The inclusion of interband transitions is discussed in Sec. 2.3.6. It is important to note that the derivation of an analytical response for a material system is always limited to the spectral region for which the model is applicable.

An intuitive derivation of the Drude model can be obtained from a simple picture [51], where an electron gas of free electrons moves against a fixed background of ion nuclei. This model is valid for many metals over a wide spectral range, particularly in the infrared to optical range that we are interested in. The equation of motion is given by

$$m\partial_t \mathbf{v} + m\gamma \mathbf{v} = -e\mathbf{E}. \quad (2.34)$$

Here, we consider the velocity $\mathbf{v}$ of electrons with mass m and charge $-e$ under the influence of an electric field $\mathbf{E}$, as they move in front of a background of ions. The velocity is damped due to electron-ion collisions with a rate of γ . From this, we define the electric current density that reads

$$\mathbf{j} = -nev, \quad (2.35)$$

where n is the electron density. From this and using Eq. (2.30), we can find prescriptions for the permittivity $\varepsilon(\omega)$ and the plasma frequency ω_p ,

$$\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega(\omega + i\gamma)}, \quad \omega_p^2 = \frac{ne^2}{\varepsilon_0 m}, \quad (2.36)$$

where n is the electron density, e is the elementary charge, ε_0 is the vacuum permittivity, and m is the electron mass. Incorporating the effects of filled d bands that cause a highly polarized environment in noble metals and core-level electrons not accounted for in the model given by Eq. (2.34), we can modify the asymptotic permittivity by adding a residual polarization, resulting in the following expression

$$\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega(\omega + i\gamma)}. \quad (2.37)$$

The parameter γ represents the electron dephasing rate and ε_∞ is the asymptotic value for high-frequencies of the permittivity [51, 204].

2.3.2. Microscopic Material Models

These equations, derived at the macroscopic level, can also be obtained at the microscopic level, allowing the inclusion of electron-electron interactions. This is achieved through the use of the Heisenberg equation of motion framework, as discussed in Sec. 2.1. By including the free Hamiltonian and the Coulomb interaction, treated within the Hartree-Fock approximation, it is straightforward to derive the dynamical equation for intraband transitions. Here, we follow Refs. [165, 167],

$$\hbar\omega f_{\mathbf{k}-\mathbf{q},\mathbf{k}} = [\tilde{\epsilon}_{\mathbf{k}} - \tilde{\epsilon}_{\mathbf{k}-\mathbf{q}}] f_{\mathbf{k}-\mathbf{q},\mathbf{k}} - V_{\mathbf{q}}(f_{\mathbf{k},\mathbf{k}} - f_{\mathbf{k}-\mathbf{q},\mathbf{k}-\mathbf{q}}) \sum_{\mathbf{K}} f_{\mathbf{K}-\mathbf{q},\mathbf{K}}. \quad (2.38)$$

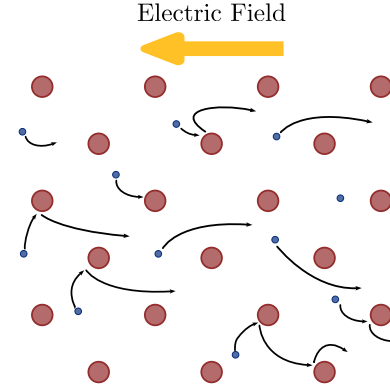


Figure 2.5.: **Conceptual Idea of Drude Theory.** This illustration shows the core concept of Drude theory. When exposed to an external electric field, electrons are accelerated by the field while scattering with the ions.

In this derivation, we deliberately neglect the spin quantum number, and the equation is linearized to include occupations and transitions only up to linear order. In addition, some mean-field contributions at the Hartree-Fock level are already incorporated in a renormalized dispersion $\tilde{\epsilon}_{\mathbf{k}} = \epsilon_{\mathbf{k}} + \delta\epsilon_{\mathbf{k}}$, where $\delta\epsilon_{\mathbf{k}} = -\sum_{\mathbf{q}} V_{\mathbf{q}} f_{\mathbf{k}-\mathbf{q},\mathbf{k}-\mathbf{q}}$. By summing over $\mathbf{k}$, we obtain an implicit equation to determine the eigenfrequencies of the electron gas,

$$F_{\mathbf{q}}(\omega) \equiv \sum_{\mathbf{k}} V_{\mathbf{q}} \frac{f_{\mathbf{k}-\mathbf{q},\mathbf{k}-\mathbf{q}} - f_{\mathbf{k},\mathbf{k}}}{\hbar\omega + \tilde{\epsilon}_{\mathbf{k}-\mathbf{q}} - \tilde{\epsilon}_{\mathbf{k}}} = 1. \quad (2.39)$$

The equation derived above has several simple poles at electron-hole excitation energies $\tilde{\epsilon}_{\mathbf{k}-\mathbf{q}} - \tilde{\epsilon}_{\mathbf{k}}$. Between these poles, the implicit equation is fulfilled at least once, as shown in Fig. 2.6.

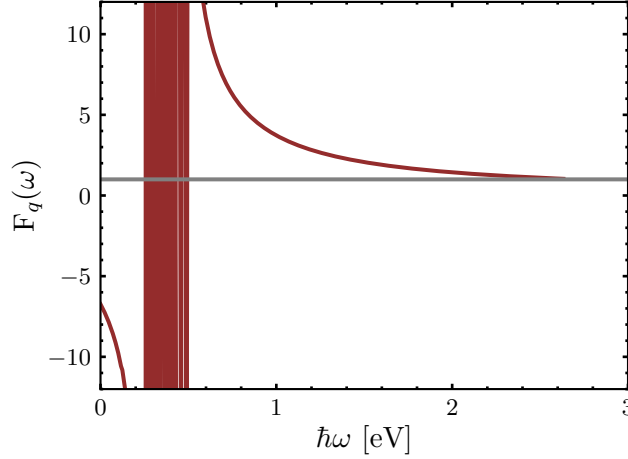


Figure 2.6.: **Visualization of the Implicit Equation for the Plasma Frequency.**

This graph shows the function $F_{\mathbf{q}}(\omega)$, revealing two characteristic parts. At low frequencies, multiple poles are observed, indicating electron-hole excitations. Conversely, at high energies, a slowly decaying branch proportional to ω^{-1} appears. This branch corresponds to the collective excitation of the electron gas.

This excitation creates the continuum of excited electron-hole states, which is difficult to visualize graphically. In addition to this continuum, an additional mode is found, which corresponds to a collective excitation of the electron gas. This generalizes the conceptual idea of the Drude model to include electron-hole excitations through Coulomb interaction. In the regime of the collective mode, $\hbar\omega \gg \epsilon_{\mathbf{k}+\mathbf{q}} - \epsilon_{\mathbf{k}} \approx \frac{\hbar^2}{m}(\mathbf{k} \cdot \mathbf{q} + q^2/2)$. From this, the plasma frequency can be derived easily,

$$1 = \frac{V_{\mathbf{q}}}{(\hbar\omega)^2} \sum_{\mathbf{k}} f_{\mathbf{k},\mathbf{k}} \frac{2\hbar^2}{m}(\mathbf{k} \cdot \mathbf{q} + q^2/2) = \frac{e^2}{m\epsilon_0 V \omega^2} \sum_{\mathbf{k}} f_{\mathbf{k},\mathbf{k}} \rightarrow \omega_p^2 \equiv \frac{ne^2}{m\epsilon_0} \quad (2.40)$$

From this description, it is possible to derive the first dispersive correction $\propto q^2$ to the plasma frequency. Interested readers are referred to Refs. [165, 167] for further details on this topic.

Furthermore, in the same spirit, an equation for the dielectric function can be derived

as the effective screening of the Coulomb potential,

$$\varepsilon_{\mathbf{q}}(\omega) = 1 - V_{\mathbf{q}} \sum_{\mathbf{k}} \frac{f_{\mathbf{k}+\mathbf{q},\mathbf{k}+\mathbf{q}} - f_{\mathbf{k},\mathbf{k}}}{\epsilon_{\mathbf{k}+\mathbf{q}} - \epsilon_{\mathbf{k}} - \hbar\omega}. \quad (2.41)$$

This equation is commonly known as the *Lindhard equation* for the dielectric constant of the electron gas.

On a final note, it is also possible to define bosonic annihilation (creation) operators for the plasmons themselves by distinguishing between the long and short range Coulomb interactions. An excellent introduction can be found in Ref. [205].

2.3.3. Thermalization in Metals and Semiconductors

When an optical pulse interacts with a material, the optical pulse primarily interacts with the electrons, which thermalize on the short timescale of electron-electron interaction and then dissipate their energy to the lattice through electron-phonon interaction. Depending on the timescales of pulse length and electron-phonon coupling, the electron and lattice remain in equilibrium and can intuitively be described by a single equation. However, when this timescale becomes short compared to the electron-phonon coupling, the two have to be distinguished for a sensible theoretical description. For this purpose, the two-temperature model has been very successfully introduced, which reads as follows [206–208]

$$C_e(T_e)\partial_t T_e = -G(T_e - T_\ell) + P_{\text{abs}}(\mathbf{r}, t), \quad (2.42a)$$

$$C_\ell\partial_t T_\ell = G(T_e - T_\ell). \quad (2.42b)$$

Here, C_e and C_ℓ represent the electron and lattice heat capacity, while T_e and T_ℓ are the electron and lattice temperatures, respectively. The model also includes the electron-phonon coupling G and the general heat source P_{abs} . This model has proven extremely successful in various experimental situations, with the first values for femtosecond excitation recorded in Refs. [209, 210]. Spatial derivatives incorporating diffusion have been neglected at this stage, but will be reintroduced later.

This temperature-based description inherently neglects nonthermal contributions that become significant during electron thermalization on a femtosecond timescale [211]. To incorporate these nonthermal processes, the theoretical model has been extended to what is known as the three-temperature model (3TM) [212, 213],

$$\partial_t N = -aN - bN + P_{\text{abs}}(\mathbf{r}, t), \quad (2.43a)$$

$$C_e\partial_t T_e = -\nabla \cdot (-\kappa_e \nabla T_e) - G(T_e - T_\ell) + aN, \quad (2.43b)$$

$$C_\ell\partial_t T_\ell = \kappa_\ell \nabla^2 T_\ell + G(T_e - T_\ell) + bN. \quad (2.43c)$$

In this model, N represents the energy stored in the nonthermalized part of the electron distribution, while κ_e and κ_ℓ are the thermal conductivities. The first experiments to verify this model were conducted in Refs. [211, 213, 213, 214]. According to Ref. [212], a is the electron gas heating rate, and b is the electron-phonon coupling rate. In Eq. (2.43), T_e , T_ℓ and N depend on space and time, but in most cases their spatial dependence is not needed and is therefore omitted in the description for clarity. Recently, researchers have explored the spatial dependence, leading to the rediscovery of the inhomogeneous three-temperature model (I3TM) [215–219].

The obtained results demonstrate good agreement with a more sophisticated model [220, 221], which relies on numerical solutions of the Boltzmann equation [222, 223], sometimes referred to as the Bloch-Boltzmann-Peierls formula [222]. This comprehensive approach has been highly successful in describing the complex dynamics of semiconductors [173, 224–228] and metals [220, 229–232], overcoming the limitations of temperature-based models.

In the context of metals, the equations are often formulated in terms of energy [224, 231, 233–235], significantly reducing the dimensionality of the problem while assuming isotropy and homogeneity for physical simplicity. Detailed calculations can be found in Refs. [236, 237].

In contrast, these descriptions in their full momentum dependent complexity have proven to be highly effective to model the dynamics in graphene and carbon nanotubes [174, 238–242], as well as transition metal dichalcogenides [19, 176, 180, 243], where they allow for the inclusion of non-isotropic situations and electron-electron interactions [244, 245].

As an illustrative example, Fig. 2.7 depicts the thermalization process of a classical Boltzmann scattering equation, revealing the prominent non-thermal distribution that arises in the system.

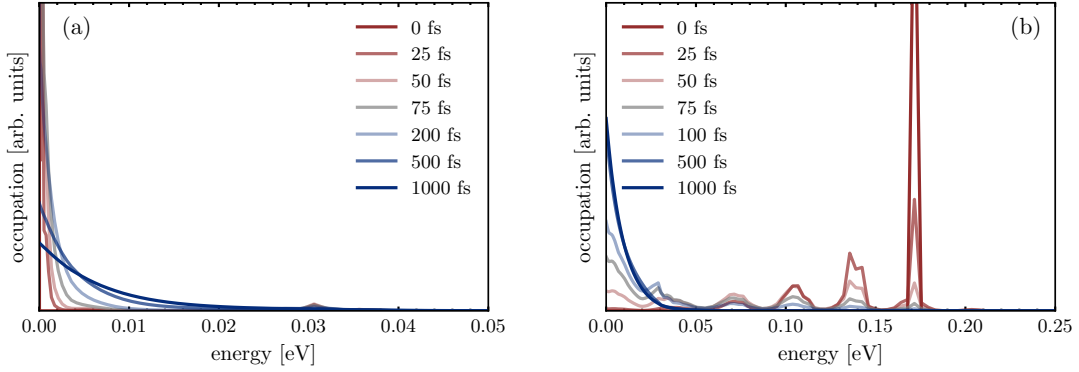


Figure 2.7.: **Example for a Classical Boltzmann Scattering Process.** Depiction of the thermalization dynamics of the classical Boltzmann equation for monolayer MoSe₂ at a lattice temperature of $T = 100$ K. (a) depicts the excitation of the $Q = 0$ mode and (b) the excitation of a higher mode. In both figures, the action of acoustic and optical phonons can clearly be distinguished. Data courtesy of Manuel Katzer.

2.3.4. Nonlocal Hydrodynamic Model

At the microscopic level, the perturbation at a spatial point $\mathbf{r}$ immediately affects its surroundings. By construction, any mesoscopic, purely local theory such as the Drude model falls short of incorporating these effects.

One approach to improve this local, mesoscopic theory is to include nonlocal hydrodynamic effects in the description of the electrons at the mesoscopic level. This effectively describes the collective behavior of electrons in a system when they exhibit hydrodynamic-like flow properties. In this limit, the electrons can be described by macroscopic quantities such as density and velocity, similar to a fluid. In the hydrodynamic

limit, the electron system is governed by the hydrodynamic equations, such as the continuity equation and an Euler equation that captures the conservation of charge and momentum, respectively [246–252]. The hydrodynamic equation of motion that we will use can then be given by

$$m\partial_t \mathbf{v} + m(\mathbf{v} \cdot \nabla) \mathbf{v} = -m\gamma \mathbf{v} - e\mathbf{E} - \nabla \left[\frac{\delta G[n]}{\delta n} \right],$$

which now includes the full substantial derivative on the left-hand side and a gradient of the energy functional $G[n]$ which describes the kinetic, exchange and correlation energy of the system and effectively incorporates quantum corrections into the description. In its simplest formulation, this can be approximated by the Thomas-Fermi functional [202], which allows a formulation in terms of the internal pressure in the system [145, 253]. In a later section, we will also present an approach to derive this equation from a microscopic Boltzmann transport equation by an appropriate momentum expansion [254]. In the usual quantum hydrodynamics literature [145, 250–253, 255–257], this equation is then linearized with the assumption [249, 250]

$$\nabla \left[\frac{\delta G[n]}{\delta n} \right] \approx \frac{m\beta^2}{n_0} \nabla n_1, \quad (2.44)$$

where β is a constant usually identified as $\beta^2 = \frac{3}{5}v_F^2$ in the high-frequency limit [145], derived via the adiabatic constant in the equation of state for a Fermi gas [246, 258]. The parameter β is usually understood as the speed of sound in the considered material. With this, we obtain an equation for the polarization,

$$\frac{\beta^2}{\omega^2 + i\gamma\omega} \nabla(\nabla \cdot \mathbf{P}_1) + \mathbf{P}_1 = -\frac{\varepsilon_0\omega_p^2}{\omega^2 + i\gamma\omega} \mathbf{E}. \quad (2.45)$$

This *hydrodynamic Drude model* constitutes an extension of the standard local Drude model, Eq. (2.34), and contains a correction resulting from the inclusion of nonlocal effects, expressed in terms of spatial gradients. From Eq. (2.45), one can typically obtain the permittivity, $\varepsilon_{\mathbf{Q}}(\omega)$, by distinguishing between the longitudinal and transverse components [147, 250, 253, 259] in Fourier space [140, 146, 260–263],

$$\varepsilon_{\mathbf{Q}}^L(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\gamma\omega - \beta^2|\mathbf{Q}|^2}. \quad (2.46)$$

This means that the electron pressure contribution affects the $\mathbf{Q}$ modes in a generalized nonlocal optical response (GNOR) theory [151] that affects only the longitudinal component while leaving the transverse component invariant. The inclusion of these terms becomes apparent for small particles with large surface-to-volume ratios, where a blue shift of the nanoparticle resonance can be observed [264]. This approach is also applicable to highly doped semiconductors [265] and finds applications in higher harmonic generation [152, 263].

2.3.5. Surface Response Formalism

In contrast to the previous section, where nonlocality was incorporated as an additional term in the differential equation, cf. Eq. (2.45), this section presents the surface response

formalism. This formalism incorporates (quantum) corrections to the local response approximation (LRA) solely via the boundary conditions, while leaving the differential equations unchanged [252]. As demonstrated in Ref. [155], this formulation effectively represents nonlocal and quantum corrections as an infinitely thin dipole layer surrounding the structure and has been shown to agree well with calculations in time-dependent density functional theory (TDDFT). Ref. [154] establishes that these boundary conditions are given by

$$D_{\perp}^{+} - D_{\perp}^{-} = d_{\parallel} \nabla \cdot (\mathbf{D}_{\parallel}^{+} - \mathbf{D}_{\parallel}^{-}), \quad (2.47a)$$

$$B_{\perp}^{+} - B_{\perp}^{-} = 0, \quad (2.47b)$$

$$\mathbf{E}_{\parallel}^{+} - \mathbf{E}_{\parallel}^{-} = -d_{\perp} \nabla_{\parallel} (E_{\perp}^{+} - E_{\perp}^{-}), \quad (2.47c)$$

$$\mathbf{H}_{\parallel}^{+} - \mathbf{H}_{\parallel}^{-} = i\omega d_{\parallel} (\mathbf{D}_{\parallel}^{+} - \mathbf{D}_{\parallel}^{-}) \times \hat{\mathbf{n}}. \quad (2.47d)$$

Here, $d_{\perp}$ and $d_{\parallel}$ represent the Feibelman d -parameters [136, 153, 266], which are defined as [153, 252]

$$d_{\perp}(\omega) = \frac{\int dx x \rho_{\text{ind}}(x)}{\int dx \rho_{\text{ind}}(x)}, \quad (2.48a)$$

$$d_{\parallel}(\omega) = \frac{\int dx x \partial_x J_y^{\text{ind}}(x, \omega)}{\int dx \partial_x J_y^{\text{ind}}(x, \omega)}. \quad (2.48b)$$

It is important to note that we adopt the description provided in Ref. [156], which clearly distinguishes between the equilibrium charge density ρ_0 and the induced charge density ρ^{ind} that the system exhibits in response to an external perturbation. This distinction is made to avoid confusion with the description used in later parts of this thesis, where we will refer to ρ^{ind} as ρ_1 . The quantities denoted by $d_{\parallel}$ and $d_{\perp}$ correspond, respectively, to the effective mesoscopic surface charge density and its first moment. The latter can also be interpreted as the center position of the induced charge density with respect to the jellium edge [202].

These parameters capture the dynamics at the surface region characterized by electron gas inhomogeneities, while classical (local) response functions describe the bulk behavior. The formulation based on the Feibelman d -parameters exhibits considerable strength, enabling the incorporation of nonlocality, electronic spill-out (or equivalently “spill-in”), and surface-enabled Landau damping effects [202, 252]. As such, this formulation overcomes the limitations of local theories highlighted by Feibelman [153], in particular discontinuity and locality. Notably, this framework has recently been applied successfully to describe various experimental and TDDFT scenarios [262, 267–269]. For a more detailed introduction, the interested reader may be referred to Refs. [156, 252]

2.3.6. Interband Transitions

So far, the description has been limited to including intraband transitions via the Drude model [119], which provides a good approximation of material properties over a certain spectral range. However, for noble metals (Au, Ag, Cu) it becomes necessary to include interband transitions in the description when studying the high-energy side of the visible spectrum [270]. The specific energy at which interband transitions become significant varies with the material. According to Ref. [271], interband transitions become important above $\gtrsim 2.1$ eV for copper, $\gtrsim 2.47$ eV for gold, and $\gtrsim 3.8$ eV for silver.

For energies below these values, a description based purely on the Drude model is sufficient to represent the macroscopic permittivity of the material, as shown by comparison with experimental data from Refs. [272, 273]. Therefore, the Drude model provides a reliable approximation for describing the optical properties of noble metals in the lower energy regime. However, as interband transitions become relevant in the visible regime, which is the focus of this work, it becomes essential to account for them in order to obtain accurate material descriptions.

As permittivities are additive, we may add contributions from interband transitions modeled as Lorentzian oscillators. Mostly, these interband transitions are modeled as Lorentzian oscillators, leading to the full permittivity,

$$\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega(\omega + i\gamma)} - \sum_{i=1}^N \frac{f_i \omega_i^2}{\omega^2 - \omega_i^2 + i\gamma_i \omega}, \quad (2.49)$$

where ω_i is the resonance frequency, f_i is the oscillator strength, and γ_i is the damping of the i th Lorentz oscillator. The parameter N denotes the number of interband transitions incorporated into the model. Depending on the material system and the desired level of accuracy, it may be necessary to include one or more interband transitions. Several authors in the literature have used different numbers of incorporated interband transitions, ranging from only one to up to eight [274–280]. The choice of the number of interband transitions is determined by numerical simplicity and the desired accuracy of the model.

Another analytical model proposed by Ref. [277, 281] utilizes a critical point transition model, cf. [276], which includes two interband transitions,

$$\varepsilon_{\text{Au}}(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega(\omega + i\gamma)} + \sum_{i=1,2} A_i \omega_i \left[\frac{e^{i\phi_i}}{\omega_i - \omega - i\gamma_i} + \frac{e^{-i\phi_i}}{\omega_i + \omega + i\gamma_i} \right]. \quad (2.50)$$

Here A_i represents the amplitudes, ω_i the resonance frequencies, and γ_i the damping rates, as already described in Eq. (2.49). This approach allows the description of asymmetric line shapes of the interband resonances and provides a better description of the experimental results compared to other publications, considering the number of fitting parameters.

However, it is essential to emphasize that all the models presented are essentially phenomenological fit models, and their parameters are adjusted to match the available experimental data from Ref. [272]. As a result, these models provide limited direct physical information, since no actual physical meaning is conveyed through the fit parameters. The fitting parameters for the critical point transition model for gold can be found in Tab. A.1.

2.4. Plasmonics - Geometrical Effects

In the previous section, we presented a comprehensive analysis of the plasmonic response of bulk materials, i.e., the system was assumed to be translationally invariant. There,

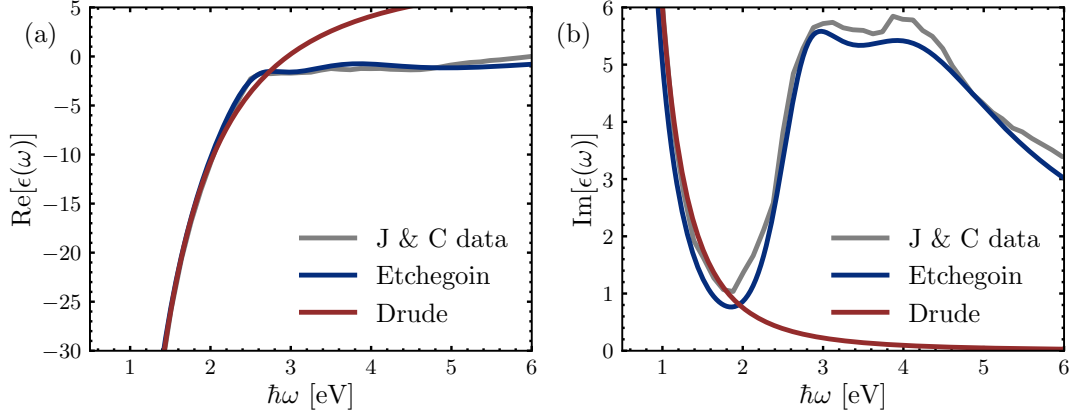


Figure 2.8.: **Gold Permittivity.** Comparison of the Johnson and Christy data [272] for the permittivity of gold in the optical regime with analytical fits obtained using the Drude model (fit parameters from Ref. [274]), and the critical point model from Ref. [277].

the behavior of the material was characterized by the plasma frequency ω_p in the Drude model. Now, in this section, we consider the effect of geometry and explore the two fundamental excitations in plasmonics - localized surface plasmons (LSPs) and surface plasmon polaritons (SPPs).

The first of these excitations, SPPs, are propagating and dispersive electromagnetic waves coupled to the electron plasma of a conductor at a dielectric interface. In contrast, LSPs are non-propagating excitations of the conduction electrons in metallic nanostructures. Here, the spatial confinement imposed by the surface of the nanoparticle exerts an effective restoring force on the driven electrons, resulting in a resonance phenomenon that leads to significant field enhancement both inside the nanoparticle and in the near-field zone outside it.

2.4.1. Localized Surface Plasmons (LSP)

The first geometry resonance we will consider are localized surface plasmons, also known as localized plasmons or simply plasmons in our context. These resonances arise naturally in the scattering of small conductive nanoparticles when exposed to oscillating electromagnetic fields. Their optical response is well characterized using Mie scattering [1, 201, 270, 282], but more sophisticated approaches using quasinormal modes also describe these plasmonic resonators well [126–128].

The remarkable advantage of LSPs lies in their ability to generate tremendous near-field field enhancements outside the particle, opening up promising technological applications. By controlling the size and shape of nanoparticles, the localized surface plasmon resonance can be finely tuned, allowing the design of novel materials with unique optical properties. This versatility leads to a wide range of applications [71, 144, 283], including nanoscale optical [284], biosensors [87], energy harvesting [67, 285–287], and even cancer treatment through photothermal therapy [288–290].

Another advantage of LSPs is their ability to be directly excited from the far field,

which distinguishes them from propagating SPPs, which cannot be easily excited from the far field.

2.4.2. Mie Scattering

In his pioneering work in 1908 [1], Gustav Mie formulated the solution to Maxwell's equations for the scattering of an electromagnetic wave by a sphere. This seminal work, aimed at describing colloidal gold solutions, laid the foundation for understanding how electromagnetic radiation interacts with particles, now known as Mie scattering or Mie theory.

Mie theory involves a complex mathematical treatment that allows the calculation of different scattering coefficients for arbitrarily complex modes. In our context, we will limit the discussion to a sphere much smaller than the wavelength of the incident light. However, we will also discuss how this treatment can be extended to more complex objects.

Assuming that the scattered field in the far field approaches a transverse radial wave, the relation between the incident electric field $\mathbf{E}^{\text{inc}}$ and the scattered electric field $\mathbf{E}^{\text{scat}}$ is usually expressed in terms of the *amplitude scattering matrix*,

$$\begin{pmatrix} E_{\parallel}^{\text{scat}} \\ E_{\perp}^{\text{scat}} \end{pmatrix} = \frac{e^{ik(r-z)}}{-ikr} \begin{pmatrix} S_2 & S_3 \\ S_4 & S_1 \end{pmatrix} \cdot \begin{pmatrix} E_{\parallel}^{\text{inc}} \\ E_{\perp}^{\text{inc}} \end{pmatrix}. \quad (2.51)$$

This treatment is typically extended and formulated in terms of the *Stokes parameters* I_s , Q_s , U_s , and V_s . However, in this discussion we will not go into the details and instead refer the interested reader to Refs. [201, 270].

This extended treatment makes it possible to derive the extinction, absorption, and scattering cross sections using the Poynting vector for arbitrary geometries. For the specific case of a sphere, the symmetry of the problem allows us to expand the solutions of the scalar wave equation in terms of spherical harmonics and spherical Bessel functions [1, 270]. Under the use of the boundary conditions that the tangential components are continuous,

$$(\mathbf{E}_{\text{inc}} + \mathbf{E}_{\text{scat}} - \mathbf{E}_{\text{in}}) \times \mathbf{e}_r = 0, \quad (\mathbf{H}_{\text{inc}} + \mathbf{H}_{\text{scat}} - \mathbf{H}_{\text{in}}) \times \mathbf{e}_r = 0, \quad (2.52)$$

one can accurately analyze the scattering, absorption, and extinction phenomena of the incident electromagnetic wave interacting with the spherical particle. To achieve this, one usually derives equations for the expansion coefficients of the individual field components, cf. Ref. [201, 270, 282, 291–294]. These equations allow the inclusion of higher multipole orders, but for our purposes we will limit ourselves to the dipolar case.

For this order, the induced dipole moment $\mathbf{p}$ in response to the external electric field $\mathbf{E}$ can be expressed in terms of the polarizability α of the object. For the isotropic case, the polarizability is a scalar quantity and the equation simply reads

$$\mathbf{p} = \alpha(\omega) \cdot \mathbf{E}. \quad (2.53)$$

In a general treatment using Mie scattering, the expansion coefficients can be related to the polarizability of the sphere. The polarizability α is given by the formula $\alpha = \frac{3}{2k^3} t_1^E$, where t_ℓ^E is determined as follows

$$t_\ell^E = \frac{-j_\ell(\rho_0)\alpha_\ell^E + [\rho_0 j_\ell(\rho_0)]' \beta_\ell^E}{h_\ell^{(+)}(\rho_0)\alpha_\ell^E - [\rho_0 h_\ell^{(+)}(\rho_0)]' \beta_\ell^E}. \quad (2.54)$$

In this equation, we used the definitions $\alpha_\ell^E = \varepsilon_0[\rho_1 j_\ell(\rho_1)]'$, $\beta_\ell^E = \varepsilon_1 j_\ell(\rho_1)$, and $\rho_\ell = k_j a$ with j_ℓ being the spherical Bessel functions and $h_\ell^{(+)}$ representing the Hankel functions of the first kind. The prime notation denotes a derivative with respect to the argument, and $k_j = k\sqrt{\varepsilon_j \mu_j}$. For our purposes of a non-magnetic material, we will always assume $\mu_j = 1$.

From a series expansion of the spherical Bessel functions for the case of a sphere with a small size compared to the wavelength, $\rho_\ell \ll 1$, we can obtain a simplified result for the polarizability

$$\alpha(\omega) = 4\pi\varepsilon_0\varepsilon_{\text{out}}r^3 \frac{\varepsilon(\omega) - \varepsilon_{\text{out}}}{\varepsilon(\omega) + 2\varepsilon_{\text{out}}}. \quad (2.55)$$

The fraction in this expression is commonly referred to as the *Clausius-Mosotti factor*, which also arises from the problem of a sphere embedded in a uniform static electric field [201, 270]. In the equation, $\varepsilon(\omega)$ is the permittivity of the sphere, ε_{out} is the surrounding permittivity, and $\mathbf{r}$ is the radius of the sphere. Because of this similarity, this approximation is often referred to as the *quasi-static approximation*. This simplified expression provides a useful and practical way of describing the polarizability of a small sphere and gives qualitatively good results for spheres much smaller than the wavelength without the need for complex calculations involving full Mie scattering theory.

The spectral position of the localized surface plasmon resonance is typically obtained using the Fröhlich condition $\text{Re}[\varepsilon(\omega)] + 2\varepsilon_{\text{out}} = 0$ [51, 201, 252, 279]. This condition allows us to find the roots of the denominator, which correspond to the singularities of the polarizability. As a result, we obtain what is commonly referred to as the plasmon frequency

$$\omega_{\text{LSP}} = \frac{\omega_p}{\sqrt{\varepsilon_\infty + 2\varepsilon_{\text{out}}}}, \quad (2.56)$$

from which we can straightforwardly calculate the resonance position. The polarizability in Eq. (2.55) generalizes to spheroids as well [201, 270, 295]. In this context, we present the specific expressions for an oblate spheroid that we will use in Ch. 3, where the x and y semi-axes are equal, and the z semi-axis is shorter, as depicted in Fig. 2.9(a). Here, the polarizability becomes a diagonal tensor denoted by $\boldsymbol{\alpha}(\omega)$, with its diagonal components given by [270, 295]

$$\alpha_i(\omega) = 4\pi\varepsilon_0\varepsilon_{\text{out}} \frac{r_x r_y r_z}{3} \frac{\varepsilon_{\text{Au}}(\omega) - \varepsilon_{\text{out}}}{L_i \varepsilon_{\text{Au}}(\omega) + \varepsilon_{\text{out}}(1 - L_i)}. \quad (2.57)$$

This expression is what we will refer to as *Mie-Gans theory* [1, 295]. The aspect ratio and such the lengths of the spheroid's semi-axes, r_i , determine the strength of the individual components via the depolarization factors L_i , which change the optical

response via the respective semi-axes [270, 281],

$$L_x = L_y = \frac{1}{2e_0^2} \left(\frac{\sqrt{1-e_0^2}}{e_0} \arcsin(e_0) - (1-e_0^2) \right), \quad (2.58a)$$

$$\text{and } L_z = \frac{1}{e_0^2} \left(1 - \frac{\sqrt{1-e_0^2}}{e_0} \arcsin(e_0) \right). \quad (2.58b)$$

For the oblate spheroid, the x and y component coincide due to symmetry. The eccentricity e_0 is defined to be

$$e_0 = 1 - \frac{r_z^2}{r_{xy}^2}. \quad (2.59)$$

Tuning the aspect ratio of the nanoparticle, the resonance of the localized plasmon can be tuned over a wide spectral range as we illustrate in Fig. 2.9(b).

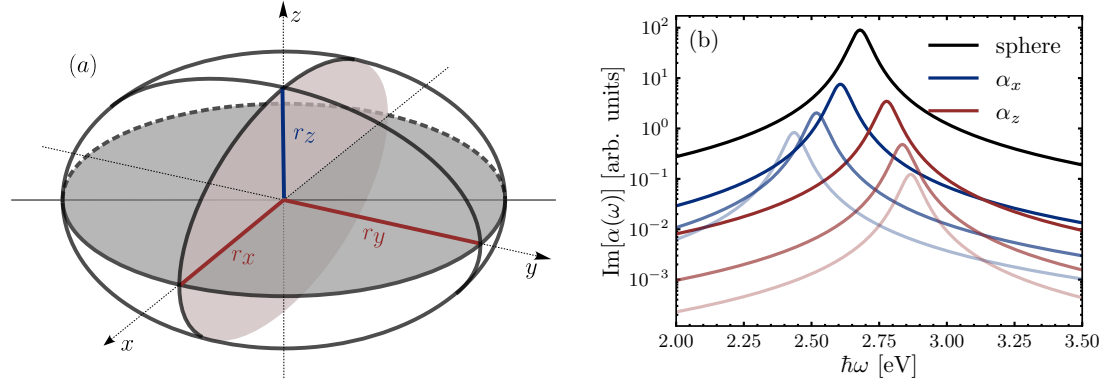


Figure 2.9.: **Resonance Behavior of Gold Spheroid under Changing Aspect Ratio.** (a) depicts the semi-axes of an oblate spheroid. (b) illustrates the imaginary part of the x and z components of a spheroid, varying the aspect ratio from 1 (sphere) to 2 : 1, 3 : 1, and 4 : 1. As the aspect ratio increases, a significant redshift of the α_x resonance is observed, while a blue shift is noticeable in the α_z resonance.

2.4.3. Nonlocal Mie Theory

In the Drude model, one usually assumes locality and hard wall boundary conditions for the electrons within the nanoparticle, i.e., no spill-out beyond its surface. However, by relaxing this assumption and considering nonlocal effects through the hydrodynamic equation, Eq. (2.45), it has been shown in Ref. [264] that the concentration of excited electrons is no longer confined to the nanoparticle surface. Instead, it extends into the nanoparticle, effectively smoothing the electron distribution.

As a consequence of these nonlocal effects, an update of the polarizability described in Eq. (2.55) is necessary,

$$\alpha(\omega) = 4\pi\epsilon_0\epsilon_{\text{out}}r^3 \frac{\epsilon(\omega) - \epsilon_{\text{out}}(1 + \delta_{\text{NL}})}{\epsilon(\omega) + 2\epsilon_{\text{out}}(1 + \delta_{\text{NL}})}, \quad (2.60)$$

where

$$\delta_{\text{NL}} = \frac{\varepsilon(\omega) - \varepsilon_\infty}{\varepsilon_\infty} \frac{j_1(k_{\text{NL}}r)}{k_{\text{NL}}r j_1'(k_{\text{NL}}r)}, \quad k_{\text{NL}}^2 = \frac{\omega^2 + i\gamma\omega - \omega_p^2/\varepsilon_\infty}{\beta^2}. \quad (2.61)$$

In this context, k_{NL} is the nonlocal longitudinal wave vector, while $\beta^2 = \frac{3}{5}v_F^2$, as discussed in Sec. 2.3.4. In the limit where $\beta \rightarrow 0$, the term $\delta \rightarrow 0$ also vanishes. Accordingly, we approach the local theory as expected. In Fig. 2.10, in analogy to Ref. [264], we plot the normalized extinction cross section,

$$\sigma_{\text{ext}}(\omega) = \frac{1}{\pi r^2} \left[\frac{1}{6\pi} \left(\frac{\omega}{c} \right)^4 |\varepsilon_0^{-1} \alpha_{\text{NL}}(\omega)|^2 + \frac{\omega}{c} \text{Im}[\varepsilon_0^{-1} \alpha_{\text{NL}}(\omega)] \right] \quad (2.62)$$

In Fig. 2.10 we can observe that for small particle radii the resonance position is significantly blueshifted. As the particle radii increase, the resonance gradually approaches the value obtained from local Mie theory, $\omega_{\text{LSP}} \rightarrow \frac{\omega_p}{\sqrt{3}}$. From this observation, we can conclude that hydrodynamics play a crucial role for metal nanoparticles, in particular those with large surface-to-volume ratios. As the surface area becomes dominant relative to the volume, the impact of hydrodynamic effects becomes increasingly important, leading to significant deviations from local Mie theory predictions.

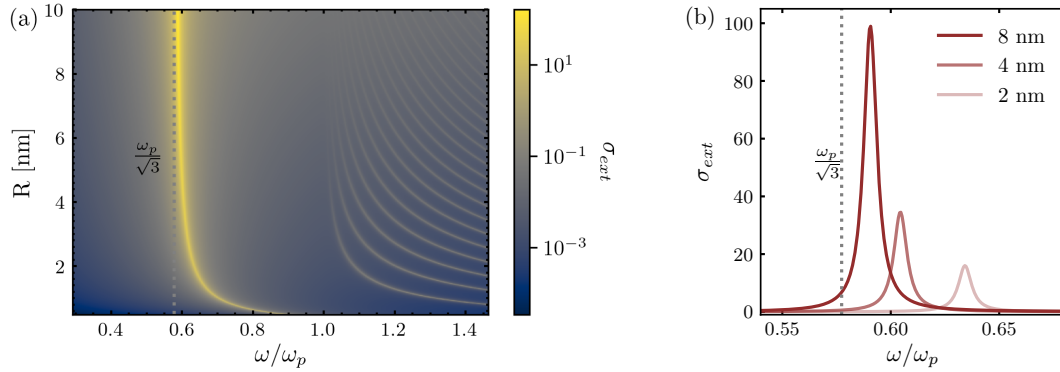


Figure 2.10.: **Extinction Cross Section from Nonlocal Polarizability.** The figure presents the extinction cross section, calculated using Eq. (2.62), so that the extinction cross section is unitless to compare different radii. (a) The prominent golden line refers to the localized surface plasmon (LSP) resonance and shows a significant shift of the resonance position. At higher energies, one additionally observes peaks resulting from the spherical Bessel function in Eq. (2.61). (b) We show the extinction cross section for individual particle radii.

2.4.4. Self-Consistent Electric Field Approach

In order to treat the self-consistent electric field $\mathbf{E}_{\text{tot}}$ inside the sphere, we use Mie theory to incorporate the geometric boundary conditions resulting from the dielectric environment. We distinguish between the externally applied field $\mathbf{E}_{\text{ext}}$, the background polarization of the sphere $\mathbf{P}_\infty$ and the Drude polarization $\mathbf{P}_d$ of the conduction electrons inside the sphere. In the following, we denote the dielectric constants of the inner and

outer environment of the MNP by ε_∞ and ε_{out} . The self-consistent field within the nanoparticle then reads [296]

$$\mathbf{E}_{\text{tot}} = \mathbf{E}_{\text{ext}} - \frac{1}{3\varepsilon_0\varepsilon_{\text{out}}}\mathbf{P}_\infty - \frac{1}{3\varepsilon_0\varepsilon_{\text{out}}}\mathbf{P}_d. \quad (2.63)$$

The background polarization density $\mathbf{P}_\infty$ is given by the total electric field in the sphere multiplied with the effective background susceptibility $\tilde{\chi}_\infty = \chi_\infty - \chi_{\text{out}} = \varepsilon_\infty - \varepsilon_{\text{out}}$. $\tilde{\chi}_\infty$ contains the correction of the susceptibility ε_∞ inside the sphere compared to the surrounding ε_{out} ,

$$\mathbf{P}_\infty = \varepsilon_0\tilde{\chi}_\infty\mathbf{E}_{\text{tot}}. \quad (2.64)$$

With this, the total field can be written as

$$\mathbf{E}_{\text{tot}} = \frac{3\varepsilon_{\text{out}}}{\varepsilon_\infty + 2\varepsilon_{\text{out}}}\left[\mathbf{E}_{\text{ext}} - \frac{1}{3\varepsilon_0\varepsilon_{\text{out}}}\mathbf{P}_d\right]. \quad (2.65)$$

The relation between Drude polarization density $\mathbf{P}_d$ and the self-consistent electric field $\mathbf{E}_{\text{tot}}$ is classically derived in Drude theory, cf. Eq. (2.36), and is given by

$$\mathbf{P}_d = -\frac{\varepsilon_0\omega_p^2}{\omega^2 + i\gamma_v\omega}\mathbf{E}_{\text{tot}}, \quad (2.66)$$

with the plasma frequency $\omega_p = \sqrt{ne^2/m\varepsilon_0}$. Inserting this definition in Eq. (2.65), an oscillator equation for the Drude polarization density in frequency space depending on the external electric field $\mathbf{E}_{\text{ext}}$ is obtained,

$$(\omega^2 + i\gamma_v\omega - \omega_{\text{LSP}}^2)\mathbf{P}_d = -3\varepsilon_0\varepsilon_{\text{out}}\omega_{\text{LSP}}^2\mathbf{E}_{\text{ext}}, \quad (2.67)$$

where we have identified the plasmon frequency,

$$\omega_{\text{LSP}} = \frac{\omega_p}{\sqrt{\varepsilon_\infty + 2\varepsilon_{\text{out}}}}, \quad (2.68)$$

and the fact that the external electric field is renormalized $\mathbf{E}_{\text{ext}} \rightarrow \frac{3\varepsilon_{\text{out}}}{\varepsilon_\infty + 2\varepsilon_{\text{out}}}\mathbf{E}_{\text{ext}}$. Eq. (2.67) shows that the geometry of our structure renormalizes the resonance frequency of our system to the plasmon frequency ω_{LSP} . As we have shown previously, this is usually derived from the resonance of the polarizability, $\alpha(\omega)$, in terms of the Fröhlich condition: $\text{Re}[\varepsilon(\omega)] + 2\varepsilon_{\text{out}} = 0$ [51, 201, 252, 279].

2.4.5. Surface Plasmon Polaritons (SPPs)

In this section, we introduce the second fundamental excitation of plasmonics - surface plasmon polaritons (SPPs). SPPs are propagating, dispersive electromagnetic waves coupled to the electron plasma of a conductor at a dielectric interface. These modes are confined at the surface below the optical wavelength and can travel along it. The variety of ways to manipulate SPPs makes them interesting for technological applications such as biomedical sensors [87] and quantum information processing schemes [297].

SPPs can be sustained in thin films and at interfaces between materials with permittivities of opposite sign [33, 66, 134, 135, 297]. In this section, we will focus on SPPs at

dielectric-metal interfaces. These SPPs are generally described by an *ansatz* for the electric and magnetic fields, which, for an interface at $z = 0$, with surrounding non-magnetic media of permittivity ε_1 and ε_2 , can be written as [135]

$$\mathbf{E}(\mathbf{r}, t) = (E_x \hat{\mathbf{x}} + E_z \hat{\mathbf{z}}) e^{-\kappa|z|} e^{i(qx - \omega t)}, \quad (2.69a)$$

$$\mathbf{B}(\mathbf{r}, t) = B_y \hat{\mathbf{y}} e^{-\kappa|z|} e^{i(qx - \omega t)}. \quad (2.69b)$$

This corresponds to a transverse magnetic (TM) solution. In the above, κ represents the confinement factor, determining the rate at which the field decays in the z direction.

Under the usual assumption of a nonmagnetic, linear medium, together with Maxwell's equations and the boundary conditions in Eq. (2.52) for the continuity of the tangential components, we obtain the typical condition for the existence of SPPs,

$$\frac{\varepsilon_1}{\kappa_1} + \frac{\varepsilon_2}{\kappa_2} = 0. \quad (2.70)$$

As can be seen from Eq. (2.70), solutions for real κ exist only if the signs of the permittivities are reversed. For this reason, SPPs are typically confined to dielectric-metal interfaces, where the permittivities have opposite signs. A similar derivation can be done for a transverse electric (TE) mode *ansatz*, but the boundary conditions, Eq. (2.52), impose that the electric field must vanish, so TE modes cannot exist in this type of system.

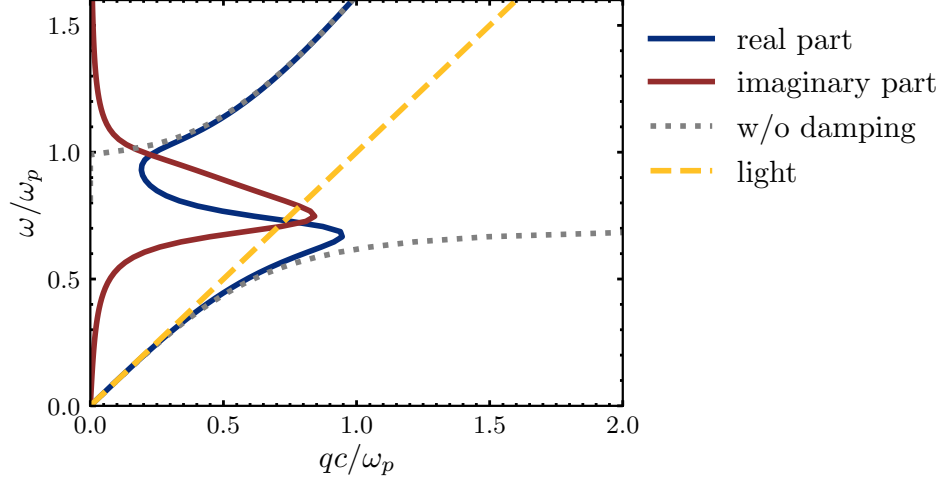


Figure 2.11.: Dispersion Relation of Surface Plasmon Polaritons (SPPs) at an Air-Metal Interface. The figure displays the dispersion relation, obtained from Eq. (2.70), for two cases: one with damping ($\gamma/\omega_p = 0.1$) and one without damping. In the undamped case, distinct upper and lower branches are observed, connected by a region where no modes can exist. The upper branch corresponds to radiative modes, while the lower branch represents SPPs confined to the interface.

Using a Drude model for the metal and $\varepsilon_1 = 1$ for the case of air, we can plot the dispersion relation for SPPs in Fig. 2.11. For frequencies, $\omega < \omega_p$, the SPP mode is observed and there is a maximum allowed value of q for this mode. On the other hand,

for frequencies $\omega > \omega_p$ the confinement factor κ becomes complex, indicating that the field begins to propagate through the bulk material in the z direction and is no longer confined at the surface.

3. Plasmon-Induced Exciton Localization and Hybridization in 2D Materials

In recent years, there has been significant interest in combining systems that support excitonic and plasmonic resonances into hybrid structures. These hybrid systems aim to take advantage of the unique properties of both excitonic and plasmonic materials, allowing for the design of novel material systems with tailored properties.

By combining excitonic and plasmonic materials in hybrid systems, the complementary properties of both types of materials can be harnessed. For example, the strong light absorption of excitonic materials can be enhanced by coupling them with plasmonic nanostructures [27, 298–300]. In these structures, various coupling regimes have been extensively studied, encompassing the weak coupling limit, the strong coupling regime, and even extending to the ultra-strong ($g > 0.1\omega$) and deep-strong coupling regime ($g > \omega$) [109, 116, 301–308]. In the ultra-strong and deep-strong coupling regimes, the light-matter interaction can no longer be treated perturbatively.

In the strong coupling regime, there has been much interest in creating joint states of excitonic and plasmonic excitations, known as *plexcitonic* states [111, 157, 160, 161, 298, 309–311]; these hybrid states can be observed in strongly interacting systems that support both excitons and plasmons. Most works have focused on systems where an excitonic system is located inside a (plasmonic) cavity to take advantage of the local field enhancement [116, 312–314]. For example, the group of Jeremy Baumberg has utilized their picocavities/particle-on-mirror systems to achieve strong exciton-plasmon interaction [108, 143, 306, 314–316], and the group of Bert Hecht mostly used their plasmonic nanoresonator [116, 117], where excitons couple to the quadrupole mode of the resonator.

In addition to the previous systems, the past few years have witnessed a significant surge in interest towards a variety of systems, in particular, systems consisting of individual nanoparticles interacting with excitonic systems, which were shown to reach the strong coupling regime without requiring a typical dipole-cavity interaction commonly used in cavity-QED [157, 160, 161, 309]: In particular, experiments revealed impressive Rabi splittings on the order of 100 meV [317–319] for systems consisting of nanorods [320], resonators [314, 321], nanodisks [318, 322], bipyramids [319] and nanocubes [317].

On the theoretical side, these interacting systems are mostly treated using a classical coupled mode theory with the interaction strength as fitting parameter [110, 318, 323]. However, there have been two recent studies that investigate the strong coupling of a metal nanorod with a TMDC monolayer [111, 324] based on a quasinormal mode analysis and quantum reaction coordinate approach, respectively, which reproduce the experimentally observed spectral splittings [318, 319, 325]. However, the modifications of the excitonic properties are so far not well investigated.

In this part of the thesis, we consider a hybrid nanostructure consisting of a spheroidal gold nanoparticle (AuNP) and a monolayer of transition metal dichalcogenides (TMDC), as illustrated in Fig. 3.1. To model this system quantitatively, both the TMDC and the

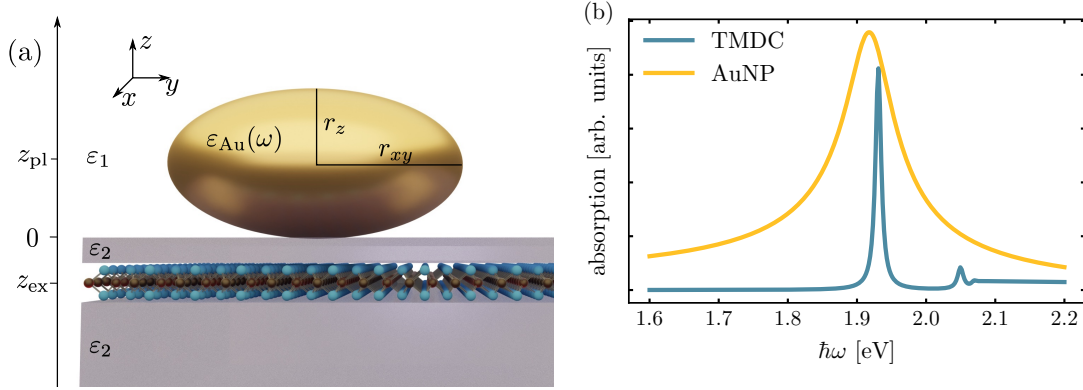


Figure 3.1.: **(a) Coupled Nanostructure.** The system consists of a gold nanoparticle (AuNP) positioned at z_{pl} and a two-dimensional TMDC monolayer at z_{ex} . The half spaces above and below the interface at $z = 0$ have constant background permittivity values ε_1 and ε_2 , respectively. The eccentricity of the AuNP can be adjusted, influencing the interaction strength. **(b) Absorption spectra of constituents.** The figure displays the absorption spectrum of a MoSe₂ monolayer (blue), calculated using the microscopic approach presented in this chapter, and the polarizability of a spheroidal AuNP (gold) individually, calculated using the permittivity function from Ref. [277] and Mie theory [1, 295].

AuNP are encapsulated in two different media with homogeneous and isotropic permittivities ε_1 and ε_2 , respectively. In contrast to previous works, we treat the entire system using a semi-classical microscopic model based on the framework of Maxwell-Heisenberg equations of motion. We analytically identify an eigenvalue equation in the composite system, which describes the center-of-mass motion of the excitons in the potential induced by the plasmonic excitation. Our derived eigenvalue equation can be used to drastically reduce the numerical complexity of the problem, and offers new physical insight into the character of the hybridization. As an example, it allows us to connect to the strong coupling limit with the occurrence of bound exciton states induced by the AuNP.

This chapter is organized as follows: we start with a description of the quantum mechanical description of the carrier dynamics within monolayers of transition metal dichalcogenides. We work in the framework of second quantization (cf. Sec. 2.1) to understand the microscopic dynamics, in particular focusing on the excitonic dynamics as they are very prominent and for our range of interest sufficient to describe the dynamics within the monolayer and its optical response. Hence, we start out in Sec. 3.1 and motivate the Hamiltonian used for our system. This is succeeded by a discussion of the macroscopic polarization, which we use as an observable in Sec. 3.2 and allows us to define the macroscopic quantity, the interband polarization, for which we use Heisenberg's equation of motion to derive the full Bloch equation in an excitonic basis in Sec. 3.3.

After having introduced the excitonic subsystems, we start Sec. 3.4 with an introduction to the second subsystem — the localized plasmons — by discussing Mie-Gans theory for the AuNP in Sec. 3.4.1. We proceed with introducing a Green's function solution of Maxwell's equations in Sec. 3.4.3 that is used to couple the constituents and find equations that describe the dynamics of the coupled system. In Sec. 3.5, we discuss the occurring eigenvalue equation that characterizes the interaction within the nanoparticle

and analyze the corresponding eigenvalues and eigenvectors. In Sec. 3.6, we then study the implications of the interaction and the arising eigenstates on the macroscopic polarization within the TMDC monolayer. Section 3.7 computes the electric near-field around the nanostructures and finds a peak splitting of the excitonic and plasmonic modes that for artificially detuned exciton resonance is shown to result in an avoided crossing behavior of the two resonances. Finally, in Sec. 3.9, we provide our conclusions and discuss the utility of our analytical plexcitonic approach to describe the interaction in nanostructures and their implications on localization and strong coupling and provide two possible extensions/applications of the theory that we developed.

3.1. Hamiltonian

To describe the dynamics of excitons in the given geometry, we will employ the framework of Maxwell-Heisenberg equations of motion, based on a second quantization Hamiltonian consisting of three contributions,

$$H = H_0 + H_{\mathbf{r}\mathbf{E}} + H_C. \quad (3.1)$$

The individual contributions consist of the free Hamiltonian, denoted as H_0 , the carrier-light coupling represented by $H_{\mathbf{r}\mathbf{E}}$ in the $\mathbf{r} \cdot \mathbf{E}$ coupling scheme, and the carrier-carrier coupling mediated via Coulomb interaction, denoted as H_C . As the microscopic specifics of dephasing processes are not essential for the investigated effects, they will be introduced at the level of the equation of motions through an effective relaxation time approximation [171] to account for non-radiative scattering processes. In the following subsections, we will individually describe the terms of the Hamiltonian.

3.1.1. Free TMDC Hamiltonian

In the second quantization scheme discussed in Sec. 2.1, the **free Hamiltonian** characterizes the band structure of the system, representing the energy landscape on which carriers can move. In general, it is given by

$$H_0 = \sum_{\mathbf{k}_{\parallel} \lambda} \epsilon_{\mathbf{k}_{\parallel}}^{\lambda} \lambda_{\mathbf{k}_{\parallel}}^{\dagger} \lambda_{\mathbf{k}_{\parallel}}. \quad (3.2)$$

Throughout this chapter, we use an abbreviated notation, since all our operators are fermionic. The standard creation and annihilation operators, $a^{\dagger}$ and a , are replaced by $\lambda^{\dagger}$ and λ . Here, λ can be seen as a compound index comprising the band and spin quantum numbers, with $\epsilon_{\mathbf{k}_{\parallel}}^{\lambda}$ representing the dispersion of the respective band. The second index, $\mathbf{k}_{\parallel}$, denotes the in-plane carrier momentum. The full band structure, as shown in Figure 2.3, exhibits a minimum (maximum) at the K/K' points for the conduction (valence) band. This allows us to approximate the dispersion as parabolic around the K/K' points, which we will utilize throughout this thesis. As mentioned in Sec. 2.2, the approximation shown in Fig. 3.2 reveals a slight spin-splitting of the band structure in both valleys due to spin-orbit coupling [326]. Consequently, an effective eight-band model well-describes the dynamics [11, 189, 327]. A plot of this approximation, which is referred to as the effective eight band model, can be found in Fig. 3.2. Since the spin-splitting of the

valence band is approximately one order of magnitude larger than that of the conduction band [188, 328, 329], it is in most cases reasonable to consider the conduction band as spin-degenerate. Interestingly, the order of the bands is reversed in terms of spin between K and K' valley [330, 331].

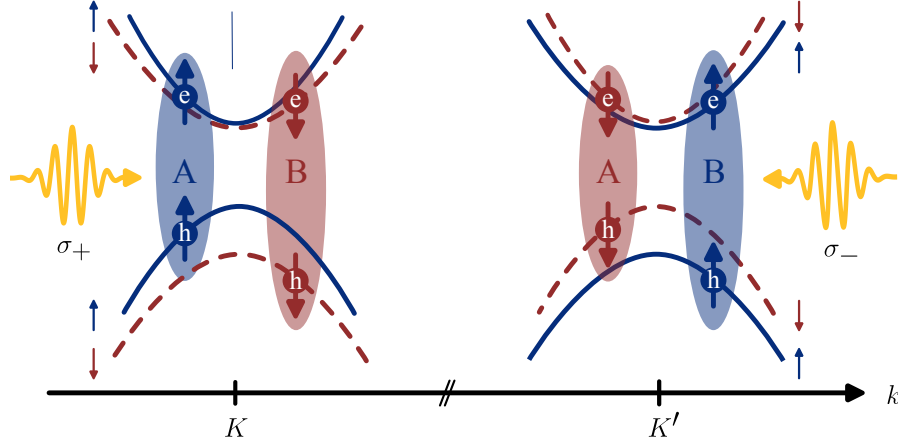


Figure 3.2.: **Effective Parabolic Eight Band Model for the TMDC Band Structure.** Due to spin-orbit coupling, valence and conduction band are spin-split, resulting in eight different bands. The band gap E_G corresponds to the energy difference of bands with the same spin. Optical transitions at the K/K' points can only be excited by σ_+/σ_- polarized light (circular dichroism) which makes them interesting for device applications [330, 331].

3.1.2. Carrier-Light Interaction

In the field of nano-optics, our focus lies in studying how electromagnetic radiation interacts with various materials at the nanoscale. Since the dimensions of these materials are small, a quantum description of the material properties becomes necessary. Similarly, the electromagnetic radiation itself can be described using a quantum theory [172]. However, in many instances, classical field theory, which is based on Maxwell's equations, proves sufficient in explaining the observed effects. Therefore, we will operate within the framework of a semi-classical theory in the following, which combines a classical representation for the electromagnetic radiation fields with a quantum theory for matter based on a second quantization approach [170, 332].

In this semi-classical description of light-matter interaction, two equivalent formalisms are commonly employed [333]. These formalisms, known as $\mathbf{p} \cdot \mathbf{A}$ and $\mathbf{r} \cdot \mathbf{E}$ coupling, differ in terms of which field quantity is coupled to which matter quantity. These formalisms have been used in our group mostly interchangeably over the years [28, 29, 180, 243, 245, 334–336]. In this thesis, we adopt the $\mathbf{r} \cdot \mathbf{E}$ coupling formalism, where the position $\mathbf{r}$ is coupled to the electric field $\mathbf{E}$ through the Hamiltonian, which can be derived using various methods. The interested reader shall be referred to Refs. [333, 337] for a derivation based on the Power-Zienau-Wooley transformation framework. For our purposes, we adopt the final definition of the carrier-light Hamiltonian in $\mathbf{r} \cdot \mathbf{E}$ coupling, given by

$$\hat{H}_{\mathbf{r}\mathbf{E}} = -\frac{1}{A} \sum_{\mathbf{k}_{\parallel}, \mathbf{Q}_{\parallel}} \mathbf{d}_{\mathbf{k}_{\parallel}, \mathbf{k}_{\parallel} - \mathbf{Q}_{\parallel}}^{\lambda\bar{\lambda}} \cdot \mathbf{E}_{\mathbf{Q}_{\parallel}}(z_{\text{ex}}) \lambda_{\mathbf{k}_{\parallel}}^{\dagger} \bar{\lambda}_{\mathbf{k}_{\parallel} - \mathbf{Q}_{\parallel}}, \quad (3.3)$$

where we defined the dipole matrix element $\mathbf{d}_{\mathbf{k}_{\parallel}, \mathbf{k}_{\parallel} - \mathbf{Q}_{\parallel}}^{\lambda\bar{\lambda}}$ as the expectation value of the position operator

$$\mathbf{d}_{\mathbf{k}_{\parallel}, \mathbf{k}_{\parallel} - \mathbf{Q}_{\parallel}}^{\lambda\bar{\lambda}} = -\frac{e}{\Omega} \int_{\Omega} d^2\mathbf{r}_{\parallel} u_{\lambda\mathbf{k}_{\parallel}}^*(\mathbf{r}) \mathbf{r} u_{\bar{\lambda}\mathbf{k}_{\parallel} - \mathbf{Q}_{\parallel}}(\mathbf{r}). \quad (3.4)$$

Here, e is the elementary charge, $u_{\lambda\mathbf{k}_{\parallel}}(\mathbf{r})$ are the lattice periodic functions in the Bloch expansion, and $\mathbf{E}_{\mathbf{Q}_{\parallel}}(z_{\text{ex}}) = \int d^2\mathbf{Q}_{\parallel} e^{-i\mathbf{Q}_{\parallel} \cdot \mathbf{r}_{\parallel}} \mathbf{E}(\mathbf{r}; \omega)$ is the Fourier component of the electric field with in-plane wave vector $\mathbf{Q}_{\parallel}$ at the position of the TMDC layer z_{ex} . Characteristically for TMDCs, their interaction with light exhibits circular dichroism, meaning that σ_{+}/σ_{-} light can only excite optical transitions in the K/K' valley [10, 11]. Thus, we find two possible optical transitions per valley that obey spin-conservation. Due to the spin-splitting, they differ in energy and will be labeled A exciton for the transition of lower energy and B exciton for the transition of higher energy, cf. Fig. 3.2. Assuming that the matrix elements are known, this prescription allows a straightforward description of the light-matter interaction. Unfortunately, the computation of the optical dipole matrix elements requires the knowledge of the lattice periodic functions, $u_{\bar{\lambda}\mathbf{k}_{\parallel}}(\mathbf{r})$ which can be obtained from explicit solution of the Schrödinger equation in density functional theory [11].

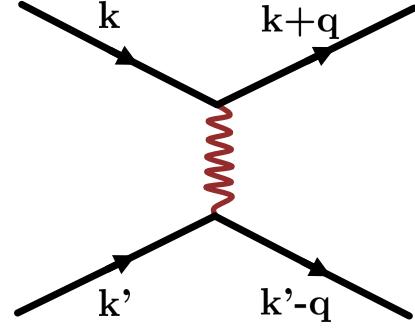


Figure 3.3.: **Illustration of Coulomb-Mediated Electron-Electron Scattering Process.** Schematic illustration of the momentum transfer process between two carriers with initial momenta $\mathbf{k}$ and $\mathbf{k}'$, exchanging momentum $\mathbf{q}$ through Coulomb interaction.

3.1.3. Carrier-Carrier Interaction

In this thesis, our focus is on the **carrier-carrier coupling** mediated through Coulomb interaction, which plays a dominant role in TMDC monolayers and is responsible for exciton formation. The Coulomb interaction is quantized using a two-particle operator, given by

$$H_C = \frac{1}{2} \sum_{\substack{\mathbf{k}_{\parallel}, \mathbf{k}'_{\parallel}, \mathbf{q}_{\parallel} \\ \lambda\lambda'}} V_{\mathbf{q}_{\parallel}} \lambda_{\mathbf{k}_{\parallel} + \mathbf{q}_{\parallel}}^{\dagger} \lambda_{\mathbf{k}'_{\parallel} - \mathbf{q}_{\parallel}}^{\dagger} \lambda'_{\mathbf{k}'_{\parallel}} \lambda_{\mathbf{k}_{\parallel}}, \quad (3.5)$$

with the Coulomb matrix element $V_{\mathbf{q}_{\parallel}}$ which can be derived as the Fourier component of the Coulomb interaction in the respective geometry, which we illustrate at the end of this section. For details on the quantization process for two-particle quantities, please refer to references [170, 171, 338]. This Hamiltonian describes an effective transfer of momentum $\mathbf{q}_{\parallel}$ between two carriers with momenta $\mathbf{k}_{\parallel}$ and $\mathbf{k}'_{\parallel}$. This momentum conserving process is mediated via Coulomb interaction, as depicted in Fig. 3.3.

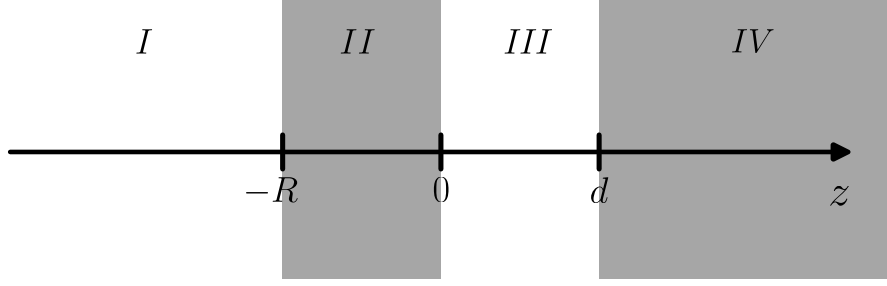


Figure 3.4.: **Schematic of the Four-Layer System.** This figure illustrates the four-layer configuration required to derive the Rytova potential for our geometry, cf. Fig. 3.1. The dimensions of each layer are provided, with layer III representing the TMDC layer.

Rytova-Keldysh Potential

The carrier-carrier potential $V_{\mathbf{q}_{\parallel}}$ is given by the Coulomb interaction of the interacting carriers. For the case of the effectively two-dimensional TMDC, this interaction is only screened within the monolayer and can propagate more freely in the adjacent materials. Thus, the Coulomb interaction in 2D materials is only weakly screened and results in strong electron-hole interaction and formation of excitons, which explains the dominance of excitonic effects in these materials. Accordingly, neither a pure 2D nor a 3D description is appropriate, and hence we follow the approach taken by Rytova in Ref. [22] and later by Keldysh in Ref. [23] to calculate the potential by considering a thin material encapsulated in between two areas of constant permittivity. The potential can be viewed as an effective 3D potential for large momenta and a 2D potential for small momenta, with an interpolation between the two in the mid-range [339–341]. In our geometry, which can be effectively represented as a four-layer system, cf. Fig. 3.1, we incorporate an additional layer compared to the standard Rytova case to provide a more accurate quantitative description of the optical response of the TMDC layer, which is strongly influenced by the substrate. However, the qualitative characteristics described earlier will remain unchanged. The potential for a system as depicted in Fig. 3.4 reads

$$V_{\mathbf{q}_{\parallel}}(z, z') = -\frac{e}{2\varepsilon_0\varepsilon_i q_{\parallel}} \left\{ e^{-q_{\parallel}|z-z'|} + \frac{1}{e^{2q_{\parallel}d} - \delta_{34}\delta_{31}} \right. \\ \left. \times \left[2\delta_{31}\delta_{34} \cosh q_{\parallel}(z - z') + e^{q_{\parallel}d} \left(\delta_{34}e^{q_{\parallel}(z+z'-d)} + \delta_{31}e^{-q_{\parallel}(z+z'-d)} \right) \right] \right\}, \quad (3.6)$$

with the definitions

$$\delta_{31} = \frac{\varepsilon_3 - \varepsilon_2 \Delta_{21}}{\varepsilon_3 + \varepsilon_2 \Delta_{21}}, \quad \Delta_{21} = \frac{e^{2kR} - \delta_{21}}{e^{2kR} + \delta_{21}}, \quad \delta_{21} = \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1 + \varepsilon_2}, \quad \delta_{34} = \frac{\varepsilon_3 - \varepsilon_4}{\varepsilon_3 + \varepsilon_4}. \quad (3.7)$$

Here, d is the thickness of the TMDC layer and R the thickness of the adjacent layer, cf. Fig. 3.4. This potential resembles the typical Rytova-type potential, which we were using multiple times throughout my PhD journey. In App. E.2, we generalize this expression to a system consisting of N layers, which might become useful to describe the Coulomb potential in artificially designed heterostructures.

3.2. Macroscopic TMDC Polarization

Now that we have discussed the Hamiltonian of our system, the remaining question is which observable we need to define to describe the excitonic dynamics within the TMDC monolayer. Here, we start from a macroscopic, experimentally accessible perspective and relate that to a microscopic quantity: The physical quantity which can be related to experiments is the macroscopic polarization, $\mathbf{P}(\mathbf{r}, t)$, from which one can derive the material susceptibility $\chi(\omega)$. In comparison with a general Hamiltonian [201, 333], we can define the macroscopic polarization as the functional derivative of the Hamiltonian density

$$H = - \int d^3\mathbf{r} \mathbf{P}(\mathbf{r}, t) \cdot \mathbf{E}(\mathbf{r}, t) \quad \text{and} \quad \mathbf{P}(\mathbf{r}, t) = -\nabla_{\mathbf{E}} \mathcal{H}(\mathbf{r}, t). \quad (3.8)$$

We want to use this expression on the semi-classical light-matter Hamiltonian in Eq. (3.5), which we Fourier transform and make three-dimensional utilizing a delta distribution so that it can be written as

$$H = - \int d^3\mathbf{r} \left[\frac{1}{A} \sum_{\mathbf{k}_{\parallel}, \mathbf{Q}_{\parallel}} \delta(z - z_{\text{ex}}) e^{-i\mathbf{Q}_{\parallel} \cdot \mathbf{r}_{\parallel}} \mathbf{d}_{\mathbf{k}_{\parallel}, \mathbf{k}_{\parallel} - \mathbf{Q}_{\parallel}}^{\lambda\bar{\lambda}} \lambda_{\mathbf{k}_{\parallel}}^{\dagger} \bar{\lambda}_{\mathbf{k}_{\parallel} - \mathbf{Q}_{\parallel}} \right] \cdot \mathbf{E}(\mathbf{r}). \quad (3.9)$$

The expression in parentheses corresponds to the Hamiltonian density, $\mathcal{H}(\mathbf{r}, t)$ which allows us to identify the macroscopic polarization operator after taking the quantum mechanical expectation value,

$$\mathbf{P}(\mathbf{r}, t) = \delta(z - z_{\text{ex}}) \frac{1}{A} \sum_{\mathbf{k}_{\parallel}, \mathbf{Q}_{\parallel}} e^{i\mathbf{Q}_{\parallel} \cdot \mathbf{r}_{\parallel}} \mathbf{d}_{\mathbf{k}_{\parallel}, \mathbf{k}_{\parallel} + \mathbf{Q}_{\parallel}}^{\lambda\bar{\lambda}} \left\langle \lambda_{\mathbf{k}_{\parallel}}^{\dagger} \bar{\lambda}_{\mathbf{k}_{\parallel} + \mathbf{Q}_{\parallel}} \right\rangle. \quad (3.10)$$

After Fourier transformation of the in-plane momenta, we make use of the 2D character of the TMDC, using a Delta distribution to express the 3D polarization through the 2D polarization

$$\mathbf{P}_{\mathbf{Q}_{\parallel}}(z) = \mathbf{P}_{\mathbf{Q}_{\parallel}}^{2D} \delta(z - z_{\text{ex}}). \quad (3.11)$$

From the previous calculation, we find the straightforward expression for the 2D polarization

$$\mathbf{P}_{\mathbf{Q}_{\parallel}}^{2D} \equiv \frac{1}{A} \sum_{\mathbf{k}_{\parallel}, \lambda} \mathbf{d}_{\mathbf{k}_{\parallel}, \mathbf{k}_{\parallel} + \mathbf{Q}_{\parallel}}^{\lambda\bar{\lambda}} \left\langle \lambda_{\mathbf{k}_{\parallel}}^{\dagger} \bar{\lambda}_{\mathbf{k}_{\parallel} + \mathbf{Q}_{\parallel}} \right\rangle. \quad (3.12)$$

Here, we identify the microscopic interband polarization of the TMDC,

$$p_{\mathbf{k}_1, \mathbf{k}_2} \equiv \left\langle v_{\mathbf{k}_1}^{\dagger} c_{\mathbf{k}_2} \right\rangle \quad (3.13)$$

which we will be the microscopic observable of this chapter to describe the exciton dynamics within the TMDC layer. Later, we will make use of Eq. (3.12) to derive an expression for the microscopically based susceptibility of the system.

All in all, we have deduced the definition of the macroscopic polarization in terms of the microscopic interband polarization, denoted as $p_{\mathbf{k}_1 \mathbf{k}_2}$. For our purposes, we will neglect the spin dependence, so that λ describes the band quantum number only.

3.3. Semiconductor Bloch Equations

In this section, we derive the dynamical semiconductor Bloch equations [170, 173, 338] to describe the exciton dynamics in our system, based on the previously stated Hamiltonian in Eq. (3.1). The microscopic interband polarization $p_{\mathbf{k}_1\mathbf{k}_2}$, discussed in the previous section, serves as the dynamical observable and can be connected to the macroscopic material polarization. To account for the distinction between the K and K' valleys, which was not considered in the previous section, the microscopic polarization will feature an additional index ξ .

We begin in Sec. 3.3.1 by deriving the equations in the electron picture [171, 342]. Subsequently, in Sec. 3.3.2, we study the Wannier equation, which we use in Sec. 3.3.3 to transform all equations into the excitonic picture [176, 243, 343] by projecting them onto exciton wave functions, which serve as solutions of the Wannier equation [170, 344].

3.3.1. Electron Picture

We begin by deriving the Bloch equation in the electron picture, employing annihilation (creation) operators for the valence band, $v_{\mathbf{k}}^{(\dagger)}$, and the conduction band, $c_{\mathbf{k}}^{(\dagger)}$. These operators describe the microscopic interband polarization, as given in Eq. (3.13). To characterize the dynamics of excitons in a monolayer of transition metal dichalcogenides, we make a series of approximations that we discuss individually:

- i) We adopt an effective **four-band model**, neglecting the spin in the system. Consequently, each valley is represented by one valence band and one conduction band, resulting in a total of four bands.
- ii) During our calculations, we encounter densities associated with the occupation of the conduction or valence band. As we are operating in the **linear optical regime**, we assume these densities to be small.
- iii) The two-particle interaction in the carrier-carrier Hamiltonian poses a hierarchy problem, which we address by employing a **Hartree-Fock approximation**.
- iv) We determine the **band gap energy** either from experimental data or *ab initio* calculations. This choice allows us to absorb all the terms contributing to band gap renormalization, e.g, some Coulomb terms on the Hartree-Fock level, into the band gap energy.
- v) We have neglected non-resonant counter-rotating contributions.

Combining all the individual contributions, the full semiconductor Bloch equation in the electron picture for our problem reads

$$\begin{aligned} \partial_t p_{\mathbf{k}_1\parallel, \mathbf{k}_2\parallel} = & -\frac{i}{\hbar} \left(\epsilon_{\mathbf{k}_2\parallel}^c - \epsilon_{\mathbf{k}_1\parallel}^v \right) p_{\mathbf{k}_1\parallel, \mathbf{k}_2\parallel} + \frac{i}{\hbar A} \mathbf{d}_{\mathbf{k}_2\parallel, \mathbf{k}_1\parallel} \cdot \mathbf{E}_{\mathbf{k}_2\parallel - \mathbf{k}_1\parallel}(z_{\text{ex}}) \\ & + \frac{i}{\hbar} \sum_{\mathbf{q}\parallel} V_{\mathbf{q}\parallel} p_{\mathbf{k}_1\parallel + \mathbf{q}\parallel, \mathbf{k}_2\parallel + \mathbf{q}\parallel} + \partial_t p_{\mathbf{k}_1\parallel, \mathbf{k}_2\parallel} \Big|_{\text{scat}}. \end{aligned} \quad (3.14)$$

The dynamics of the interband polarization, denoted as $p_{\mathbf{k}_1\parallel, \mathbf{k}_2\parallel}$, are governed by four key factors: Firstly, the oscillation of the interband polarization is captured by the first term in Eq. (3.14), which depends on the energy difference between the conduction band $\epsilon_{\mathbf{k}_2\parallel}^c$ and the valence band $\epsilon_{\mathbf{k}_1\parallel}^v$. the contribution of the external electric field is represented

by the second term, which acts as a driving force. Here we can define a Rabi frequency $\Omega_{\mathbf{k}_1^\parallel \mathbf{k}_1^\parallel} = \mathbf{d}_{\mathbf{k}_2^\parallel \mathbf{k}_1^\parallel} \cdot \mathbf{E}_{\mathbf{k}_2^\parallel - \mathbf{k}_1^\parallel} (z_{\text{ex}}) / \hbar$. The third term accounts for the Coulomb coupling contribution between individual carriers, summed over all possible exchange momenta $\mathbf{q}_\parallel$. Lastly, we include a phenomenological scattering term as the fourth term, as the specifics of scattering are not crucial to the effects we investigate.

Parabolic Band Structure

In the following, we will make use of the fact that the band structure of the monolayers of transition metal dichalcogenides is parabolic around the K and K' points which dominate their optical response in the optical range that we are interested in and mathematically implement the eight-band model we discussed in Sec. 3.1. Accordingly, the reference point of the momentum vector will be moved from the center of the Brillouin zone to one of the high symmetry points K/K' : $\mathbf{k} \rightarrow K^\xi + \mathbf{k}$ in our analytical calculations. This introduces the additional index $\xi \in \{1, -1\}$ as the new valley index for the individual K (1) or K' (-1) valley. This approximation has been demonstrated to be in excellent agreement with the full band structure around these high symmetry points [11, 188, 243]. It provides a sufficient approximation for describing the dynamics in the optical range that we are interested in. The band structure at the respective ξ can then be effectively approximated as a parabola [171],

$$\epsilon_{\mathbf{k}_\parallel}^{c\xi} \approx \frac{E_G^\xi}{2} + \frac{\hbar^2 \mathbf{k}_\parallel^2}{2m_e}, \quad \epsilon_{\mathbf{k}_\parallel}^{v\xi} \approx -\frac{E_G^\xi}{2} - \frac{\hbar^2 \mathbf{k}_\parallel^2}{2m_h}. \quad (3.15)$$

Here, we have taken into account the influence of spin-orbit coupling, which leads to distinct band gap energies E_G^ξ at the respective valleys. m_e and m_h are the electron or hole mass. By distinguishing between the K and K' valleys, our chosen observable, the interband polarization, acquires an additional valley index, cf. Eq. (3.13),

$$p_{\mathbf{k}_1^\parallel, \mathbf{k}_2^\parallel}^\xi = \left\langle v_{\mathbf{k}_1^\parallel}^{\xi\dagger} c_{\mathbf{k}_2^\parallel}^\xi \right\rangle. \quad (3.16)$$

In this study, we consider polarizations describing interband coherences within the same valley, assuming that ξ is the same in both valence and conduction band. This assumption is reasonable since we are primarily interested in the linear optical response of the system at this stage. Accordingly, we also obtain distinct Bloch equations at each valley that we can generally express as

$$\begin{aligned} \partial_t p_{\mathbf{k}_1^\parallel, \mathbf{k}_2^\parallel}^\xi = & -\frac{i}{\hbar} \left(\epsilon_{\mathbf{k}_2^\parallel}^{c\xi} - \epsilon_{\mathbf{k}_1^\parallel}^{v\xi} \right) p_{\mathbf{k}_1^\parallel, \mathbf{k}_2^\parallel}^\xi + \frac{i}{\hbar A} \mathbf{d}_{\mathbf{k}_2^\parallel, \mathbf{k}_1^\parallel}^\xi \cdot \mathbf{E}_{\mathbf{k}_2^\parallel - \mathbf{k}_1^\parallel} \\ & + \frac{i}{\hbar} \sum_{\mathbf{q}_\parallel} V_{\mathbf{q}_\parallel} p_{\mathbf{k}_1^\parallel + \mathbf{q}_\parallel, \mathbf{k}_2^\parallel + \mathbf{q}_\parallel}^\xi + \partial_t p_{\mathbf{k}_1^\parallel, \mathbf{k}_2^\parallel}^\xi \Big|_{\text{scat}}. \end{aligned} \quad (3.17)$$

In general, we reproduce the same equation obtained in Eq. (3.14) but include an additional index. The circular dichroism will be included in the dipole matrix element.

Relative and Center-of-Mass Coordinates

As the dynamical equations for an electron-hole pair by construction resemble a two-body problem, it feels natural to transform to a coordinate system of relative and center-of-mass coordinates to distinguish the motion of the exciton as a new quasiparticle from its

relative motion. This can be done using the transformation

$$\mathbf{Q}_{\parallel} = \mathbf{k}_2^{\parallel} - \mathbf{k}_1^{\parallel}, \quad \mathbf{q}_{\parallel} = \alpha \mathbf{k}_1^{\parallel} + \beta \mathbf{k}_2^{\parallel}, \quad (3.18a)$$

$$\mathbf{k}_1^{\parallel} = \mathbf{q}_{\parallel} - \beta \mathbf{Q}_{\parallel}, \quad \mathbf{k}_2^{\parallel} = \mathbf{q}_{\parallel} + \alpha \mathbf{Q}_{\parallel}, \quad (3.18b)$$

with $\alpha = \frac{m_e}{m_e + m_h}$ and $\beta = \frac{m_h}{m_e + m_h}$ which represent the relative masses. At this point, we want to comment on the unintuitive form of the transformation, which one would assume to feature the reversed sign of the $\mathbf{k}_1$ term in Eq. (3.18a). This results from our implicit assumption that, $v_{\mathbf{k}}^{\dagger} = h_{\mathbf{k}}$ as opposed to the usual, $v_{\mathbf{k}}^{\dagger} = h_{-\mathbf{k}}$ which effectively results in $\mathbf{Q} = \mathbf{q}_e + \mathbf{q}_h \rightarrow \mathbf{q}_c - \mathbf{q}_v$. In relative and center-of-mass coordinates, the Bloch equation in Eq. (3.17) reads

$$i\hbar\partial_t p_{\mathbf{q}_{\parallel}\mathbf{Q}_{\parallel}}^{\xi} = \left[E_G^{\xi} + \frac{\hbar^2 \mathbf{q}_{\parallel}^2}{2\mu} + \frac{\hbar^2 \mathbf{Q}_{\parallel}^2}{2M} \right] p_{\mathbf{q}_{\parallel}\mathbf{Q}_{\parallel}}^{\xi} - \frac{1}{A} \mathbf{d}_{\mathbf{q}_{\parallel} + \alpha \mathbf{Q}_{\parallel}, \mathbf{q}_{\parallel} - \beta \mathbf{Q}_{\parallel}}^{\xi*} \cdot \mathbf{E}_{\mathbf{Q}_{\parallel}}(z_{\text{ex}}) \quad (3.19)$$

$$- \sum_{\mathbf{k}_{\parallel}} V_{\mathbf{k}_{\parallel}} p_{\mathbf{q}_{\parallel} - \mathbf{k}_{\parallel}, \mathbf{Q}_{\parallel}}^{\xi} + \partial_t p_{\mathbf{q}_{\parallel}\mathbf{Q}_{\parallel}}^{\xi} \Big|_{\text{scat}}.$$

Here, we have introduced the total mass, $M = m_e + m_h$, and the reduced mass, $\mu = \frac{m_e m_h}{m_e + m_h}$, as commonly done in solutions of the two-body problem. The momentum indices of the polarization were transformed in agreement with Eq. (3.18a).

At this stage, we reconsider the momentum dependence of the dipole moment. As the light dispersion (light cone) is very steep compared to the material dispersion, we assume that only vertical transitions are relevant for the optical matrix element so that $\mathbf{d}_{\mathbf{q}_{\parallel} + \alpha \mathbf{Q}_{\parallel}, \mathbf{q}_{\parallel} - \beta \mathbf{Q}_{\parallel}}^{\xi} \approx \mathbf{d}_{\mathbf{q}_{\parallel}, \mathbf{q}_{\parallel}}^{\xi} \equiv \mathbf{d}_{\mathbf{q}_{\parallel}}^{\xi}$. In addition, we expand the momentum dependent dipole moment $\mathbf{d}_{\mathbf{q}_{\parallel}}^{\xi}$ around the K/K' valley, keeping only the zeroth order in the expansion so that we can effectively approximate it with its value at the K/K' points $\mathbf{d}_{\mathbf{q}_{\parallel}}^{\xi} \approx \mathbf{d}_{\mathbf{K}^{\xi}}^{\xi} \equiv \mathbf{d}^{\xi}$. The dipole element can be obtained from numerical calculations using density functional theory [11].

3.3.2. Wannier Equation

Since the dynamics in TMDCs are dominated by excitonic features in the optical regime, we can expand to a good approximation the equations of motion in exciton wave functions, $\varphi_{\mathbf{q}_{\parallel}}^{\xi\nu}$, which are solutions of the Wannier equation describing the excitonic dynamics in 2D materials [170]. It reads

$$\left[E_G^{\xi} + \frac{\hbar^2 \mathbf{q}_{\parallel}^2}{2\mu} \right] \varphi_{\mathbf{q}_{\parallel}}^{\xi\nu} - \sum_{\mathbf{k}_{\parallel}} V_{\mathbf{k}_{\parallel}} \varphi_{\mathbf{q}_{\parallel} - \mathbf{k}_{\parallel}}^{\xi\nu} = E^{\xi\nu} \varphi_{\mathbf{q}_{\parallel}}^{\xi\nu}. \quad (3.20)$$

This equation describes the relative motion of electron and hole, which make up an exciton, similar to the situation in a two-body problem. The relative coordinate of the exciton problem with mass μ evolves in the Coulomb potential $V_{\mathbf{k}_{\parallel}}$. The ν index in Eq. (3.20) is the quantum number of the excitonic state. This equation allows to disentangle relative and center-of-mass motion in Eq. (3.19). This can be done by projecting

the polarization, $p_{\mathbf{q}_{\parallel}\mathbf{Q}_{\parallel}}^{\xi}$, on a complete set of eigenfunctions that solve the Wannier equation, which we will touch upon in Sec. 3.3.3. Before we do so, we take some time to study the Wannier equation, Eq (3.20) in detail.

The solution of the Wannier equation is typically obtained straightforwardly in our group through eigendecomposition, and more details regarding this approach can be found in App. D.2. As obvious from Eq. (3.20), the characterizing feature for the Wannier equation is the Coulomb potential, which will significantly affect the eigenvalues and eigenfunctions. The traditional analytical description, as outlined in Refs. [22, 23], has been commonly employed to study the case of a TMDC layer surrounded by a medium of constant permittivity on both sides. This has been treated to great accuracy in Refs. [22, 23, 345–347] where a corrected version of the standard Rytova-Keldysh potential for the three layer case has been used in our group. For the scope of this work, we generalized this approach to an effective four layer system, described using the Coulomb potential in Eq. (3.6). Qualitatively, the results are unchanged compared to the three layer case, with slight quantitatively corrections to the binding energies and excitonic wave functions due to changing screening effects.

3.3.3. Exciton Picture

In the full microscopic dynamical equation in Eq. (3.19), it is possible to identify the Wannier equation, Eq. (3.20). This allows us to map the full dynamical equation on exciton wave functions, $\varphi_{\mathbf{q}_{\parallel}}^{\xi\nu}$, that are solutions of the Wannier equation to separate relative and center-of-mass motion. This can be achieved using the expansion [344],

$$p_{\mathbf{q}_{\parallel}\mathbf{Q}_{\parallel}}^{\xi} = \sum_{\nu} \varphi_{\mathbf{q}_{\parallel}}^{\xi\nu} p_{\mathbf{Q}_{\parallel}}^{\xi\nu}. \quad (3.21)$$

Normally, the full Wannier equation reveals left- and right-handed solutions due to the appearance of the valence and conduction band densities [171]. This makes it necessary to distinguish left-handed and right-handed exciton wave functions [171]. However, as we work in the weak excitation limit, meaning vanishing densities, left-handed and right-handed solutions coincide so that we use exciton wave functions, $\varphi_{\mathbf{q}_{\parallel}}^{\xi\nu}$, and their complex conjugates in our calculations.

Expanding in the new basis and under the use of the Wannier equation, the entire relative motion on the left-hand side of Eq. (3.19) can be absorbed in the eigenvalues $E^{\xi\nu}$ of the Wannier equation, so that only the inhomogeneous part in Eq. (3.19) depends on $\mathbf{q}_{\parallel}$ which enables us to map on the excitonic wave functions $\varphi_{\mathbf{q}_{\parallel}}^{\xi\nu}$ by multiplying with $(\varphi_{\mathbf{q}_{\parallel}}^{\xi\nu})^*$ from the left and summing over all relative momenta. Using the orthonormality relation $1/A \sum_{\mathbf{q}_{\parallel}} (\varphi_{\mathbf{q}_{\parallel}}^{\xi\lambda})^* \varphi_{\mathbf{q}_{\parallel}}^{\xi\nu} = \delta^{\lambda\nu}$, we find

$$\hbar\omega p_{\mathbf{Q}_{\parallel}}^{\xi\nu} = \left[E^{\xi\nu} + \frac{\hbar^2 \mathbf{Q}_{\parallel}^2}{2M} - i\gamma^{\nu} \right] p_{\mathbf{Q}_{\parallel}}^{\xi\nu}(\omega) - \varphi_{\nu}^*(\mathbf{r}_{\parallel} = 0) \sum_{\sigma} (d^{\xi\sigma})^* E_{\mathbf{Q}_{\parallel}}^{\sigma}(z_{\text{ex}}; \omega). \quad (3.22)$$

Here, the sum over all relative momenta can be interpreted as a Fourier transform of the relative coordinate of electron and hole $\mathbf{r}_{\parallel}$ to real space and used the identity

$\sum_{\mathbf{q}_{\parallel}} \varphi_{\mathbf{q}_{\parallel}}^{\xi\nu} = \varphi_{\xi\nu}^*(\mathbf{r}_{\parallel} = \mathbf{0})$. Here, $\varphi_{\nu}(\mathbf{r}_{\parallel})$ is the exciton wave function depending on the relative coordinate of electron and hole $\mathbf{r}_{\parallel}$ and can be obtained by solution of the Wannier equation in Eq. (3.20). The excitonic wave function is evaluated at $\mathbf{r}_{\parallel} = \mathbf{0}$, which accounts for the probability of finding electron and hole at the same position [348]. At this stage, we introduce a couple of simplifying assumptions applicable for our case. We assume the band gap to be equivalent for both valleys, such that the wave function and the eigenvalues of the Wannier equation will not be valley-dependent and depend solely on the excitonic quantum number ν . The circular dichroism of the TMDC is introduced via $d^{\sigma\xi} = d^{\sigma}\delta_{\sigma\xi}$. The dephasing rates γ^{ν} are added to account for phonon-induced dephasing as calculated microscopically in Ref. [176] using a phenomenological effective relaxation time approximation.

Thus, we have derived a Bloch equation in an excitonic picture that only contains the center-of-mass momentum $\mathbf{Q}_{\parallel}$ of the exciton. The first term on the right-hand side of the equation is the oscillation of interband polarization with the characteristic energy that is composed of the excitonic energies E^{ν} , consisting of the band gap energy and the exciton binding energy, the parabolic momentum contribution and a dephasing γ^{ν} that we added phenomenologically to account for damping and excitonic dephasing. The second term describes the excitation of the polarization by an external classical electric field $E_{\mathbf{Q}_{\parallel}}^{\sigma}$ at the position of the TMDC.

TMDC Polarization - Exciton Picture

The expansion in exciton wave functions in Eq. (3.21) also has to be considered in the definition of the macroscopic polarization that we discussed in Sec. 3.2. Here, we find

$$\mathbf{P}_{\mathbf{Q}_{\parallel}}^{2D}(\omega) = \frac{1}{A} \sum_{\xi\nu} \sum_{\mathbf{q}_{\parallel}} \mathbf{d}^{\xi} \varphi_{\mathbf{q}_{\parallel}}^{\xi\nu} p_{\mathbf{Q}_{\parallel}}^{\xi\nu}(\omega) + c.c., \quad (3.23)$$

Similar to the calculations for the microscopic polarization, we can also identify the exciton wave function at $\mathbf{r}_{\parallel} = \mathbf{0}$ in real space. This allows us to express the chiral components of the macroscopic polarization as

$$P_{\mathbf{Q}_{\parallel}}^{\sigma,2D}(\omega) = \sum_{\xi\nu} d^{\xi\sigma} \varphi_{\xi\nu}(\mathbf{r}_{\parallel} = \mathbf{0}) p_{\mathbf{Q}_{\parallel}}^{\xi\nu}(\omega) + c.c., \quad (3.24)$$

which gives the macroscopic polarization in terms of the dipole element $d^{\xi\sigma}$, the wave function for vanishing relative electron-hole coordinate $\varphi_{\nu}(\mathbf{r}_{\parallel} = \mathbf{0})$, i.e., electron and hole at the same position in real space, and the microscopic interband polarization $p_{\mathbf{Q}_{\parallel}}^{\xi\nu}$. Thus, we can deduce that only excitonic states contribute to the macroscopic polarization that have a non-vanishing wave function at $\mathbf{r}_{\parallel} = \mathbf{0}$. Many times, the exciton wave function and the dipole moment are combined into an effective excitonic dipole moment [28]. At this stage, the circular dichroism of the TMDC is introduced using the identity $d^{\xi\sigma} = d^{\xi}\delta_{\xi\sigma}$.

Absorption Spectrum – Elliott Formula

From the previously defined macroscopic polarization, cf. Eq. (3.24), one can deduce the absorption spectrum via the well-known Elliott formula [171]

$$\chi(\omega) = \frac{1}{\varepsilon_0} \sum_{\xi\nu} \frac{|\mathbf{d}^{\xi}|^2 |\varphi_{\xi\nu}(\mathbf{r}_{\parallel} = \mathbf{0})|^2}{E^{\nu} - \hbar\omega - i\gamma}, \quad (3.25)$$

where the valley-specific and due to the circular dichroism also the σ^+/σ^- -specific polarization can be obtained as the individual components of the ξ sum. This equation contains the usual step-like absorption spectrum generally expected for two-dimensional structures. However, due to the strong electron-hole interaction, the optical spectrum is dominated by excitonic features below the band gap and the free particle band gap is merely visible [18]. The spectral positions of the excitonic peaks are given by the excitonic eigenenergies E^ν . In Fig. 3.5, we exemplarily plot the imaginary part of the susceptibility in Eq. (3.25) that is proportional to the TMDC absorption.

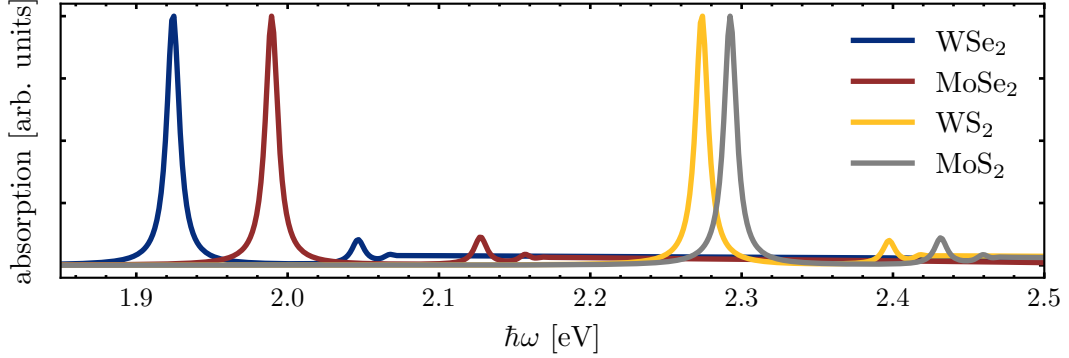


Figure 3.5.: **Calculated TMDC Absorption Spectra.** TMDC absorption spectra, calculated for the most used TMDCs using the microscopic approach presented in this chapter.

This would be sufficient if we would just model the case of plane wave excitation and translationally invariant systems without other sources. However, as we consider additional sources and dynamical interactions of the TMDC excitons with external scatterers, more efforts will be taken in the following subsections to include other than just the purely excitonic effects.

3.4. Self-Consistent Maxwell-Bloch Approach

Now that we have extensively introduced the excitonic description of the TMDC, we need to start thinking about how to describe the optical response of the gold nanoparticle (AuNP) and how to treat the interaction with it. Therefore, we extend the Bloch approach, we have described previously, to self-consistently include Maxwell's equations. The plasmonic response of the metal nanoparticle will be described using Mie theory and the electromagnetic field that mediates the interaction by Maxwell's equations. This will briefly be introduced in the subsequent two chapters.

In our approach, we use real space for the out-of-plane component (in the z direction) and the Fourier transform for the in-plane components (in the x and y directions). In addition, we transform the temporal dynamics into the frequency domain, which allows us to work with one set of coordinates $(\mathbf{Q}_\parallel, z; \omega)$. This transformation allows us to solve the differential equations algebraically.

3.4.1. Optical Response of Nanoparticle Plasmons

For the scope of this thesis, we use an oblate spheroid in a dipole approximation using Mie-Gans theory [1, 295]. This condenses the light-matter interaction in response to the external field $\mathbf{E}_{\mathbf{Q}_{\parallel}}^0$ for a spheroid in a diagonal polarizability tensor, $\boldsymbol{\alpha}(\omega)$, whose diagonal components are given in Eq. (2.57). The gold permittivity $\varepsilon_{\text{Au}}(\omega)$ is analytically modeled using the approach from Ref. [277], that incorporates two interband transitions in the visible regime to accurately describe the experimental data found in Ref. [272]. Its analytical expression is given in Eq. (2.50).

The choice of an oblate spheroid allows for enhanced interaction of AuNP and TMDC, since it reduces the effective separation while keeping the volume and thus the polarizability large. In Fig. 3.1b, the absolute value of the in-plane polarizability of the considered spheroid is shown as an example. All used parameters can be found in Tab. A.2.

In this dipole approximation, the AuNP polarization can be written as

$$\mathbf{P}_{\mathbf{Q}_{\parallel}}^{\text{AuNP}}(z; \omega) = \frac{\boldsymbol{\alpha}(\omega)}{(2\pi)^2} \cdot \int d^2\mathbf{Q}'_{\parallel} e^{-i(\mathbf{Q}_{\parallel}-\mathbf{Q}'_{\parallel})\cdot\mathbf{r}_{\parallel}^{\text{pl}}} \mathbf{E}_{\mathbf{Q}'_{\parallel}}(z_{\text{pl}}) \delta(z - z_{\text{pl}}), \quad (3.26)$$

which describes the polarization of a point dipole located at $\mathbf{r}_{\text{pl}} = (\mathbf{r}_{\parallel}^{\text{pl}}, z_{\text{pl}})$. The polarizability $\boldsymbol{\alpha}(\omega)$ incorporates the electric field generated by the AuNP. Thus, $\mathbf{E}_{\mathbf{Q}'_{\parallel}}(z_{\text{pl}})$ corresponds to the electric field at the position of the AuNP, excluding the field contributed by itself. For simplicity reason, we will assume $\mathbf{r}_{\parallel}^{\text{pl}} = 0$. Combining the two polarizations given in Eqs. (3.48) and (3.26), the full polarization is given by

$$\mathbf{P}_{\mathbf{Q}_{\parallel}}(z; \omega) = \mathbf{P}_{\mathbf{Q}_{\parallel}}^{\text{TMDC}}(z; \omega) + \mathbf{P}_{\mathbf{Q}_{\parallel}}^{\text{AuNP}}(z; \omega), \quad (3.27)$$

which enters Maxwell's equations to compute the electric field close to the nanostructure.

3.4.2. Green's Function Approach to Electromagnetic Interaction

In our description, the interaction of TMDC and AuNP is mediated by the electric field, as can be seen in Eqs. (3.32) and (3.26), which has to be determined self-consistently from Maxwell's equations. The starting point for the investigation is the wave equation

$$\left(\nabla^2 - \frac{\varepsilon(z)}{c^2} \frac{\partial^2}{\partial t^2} \right) \mathbf{E}(\mathbf{r}, t) = \frac{1}{\varepsilon_0 c^2} \frac{\partial^2}{\partial t^2} \mathbf{P}(\mathbf{r}, t) - \frac{1}{\varepsilon(z) \varepsilon_0} \nabla(\nabla \cdot \mathbf{P}(\mathbf{r}, t)), \quad (3.28)$$

for the polarization $\mathbf{P}(\mathbf{r}, t)$ in a background medium with spatially piecewise-constant permittivity $\varepsilon(z)$, which is ε_1 in the upper half plane and ε_2 in the lower half plane. A general solution of this equation can be provided via the Green's function using the coordinates $(\mathbf{Q}_{\parallel}, z; \omega)$ which we obtain by Fourier transformation according to $\mathbf{E}(\mathbf{r}; \omega) = \frac{1}{(2\pi)^2} \int d^2\mathbf{Q}_{\parallel} e^{i\mathbf{Q}_{\parallel}\cdot\mathbf{r}_{\parallel}} \mathbf{E}_{\mathbf{Q}_{\parallel}}(z; \omega)$. Hence, the electric field can be expressed as

$$\mathbf{E}_{\mathbf{Q}_{\parallel}}(z; \omega) = \int_{\mathbb{R}} dz' \mathcal{G}_{\mathbf{Q}_{\parallel}}(z, z'; \omega) \cdot \mathbf{P}_{\mathbf{Q}_{\parallel}}(z'; \omega) + \mathbf{E}_{\mathbf{Q}_{\parallel}}^0(z; \omega), \quad (3.29)$$

with the dyadic Green's function $\mathcal{G}_{\mathbf{Q}_{\parallel}}(z, z'; \omega)$ and the external electric field $\mathbf{E}_{\mathbf{Q}_{\parallel}}^0(z; \omega)$. For Eq. (3.28), the dyadic Green's function is given by

$$\mathcal{G}_{\mathbf{Q}_{\parallel}}(z, z'; \omega) = \left[-\frac{\omega^2}{\varepsilon_0 c^2} \mathbb{1} + \frac{1}{\varepsilon_0 \varepsilon(z)} \begin{pmatrix} \mathbf{Q}_{\parallel} \otimes \mathbf{Q}_{\parallel} & i\mathbf{Q}_{\parallel} \partial_{z'} \\ i\mathbf{Q}_{\parallel}^T \partial_{z'} & \partial_{z'}^2 \end{pmatrix} \right] G_{\mathbf{Q}_{\parallel}}(z, z'; \omega), \quad (3.30)$$

where the symbol $\mathbb{1}$ denotes the three-dimensional identity matrix. The second matrix has a 2 by 2 matrix as its first entry, and the resulting matrix is also three-dimensional. Here, the scalar Green's function $G_{\mathbf{Q}_{\parallel}}(z, z'; \omega)$ is defined as

$$G_{\mathbf{Q}_{\parallel}}(z, z'; \omega) = -\frac{i}{2k_{\mathbf{Q}_{\parallel}}} e^{ik_{\mathbf{Q}_{\parallel}}|z-z'|}, \quad (3.31)$$

where $k_{\mathbf{Q}_{\parallel}} \equiv \sqrt{\varepsilon(z) \frac{\omega^2}{c^2} - Q_{\parallel}^2}$. This can be obtained from complex contour integration, details will be provided in App. D.1. Eqs. (3.30) and (3.31) allow one to calculate the self-consistent electric field at the TMDC and the AuNP position which enters the dynamical equation for the microscopic TMDC polarization $p_{\mathbf{Q}_{\parallel}}^{\xi\nu}(\omega)$, cf. Eq. (3.32), and the AuNP polarization, cf. Eq. (3.26).

3.4.3. Optical Response of the Coupled Nanostructure

To obtain a self-consistent set of solutions for our system, we need to combine all the equations introduced thus far. In our analysis, we will specifically focus on the 1s resonance of TMDC in the context of our interacting system. This is a good approximation when the 1s resonance is spectrally clearly separated and the spectral range is limited to the one dominated by the 1s resonance, as it is for our case. For clarity, we will omit the index ν in our notation, use φ_0 to represent the value of φ^{1s} at the origin ($\mathbf{r}_{\parallel} = 0$), and γ^{1s} to denote the corresponding damping coefficient for the 1s resonance. By incorporating these variables and equations into our overall framework, we can derive a self-consistent solution that captures the dynamics and behavior of the system accurately.

Restating Eq. (3.22) for didactic purposes, we describe the microscopic dynamics in TMDC monolayers using the excitonic Bloch equations, cf. Refs. [179, 226, 243],

$$\left(E^{1s} + \frac{\hbar^2 \mathbf{Q}_{\parallel}^2}{2M} - \hbar\omega - i\gamma \right) p_{\mathbf{Q}_{\parallel}}^{\xi}(\omega) = \varphi_0^* (\mathbf{d}^{\xi})^* \cdot \mathbf{E}_{\mathbf{Q}_{\parallel}}(z_{\text{ex}}; \omega). \quad (3.32)$$

The left-hand side accounts for the oscillation of the microscopic 1s exciton polarization, $p_{\mathbf{Q}_{\parallel}}^{\xi}$, with excitonic energy, E^{1s} , where we use a valley index $\xi = \pm 1$ for the K/K' valley, respectively and the Fourier component of the center-of-mass motion $\mathbf{Q}_{\parallel}$. Furthermore, the left-hand side accounts for the dispersion of excitons (second term) with the exciton mass M . The dephasing rates γ were added to account for phonon-induced dephasing as calculated microscopically in Ref. [176]. The TMDC excitons are driven by the electric field $\mathbf{E}_{\mathbf{Q}_{\parallel}}(z_{\text{ex}}; \omega)$ via the electronic transition dipole moment $\mathbf{d}^{\xi}$ at the respective valley [11] and the 1s exciton wave function at the origin φ_0 . The entire interaction is now mediated via the electric field. In the hybrid structure, the total field at the TMDC position $\mathbf{E}_{\mathbf{Q}_{\parallel}}(z_{\text{ex}})$ includes the external field $\mathbf{E}_{\mathbf{Q}_{\parallel}}^0$, a contribution caused by the AuNP-TMDC interaction as well as the inter- and intra-valley exchange coupling within the monolayer [349].

By inserting Eq. (3.29) into Eq. (3.32), we find the following equation of motion for the microscopic TMDC polarization,

$$\begin{aligned}
 & \left[E^{1s} + \frac{\hbar^2 \mathbf{Q}_{\parallel}^2}{2M} - \hbar\omega - i\gamma \right] p_{\mathbf{Q}_{\parallel}}^{\xi}(\omega) \\
 &= \varphi_0^* \mathbf{d}^{\xi*} \cdot \left[\mathbf{E}_{\mathbf{Q}_{\parallel}}^0(z_{\text{ex}}; \omega) + \mathcal{G}_{\mathbf{Q}_{\parallel}}(z_{\text{ex}}, z_{\text{pl}}; \omega) \cdot \boldsymbol{\alpha}(\omega) \cdot \mathbf{E}^0(\mathbf{r}_{\text{pl}}; \omega) \right] \\
 & \quad + |\varphi_0|^2 \mathbf{d}^{\xi*} \cdot \sum_{\xi'} \left[\mathcal{G}_{\mathbf{Q}_{\parallel}}(z_{\text{ex}}, z_{\text{ex}}; \omega) \cdot \mathbf{d}^{\xi'} p_{\mathbf{Q}_{\parallel}}^{\xi'}(\omega) \right. \\
 & \quad \left. + \mathcal{G}_{\mathbf{Q}_{\parallel}}(z_{\text{ex}}, z_{\text{pl}}; \omega) \cdot \frac{\boldsymbol{\alpha}(\omega)}{(2\pi)^2} \cdot \int d^2 \mathbf{Q}'_{\parallel} \mathcal{G}_{\mathbf{Q}'_{\parallel}}(z_{\text{pl}}, z_{\text{ex}}; \omega) \cdot \mathbf{d}^{\xi'} p_{\mathbf{Q}'_{\parallel}}^{\xi'}(\omega) \right].
 \end{aligned} \tag{3.33}$$

In Eq. (3.33), the coupling between TMDC excitons and the AuNP plasmon induced by the electric field is given in terms of the Green's functions, including the self-interaction of the excitonic polarization. In Eq. (3.33), the first term on the right-hand side is the interaction with the external electric field $\mathbf{E}_{\mathbf{Q}_{\parallel}}^0(z_{\text{ex}})$ at the TMDC position z_{ex} . The second term is the external electric field at the AuNP position, which is resonantly enhanced by the AuNP and then coupled to the TMDC. In the second line, we see that the electric field also mediates a dipole-dipole coupling between the excitons at the K/K' point, widely known as the inter- and intra-valley exchange coupling [350]. The final term in the equation describes a self-interaction of the TMDC that is mediated by the AuNP, as evidenced by the appearance of two Green's functions. This term can be interpreted as an effective exciton-exciton interaction.

In our particular setup, special care is required to include the dielectric interface at $z = 0$, which arises due to the piecewise constant background permittivity. Since the distance between the TMDC and the AuNP is only a few nanometers and the wavelengths used are in the optical range, we have opted to utilize the quasi-static Green's function, provided in Eq. (3.35), which also incorporates the change in background permittivity. This leads to the fact that the quasi-static Green's function can only be defined piecewise. Due to the interface, the Green's function also contains additional mirror charge terms. The Green's function is derived following Ref. [351] and takes into account the individual positions of the scatterers.

In the quasi-static limit, i.e., $c \rightarrow \infty$, the dyadic Green's function can be expressed as

$$\mathcal{G}_{\mathbf{Q}_{\parallel}}^{\text{st}}(z, z') = \frac{1}{\varepsilon_0 \varepsilon(z)} \begin{pmatrix} \mathbf{Q}_{\parallel} \otimes \mathbf{Q}_{\parallel} & i\mathbf{Q}_{\parallel} \partial_{z'} \\ i\mathbf{Q}_{\parallel}^T \partial_z & \partial_{z'}^2 \end{pmatrix} G_{\mathbf{Q}_{\parallel}}^{\text{st}}(z, z'). \tag{3.34}$$

Evaluating Eq. (3.33) with the quasi-static scalar Green's function

$$G_{\mathbf{Q}_{\parallel}}^{\text{st}}(z, z') = \begin{cases} -\frac{1}{2Q_{\parallel}} e^{-Q_{\parallel}|z-z'|} - \frac{1}{2Q_{\parallel}} \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} e^{-Q_{\parallel}|z+z'|} & , \quad z, z' > 0 \\ -\frac{1}{Q_{\parallel}} \frac{\varepsilon(z)}{\varepsilon_1 + \varepsilon_2} e^{-Q_{\parallel}|z-z'|} & , \quad \text{sgn}(z) \neq \text{sgn}(z') , \\ -\frac{1}{2Q_{\parallel}} e^{-Q_{\parallel}|z-z'|} - \frac{1}{2Q_{\parallel}} \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1 + \varepsilon_2} e^{-Q_{\parallel}|z+z'|} & , \quad z, z' < 0 \end{cases} \tag{3.35}$$

we obtain individual equations for the respective valley K/K' . For a derivation of the Green's function, we refer to Ref. [351]. To investigate the effects resulting from the coupling of TMDC and AuNP, we first diagonalize our system of equations by performing a transformation with respect to the inter-valley exchange coupling,

$$\begin{pmatrix} p_{\mathbf{Q}_{\parallel}}^U \\ p_{\mathbf{Q}_{\parallel}}^V \end{pmatrix} \equiv \frac{1}{\sqrt{2}} \begin{pmatrix} -e^{i\phi} & e^{-i\phi} \\ e^{i\phi} & e^{-i\phi} \end{pmatrix} \cdot \begin{pmatrix} p_{\mathbf{Q}_{\parallel}}^K \\ p_{\mathbf{Q}_{\parallel}}^K \end{pmatrix}. \quad (3.36)$$

This is analogous to Ref. [349]. ϕ represents the angle coordinate in polar coordinates corresponding to $\mathbf{Q}_{\parallel}$. The same matrix transformation is used to transform the circularly polarized external electric field $\mathbf{E}_{\mathbf{Q}_{\parallel}}^0$ in Eq. (3.33) into its new basis $\{E_{\mathbf{Q}_{\parallel}}^{0,U}, E_{\mathbf{Q}_{\parallel}}^{0,V}\}$. We find two decoupled equations, Eqs. (3.37) and (3.38), for the new polarizations $p_{\mathbf{Q}_{\parallel}}^U(\omega)$ and $p_{\mathbf{Q}_{\parallel}}^V(\omega)$,

$$\left[E^{1s} + \frac{\hbar^2 \mathbf{Q}_{\parallel}^2}{2M} - \hbar\omega - i\gamma \right] p_{\mathbf{Q}_{\parallel}}^U(\omega) = d^* \varphi_0^* E_{\mathbf{Q}_{\parallel}}^{0,U}(z_{\text{ex}}; \omega). \quad (3.37)$$

In Eq. (3.37), $p_{\mathbf{Q}_{\parallel}}^U$ is unaffected by the exchange coupling. The left-hand side of Eq. (3.37) exhibits a free parabolic exciton dispersion that is consistent with previous literature [349]. Accordingly, we will refer to Eq. (3.37) as the parabolic Bloch equation. It's worth noting that both the exchange coupling contributions and the coupling contributions between TMDC and AuNP cancel each other out. This is due to the quasi-static approach, which reduces the interaction to longitudinal components that appear under the transformation in Eq. (3.36) only in the V component, cf. Ref. [349]. Hence, the right-hand side only accounts for the excitation by the external electric field $E_{\mathbf{Q}_{\parallel}}^{0,U}(z_{\text{ex}}; \omega)$ at the TMDC position and accordingly has the same form as the pristine TMDC case without exchange and TMDC-AuNP coupling. In contrast, the equation for $p_{\mathbf{Q}_{\parallel}}^V(\omega)$, Eq. (3.38), reads

$$\begin{aligned} & \left[E^{1s} + \frac{\hbar^2 \mathbf{Q}_{\parallel}^2}{2M} + X_{\mathbf{Q}_{\parallel}}(z_{\text{ex}}) - \hbar\omega - i\gamma \right] p_{\mathbf{Q}_{\parallel}}^V(\omega) \\ & - \frac{1}{(2\pi)^2} \int d^2 \mathbf{Q}'_{\parallel} V_{\mathbf{Q}_{\parallel} \mathbf{Q}'_{\parallel}}(z_{\text{ex}}, z_{\text{pl}}; \omega) p_{\mathbf{Q}'_{\parallel}}^V(\omega) \\ & = d^* \varphi_0^* \left(E_{\mathbf{Q}_{\parallel}}^{0,V}(z_{\text{ex}}; \omega) + S_{\mathbf{Q}_{\parallel}}(z_{\text{pl}}, z_{\text{ex}}; \omega) \right). \end{aligned} \quad (3.38)$$

Comparing to Eq. (3.37), where all interaction contributions cancel, we find three additional terms. The first one is the intra- and inter-valley exchange term, which renormalizes the parabolic dispersion

$$X_{\mathbf{Q}_{\parallel}}(z_{\text{ex}}) = -|\varphi_0|^2 |d|^2 \frac{Q_{\parallel}^2}{\varepsilon_0 \varepsilon_2} G_{\mathbf{Q}_{\parallel}}^{\text{rst}}(z_{\text{ex}}, z_{\text{ex}}). \quad (3.39)$$

As can be seen in Fig. 3.6, where we depict the further relevant momentum range from $(-1 \text{ to } 1) \text{ nm}^{-1}$, $X_{\mathbf{Q}_{\parallel}}(z_{\text{ex}})$ changes the parabolic dispersion to a conical one depending on the exchange coupling among the K/K' valleys, cf. Ref. [349]. Hence, we refer to Eq. (3.38) as the conical Bloch equation. The other additional terms, $V_{\mathbf{Q}_{\parallel}\mathbf{Q}'_{\parallel}}(z_{\text{ex}}, z_{\text{pl}}; \omega)$ and $S_{\mathbf{Q}_{\parallel}}(z_{\text{pl}}, z_{\text{ex}}; \omega)$, are given by

$$V_{\mathbf{Q}_{\parallel}\mathbf{Q}'_{\parallel}}(z_{\text{ex}}, z_{\text{pl}}; \omega) = |\varphi_0|^2 |d|^2 \frac{Q_{\parallel}^2}{\varepsilon_0 \varepsilon_2} G_{\mathbf{Q}_{\parallel}}^{\text{st}}(z_{\text{ex}}, z_{\text{pl}}) \times \frac{Q'_{\parallel}{}^2}{\varepsilon_0 \varepsilon_1} G_{\mathbf{Q}'_{\parallel}}^{\text{st}}(z_{\text{pl}}, z_{\text{ex}}) [\alpha_{\parallel}(\omega) \cos(\phi - \phi') + \alpha_z(\omega)], \quad (3.40a)$$

$$S_{\mathbf{Q}_{\parallel}}(z_{\text{ex}}, z_{\text{pl}}; \omega) = \frac{Q_{\parallel}^2}{\varepsilon_0 \varepsilon_2} G_{\mathbf{Q}_{\parallel}}^{\text{st}}(z_{\text{ex}}, z_{\text{pl}}) [\alpha_{\parallel}(\omega) E_0^V(\mathbf{r}_{\text{pl}}; \omega) - i\alpha_z(\omega) E_0^z(\mathbf{r}_{\text{pl}}; \omega)]. \quad (3.40b)$$

The first of the two terms, $V_{\mathbf{Q}_{\parallel}\mathbf{Q}'_{\parallel}}$, describes the effects of the effective exciton-exciton interaction mediated by the plasmonic nanoparticle. This has the form of coupling between induced dipoles, as apparent from the characteristic cosine dependence on the relative angle $\phi - \phi'$. In the following, it is interpreted as an additional potential for the center-of-mass motion of the excitons. Due to the symmetry of the system, we chose $\alpha_{\parallel} = \alpha_x = \alpha_y$. The term on the right-hand side, $S_{\mathbf{Q}_{\parallel}}(z_{\text{pl}})$, represents the excitation caused by the external electric field. This excitation is initially scattered and enhanced by the AuNP before coupling to the TMDC. The interaction mediated via the in-plane and the z -axis of the AuNP, respectively, is qualitatively different, as can be seen from the additional imaginary unit in front of the z -component.

In agreement with Ref. [349], we show in Fig. 3.6 that the exchange coupling in Eq. (3.38) leads to the formation of a parabolic lower band and a conical upper band in the excitonic dispersion. For this reason, we have chosen U and V as indices for the parabolic and conical dispersion, respectively. We define their dispersion from

$$\mathcal{E}_{\mathbf{Q}_{\parallel}}^U = E^{1s} + \frac{\hbar^2 \mathbf{Q}_{\parallel}^2}{2M}, \quad (3.41a)$$

$$\mathcal{E}_{\mathbf{Q}_{\parallel}}^V = E^{1s} + \frac{\hbar^2 \mathbf{Q}_{\parallel}^2}{2M} + X_{\mathbf{Q}_{\parallel}}(z_{\text{ex}}). \quad (3.41b)$$

Summarizing our analytical advances so far, we have found that our equations can be diagonalized such that only one of the TMDC exciton components, Eq. (3.38), is affected by the AuNP, while the other component, Eq. (3.37), is completely unchanged compared to the purely excitonic case in Eq. (3.32).

3.5. Plexcitonic States

Similar to identifying the Wannier equation in the semiconductor Bloch equation (SBE) [170, 173, 348] which captures the relative motion of electron and hole. In the conical Bloch equation, In the conical Bloch equation, Eq. (3.38), we encounter an eigenvalue equation that includes the complete excitonic center-of-mass motion with in-plane momentum $\mathbf{Q}_{\parallel}$. This equation captures both the changes in exciton dispersion caused by exchange coupling and the interaction between the plasmon of AuNP and the excitons of TMDC.

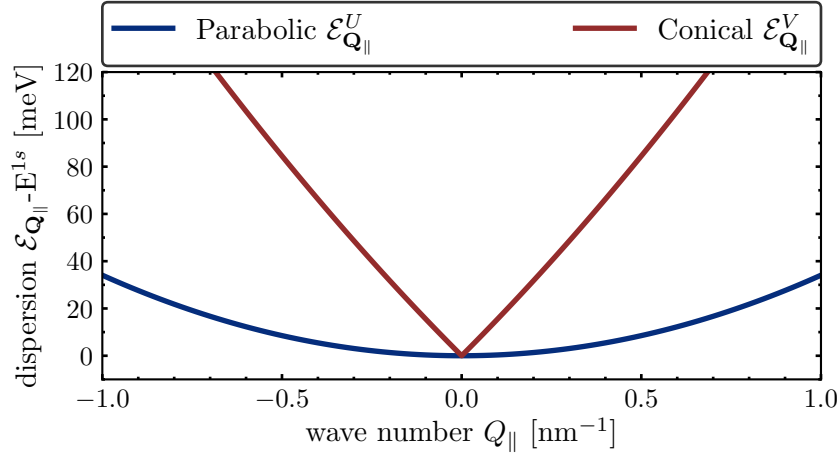


Figure 3.6.: **Excitonic Dispersion.** The exchange coupling causes a split in the dispersion, resulting in a parabolic dispersion for the non-interacting $p_{\mathbf{Q}_{\parallel}}^U$, and a conical dispersion for $p_{\mathbf{Q}_{\parallel}}^V$, which experiences interaction with the gold nanoparticle. The distinctive shape of the dispersion has also influenced its nomenclature.

$$\left[\frac{\hbar^2 \mathbf{Q}_{\parallel}^2}{2M} + X_{\mathbf{Q}_{\parallel}}(z_{\text{ex}}) \right] \Psi_{\mathbf{Q}_{\parallel}}^{\text{R},\lambda} - \frac{1}{(2\pi)^2} \int d^2 \mathbf{Q}'_{\parallel} V_{\mathbf{Q}_{\parallel} \mathbf{Q}'_{\parallel}}(z_{\text{ex}}, z_{\text{pl}}; \omega) \Psi_{\mathbf{Q}'_{\parallel}}^{\text{R},\lambda} = E^{\lambda} \Psi_{\mathbf{Q}_{\parallel}}^{\text{R},\lambda}, \quad (3.42)$$

The nonlocal plasmon-induced potential $V_{\mathbf{Q}_{\parallel} \mathbf{Q}'_{\parallel}}$ determines the center-of-mass motion $\mathbf{Q}_{\parallel}$ on the dispersion modified by the exchange coupling (left side in Eq. (3.42)). Although the Wannier equation and the plexcitonic eigenvalue equation, Eq. (3.42), which we treat as a Schrödinger equation, share formal similarities, they differ qualitatively because the plasmon-induced potential $V_{\mathbf{Q}_{\parallel} \mathbf{Q}'_{\parallel}}$ is complex due to the complex-valued polarizability $\alpha(\omega)$, cf. Eq. (3.40a).

Accordingly, the eigenvalue equation, Eq. (3.42), becomes non-Hermitian which results in complex-valued eigenvalues and requires distinguishing left and right eigenvectors $\Psi_{\mathbf{Q}_{\parallel}}^{\text{L},\lambda}$ and $\Psi_{\mathbf{Q}'_{\parallel}}^{\text{R},\lambda}$ [352, 353] as will be done in Sec. 3.5.2. We will refer to these new eigenstates as *plexcitonic states*, as they describe the hybridized plasmon-exciton states of plasmonic and excitonic character.

In this section, we study the eigenvalue equation numerically and analyze the eigenvalues and eigenvectors in detail, which we will use in subsequent sections to define macroscopic quantities. For this purpose, we choose an oblate spheroid as depicted in Fig. 3.1. The explicit parameters can be found in Tab. A.2.

3.5.1. Plexcitonic Eigenvalues

The eigenvalue analysis of Eq. (3.42) by numerical eigendecomposition in analogy to established methods for the Wannier equation [179, 327] reveals a finite number of eigen-

values with negative real part representing bound states (discussion below). The eigenvalues with positive real part are distributed quasi-continuously along $\mathcal{E}_{\mathbf{Q}_{\parallel}}^{U/V}$. Figure 3.6 shows the dispersion: $\mathcal{E}_{\mathbf{Q}_{\parallel}}^V$ is conical for the parameter range of interest, consistent with recent work [349]. For increasing background permittivity ε_2 , the dispersion interpolates between a cone and a parabola.

Through a parameter study of the background permittivities ε_1 and ε_2 , the aspect ratio of the ellipsoid r_{xy}/r_z , and the distance between AuNP and TMDC $|z_{\text{pl}} - z_{\text{ex}}|$, we observe up to three eigenvalues with negative real part up to 100 meV as well as associated eigenvectors (discussion below). The imaginary contribution (broadening in the spectrum) is on the same order of magnitude. These eigenvalues correspond to an attractive interaction mediated by the plasmon-induced potential $V_{\mathbf{Q}_{\parallel}\mathbf{Q}'_{\parallel}}$ in Eq. (3.42) that spatially localize excitons. We found that each of these eigenvalues originates from the interaction with the plasmonic mode along one of the three Cartesian axes of the nanoparticle. The frequency dependence of the binding energies is discussed in Fig. 3.8. To illustrate these results, we calculate the excitonic density of states (DOS),

$$\text{DOS}(E) = \frac{1}{A} \sum_{\lambda} \delta(E - E^{\lambda}), \quad (3.43)$$

by evaluating the Dirac delta distribution, $\delta(E - E^{\lambda})$, for the real part of the eigenvalues only. To be able to plot the DOS, we approximate the delta distribution with Lorentzian functions $\mathcal{L}_{\gamma_{\ell}}(E, E^{\lambda})$, which introduces an artificial linewidth γ_{ℓ} . Using $\gamma_{\ell} = 1$ meV, Fig. 3.7 shows that only the eigenvalues with negative real parts deviate from the quasi-continuous spectrum. By switching the interaction with the external particle on and off in our numerical implementation, we can compare the purely excitonic system to the interacting plexcitonic one that includes the effective exciton-exciton interaction $V_{\mathbf{Q}_{\parallel}\mathbf{Q}'_{\parallel}}$, mediated via the plasmonic nanoparticle. For our choice of parameters (oblate spheroid), cf. Tab. A.2, we find two interaction-induced peaks at negative energies that result in a non-vanishing density of states at the respective eigenvalue energy. Due to the symmetry of the spheroid, we find that the eigenvalues corresponding to the interaction via the in-plane axes are degenerate and cause the peak at -39 meV, while the peak at -8 meV originates from interaction via the out-of-plane AuNP axis. A detailed parameter study for which parameters we obtain negative eigenvalues and localized eigenstates is provided in Fig. 3.8.

Figure 3.7 displays the excitonic DOS for the conical excitonic dispersion without interaction with the nanoparticle, represented by the blue line. The real and positive eigenvalues are quasi-continuously distributed among the dispersion $\mathcal{E}_{\mathbf{Q}_{\parallel}}^V$. In contrast to strictly two-dimensional systems with parabolic dispersion, the DOS is not a step function due to the presence of a linear term in the dispersion relation, cf. Eq. (3.41b), that depends on the center-of-mass momentum $\mathbf{Q}_{\parallel}$.

For the plexcitonic case (red), a numerical analysis proves that all eigenvalues with positive real part distribute on the conical dispersion and have negligible imaginary parts (on the order of the numerical accuracy). However, the eigenvalues with negative real part deviate significantly from the conical excitonic case, as seen in Fig. 3.7, and have non-negligible imaginary parts. The imaginary parts of the eigenvalues originate from the nature of the lossy plasmon resonance and Förster-type processes between TMDC exciton and AuNP plasmon and introduce additional dephasing channels [28, 30].

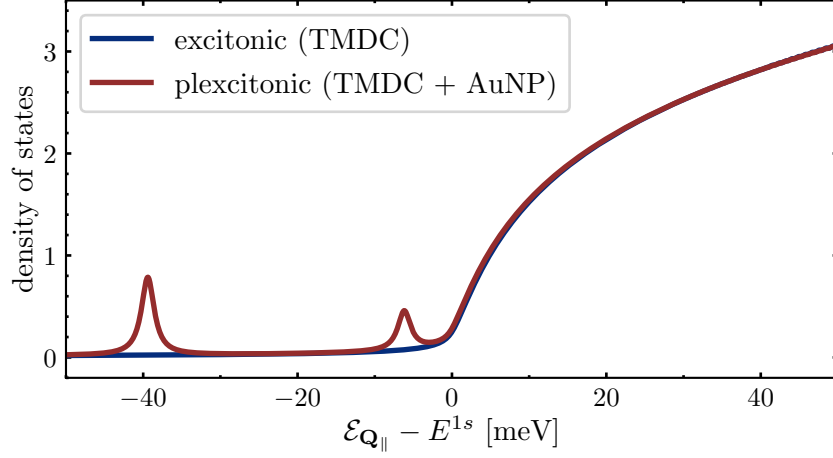


Figure 3.7.: **Excitonic Density of States (DOS)**. Comparison of the excitonic density of states for the interacting plexcitonic and the purely excitonic system, where the potential $V_{\mathbf{Q}_{||}\mathbf{Q}_{||}}$ in Eq. (3.42) was set to zero artificially for a spheroid with $r_{xy} = 8$ nm and $r_z = 4$ nm. The plexcitonic plot exhibits two additional peaks at negative energy, corresponding to the coupling via the in-plane component $\alpha_{||}$ of the AuNP, with a multiplicity of two, and the z component α_z with a multiplicity of one. The peak at ≈ -39 meV corresponds to the in-plane coupling, while the one at ≈ -8 meV is caused by the interaction via the z component. For the graphical representation, we used $\gamma_\ell = 1$ meV.

Based on our findings, we can conclude that the plasmon-mediated exciton-exciton interaction leads to the formation of plexcitonic states, exhibiting negative real part of the eigenvalue. We interpret this feature as the formation of bound states, where the real part of the eigenvalue represents the binding energy. These states cause the deviation in the density of states from the conical excitonic case in Fig. 3.7.

In the following analysis, we examine the plexcitonic eigenvalues that deviate from the dispersion and become negative. This occurs when the TMDC exciton and AuNP plasmon are in resonance. Here, we focus on the distribution of the lowest eigenvalues, which we present in Fig. 3.8. Specifically, we explore two distinct distributions based on the interaction through the in-plane polarizability axis $\alpha_{||}$ of the nanoparticle and the out-of-plane axis α_z .

As anticipated, one can clearly distinguish the distributions of eigenvalues resulting from in-plane and out-of-plane interaction, respectively. We observe spectral ranges where negative eigenvalues are absent, either due to interaction via a single axis or in a narrow spectral range for both axes. In the absence of negative eigenvalues, the individual components are out of resonance, which prevents attractive interactions. However, when the components are in resonance, we detect negative eigenvalues, which we interpret as the binding energy of the exciton in the potential induced by the AuNP. Notably, at certain spectral positions, these binding energies amount to several tens of meV.

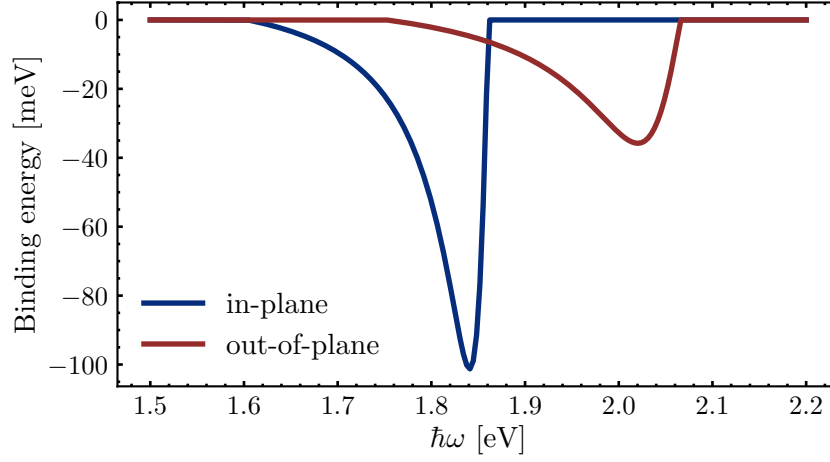


Figure 3.8.: **Plexcitonic Eigenvalue Spectrum.** The lowest eigenvalue of the plexcitonic eigenvalue equation, cf. Eq. (3.42), highly depends on the choice of the spectral position of the excitonic 1s resonance. Here, the lowest eigenvalue for interacting via the in-plane/out-of-plane axis is given.

3.5.2. Plexcitonic Eigenvectors and Probability Density

In this subsection, we analyze the eigenvectors corresponding to the negative eigenvalues presented in the previous section. In the usual excitonic picture, solutions of the Wannier equation [176] describe the relative electron-hole motion and their wave functions represent the probability amplitudes of their motion. Due to its non-Hermitian nature, the physical interpretation of the plexcitonic eigenvalue equation is not straightforward. It generates left and right eigenvectors $\Psi_{\mathbf{Q}_{\parallel}}^{L,\lambda}$, $\Psi_{\mathbf{Q}_{\parallel}}^{R,\lambda}$.

To address this issue, we follow the approach presented in Ref. [354] and define the probability density,

$$\rho^{\lambda}(\mathbf{r}_{\parallel}) \equiv \Psi_{\mathbf{Q}_{\parallel}}^{L,\lambda}(\mathbf{r}_{\parallel}) \Psi_{\mathbf{Q}_{\parallel}}^{R,\lambda}(\mathbf{r}_{\parallel}), \quad (3.44)$$

where we use the normalization scheme

$$\langle \Psi_{\mathbf{Q}_{\parallel}}^{L,\lambda} | \Psi_{\mathbf{Q}_{\parallel}}^{R,\mu} \rangle = \delta^{\lambda\mu}, \quad (3.45)$$

for the left and right eigenvectors $\Psi_{\mathbf{Q}_{\parallel}}^{L,\lambda}$, $\Psi_{\mathbf{Q}_{\parallel}}^{R,\lambda}$ with the scalar product defined as a 2D momentum integral over $\mathbf{Q}_{\parallel}$. Our analysis reveals that the eigenvectors $\Psi_{\mathbf{Q}_{\parallel}}^{L,\lambda}$ and $\Psi_{\mathbf{Q}_{\parallel}}^{R,\lambda}$, respectively, belonging to the three negative eigenvalues (bound states), correspond to the degeneracy of the spatial axes of the gold nanoparticle polarizability $\alpha(\omega)$. They accurately reflect the symmetry of the coupling axis, showing either an x - or y -orientation or a radial symmetry for coupling via the out-of-plane component. We observe that the eigenvectors corresponding to negative eigenvalues are localized near the origin and thus represent bound states, while the eigenvectors corresponding to positive eigenvalues are distributed throughout the momentum space and represent the discretization of the considered Hilbert space. Therefore, the AuNP allows studying exciton localization near the AuNP. To illustrate this, we discuss the real space probability density $\rho(\mathbf{r}_{\parallel})$, defined

in Eq. (3.44). In Fig. 3.9, we plot the real part of the sum of the probability densities, cf. Eq. (3.44), associated with the degenerate eigenvalue from the in-plane coupling, resulting in a ring-shaped distribution around the origin. The x and y components individually exhibit orientation along their respective axes.

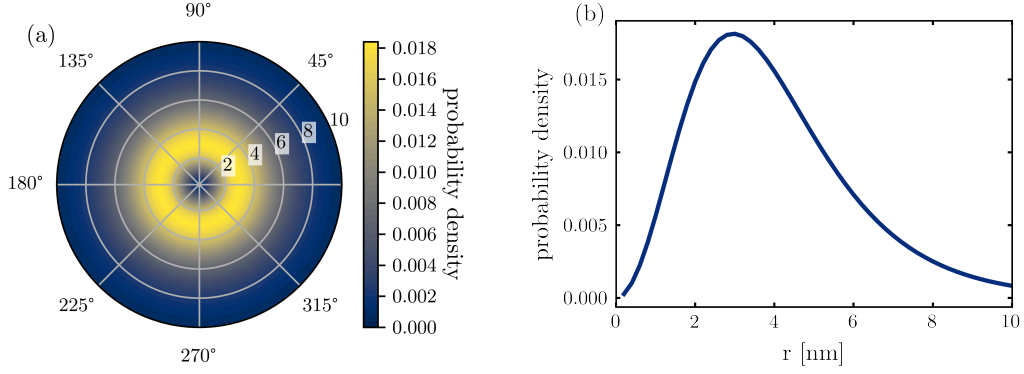


Figure 3.9.: In-Plane Probability Density in Real Space. The eigenvalues corresponding to in-plane interaction are degenerate, here we plot the superposition of the two probability densities corresponding to this attractive in-plane interaction. (a) shows the two-dimensional distribution, while (b) depicts the radial profile of the probability density.

The ring-shaped feature is a result of the in-plane dipole-dipole interaction between the spatially fixed dipole (plasmon) and the dipole that is free to move in a 2D plane (exciton). In contrast to the probability density resulting from in-plane interaction, the probability density for out-of-plane interaction, provided in Fig. 3.10, exhibits a Gaussian distribution centered around the origin of the AuNP position. This outcome can also be derived from the minimization of the dipole-dipole potential for dipoles that are perpendicular to one other.

In summary, we find that the additional states in the density of states reveal negative eigenenergies, cf. Fig. 3.7. These states are spatially confined near the gold nanoparticle, indicating that they correspond to bound states. In Sec. 3.6 and 3.7, we will analyze the implications of these states on macroscopic observables such as the macroscopic TMDC polarization and the electric near-field in more detail.

In contrast to the probability density resulting from in-plane interaction, the probability density for out-of-plane interaction exhibits a Gaussian distribution centered around the origin of the AuNP position. This outcome can also be derived from the minimization of the dipole-dipole potential for dipoles that are perpendicular to one other.

3.6. Exciton Localization

In this section, we analyze the impact of the external nanoparticle on the macroscopic polarization within the TMDC layer, contributing to optical observables via Maxwell's equations. As a macroscopic observable, we use the absolute value of the TMDC polarization in Eq. (3.12) that we map on the plexcitonic eigenstates defined by Eq. (3.42)

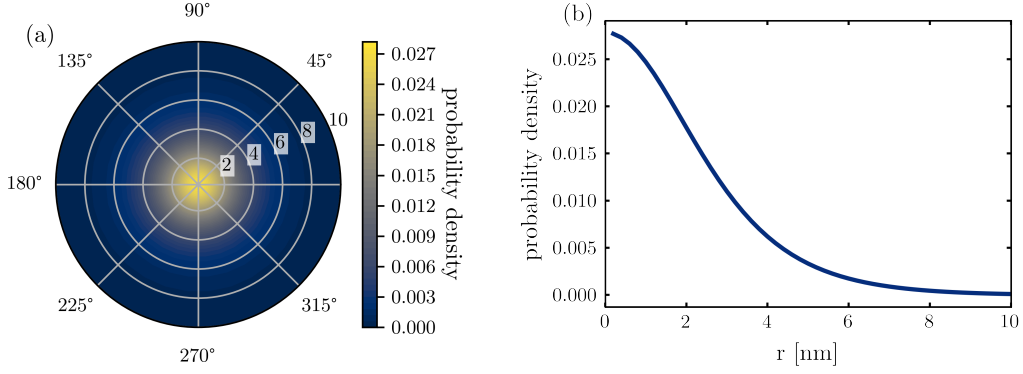


Figure 3.10.: **Out-of-Plane Probability Density in Real Space.** Here, we plot the probability corresponding to interaction via the out-of-plane axis of the AuNP. (a) shows the two-dimensional distribution, while (b) depicts the radial profile of the probability density.

using the plexcitonic expansion

$$p_{\mathbf{Q}_{\parallel}}^V(\omega) = \sum_{\lambda} \Psi_{\mathbf{Q}_{\parallel}}^{R,\lambda} p^{\lambda}(\omega), \quad (3.46)$$

with suitable expansion coefficients p^{λ} . We expand Eq. (3.38) using the plexcitonic expansion in Eq. (3.46), expressing it in terms of right eigenvectors $\Psi_{\mathbf{Q}_{\parallel}}^{R,\lambda}$ which form a complete basis in momentum space. We then project this expanded equation onto the corresponding left eigenvectors $\Psi_{\mathbf{Q}_{\parallel}}^{L,\lambda}$ and utilize the biorthonormality relation [see Eq. (3.45)].

This approach yields a dynamical equation for the expansion coefficient p^{λ} , which we term the *plexcitonic polarization equation*,

$$p^{\lambda}(\omega) = \frac{d^* \varphi_0^*}{(2\pi)^2} \int d^2 \mathbf{Q}'_{\parallel} \frac{\left(\Psi_{\mathbf{Q}'_{\parallel}}^{L,\lambda} \right)^* \left(E_{\mathbf{Q}'_{\parallel}}^{0,V}(z_{\text{ex}}) + S_{\mathbf{Q}'_{\parallel}} \right)}{E^{1s} + E^{\lambda} - \hbar\omega - i\gamma}. \quad (3.47)$$

We observe that the plexcitonic polarization p^{λ} can be excited by two external source terms: the external field at the position of the TMDC, $E_{\mathbf{Q}'_{\parallel}}^{0,V}(z_{\text{ex}})$, and the field scattered by the AuNP, $S_{\mathbf{Q}'_{\parallel}}$, as described in Eq. (3.40b). The latter carries a non-vanishing in-plane momentum $\mathbf{Q}_{\parallel}$. To simplify the notation, we no longer explicitly mention the dependencies of $S_{\mathbf{Q}'_{\parallel}}$. Notably, the complex-valued plexcitonic eigenvalues E^{λ} renormalize not only the resonance energy, as seen in the denominator, but also the dephasing of the nanostructure, through their imaginary part which are negative and thus increase the effective dephasing of the nanostructure.

By Fourier transformation of Eq. (3.12), we find that the macroscopic TMDC polar-

ization, including all contributions from $p_{\mathbf{Q}_{\parallel}}^U(\omega)$ and $p_{\mathbf{Q}_{\parallel}}^V(\omega)$, can be written as

$$\begin{aligned}
 \mathbf{P}_{\text{TMDC}}^{\pm}(\mathbf{r}; \omega) = & \quad (3.48) \\
 & \frac{|d|^2 |\varphi_0|^2}{2} \frac{1}{(2\pi)^2} \int d^2 \mathbf{Q}_{\parallel} \left\{ e^{i\mathbf{Q}_{\parallel} \cdot \mathbf{r}_{\parallel}} \left[\frac{1}{E^{1s} + \frac{\hbar^2 \mathbf{Q}_{\parallel}^2}{2M} - \hbar\omega - i\gamma} \begin{pmatrix} 1 & -e^{-2i\phi} \\ -e^{2i\phi} & 1 \end{pmatrix} \cdot \mathbf{E}_{\mathbf{Q}_{\parallel}}^{0,\pm}(z_{\text{ex}}) \right. \right. \\
 & + \frac{1}{(2\pi)^2} \int d^2 \mathbf{Q}'_{\parallel} \sum_{\lambda} \frac{\Psi_{\mathbf{Q}_{\parallel}}^{R,\lambda} \left(\Psi_{\mathbf{Q}'_{\parallel}}^{L,\lambda} \right)^*}{E^{1s} + E^{\lambda} - \hbar\omega - i\gamma} \begin{pmatrix} e^{-i\phi} e^{i\phi'} & e^{-i\phi} e^{-i\phi'} \\ e^{i\phi} e^{i\phi'} & e^{i\phi} e^{-i\phi'} \end{pmatrix} \cdot \mathbf{E}_{\mathbf{Q}'_{\parallel}}^{0,\pm}(z_{\text{ex}}) \\
 & + \frac{1}{(2\pi)^2} \int d^2 \mathbf{Q}'_{\parallel} \sum_{\lambda} \frac{Q_{\parallel}^2}{\varepsilon_0 \varepsilon_2} \frac{\Psi_{\mathbf{Q}_{\parallel}}^{R,\lambda} \left(\Psi_{\mathbf{Q}'_{\parallel}}^{L,\lambda} \right)^*}{E^{1s} + E^{\lambda} - \hbar\omega - i\gamma} G_{\mathbf{Q}_{\parallel}}^{\text{st}} \begin{pmatrix} e^{-i\phi} e^{i\phi'} & e^{-i\phi} e^{-i\phi'} & -e^{-i\phi} \\ e^{i\phi} e^{i\phi'} & e^{i\phi} e^{-i\phi'} & -e^{i\phi} \end{pmatrix} \\
 & \left. \times \begin{pmatrix} \alpha_{\parallel} E_0^+(\mathbf{r}_{\text{pl}}) \\ \alpha_{\parallel} E_0^-(\mathbf{r}_{\text{pl}}) \\ i\sqrt{2} \alpha_z E_0^z(\mathbf{r}_{\text{pl}}) \end{pmatrix} \right] + \text{c.c.} \left. \right\}.
 \end{aligned}$$

In Eq. (3.48), we can identify three distinct contributions to the macroscopic TMDC polarization. The first term corresponds to half the unperturbed response of the TMDC, which is independent of any interaction with the AuNP. The second term captures the interaction between the TMDC and the AuNP, as well as the TMDC self-interaction, which is described by the plexcitonic eigenvalues E^{λ} and eigenvectors $\Psi_{\mathbf{Q}_{\parallel}}^{L,\lambda}$ and $\Psi_{\mathbf{Q}_{\parallel}}^{R,\lambda}$. The third term represents the external electric field scattered and enhanced by the AuNP and subsequently transferred to the TMDC position, where it contributes to the TMDC polarization. In the limit of vanishing AuNP, the third term vanishes and the second one reproduces the second half of the unperturbed TMDC response.

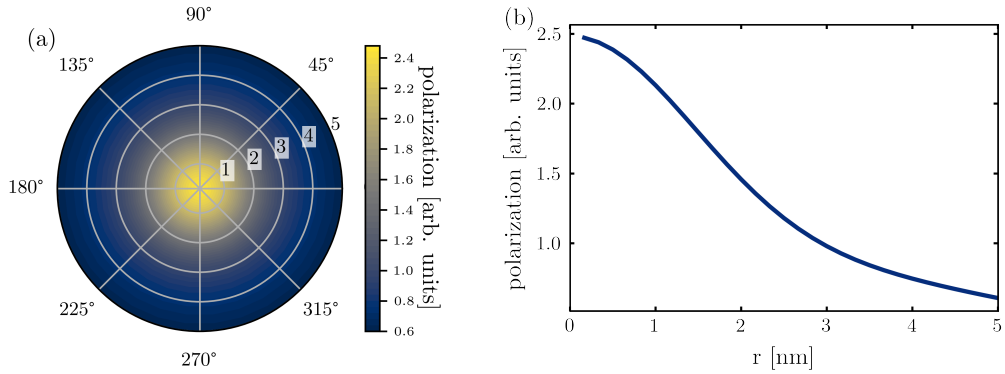


Figure 3.11.: **Full TMDC polarization in Real Space.** In the figure, we see for σ^+ excitation that full TMDC polarization localizes in a radially symmetric way below the metal nanoparticle.

In Fig. 3.11, we plot the absolute value of the resulting macroscopic polarization of the TMDC from Eq. (3.48) when excited by a σ^+ -polarized plane wave and find a radially symmetric distribution of the polarization around the nanoparticle location. According to Eq. (3.48), the spatial localization is mainly attributed to two key processes. The first one is the dipole-dipole interaction between the TMDC exciton and the AuNP

plasmon, leading to the localized plexcitonic states discussed in Sec. 3.5. The second one is the locally enhanced electric field in the TMDC layer, which occurs due to the scattering of the field by the AuNP. These processes can be observed in the individual σ^+/σ^- components of the TMDC polarization excitation with a σ^+ pulse and are given in Fig. 3.12. The results are analogous for σ^- excitation.

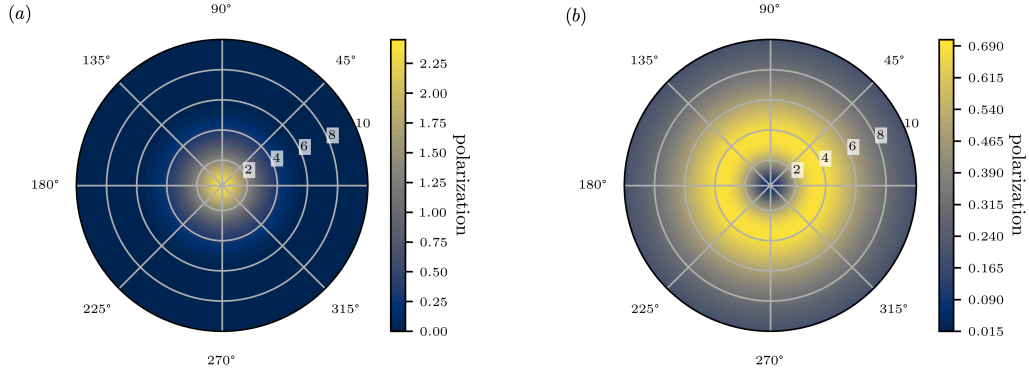


Figure 3.12.: **Circular Components of Macroscopic TMDC Polarization in Real Space.** We plot σ^+ polarization in (a) and σ^- polarization in (b) for the case of σ^+ excitation. In (a), the σ^+ contribution is centered around the origin, while in (b), the σ^- contribution forms a ring around the origin. The full polarization, shown in Fig. 3.11, is obtained as the sum of both contributions.

Our analysis reveals two distinct shapes for the spatial distribution of the macroscopic TMDC polarization. The absolute value of the σ^+ polarization is Gaussian distributed and centered around the origin. For the absolute value of the σ^- polarization, a ring-shaped feature is observed, similar to the probability density investigated in Sec. 3.5.2, with vanishing polarization at the origin. These findings suggest that the selection rules are modified in the electric near-field [355], enabling the excitation of oppositely polarized light. Furthermore, we interpret our results as indicating that polarization of the same direction is primarily induced by the external field that scatters off the AuNP, whereas polarization of the opposite direction mostly originates from the dipole-dipole interaction between the TMDC exciton and AuNP plasmon, reproducing the shape of the probability density from Sec. 3.5.2.

This analysis reveals that proper selection of parameters, positioning a gold nanoparticle on a TMDC monolayer, can induce the formation of plexcitonic states through dipole-dipole interactions. The resulting polarization enhancement in the TMDC underneath the nanoparticle effectively localizes carriers near the AuNP.

3.7. Strong Coupling

This section focuses on the study of the electric field emitted by the nanostructure in response to an external electric field. To calculate the electric field outside the nanostructure, we use the Green's method to solve the wave equation described in Eq. (3.28).

We find for the electric field distribution surrounding the nanostructure,

$$\mathbf{E}_{\mathbf{Q}_{\parallel}}(z; \omega) = \mathcal{G}_{\mathbf{Q}_{\parallel}}^{\text{st}}(z, z_{\text{ex}}) \cdot \mathbf{P}_{\mathbf{Q}_{\parallel}}^{\text{TMDC}}(z_{\text{ex}}; \omega) + \mathcal{G}_{\mathbf{Q}_{\parallel}}^{\text{st}}(z, z_{\text{pl}}) \cdot \mathbf{P}_{\mathbf{Q}_{\parallel}}^{\text{AuNP}}(z_{\text{pl}}; \omega) + \mathbf{E}_{\mathbf{Q}_{\parallel}}^0(z; \omega). \quad (3.49)$$

The TMDC polarization is defined in Eq. (3.48) and the gold polarization is defined as

$$\begin{aligned} \mathbf{P}_{\mathbf{Q}_{\parallel}}^{\text{AuNP}, \pm}(z_{\text{pl}}; \omega) &= \frac{1}{(2\pi)^2} \int d^2 \mathbf{Q}'_{\parallel} \begin{pmatrix} \alpha_{\parallel} E_{\mathbf{Q}'_{\parallel}}^+(z_{\text{pl}}) \\ \alpha_{\parallel} E_{\mathbf{Q}'_{\parallel}}^-(z_{\text{pl}}) \\ \alpha_z E_{\mathbf{Q}'_{\parallel}}^z(z_{\text{pl}}) \end{pmatrix} \\ &\quad + \frac{|d|^2 |\varphi_0|^2}{2} \sum_{\lambda} \frac{1}{E + E^{\lambda} - \hbar\omega - i\gamma} \frac{1}{(2\pi)^2} \int d^2 \mathbf{Q}'_{\parallel} \psi_{\mathbf{Q}'_{\parallel}}^R \frac{Q_{\parallel}'^2}{\varepsilon_0 \varepsilon_1} G_{\mathbf{Q}'_{\parallel}}^{\text{st}}(z_{\text{pl}}, z_{\text{ex}}) \begin{pmatrix} e^{-i\phi'} \alpha_{\parallel} \\ e^{i\phi'} \alpha_{\parallel} \\ i\alpha_z \end{pmatrix} \\ &\quad \times \frac{\alpha_{\parallel}}{(2\pi)^2} \int d^2 \mathbf{Q}''_{\parallel} \left(\psi_{\mathbf{Q}''_{\parallel}}^L \right)^* \left[(e^{i\phi''} E_{\mathbf{Q}''_{\parallel}}^+(z_{\text{ex}}) + e^{-i\phi''} E_{\mathbf{Q}''_{\parallel}}^-(z_{\text{ex}})) \right. \\ &\quad \left. + \frac{Q_{\parallel}^2}{\varepsilon_0 \varepsilon_2} G_{\mathbf{Q}''_{\parallel}}^{\text{st}}(z_{\text{ex}}, z_{\text{pl}}) (e^{i\phi''} E^+(\mathbf{r}_{\text{pl}}) + e^{-i\phi''} E^-(\mathbf{r}_{\text{pl}})) \right]. \end{aligned}$$

The polarization of the system is composed of three contributions. The first one is the dipole response of the AuNP, which is determined by its polarizability α and the external electric field at the AuNP position $\mathbf{E}_{\mathbf{Q}'_{\parallel}}(z_{\text{pl}})$. The second contribution arises from the interaction of the external electric field with the TMDC layer, which is then mediated to the AuNP. The third contribution arises from the effective self-interaction of the plasmon, mediated via the TMDC layer. Importantly, our analysis in Sec. 3.4 relies on the quasi-static approximation, which accurately describes the electric near-field where $\mathbf{Q}_{\parallel} \neq 0$ is dominant. Therefore, our analysis is limited to the electric near-field, which is well-captured by our approach. Note, that to accurately describe the electric far-field and account for radiative processes, it would be necessary to include the $\mathbf{Q}_{\parallel} = 0$ case in the calculation. Numerical evaluation of the electric near-field from Eq. (3.49) yields an optical near-field spectrum.

In Fig. 3.13, we plot the Fourier transformed (purely real space) absolute value of the electric field intensity $|\mathbf{E}(\mathbf{r}; \omega)|^2$ for excitation by plane waves. In contrast to TMDC excitation with a plane wave that only has a vanishing in-plane momentum, scattering off the AuNP generates electric field components in the near-field that possess a non-vanishing center-of-mass momentum $\mathbf{Q}_{\parallel} \neq 0$. These components can interact with momentum-dark excitonic states $\mathbf{Q}_{\parallel} \neq 0$ in the TMDC, illustrating that the observed features result from dark excitons. The spectra in Fig. 3.13 show that the individual non-interacting energy transitions of TMDC exciton and AuNP plasmon are designed so that their respective resonances, excitonic and plasmonic, occur at the same spectral location, cf. Tab. A.2, as depicted in the individual plasmon/exciton plots presented in Fig. 3.1. However, for both systems in contact we observe spectral peak splitting, which is a sign of strong coupling between the individual TMDC exciton and AuNP plasmon oscillators [111, 324]. Since our description relies on the excitation of dark excitons in the near-field, we attribute the occurrence of strong coupling to the spatial localization of near-field excited dark excitons.

We also highlight that our numerical approach allows us to artificially tune the excitonic resonance while keeping the plasmonic resonance fixed. Figure 3.14 shows the two peak

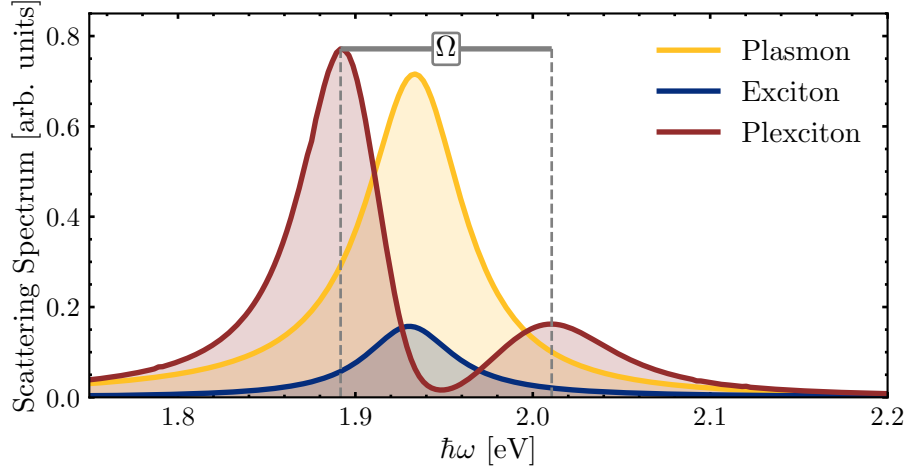


Figure 3.13.: **Peak Splitting** For comparable excitonic and plasmonic resonance energies, the response of the joint system splits into two distinct peaks at lower and higher energy compared to the shared resonance. The scattered electric field is detected at $x = 2$ nm, $y = 0$ nm and $z = -5$ nm. The excitonic resonance energy is $E^{1s} = 1.93$ eV, other parameters for room temperature can be found in Tab. A.2. The plasmonic and plexcitonic spectra are presented in the correct ratio, the excitonic spectrum is scaled for display in the same plot.

positions with varying 1s excitonic resonance. Resonance energies far away from each other have little influence on one another, while we observe a significant peak splitting once the spectral separation of their peaks approaches their linewidths. Compared to the uncoupled case, the interaction leads to a minimum value of the spectral splitting of the observed spectral peaks, which we call effective Rabi splitting. This can be interpreted as avoided crossing behavior and supports the finding that the system behaves in a strong coupling regime.

In Fig. 3.14, we observed that our system reveals a Rabi splitting of several tens of meV and thus clearly operates in the strong coupling regime. The Rabi splitting can be tuned via various system parameters, which we analyze individually to understand their impact on the effective Rabi splitting Ω in Fig. 3.15.

In our study, we observe a decrease in the Rabi splitting as the TMDC/AuNP spacing increases, consistent with the findings in Ref. [111]. This decrease can be attributed to the significant reduction in the interaction strength as the separation between the materials increases.

Furthermore, we investigate the impact of increasing background permittivity ϵ_1 in the upper half-space on the Rabi splitting. We find that as the background permittivity increases, the Rabi splitting decreases. This can be interpreted as the enhanced screening effect resulting from the increased background permittivity, which weakens the overall interaction.

Lastly, we consider the influence of particle radius on the Rabi splitting, which exhibits a scaling behavior similar to the dependence of the plexcitonic eigenvalues E^λ on the radius. Increasing the radius leads to a cubic increase in volume, enhancing the interaction strength. However, this is counteracted by the increase in effective separation, leading to an exponential decrease in the interaction strength.

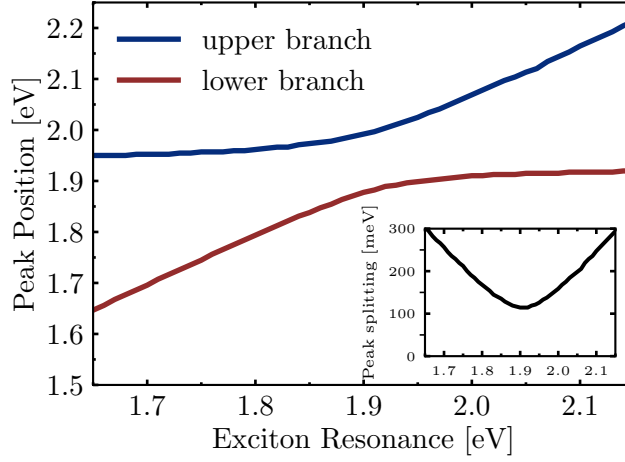


Figure 3.14.: **Avoided Crossing.** Numerically tuning the excitonic resonance allows investigating the peak splitting in the plexcitonic spectrum and shows the avoided crossing behavior of the system, indicating a strong-coupling regime. The given spectrum displays the peak positions, cf. Fig. 3.13, over a wide exciton resonance range. The inset illustrates the peak separation, with its lowest value being the Rabi splitting that is approximately 110 meV in this case. All parameters used in the numerical implementation can be found in Tab. A.2.

3.8. Conclusions

We have presented a self-consistent theoretical approach for the near-field optical interaction between a monolayer of TMDC and a gold nanoparticle. Starting from the excitonic and plasmonic picture, we identified a novel eigenvalue equation that describes the center-of-mass motion of the excitons in an effective potential that features hybridized exciton-plasmon states. In this context, strong coupling is related to the excitation of momentum-dark excitons and their spatial localization in the monolayer near the AuNP: the density of states contains bound states below the excitonic 1s resonance. This interpretation is supported by the plexcitonic probability density and its influence on the spectral and spatial properties of the macroscopic TMDC polarization.

Our analysis strongly suggests that the strong localization near the external particle leads to a strong coupling behavior visible in the electric near-field. Through a detailed parameter study, we establish a connection between the existence of these common states and an avoided crossing behavior in the spectral representation of the system. Our findings provide evidence that metal nanoparticles can be used to effectively localize excitons in two-dimensional TMDC layers.

3.9. Perspectives

For the scope of this thesis, our results of the developed model are limited to the observation of localized excitons close to the metal nanoparticle and strong coupling features in the electrical near-field of the particle. However, the microscopic approach we developed here may be extended to other physical systems or effects. For example, in Ref. [356], we extended the description to a system of a plasmonic crystal, meaning a

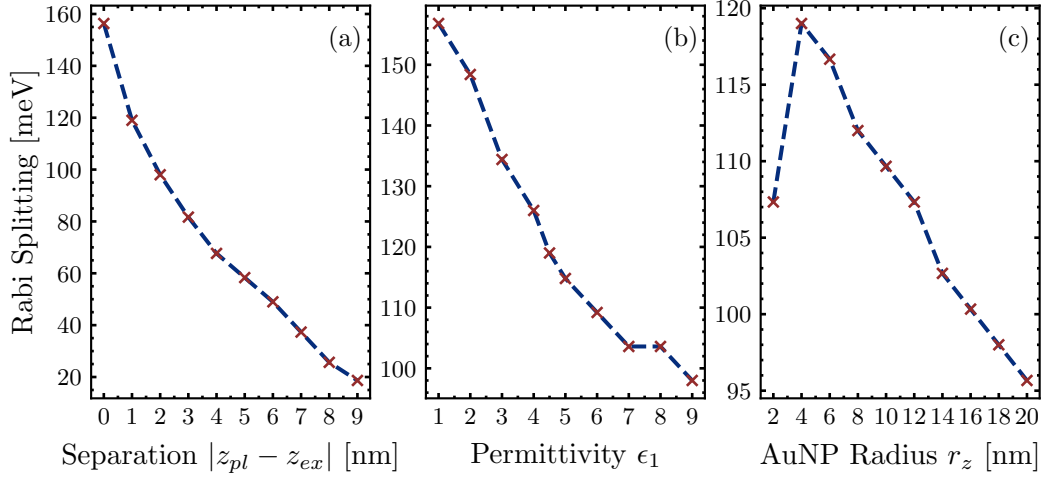


Figure 3.15.: **Parameter Dependencies of Rabi Splitting.** The graphs display the dependence of the Rabi splitting over a parameter range that results in strong coupling. (a) illustrates that an increase in the separation of TMDC and AuNP results in a decrease in the splitting. (b): For an increasing background permittivity ϵ_1 in the upper half space, the Rabi splitting decreases. (c): For an increasing AuNP radius r_z , the Rabi splitting reaches a maximum at ≈ 4 nm. This behavior qualitatively agrees with the dependence of the lowest eigenvalue on the AuNP radius.

meta-crystal consisting of individual nanoparticles coupled to a TMDC monolayer which allowed to compute also the far-field and effectively compare the coupling to bright and dark excitons. Furthermore, as it theoretically resembles a similar physical system, the model might also be used to describe SNOM experiments and the launch of propagating exciton-polaritons which we will describe in Sec. 3.9.1. In addition, to further study localization effects in that theoretical framework it might be useful to upgrade the description to a spatio-temporal description in the Wigner function framework, which we will sketch in Sec. 3.9.2. Finally, a very exciting observation has been the prediction of cross polarized light, e.g., $\sigma_+ \rightarrow \sigma_-$. This is caused by the break-up of the selection rules in the near-field, which is enhanced by the metal nanoparticle and allows for an effective inter-valley exchange. This effect should be observed as a reduction in the degree of polarization. Further investigation of this phenomenon may shed more light on the coupling mechanisms within the TMDC.

3.9.1. Propagating Surface Polaritons

As pointed out in Sec. 2.4.5, one of two main excitations discussed in plasmonics are surface plasmon-polaritons (SPP) that form at metal-dielectric interfaces and can propagate as evanescent wave along the interface. The existence of these SPPs is linked to a sign change of the real part of the permittivity at the interface [51]. Experimental excitation of these polaritons has been found to be challenging using far-field methods alone. Instead, external couplers are typically required to generate in-plane momentum for the excitation. Examples of such couplers include grating couplers, plasmonic metastructures, and all-optical methods utilizing interference effects. These techniques enable efficient excitation of the polaritons and facilitate their study in various experimental se-

tups. This framework has been extended to 2D systems [134, 357], in particular graphene, where travelling surface plasmon-polaritons have been observed experimentally [297] and described theoretically [135].

Recently, there were also experimental evidence of propagating surface exciton-polaritons that were usually excited in SNOM experiments [33, 134, 297, 358–360] which are linked to the negativity of the real part of the TMDC susceptibility. Models for these systems were at most phenomenological [33].

Due to the schematic similarities of our approach to the standard SNOM setup [361, 362], our theory can potentially also be adapted to additionally consider the microscopic degrees of freedom in a SNOM measurements, in particular the material dispersion, and describe the excitation of in-plane propagating polaritons. Therefore, a comparison with the classical theories in Refs. [33, 134, 297, 357–360] would allow describing these materials effectively.

However, the problems are that the description would be limited to propagating surface exciton-polaritons as for finite thickness, the material properties dramatically change and 3D or at least an effective 2D theory have to be employed for an appropriate description of these systems.

3.9.2. Spatio-Temporal Description in Wigner Function Framework

The quantum mechanical probability density is given by

$$\rho(\mathbf{r}, t) = \left| \Psi^\dagger(\mathbf{r}, t) \Psi(\mathbf{r}, t) \right|, \quad (3.50)$$

where the individual wave functions $\Psi(\mathbf{r}, t)$ can be expressed as

$$\Psi(\mathbf{r}, t) = \sum_{\mathbf{k}} \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}} u_{\mathbf{k}\lambda}(\mathbf{r}) \lambda_{\mathbf{k}}(t), \quad \Psi^\dagger(\mathbf{r}, t) = \sum_{\mathbf{k}} \frac{e^{-i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}} u_{\mathbf{k}\lambda}^*(\mathbf{r}) \lambda_{\mathbf{k}}^\dagger(t). \quad (3.51)$$

Assuming that we focus on conduction band electrons only, we can make a connection between the electron density and excitonic operators $P_{\mathbf{k}_1, \mathbf{k}_2}$ using the unit operator method, as presented in Refs. [179, 363]. This allows us express the electron density similar to a three-carrier problem. In a first approximation, this can be given as

$$\rho(\mathbf{r}, t) = \frac{1}{V} \sum_{\mathbf{q}_e, \mathbf{q}_h, \Delta\mathbf{q}} e^{i\Delta\mathbf{q}\cdot\mathbf{r}} P_{\mathbf{q}_h, \mathbf{q}_e}^\dagger(t) P_{\mathbf{q}_h, \mathbf{q}_e + \Delta\mathbf{q}}(t). \quad (3.52)$$

In excitonic coordinates this would read

$$\rho(\mathbf{r}, t) = \frac{1}{V} \sum_{\mathbf{q}, \mathbf{Q}, \Delta\mathbf{q}} \sum_{\nu\nu'} e^{i\Delta\mathbf{q}\cdot\mathbf{r}} \varphi_{\mathbf{q}}^{\nu,*} \varphi_{\mathbf{q}+\beta\Delta\mathbf{q}}^{\nu'} p_{\mathbf{Q}}^{\nu,\dagger} p_{\mathbf{Q}-\Delta\mathbf{q}}^{\nu'}. \quad (3.53)$$

This expression exhibits formal similarities with the spatio-temporal Wigner function description, which we utilize in Sec. 4. This resemblance is not surprising, as recent advances in studying localized phenomena in TMDCs, achieved through strain engineering or Moiré potentials, have been successfully described within the Wigner distribution framework [43, 364–368]. Given the similarity of our approach, which aims to investigate localization effects, it may prove advantageous to adopt a spatio-temporal framework.

4. Spatio-Temporal Description of Microscopic Scattering Equations

Plasmonic structures have been accurately characterized by classical electrodynamics, as discussed in detail in Ch. 2. This has facilitated highly successful analytical descriptions [1, 119, 295], leading to a profound understanding of their behavior and has played a crucial role in the impressive success in numerically characterizing plasmonic structures, using techniques such as finite-difference time-domain simulations, finite-element methods, and boundary element methods.

These initially local descriptions have been very successfully extended to include nonlocal, hydrodynamic effects [145, 151, 253, 261]. More recently, this theoretical toolbox has been extended by the rediscovery of the surface response formalism in terms of Feibelman d -parameters, which effectively describes the optical response via its surface processes [153, 155], yielding qualitatively good results that are compatible with results from *ab initio* simulations [156, 252]. However, all of these approaches are inherently mesoscopic and thus represent “a macroscopic approach to a microscopic problem” [253] that does not provide access to the microscopic electron dynamics.

An initial approach to describe material properties has involved the use of a thermalized excited electron gas through a two-temperature model (2TM) [206, 207, 212, 369, 370]. Based on this, a more advanced inhomogeneous three-temperature model (3TM) [215, 216] has recently emerged, providing valuable insights into specific aspects of the microscopic dynamics, particularly focusing on the spatial electron distribution. However, due to its temperature-based formulation, the 3TM approach is inherently limited in its ability to explore non-equilibrium or non-thermal effects of the excited electron gas.

Other approaches explicitly include the momentum degree of freedom of the electrons, allowing a more detailed treatment of electron kinetics [220, 231, 371, 372]. The complexity of the treatment of the electrons ranges from effective free electron models with empirical parameters [229] to more sophisticated *ab initio* calculations [373, 374] or full numerical simulations of the electric fields [375]. However, these dynamics are usually formulated for translationally invariant systems under the additional assumption of the Thomas-Fermi model, which does not allow the inclusion of nonlocal effects or interband transitions. This was addressed by employing microscopic models for the treatment of the nonlocal response, originally developed for correlated electron-hole gases in semiconductors within the Heisenberg equations of motion formalism [376, 377]. As a result, Boltzmann transport equations were derived, allowing the spatio-temporal treatment of excited carriers in metals [378, 379]. However, as of now, these models are limited to describing dynamics in a single band and typically disregard potential momentum-related anisotropies.

We conclude that although many aspects of plasmon generation, propagation, and relaxation are discussed in the literature, a consistent theory for intra- and interband many-body excitations and nonlocal effects is not currently available, although it would

be very useful for experiments describing charge transfer, for example in catalysis, where hot electrons and holes are becoming increasingly important.

Therefore, a central part of this work will be to extend current microscopic spatio-temporal descriptions [376–380] by developing a comprehensive spatio-temporal, momentum-resolved, multiband description for metals. This extension is essential to incorporate the currently discussed nonlocal, hydrodynamic effects into the theory, while also accounting for interband transitions.

In this chapter, we establish the framework that will serve as the basis for the rest of this work. We begin by describing our fundamental Hamiltonian in Sec. 4.1, which includes multiple interaction channels of the electronic and phononic systems, as well as interactions of the electronic systems with the external electric field through intra- and interband channels. In addition, we incorporate Coulomb effects, which provide valuable insights into band gap renormalization and add geometrical information.

Next, we introduce the Wigner function framework in Sec. 4.2, which is used in Sec. 4.3 to derive spatio-temporal Bloch equations. To allow comparisons with the existing literature, we formulate a coarse-graining mechanism in Sec. 4.5, which explains how macroscopic quantities can be derived from our microscopic approach. This allows us to successfully reproduce the classical Drude model and the hydrodynamic model.

Furthermore, in Sec. 4.6 we pioneer a novel approach by integrating geometrical features into the microscopic equations instead of treating them as a later step. This method, similar to Rytova-Keldysh type approaches [22, 23], incorporates geometric information at the microscopic level.

As a final step in this chapter, in Sec. 4.7 we extend the description in terms of Wigner functions to a two-band approach, which allows including interband polarization in addition to intraband densities.

4.1. Hamiltonian

To describe our systems microscopically, using the method of second quantization as discussed in Sec. 2.1, we introduce the Hamiltonian that contains the relevant physical information of our system. We again employ a semi-classical description of the system, in which material properties are treated quantum-mechanically while the (electric) field quantities are treated using classical Maxwell theory. We assume that our system consists of electrons and phonons, interacting with one another and the electric field so that our Hamiltonian is given by

$$H = H_0 + H_{\text{el-ph}} + H_{\text{lm}} + H_C, \quad (4.1a)$$

with the free Hamiltonian H_0 , the electron-phonon interaction $H_{\text{el-ph}}$, the light-matter interaction H_{lm} , and the Coulomb-mediated electron-electron interaction H_C . In the following, we describe the terms individually. The free Hamiltonian H_0 for the electronic and phonon systems describing the respective electron and phonon dispersion reads

$$H_0 = \sum_{\mathbf{k}} \epsilon_{\mathbf{k}}^{\lambda} \lambda_{\mathbf{k}}^{\dagger} \lambda_{\mathbf{k}} + \sum_{\mathbf{q}\alpha} \hbar\omega_{\mathbf{q}}^{\alpha} b_{\mathbf{q}\alpha}^{\dagger} b_{\mathbf{q}\alpha}, \quad (4.1b)$$

with the electron annihilation (creation) operators $\lambda_{\mathbf{k}}^{(\dagger)}$, the electron dispersion $\epsilon_{\mathbf{k}}^{\lambda}$, the phonon annihilation (creation) operators $b_{\mathbf{q}\alpha}^{(\dagger)}$, and the phonon dispersion $\hbar\omega_{\mathbf{q}}^{\alpha}$. In the

following, we will reserve $\mathbf{k}$ for electron momenta, $\mathbf{q}$ for phonon momenta, λ for electronic bands, and α for the phonon branches. In general, both electrons and phonons should contain multiple bands to adequately describe the system. In Fig. 4.1, we reproduce the electronic band structure as well as the phonon dispersion for our model material, gold. The electronic band structure can be derived using various methods in density functional theory [381–383] while the phonon interaction can be obtained from simpler methods [384–386].

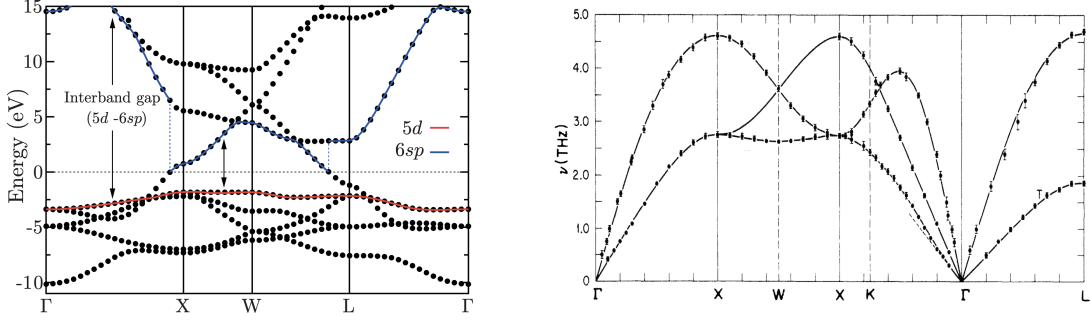


Figure 4.1.: **Electron and Phonon Band Structures of Gold.** (a) Electronic band structure of gold from DFT-PBE calculation, reprinted figure with permission from Ref. [383]. Copyright (2012) by the American Physical Society. (b) Phonon band structure, reprinted figure with permission from Ref. [384]. Copyright (1973) by the American Physical Society.

In addition, we include an interaction of electrons and phonons in the system. This is typically given by the electron-phonon Hamiltonian [168, 170, 387–389]

$$H_{\text{el-ph}} = \sum_{\mathbf{k}\mathbf{q}} g_{\mathbf{q}}^{\lambda\alpha} \lambda_{\mathbf{k}+\mathbf{q}}^{\dagger} \lambda_{\mathbf{k}} (b_{\mathbf{q}\alpha} + b_{-\mathbf{q}}^{\dagger\alpha}), \quad (4.1c)$$

where $g_{\mathbf{q}}^{\lambda\alpha} = g_{-\mathbf{q}}^{\lambda\alpha*}$, in order to be Hermitian. The interaction is usually assumed to be mediated via deformation potential coupling [220, 229] and commonly expressed as $g_{\mathbf{q}}^{\lambda\alpha} = i\sqrt{\hbar N/2M\omega_{\mathbf{q}}} \mathbf{q} \cdot \mathbf{e}_{\mathbf{q}}^{\alpha} V_{\mathbf{q}}^{\lambda}$, [388] where M is the ion mass in the unit cell and N is the ion number in the crystal [388], $V_{\mathbf{q}}^{\lambda}$ is the Fourier transformed electron-ion potential [168]. Here, due to the scalar product, $\mathbf{e}_{\mathbf{q}} \cdot \mathbf{q}$, only longitudinal phonons interact with electrons. Later, we will employ the strongly screened version of the electron-ion potential, cf. Sec. 6. In addition, we assume that the electron-phonon interaction can only lead to intraband scattering processes, which is reasonable considering that the phonon energies are generally small compared to the interband gaps, i.e., on the order of tens of meV versus single-digit eVs.

In this work, the light-matter coupling is treated semi-classically. This means that all expressions describing material quantities are treated quantum mechanically, while all terms referring to field quantities are described classically via the electric field. Thus, our full light-matter Hamiltonian in $\mathbf{r} \cdot \mathbf{E}$ coupling [390] reads

$$H_{\text{lm}} = \frac{ie}{V} \sum_{\mathbf{k}, \mathbf{K}, \lambda} \mathbf{E}_{-\mathbf{K}} \cdot \nabla_{\mathbf{K}} (\lambda_{\mathbf{k}}^{\dagger} \lambda_{\mathbf{k}+\mathbf{K}}) - \sum_{\mathbf{k}, \mathbf{K}, \lambda \neq \lambda'} \mathbf{d}_{\mathbf{k}+\mathbf{K}, \mathbf{k}}^{\lambda\lambda'} \cdot \mathbf{E}_{-\mathbf{K}} (\lambda_{\mathbf{k}}^{\dagger} \lambda'_{\mathbf{k}+\mathbf{K}}). \quad (4.1d)$$

It has two contributions: the first term describes the intraband part of the semiclassical light-matter coupling [170, 391] with the Fourier component $\mathbf{E}_{\mathbf{K}}(t)$ of the exciting electric field $\mathbf{E}(\mathbf{r}, t) = \sum_{\mathbf{K}} \exp\{i\mathbf{K} \cdot \mathbf{r}\} \mathbf{E}_{\mathbf{K}}(t)$ with the elementary charge e . The second term describes the corresponding interband electron-light coupling, similar to the term introduced in Sec. 3.1.2, which describes interband transitions with the dipole moment $\mathbf{d}_{\mathbf{k}+\mathbf{K}, \mathbf{k}}^{\lambda\lambda'}$. This dipole matrix element can be defined in agreement with Sec. 3.1.2 for the three-dimensional case as

$$\mathbf{d}_{\mathbf{k}_1, \mathbf{k}_2}^{\lambda\lambda'} = -\frac{e}{\Omega} \int_{\Omega} d^3\mathbf{r} u_{\lambda\mathbf{k}_1}^*(\mathbf{r}) \mathbf{r} u_{\lambda'\mathbf{k}_2}(\mathbf{r}). \quad (4.1e)$$

In all considered cases, the momentum transfer of the light to material will be small $\mathbf{k} \gg \mathbf{K}$, so that we usually approximate $\mathbf{d}_{\mathbf{k}+\mathbf{K}, \mathbf{k}}^{\lambda\lambda'} \approx \mathbf{d}_{\mathbf{k}, \mathbf{k}}^{\lambda\lambda'} \equiv \mathbf{d}_{\mathbf{k}}^{\lambda\lambda'}$.

For the Coulomb interaction, we account for the carrier-carrier interaction using a two-particle operator [165, 167] which can be given as a momentum transfer between two particles,

$$H_C = \frac{1}{2} \sum_{\substack{\mathbf{k}\mathbf{k}'\mathbf{q} \\ \lambda\lambda'}} V_{\mathbf{q}} \lambda_{\mathbf{k}+\mathbf{q}}^{\dagger} \lambda_{\mathbf{k}'-\mathbf{q}}^{\dagger} \lambda_{\mathbf{k}'}^{\lambda'} \lambda_{\mathbf{k}}. \quad (4.1f)$$

Here the states $\mathbf{k}$ and $\mathbf{k}'$ exchange the momentum $\mathbf{q}$ via a Coulomb process. The Coulomb matrix element contains the Fourier transformed Coulomb potential $V_{\mathbf{q}} = e^2/\varepsilon_0\Omega |\mathbf{q}|^2$ for electrons and ions, where Ω is the crystal volume. We implicitly assume that the Coulomb interaction does not allow interband transitions, since the momenta exchanged are small, and that momentum conservation is fulfilled.

4.2. Wigner Function

In this section, our focus is primarily directed towards the spatial dependence of the microscopic quantities we are investigating. To address this aspect, we introduce a new observable called the *Wigner function* [254, 392, 393].

According to Wigner, in classical statistical mechanics, the Boltzmann distribution provides the probability, denoted as P , of encountering a physical system with energy ε and temperature $\beta = 1/k_B T$, within a phase space volume x_i to $x_i + dx_i$ and p_i to $p_i + dp_i$. This probability for statistical equilibrium is represented by the Gibbs-Boltzmann formula:

$$P(x_1, \dots, x_n; p_1, \dots, p_n) dx_1 \dots dx_n dp_1 \dots dp_n = e^{-\beta\varepsilon} dx_1 \dots dx_n dp_1 \dots dp_n, \quad (4.2)$$

with momentum interval $p_i + dp_i$ and position interval $x_i + dx_i$. The Wigner function, first formulated in 1932 by E. Wigner [392], provides a quantum-statistically analogous expression for the Boltzmann distribution

$$P(x_1, \dots, x_n; p_1, \dots, p_n) = \left(\frac{1}{\hbar\pi}\right)^n \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} dy_1 \dots dy_n \psi^*(x_1 + y_1, \dots, x_n + y_n) \\ \times \psi(x_1 - y_1, \dots, x_n - y_n) e^{2i(p_1 y_1 + \dots + p_n y_n)/\hbar}, \quad (4.3)$$

which gives the correct probabilities when integrated over $x_1 \dots x_n$ or $p_1 \dots p_n$, respectively. However, it cannot be interpreted as the simultaneous probability of position and

momenta as it can take negative values and would in addition violate the Heisenberg uncertainty principle. Consequently, the Wigner function resembles a classical phase-space distribution in several ways: it is real-valued, normalized to one, and its marginal distributions are true probability distributions in either momentum or position [171].

For now, we will focus on a derivation of the dynamics in a single band approximation, so that we use electronic creation and annihilation operators, $a_{\mathbf{k}}^\dagger$ and $a_{\mathbf{k}}$, without a band index. In Sec. 4.7, we will extend this description to a multi-band theory.

We define the Wigner function as [171, 376]

$$f_{\mathbf{k}}(\mathbf{r}, t) = \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} \left\langle a_{\mathbf{k}-\mathbf{q}/2}^\dagger a_{\mathbf{k}+\mathbf{q}/2} \right\rangle (t), \quad (4.4)$$

which contains the electronic creation and annihilation operators, $a_{\mathbf{k}}^\dagger$ and $a_{\mathbf{k}}$. For the two-body problem generally associated with the off-diagonal terms of the Wigner function, the momentum $\mathbf{q}$ describes the relative momentum, while $\mathbf{k}$ describes the center-of-mass motion.

4.3. Bloch Equations for Electronic Wigner Function

In this section, we derive the fundamental equations for the Wigner function $f_{\mathbf{k}}(\mathbf{r}, t)$ that form the basis of the calculations we perform throughout this thesis. The spatio-temporal nature of these equations will be important as we aim to study spatially varying systems in this framework. On the microscopic level, we provide the Wigner function for the dynamics in a single electronic band. Later in this section, we will expand this description to a two band case so that we have Wigner functions describing the respective band occupations (valence and conduction band) and a Wigner function describing the spatio-temporal interband polarization. At the end of the section, we will discuss an approach we developed to include geometrical effects via the Coulomb interaction already at the microscopic level.

We start by deriving the equations of motion for the expectation values of the Wigner function in momentum space, $\left\langle a_{\mathbf{k}-\mathbf{q}/2}^\dagger a_{\mathbf{k}+\mathbf{q}/2} \right\rangle$, and later Fourier transform the respective dynamical equations to the phase space description represented by the Wigner function. The resulting equations are sometimes also called quantum Vlasov equations due to their similarity to the classical Vlasov equations [394, 395].

Many of these calculations follow straightforward textbook knowledge for scattering contributions that are well-known in the semiconductor community for spatially homogeneous systems like quantum wells or 2D materials [170, 173, 228, 376, 380, 396]. However, a Fourier transform from momentum space to real space is not straightforward, as it requires the use of the gradient expansion [376] and detailed knowledge of the coupling elements. This will be presented in the following subsections. We start with a derivation of the free electronic contribution in Sec. 4.3.1 under the parabolic band approximation. In Sec. 4.3.2, we proceed to study the light-matter interaction, for now only including intraband transitions. This is followed by an extensive treatment of the Coulomb-mediated electron-electron interaction, where we derive additional potentials on

the Hartree-Fock level and electron-electron scattering contribution from a second-order correlation expansion. At last, we find electron-phonon scattering contributions mediated via phonon-assisted intraband transitions in Sec. 4.3.4. All in all, this allows us to provide a spatio-temporal equation in Wigner space to describe the electron dynamics in metals.

4.3.1. Free Electronic Motion

To derive the undisturbed contribution for the Wigner function, we have to make a parabolic approximation for the band structure, $\epsilon_{\mathbf{k}} \approx \frac{\hbar^2 \mathbf{k}^2}{2m}$ where m is the effective mass of the individual electronic band. For metals, this is shown to be very close to the free electron mass m_e , which we will assume in the following [389]. Once, we include multiple bands in the description, we will also need to include a band gap in the description. From the band gap, we also derive the electron velocity that reads $\mathbf{v}_{\mathbf{k}} = \hbar \mathbf{k} / m$. This approximation allows to Fourier transform the equations, as shown in App. F.1.1 so that we find

$$\partial_t f_{\mathbf{k}}(\mathbf{r}, t) = -\mathbf{v}_{\mathbf{k}} \cdot \nabla_{\mathbf{r}} f_{\mathbf{k}}(\mathbf{r}, t). \quad (4.5)$$

Here, the temporal derivative of the Wigner function is coupled to its gradients, which scale with their velocities. Accordingly, the free movement of electron on the band structure can be seen as a standard drift equation.

4.3.2. Electron-Light Interaction

The calculation of the contributions of the light-matter Hamiltonian to the equations of motion is straightforward, since the semi-classical light-matter coupling Hamiltonian in Eq. (4.1d) has the same complexity as the free Hamiltonian in Eq. (4.1b). For now, we will only consider intraband contributions, as they are responsible for the formation of the plasmon resonance. Accordingly, we only consider the intraband Hamiltonian in Eq. (4.1d), we obtain

$$\partial_t f_{\mathbf{k}}(\mathbf{r}, t) = -\mathbf{v}_{\mathbf{k}} \cdot \nabla_{\mathbf{r}} f_{\mathbf{k}}(\mathbf{r}, t) + \frac{e}{\hbar} \mathbf{E}(\mathbf{r}, t) \cdot \nabla_{\mathbf{k}} f_{\mathbf{k}}(\mathbf{r}, t). \quad (4.6)$$

On the right-hand side, the first term is the contribution from the free Hamiltonian and the second one is an optically induced excitation that generates transitions in the momentum distribution of the electron distribution. The only assumption in its derivation is to assume that the momentum introduced by the optical field is small compared to the material dispersion, $\mathbf{K} \ll \mathbf{k}$. This dynamical equation, only including the free motion and the optical source term, will be sufficient to derive the classical Drude model in Sec. (4.5.1).

4.3.3. Electron-Electron Interaction

This section is focused on the derivation of contributions to the equations of motion that arise from Coulomb-mediated electron-electron interactions. For the scope of this thesis, we will mostly focus on mean-field effects introduced by the Coulomb interaction. For this purpose, we will start deriving equations of motion on the Hartree-Fock level and study their effect on the equations of motion. In addition, we will also provide spatio-temporal equations of motion for electron-electron scattering beyond Hartree-Fock. In momentum space, we find from the Heisenberg equations of motion framework,

$$i\hbar\partial_t \langle a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_2} \rangle = \sum_{\mathbf{k}, \mathbf{q}} V_{\mathbf{q}} \left[\langle a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}+\mathbf{q}}^\dagger a_{\mathbf{k}} a_{\mathbf{k}_2+\mathbf{q}} \rangle - \langle a_{\mathbf{k}_1-\mathbf{q}}^\dagger a_{\mathbf{k}+\mathbf{q}}^\dagger a_{\mathbf{k}} a_{\mathbf{k}_2} \rangle \right]. \quad (4.7)$$

Here, we already employed the symmetry of the Coulomb potential $V_{\mathbf{q}} = V_{-\mathbf{q}}$. This Coulomb potential results in the usual hierarchy problem resulting from interaction with multi-particle operators. We will approach this using a cluster expansion, cf. Sec. 2.1.1, into singlet states and the doublet correlation [170, 171, 228],

$$\langle a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_2}^\dagger a_{\mathbf{k}_3} a_{\mathbf{k}_4} \rangle = \langle a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_4} \rangle \langle a_{\mathbf{k}_2}^\dagger a_{\mathbf{k}_3} \rangle - \langle a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_3} \rangle \langle a_{\mathbf{k}_2}^\dagger a_{\mathbf{k}_4} \rangle + \langle a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_2}^\dagger a_{\mathbf{k}_3} a_{\mathbf{k}_4} \rangle^c. \quad (4.8)$$

The first two terms on the right-hand side are the mean-field contributions that are usually referred to as Hartree and Fock terms. The last term is the correlation contribution, which describes corrections to the mean-field factorization. The latter are not determined as easily, since one has to derive equations of motion for the correction terms themselves. Hence, as mentioned, we will mostly limit us to the mean-field contributions. For a general Wigner function in momentum space, we find

$$i\hbar\partial_t f_{\mathbf{k}_1, \mathbf{k}_2} = (\epsilon_{\mathbf{k}_2} - \epsilon_{\mathbf{k}_1}) f_{\mathbf{k}_1, \mathbf{k}_2} + \sum_{\mathbf{k}', \mathbf{q}'} V_{\mathbf{q}'} \left[f_{\mathbf{k}'+\mathbf{q}', \mathbf{k}'} f_{\mathbf{k}_1, \mathbf{k}_2+\mathbf{q}'} - f_{\mathbf{k}_1, \mathbf{k}'} f_{\mathbf{k}'+\mathbf{q}', \mathbf{k}_2+\mathbf{q}'} - f_{\mathbf{k}'+\mathbf{q}', \mathbf{k}'} f_{\mathbf{k}_1-\mathbf{q}', \mathbf{k}_2} + f_{\mathbf{k}_1-\mathbf{q}', \mathbf{k}'} f_{\mathbf{k}'+\mathbf{q}', \mathbf{k}_2} \right]. \quad (4.9)$$

This equation can be given in terms of an effective single-particle Hamiltonian with renormalized eigenenergies as has been shown in Ref. [376]. After some straightforward transformations, Eq. (4.9) can be given as

$$i\hbar\partial_t f_{\mathbf{k}_1, \mathbf{k}_2} = \sum_{\mathbf{k}'} \mathcal{E}_{\mathbf{k}_2, \mathbf{k}'} f_{\mathbf{k}_1, \mathbf{k}'} - \mathcal{E}_{\mathbf{k}', \mathbf{k}_1} f_{\mathbf{k}', \mathbf{k}_2}, \quad (4.10)$$

where we define the renormalized one-particle eigenenergy,

$$\mathcal{E}_{\mathbf{k}\mathbf{k}'} \equiv \epsilon_{\mathbf{k}} \delta_{\mathbf{k}\mathbf{k}'} + \sum_{\mathbf{q}'} [V_{\mathbf{k}-\mathbf{k}'} f_{\mathbf{q}', \mathbf{q}'-\mathbf{k}'+\mathbf{k}} - V_{\mathbf{q}'} f_{\mathbf{k}'+\mathbf{q}', \mathbf{k}+\mathbf{q}'}]. \quad (4.11)$$

The obtained results, featuring renormalized eigenenergies with two momentum indices, provide an intuitive understanding of the electron-electron interaction effects on the Hartree-Fock level. The effective one-particle self-energy $\mathcal{E}_{\mathbf{k}\mathbf{k}'}$ is the usual free electron dispersion $\epsilon_{\mathbf{k}}$ renormalized by the electron-electron interaction at the mean field level [376].

Fourier Transformation of Equations of Motion

To obtain dynamical equations of the Wigner function in agreement with the previous section, we Fourier transform Eq. (4.10) and obtain

$$\partial_t f_{\mathbf{k}}(\mathbf{r}) = \partial_t \sum_{\mathbf{q}} f_{\mathbf{k}-\mathbf{q}/2, \mathbf{k}+\mathbf{q}/2} = -\frac{i}{\hbar} \sum_{\mathbf{q}, \mathbf{k}'} e^{i\mathbf{q}\mathbf{r}} (\mathcal{E}_{\mathbf{k}+\mathbf{q}/2, \mathbf{k}'} f_{\mathbf{k}-\mathbf{q}/2, \mathbf{k}'} - \mathcal{E}_{\mathbf{k}', \mathbf{k}-\mathbf{q}/2} f_{\mathbf{k}', \mathbf{k}+\mathbf{q}/2}). \quad (4.12)$$

This Fourier transformation of a product in momentum space can be expressed in terms of a convolution in real space. Employing the convolution theorem, we find

$$\begin{aligned} \partial_t f_{\mathbf{k}}(\mathbf{r}) = & -\frac{i}{\hbar V} \int d^3\mathbf{r}' \sum_{\mathbf{q}, \mathbf{k}'} e^{i\mathbf{q}\mathbf{r}'} \left(e^{i\mathbf{k}'\mathbf{r}} \mathcal{E}_{\mathbf{k}+\mathbf{k}'/2+\mathbf{q}/2, \mathbf{k}-\mathbf{k}'/2+\mathbf{q}/2} \right. \\ & \left. - e^{-i\mathbf{k}'\mathbf{r}} \mathcal{E}_{\mathbf{k}-\mathbf{k}'/2-\mathbf{q}/2, \mathbf{k}-\mathbf{q}/2+\mathbf{k}'/2} \right) f_{\mathbf{k}-\mathbf{k}'/2}(\mathbf{r}-\mathbf{r}'). \end{aligned} \quad (4.13)$$

Here we find that due to the formulation of the dynamical equations in the Wigner phase space formulation, they are inherently nonlocal, which is evident in the space and momentum convolutions. Therefore, we will perform a Taylor expansion in real and momentum space, which we will call a gradient expansion [376, 380].

Gradient Expansion

Following the approach given in Ref. [376], the Wigner function of the form given in Eq. 4.13 is Taylor-expanded in the convolution variables using the general expression

$$f_{\mathbf{k}-\mathbf{k}'/2}(\mathbf{r}-\mathbf{r}') = \sum_{n,m=0}^{\infty} \frac{1}{2^m n! m!} \left(-\mathbf{r}' \cdot \frac{\partial}{\partial \mathbf{r}} \right)^n \left(-\mathbf{k}' \cdot \frac{\partial}{\partial \mathbf{k}} \right)^m f_{\mathbf{k}}(\mathbf{r}). \quad (4.14)$$

From this, the full integro-differential equation, Eq. (4.13), can be transformed into a set of differential equations of infinite order. For our purposes, we will limit ourselves to the first Taylor order in real and momentum space. This approximation allows us to write the Wigner function as follows

$$f_{\mathbf{k}-\mathbf{k}'/2}(\mathbf{r}-\mathbf{r}') \approx f_{\mathbf{k}}(\mathbf{r}) - \mathbf{r}' \cdot \nabla_{\mathbf{r}} f_{\mathbf{k}}(\mathbf{r}) - \mathbf{k}' \cdot \nabla_{\mathbf{k}} f_{\mathbf{k}}(\mathbf{r})/2. \quad (4.15)$$

In this approximation, the resulting dynamical equation including the first correction resulting from nonlocality for the Wigner function can be expressed as

$$\partial_t f_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\hbar} \left[-\frac{\partial \mathcal{E}_{\mathbf{k}}(\mathbf{r})}{\partial \mathbf{k}} \frac{\partial f_{\mathbf{k}}(\mathbf{r})}{\partial \mathbf{r}} + \frac{\partial \mathcal{E}_{\mathbf{k}}(\mathbf{r})}{\partial \mathbf{r}} \frac{\partial f_{\mathbf{k}}(\mathbf{r})}{\partial \mathbf{k}} \right] \quad (4.16)$$

This equation couples the real and momentum space derivatives of the Wigner function to the real and momentum space derivatives of the effective single-particle eigenenergy, $\mathcal{E}_{\mathbf{k}}(\mathbf{r})$. The real-space eigenenergy can be derived as the Fourier transform of Eq. (4.11) according to the definition of the Wigner function,

$$\begin{aligned} \mathcal{E}_{\mathbf{k}}(\mathbf{r}) &= \sum_{\mathbf{q}} e^{i\mathbf{q}\mathbf{r}} \mathcal{E}_{\mathbf{k}+\mathbf{q}/2, \mathbf{k}-\mathbf{q}/2} \\ &= \varepsilon_{\mathbf{k}} + \sum_{\mathbf{q}\mathbf{q}'} e^{i\mathbf{q}\mathbf{r}} V_{\mathbf{q}} f_{\mathbf{q}', \mathbf{q}'+\mathbf{q}} - \sum_{\mathbf{k}'} V_{\mathbf{k}'-\mathbf{k}} f_{\mathbf{k}'}(\mathbf{r}). \end{aligned} \quad (4.17)$$

At this stage, we explicitly distinguish the Hartree and the Fock contribution and introduce the Hartree potential, $\Phi^H(\mathbf{r})$, and the Fock potential, $\Phi_{\mathbf{k}}^F(\mathbf{r})$,

$$\Phi^H(\mathbf{r}) \equiv -\frac{1}{e} \sum_{\mathbf{q}\mathbf{q}'} e^{i\mathbf{q}\mathbf{r}} V_{\mathbf{q}} f_{\mathbf{q}', \mathbf{q}'+\mathbf{q}} = -\frac{1}{e\Omega} \int d^3\mathbf{r}' V(\mathbf{r}-\mathbf{r}') \sum_{\mathbf{k}'} f_{\mathbf{k}'}(\mathbf{r}'), \quad (4.18a)$$

$$\Phi_{\mathbf{k}}^F(\mathbf{r}) \equiv -\frac{1}{e} \sum_{\mathbf{k}' \neq \mathbf{k}} V_{\mathbf{k}'-\mathbf{k}} f_{\mathbf{k}'}(\mathbf{r}). \quad (4.18b)$$

Here, $V(\mathbf{r}-\mathbf{r}')$ is the Coulomb potential in real space for the respective geometry. For our purposes, this will mostly be the solution of Poisson's equation for a spherical geometry [201, 351], Ω denotes a normalization volume of the crystal. Using these definitions, the effective single-particle eigenenergy in Wigner space can be expressed as

$$\mathcal{E}_{\mathbf{k}}(\mathbf{r}) = \varepsilon_{\mathbf{k}} - e\Phi^H(\mathbf{r}) + e\Phi_{\mathbf{k}}^F(\mathbf{r}). \quad (4.19)$$

Note that the Hartree potential, which is defined by the Coulomb potential, the Green's function for a point source, must satisfy the Poisson equation

$$\nabla^2 \Phi^H(\mathbf{r}) = -\rho(\mathbf{r}) = \frac{e}{V} \sum_{\mathbf{k}} f_{\mathbf{k}}(\mathbf{r}). \quad (4.20)$$

We will touch more on the latter equality in Sec. 4.5. Having obtained the definition of the eigenenergy, we can now compute its derivatives,

$$\frac{\partial \mathcal{E}_{\mathbf{k}}(\mathbf{r})}{\partial \mathbf{k}} = \nabla_{\mathbf{k}} \varepsilon_{\mathbf{k}} + e \nabla_{\mathbf{k}} \Phi_{\mathbf{k}}^F(\mathbf{r}) = \nabla_{\mathbf{k}} \varepsilon_{\mathbf{k}} - \sum_{\mathbf{k}'} (\nabla_{\mathbf{k}} V_{\mathbf{k}'-\mathbf{k}}) f_{\mathbf{k}'}(\mathbf{r}), \quad (4.21a)$$

$$\frac{\partial \mathcal{E}_{\mathbf{k}}(\mathbf{r})}{\partial \mathbf{r}} = -e \nabla_{\mathbf{r}} \Phi^H(\mathbf{r}) + e \nabla_{\mathbf{r}} \Phi_{\mathbf{k}}^F(\mathbf{r}) = -e \nabla_{\mathbf{r}} \Phi^H(\mathbf{r}) - \sum_{\mathbf{k}'} V_{\mathbf{k}'-\mathbf{k}} (\nabla_{\mathbf{r}} f_{\mathbf{k}'}(\mathbf{r})). \quad (4.21b)$$

From this, in combination with the contributions of the electron-light interaction in Sec. 4.3.2, we can derive the spatio-temporal equations of motion at the Hartree-Fock level,

$$\begin{aligned} \partial_t f_{\mathbf{k}}(\mathbf{r}, t) + \nabla_{\mathbf{r}} f_{\mathbf{k}}(\mathbf{r}, t) \cdot \left[\mathbf{v}_{\mathbf{k}} + \frac{e}{\hbar} \nabla_{\mathbf{k}} \Phi_{\mathbf{k}}^F(\mathbf{r}) \right] \\ = \frac{e}{\hbar} \nabla_{\mathbf{k}} f_{\mathbf{k}}(\mathbf{r}, t) \cdot [\mathbf{E}(\mathbf{r}, t) - \nabla_{\mathbf{r}} \Phi^H(\mathbf{r}) + \nabla_{\mathbf{r}} \Phi_{\mathbf{k}}^F(\mathbf{r})]. \end{aligned} \quad (4.22)$$

In comparison to the case without electron-electron interaction, we observe the presence of three additional terms: On the left-hand side of the equation, we consider the drift of the electronic Wigner function with respect to the group velocity $\mathbf{v}_{\mathbf{k}} = \nabla_{\mathbf{k}} \varepsilon_{\mathbf{k}} / \hbar$, influenced by momentum gradients of the Fock potential $\Phi_{\mathbf{k}}^F(\mathbf{r})$. This phenomenon is analogous to the well-known band gap renormalization resulting from the Fock term in semiconductors. The difference lies in our consideration of the momentum difference between two states within the same band, rather than the band gap.

On the right-hand side, we observe that the Hartree and Fock potentials contribute additional terms through their spatial derivatives. These terms account for the acceleration

of electrons within these potentials and exhibit similarities to the acceleration induced by the external optical driving field $\mathbf{E}(\mathbf{r}, t)$. These similarities are to be expected, as the Hartree and Fock potentials represent mean-field effects arising from Coulomb interaction with the overall electron distribution.

Scattering Processes from Coulomb-Mediated Electron-Electron Interaction

So far, we have limited ourselves to including terms on the Hartree-Fock level, however, as shown in Eq. (4.8), the cluster expansion also results in correlation contributions which introduce additional effects that are mostly considered as particle number conserving electron-electron scattering processes. We will study these contributions in more detail in the following. This is done by considering the dynamical evolution of the correlated quantity

$$\left\langle a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_2}^\dagger a_{\mathbf{k}_3} a_{\mathbf{k}_4} \right\rangle^c = \left\langle a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_2}^\dagger a_{\mathbf{k}_3} a_{\mathbf{k}_4} \right\rangle - \left\langle a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_4} \right\rangle \left\langle a_{\mathbf{k}_2}^\dagger a_{\mathbf{k}_3} \right\rangle + \left\langle a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_3} \right\rangle \left\langle a_{\mathbf{k}_2}^\dagger a_{\mathbf{k}_4} \right\rangle. \quad (4.23)$$

To accomplish this, one needs to derive equations of motion for the two-particle operator expectation value on the right-hand side. In principle, the full Hamiltonian has to be considered again to derive this equation. However, we focus on the more fundamental contributions arising from the free-particle and carrier-carrier Hamiltonian and neglect the influences of light-matter and electron-phonon interactions on the correlations [175],

$$\begin{aligned} \partial_t \left\langle a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_2}^\dagger a_{\mathbf{k}_3} a_{\mathbf{k}_4} \right\rangle &= \frac{i}{\hbar} (\epsilon_{\mathbf{k}_1} + \epsilon_{\mathbf{k}_2} - \epsilon_{\mathbf{k}_3} - \epsilon_{\mathbf{k}_4}) \left\langle a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_2}^\dagger a_{\mathbf{k}_3} a_{\mathbf{k}_4} \right\rangle \\ &+ \frac{2i}{\hbar} \sum_{\mathbf{q}, \mathbf{k}} V_{\mathbf{q}} \left(\left\langle a_{\mathbf{k}_1+\mathbf{q}}^\dagger a_{\mathbf{k}-\mathbf{q}}^\dagger a_{\mathbf{k}} a_{\mathbf{k}_2}^\dagger a_{\mathbf{k}_3} a_{\mathbf{k}_4} \right\rangle - \left\langle a_{\mathbf{k}_1+\mathbf{q}}^\dagger a_{\mathbf{k}-\mathbf{q}}^\dagger a_{\mathbf{k}_2+\mathbf{q}}^\dagger a_{\mathbf{k}} a_{\mathbf{k}_3} a_{\mathbf{k}_4} \right\rangle \right. \\ &\quad \left. + \left\langle a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_2}^\dagger a_{\mathbf{k}_3} a_{\mathbf{k}+\mathbf{q}}^\dagger a_{\mathbf{k}_4+\mathbf{q}} a_{\mathbf{k}} \right\rangle - \left\langle a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_2}^\dagger a_{\mathbf{k}+\mathbf{q}}^\dagger a_{\mathbf{k}_3+\mathbf{q}} a_{\mathbf{k}_4} a_{\mathbf{k}} \right\rangle \right). \quad (4.24) \end{aligned}$$

We discover the usual hierarchy problem and now find six-operator expectation values. To derive an equation for $\left\langle a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_2}^\dagger a_{\mathbf{k}_3} a_{\mathbf{k}_4} \right\rangle^c$, we need to combine this with dynamical equations for the the Hartree-Fock, resulting in additional four-operator expectation values. This derivation is well documented [183] and hence, we will only sketch the derivation in the following. Once the individual terms are brought to normal order, the appearing higher-order contributions are expanded in two-operator expectation values using the cluster expansion [171, 348]. The resulting equation, as an inhomogeneous first-order ordinary differential equation, can be formally integrated according to Sec. 2.1.2. The occurring integral can be solved using the Markov approximation [170, 228] that neglects memory effects caused by wave functions overlap [397]. This is a good approximation for systems with large damping effects, such as metals, which destroy memory. In a last step, we Fourier transform the resulting equation to Wigner space under the use of the gradient expansion as presented in Eq. (4.14). In zeroth order, we find for the electron-electron scattering contributions in second-order correlation expansion,

$$\left. \partial_t f_{\mathbf{k}}(\mathbf{r}, t) \right|_{\text{Coulomb, corr.}} = \sum_{\mathbf{q}} [\mathcal{W}_{\mathbf{k}+\mathbf{q}, \mathbf{k}}^{\text{in}}(\mathbf{r}, t)(1 - f_{\mathbf{k}}(\mathbf{r}, t)) - \mathcal{W}_{\mathbf{k}, \mathbf{k}+\mathbf{q}}^{\text{out}}(\mathbf{r}, t)f_{\mathbf{k}}(\mathbf{r}, t)].$$

The scattering terms depend on the occupation of the initial state of the scattering event, i.e., in the case of in-scattering, on the electron occupation terms $f_{\mathbf{k}}$, and in the case of out-scattering, on the hole occupation terms $(1 - f_{\mathbf{k}})$. In analogy to Refs. [19, 173, 376, 380, 396, 398], we define the electron-electron in- and out-scattering rates,

$$\begin{aligned} \mathcal{W}_{\mathbf{k}+\mathbf{q}, \mathbf{k}}^{\text{in}}(\mathbf{r}, t) &= \frac{2\pi}{\hbar^2} \sum_{\mathbf{k}'} |V_{\mathbf{q}}|^2 f_{\mathbf{k}+\mathbf{q}}(\mathbf{r}, t) f_{\mathbf{k}'}(\mathbf{r}, t) \times \\ &\quad \times (1 - f_{\mathbf{k}'+\mathbf{q}}(\mathbf{r}, t)) \delta(\varepsilon_{\mathbf{k}+\mathbf{q}} + \varepsilon_{\mathbf{k}'} - \varepsilon_{\mathbf{k}'+\mathbf{q}} - \varepsilon_{\mathbf{k}}), \end{aligned} \quad (4.25)$$

$$\begin{aligned} \mathcal{W}_{\mathbf{k}, \mathbf{k}+\mathbf{q}}^{\text{out}}(\mathbf{r}, t) &= \frac{2\pi}{\hbar^2} \sum_{\mathbf{k}'} |V_{\mathbf{q}}|^2 f_{\mathbf{k}'+\mathbf{q}}(\mathbf{r}, t) (1 - f_{\mathbf{k}'}(\mathbf{r}, t)) \times \\ &\quad \times (1 - f_{\mathbf{k}+\mathbf{q}}(\mathbf{r}, t)) \delta(\varepsilon_{\mathbf{k}+\mathbf{q}} + \varepsilon_{\mathbf{k}'} - \varepsilon_{\mathbf{k}'+\mathbf{q}} - \varepsilon_{\mathbf{k}}). \end{aligned} \quad (4.26)$$

Together with the mean-field contributions via the Hartree and Fock potentials, these are all contributions resulting from the Coulomb-mediated electron-electron interaction.

4.3.4. Electron-Phonon Interaction

As electron-phonon interaction provides the dominant dephasing mechanism in metals [399, 400], we will derive microscopic electron-phonon scattering equations. In the semiconductor community, these equations have allowed to numerically calculate the linewidth of radiative and non-radiative processes [19, 176, 180, 243]. To derive the electron-phonon scattering contributions, we follow a similar derivation as previously for the electron-electron scattering processes. From the electron-phonon Hamiltonian in Eq. (4.1c), we find

$$\begin{aligned} \left. \partial_t f_{\mathbf{k}}(\mathbf{r}) \right|_{\text{el-ph}} &= -\frac{i}{\hbar} \sum_{\mathbf{q}, \mathbf{q}'} e^{i\mathbf{q} \cdot \mathbf{r}} g_{\mathbf{q}'} \left[\left\langle b_{-\mathbf{q}'}^{\dagger} a_{\mathbf{k}-\mathbf{q}/2}^{\dagger} a_{\mathbf{k}-\mathbf{q}'+\mathbf{q}/2} \right\rangle - \left\langle b_{-\mathbf{q}'}^{\dagger} a_{\mathbf{k}+\mathbf{q}'-\mathbf{q}/2}^{\dagger} a_{\mathbf{k}+\mathbf{q}/2} \right\rangle \right. \\ &\quad \left. + \left\langle b_{\mathbf{q}'} a_{\mathbf{k}-\mathbf{q}/2}^{\dagger} a_{\mathbf{k}-\mathbf{q}'+\mathbf{q}/2} \right\rangle - \left\langle b_{\mathbf{q}'} a_{\mathbf{k}+\mathbf{q}'-\mathbf{q}/2}^{\dagger} a_{\mathbf{k}+\mathbf{q}/2} \right\rangle \right]. \end{aligned} \quad (4.27)$$

Here, the Wigner function is coupled to three operator quantities, e.g. $\langle b_{\mathbf{q}_1}^{\dagger} a_{\mathbf{k}_1}^{\dagger} a_{\mathbf{q}_1} \rangle$, which represent phonon-assisted intraband transitions. Since we neglect coherent phonons at this stage, i.e. $\langle b_{\mathbf{q}}^{(\dagger)} \rangle$, the singlet factorization vanishes so that expectation values and correlations become equivalent. These correlations are treated similarly to the electron-electron correlations. By considering the contributions to the dynamics from the free particle Hamiltonian and the electron-phonon Hamiltonian to be dominant, we derive

equations of motion for the phonon assisted intraband transitions,

$$\begin{aligned} \partial_t \langle b_{\mathbf{q}_1}^\dagger a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_2} \rangle &= \frac{i}{\hbar} (\hbar\omega_{\mathbf{q}_1} + \epsilon_{\mathbf{k}_1} - \epsilon_{\mathbf{k}_2}) \langle b_{\mathbf{q}_1}^\dagger a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_2} \rangle \\ &\quad - \sum_{\mathbf{q}} \frac{ig_{\mathbf{q}}}{\hbar} \left[\langle b_{\mathbf{q}_1}^\dagger b_{\mathbf{q}} a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_2-\mathbf{q}} \rangle - \langle b_{\mathbf{q}_1}^\dagger b_{\mathbf{q}} a_{\mathbf{k}_1+\mathbf{q}}^\dagger a_{\mathbf{k}_2} \rangle \right] \\ &\quad + \frac{ig_{\mathbf{q}_1}}{\hbar} \langle a_{\mathbf{k}_1+\mathbf{k}_2}^\dagger a_{\mathbf{k}_2} \rangle - \sum_{\mathbf{k}} \frac{g_{\mathbf{q}_1}}{\hbar} \langle a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}+\mathbf{q}_1}^\dagger a_{\mathbf{k}} a_{\mathbf{k}_2} \rangle. \end{aligned} \quad (4.28)$$

Again we encounter the typical hierarchy problem. This time, we have electron and phonon operators. To address this issue, we will employ a cluster expansion up to the two-operator level. In the following, we will focus on phonon-assisted process and neglect purely electronic Hartree-Fock contributions to the phonon-assisted transitions. Similar to the treatment of electron-electron scattering, we will perform a formal integration that enables us to find a solution under a Markov approximation. After another Fourier transformation, involving a gradient expansion up to zeroth order, we can obtain an expression for the phonon-induced damping of the Wigner function

$$\partial_t f_{\mathbf{k}}(\mathbf{r}, t) \Big|_{\text{el-ph}} = \sum_{\mathbf{q}} [\Gamma_{\mathbf{k}+\mathbf{q},\mathbf{k}}^{\text{in}}(\mathbf{r}, t)(1 - f_{\mathbf{k}}(\mathbf{r}, t)) - \Gamma_{\mathbf{k},\mathbf{k}+\mathbf{q}}^{\text{out}}(\mathbf{r}, t)f_{\mathbf{k}}(\mathbf{r}, t)]. \quad (4.29)$$

The electron-phonon scattering terms also depend on the occupation of the initial state of the scattering event, i.e., in the case of in-scattering, on the electron occupation terms $f_{\mathbf{k}}$, and in the case of out-scattering, on the hole occupation terms $(1 - f_{\mathbf{k}})$. The electron-phonon scattering rates are given by [19, 376, 398, 401]

$$\Gamma_{\mathbf{k}+\mathbf{q},\mathbf{k}}^{\text{in}}(\mathbf{r}, t) = \frac{2\pi}{\hbar^2} \sum_{\pm} |g_{\mathbf{q}}|^2 f_{\mathbf{k}+\mathbf{q}}(\mathbf{r}, t) \times \quad (4.30a)$$

$$\times \left(\frac{1}{2} \pm \frac{1}{2} + n_{\mathbf{q}}(\mathbf{r}, t) \right) \delta(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}} \pm \hbar\omega_{\mathbf{q}}),$$

$$\Gamma_{\mathbf{k},\mathbf{k}+\mathbf{q}}^{\text{out}}(\mathbf{r}, t) = \frac{2\pi}{\hbar^2} \sum_{\pm} |g_{\mathbf{q}}|^2 ((1 - f_{\mathbf{k}+\mathbf{q}}(\mathbf{r}, t)) \times \quad (4.30b)$$

$$\times \left(\frac{1}{2} \pm \frac{1}{2} + n_{\mathbf{q}}(\mathbf{r}, t) \right) \delta(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}} \mp \hbar\omega_{\mathbf{q}}),$$

With this, we have discussed all contributions to the equations of motion of the Wigner function $f_{\mathbf{k}}(\mathbf{r}, t)$. Accordingly, the full equation that we will use throughout the remaining part of this thesis reads,

$$\begin{aligned}
 & \partial_t f_{\mathbf{k}}(\mathbf{r}, t) + \nabla_{\mathbf{r}} f_{\mathbf{k}}(\mathbf{r}, t) \cdot \left[\mathbf{v}_{\mathbf{k}} + \frac{e}{\hbar} \nabla_{\mathbf{k}} \Phi_{\mathbf{k}}^{\text{F}}(\mathbf{r}) \right] \\
 &= \nabla_{\mathbf{k}} f_{\mathbf{k}}(\mathbf{r}, t) \cdot \left[\frac{e}{\hbar} (\mathbf{E}(\mathbf{r}, t) - \partial_{\mathbf{r}} \Phi^{\text{H}}(\mathbf{r}) + \partial_{\mathbf{r}} \Phi_{\mathbf{k}}^{\text{F}}(\mathbf{r})) \right] \\
 &+ \sum_{\mathbf{q}} [\Gamma_{\mathbf{k}+\mathbf{q}, \mathbf{k}}^{\text{in}}(\mathbf{r}, t)(1 - f_{\mathbf{k}}(\mathbf{r}, t)) - \Gamma_{\mathbf{k}, \mathbf{k}+\mathbf{q}}^{\text{out}}(\mathbf{r}, t)f_{\mathbf{k}}(\mathbf{r}, t)] \\
 &+ \sum_{\mathbf{q}} [\mathcal{W}_{\mathbf{k}+\mathbf{q}, \mathbf{k}}^{\text{in}}(\mathbf{r}, t)(1 - f_{\mathbf{k}}(\mathbf{r}, t)) - \mathcal{W}_{\mathbf{k}, \mathbf{k}+\mathbf{q}}^{\text{out}}(\mathbf{r}, t)f_{\mathbf{k}}(\mathbf{r}, t)]. \quad (4.31)
 \end{aligned}$$

The left-hand side considers the drift of the electronic Wigner function with group velocity $\mathbf{v}_{\mathbf{k}} = \nabla_{\mathbf{k}} \epsilon_{\mathbf{k}}$ under the effect of the Fock potential $\Phi_{\mathbf{k}}^{\text{F}}(\mathbf{r})$ that we provide in Eq. (4.18b). The first term on the right-hand side accounts for the acceleration of electrons in response to the external optical driving field $\mathbf{E}(\mathbf{r}, t)$, with additional contributions from the Hartree potential $\Phi^{\text{H}}(\mathbf{r})$ and the Fock potentials $\Phi_{\mathbf{k}}^{\text{F}}(\mathbf{r})$. The terms in the last two lines consider the electron-phonon as well as the electron-electron kinetic scattering in the limit of the standard Boltzmann equations [19, 376, 398, 401]. This equation can be found under different names in the literature, for example quantum Vlasov equation or Boltzmann-Vlasov equation in analogy to momentum closure in hydrodynamic systems [394, 395].

4.4. Phonon Scattering Equations

In metals, the electron-phonon interaction has been studied on a microscopic level in Ref. [220, 371] and widely used within the literature nowadays [229, 231, 372]. For most numerical implementations, an isotropic distribution in momentum space is used, allowing for an effective treatment in terms of the energy in Debye approximation, i.e., under the assumption of a linear phonon dispersion. In many works, this treatment is reduced even further under the assumption that the phonons can be described to be in a thermal equilibrium, allowing to define a phonon temperature which is then modeled using the two-temperature model, cf. [369, 402], or more recently in terms of the three temperature model (3TM) [212, 216–218]. For the scope of this thesis, we aim towards a fully microscopic spatio-temporal description of the electron-phonon scattering processes in metals, allowing to capture the dynamical processes similar to the semiconductor community, cf. Ref. [176]. To achieve this, we introduce a momentum- and space-resolved phonon Wigner function for the phonon mode occupation $n_{\mathbf{q}}(\mathbf{r})$, defined as follows

$$n_{\mathbf{q}}(\mathbf{r}) = \sum_{\mathbf{Q}} e^{i\mathbf{Q}\cdot\mathbf{r}} \left\langle b_{\mathbf{q}-\mathbf{Q}/2}^{\dagger} b_{\mathbf{q}+\mathbf{Q}/2} \right\rangle. \quad (4.32)$$

This equation is formulated using the Wigner phase space representation. As we assume vanishing coherent phonon modes, the phonon Wigner function describes the incoherent phonon mode occupation. The incoherent phonon mode occupation can be related to the temperature of the phonon subsystem.

In a similar derivation to the previous sections, we employ a second-order correlation expansion, assuming dominant electron-phonon contributions and applying the Markov approximation. This leads to a dynamical equation, given as:

$$\partial_t n_{\mathbf{q}}(\mathbf{r}, t) = -\mathbf{v}_{\mathbf{q}}^{\text{ph}} \cdot \nabla_{\mathbf{r}} n_{\mathbf{q}}(\mathbf{r}, t) + \Gamma_{\mathbf{q}}^{\text{em}}(\mathbf{r}, t) (1 + n_{\mathbf{q}}(\mathbf{r}, t)) - \Gamma_{\mathbf{q}}^{\text{abs}}(\mathbf{r}, t) n_{\mathbf{q}}(\mathbf{r}, t). \quad (4.33)$$

The first term considers the drift of phonons with the group velocity $\mathbf{v}_{\mathbf{q}}^{\text{ph}} = \nabla_{\mathbf{q}} \omega_{\mathbf{q}}$. The last two terms describe the phonon thermalization processes via electron-phonon scattering, where the first term accounts for the emission of phonons and the second term for the absorption of phonons. The appearing rates for phonon emission or absorption are given by [174, 245, 401]

$$\Gamma_{\mathbf{q}}^{\text{em}}(\mathbf{r}, t) = \frac{2\pi}{\hbar^2} \sum_{\mathbf{k}} |g_{\mathbf{q}}|^2 f_{\mathbf{k}+\mathbf{q}}(\mathbf{r}, t) (1 - f_{\mathbf{k}}(\mathbf{r}, t)) \delta(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}} + \hbar\omega_{\mathbf{q}}), \quad (4.34a)$$

$$\Gamma_{\mathbf{q}}^{\text{abs}}(\mathbf{r}, t) = \frac{2\pi}{\hbar^2} \sum_{\mathbf{k}} |g_{\mathbf{q}}|^2 f_{\mathbf{k}}(\mathbf{r}, t) (1 - f_{\mathbf{k}+\mathbf{q}}(\mathbf{r}, t)) \delta(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}} - \hbar\omega_{\mathbf{q}}). \quad (4.34b)$$

The emission and absorption processes depend on the occupation of the initial state of the relevant electronic transition, represented by the electron occupation terms $f_{\mathbf{k}}$, and the hole occupation terms $(1 - f_{\mathbf{k}})$. The Dirac δ distributions that appear in the equations account for the conservation of energy and momentum in phonon emission and absorption processes.

4.5. Derivation of Macroscopic Quantities from Microscopic Equations

In this section, we examine the validity of our microscopic approach by investigating its ability to reproduce certain macroscopic equations. By ensuring that our microscopic model correctly captures the macroscopic behavior of the system, we can validate its reliability and applicability in describing the overall dynamics and interactions. To achieve this, we employ a momentum expansion technique [254, 403, 404] on the Wigner function, Eq. (4.4), with respect to the group velocity $\mathbf{v}_{\mathbf{k}}$. By doing so, we effectively coarse-grain the microscopic details, such as the occupation at different wave vectors of electrons $\mathbf{k}$ and phonons $\mathbf{q}$. This approach allows us to derive a mesoscopic description of the system, characterized by the electron charge density $\rho(\mathbf{r}, t)$, electron current density $\mathbf{j}(\mathbf{r}, t)$, and Cauchy stress tensor $\mathbb{P}(\mathbf{r}, t)$ that are defined as

$$\rho(\mathbf{r}, t) = -\frac{e}{V} \sum_{\mathbf{k}} f_{\mathbf{k}}(\mathbf{r}, t), \quad (4.35a)$$

$$\mathbf{j}(\mathbf{r}, t) = -\frac{e}{V} \sum_{\mathbf{k}} \mathbf{v}_{\mathbf{k}} f_{\mathbf{k}}(\mathbf{r}, t), \quad (4.35b)$$

$$\mathbb{P}(\mathbf{r}, t) = -\frac{e}{V} \sum_{\mathbf{k}} \mathbf{v}_{\mathbf{k}} \otimes \mathbf{v}_{\mathbf{k}} f_{\mathbf{k}}(\mathbf{r}, t). \quad (4.35c)$$

Intuitively, this can be seen from the fact that the marginal distributions of the Wigner function are true probability distributions [171]. Occasionally, this methodology is referred to as hydrodynamic momentum expansion. However, to prevent any potential confusion with the model commonly known as the hydrodynamic model [253, 261], we will refer to it as the mesoscopic approach. In the upcoming subsections, we will delve into the standard Drude limit and the hydrodynamic limit for further examination.

4.5.1. Microscopic Drude Model

In classical electrodynamics, the most fundamental description of metal structures is based on the Drude model, which we introduced in Sec. 2.3.1. We now show how this Drude limit can be obtained from our microscopic equations. To achieve this, we make significant simplifications to Eq. (4.31) by neglecting Coulomb effects at the Hartree-Fock level and combining scattering terms in a relaxation time approximation [171]. This leads to the introduction of a damping term γ , and the simplified equation becomes

$$\partial_t f_{\mathbf{k}}(\mathbf{r}, t) = -\mathbf{v}_{\mathbf{k}} \cdot \nabla_{\mathbf{r}} f_{\mathbf{k}}(\mathbf{r}, t) + \frac{e}{\hbar} \mathbf{E}(\mathbf{r}, t) \cdot \nabla_{\mathbf{k}} f_{\mathbf{k}}(\mathbf{r}, t) - \gamma(f_{\mathbf{k}}(\mathbf{r}, t) - f_{\mathbf{k}}^0). \quad (4.36)$$

Accordingly, the Wigner function is driven by its own spatial gradients and the electric field $\mathbf{E}(\mathbf{r}, t)$, while its motion is damped by the phenomenological damping term γ , which takes into account the joint action of all scattering terms.

To obtain an analytical solution for this Boltzmann equation, we linearize the equation in terms of the electric field, i.e., we consider $f_{\mathbf{k}}(\mathbf{r}) = f_{\mathbf{k}}^0 + f_{\mathbf{k}}^1(\mathbf{r}) + \mathcal{O}(E^2)$, where $f_{\mathbf{k}}^0$ represents the spatially homogeneous equilibrium distribution and $f_{\mathbf{k}}^1(\mathbf{r})$ is the first-order perturbation due to the applied electric field. For the first-order perturbation, we find

$$\partial_t f_{\mathbf{k}}^1(\mathbf{r}) = -\mathbf{v}_{\mathbf{k}} \cdot \nabla_{\mathbf{r}} f_{\mathbf{k}}^1(\mathbf{r}) + \frac{e}{\hbar} \mathbf{E}(\mathbf{r}) \cdot \nabla_{\mathbf{k}} f_{\mathbf{k}}^0 - \gamma f_{\mathbf{k}}^1(\mathbf{r}). \quad (4.37)$$

Since we consider spatially homogeneous systems when deriving the classical Drude model, we can neglect spatial dependence, allowing us to Fourier transform Eq. (4.37) to the frequency domain,

$$f_{\mathbf{k}}^1 = \frac{e}{\hbar(-i\omega + \gamma)} \nabla_{\mathbf{k}} f_{\mathbf{k}}^0 \cdot \mathbf{E}. \quad (4.38)$$

By utilizing Eq. (4.35b) and employing integration by parts, we obtain the expression for the current density,

$$\mathbf{j}(\mathbf{r}, t) = \frac{e^2}{mV(-i\omega + \gamma)} \sum_{\mathbf{k}} f_{\mathbf{k}}^0 \mathbf{E}. \quad (4.39)$$

This expression allows us to identify the Drude conductivity $\sigma_D(\omega)$. However, in this thesis, our main focus is on polarizations and permittivities, so we will instead identify the current density $\mathbf{j}$ as the temporal derivative of the polarization $\mathbf{P}$, leading to the well-known equation,

$$\mathbf{P}(\omega) = \varepsilon_0 \chi_D(\omega) \mathbf{E}(\omega), \quad \chi_D(\omega) = -\frac{\omega_p^2}{\omega^2 + i\omega\gamma}. \quad (4.40)$$

Here, $\chi_D(\omega)$ represents the Drude susceptibility, with the usual definition of the plasma frequency,

$$\omega_p = \sqrt{\frac{e^2 n_0}{\varepsilon_0 m}}, \quad n_0 = \frac{1}{V} \sum_{\mathbf{k}} f_{\mathbf{k}}^0. \quad (4.41)$$

Herein, the momentum sum over the Wigner function represents the equilibrium value of the conduction band electron density n_0 . Furthermore, ε_0 is the vacuum permittivity, m the free electron mass, and e the elementary charge. In Sec. 4.7.1, we will discuss how to handle this quantity when multiple bands appear in the description.

4.5.2. Microscopic Hydrodynamic Drude Model

In this section, we will revisit Eq. (4.36) without neglecting spatial derivatives, enabling us to incorporate nonlocality in the description and investigate its impact on the macroscopic polarization $\mathbf{P}$. The main motivation for using the Wigner function approach was to account for nonlocalities at the microscopic level. Here we show how these nonlocal effects are transferred to the mesoscopic regime, leading to a rederivation of the hydrodynamic equations of motion. Once we move to the mesoscopic level, the calculations closely follow the current state of the literature as reported in Refs. [149, 151, 251–253, 259, 261, 264, 405].

As scattering terms conserve the local electronic density in the gradient approximation, they vanish under the momentum sum. This results in a continuity equation for the electron charge density $\rho(\mathbf{r}, t)$ and the electron current density $\mathbf{j}(\mathbf{r}, t)$,

$$\partial_t \rho(\mathbf{r}, t) = -\nabla_{\mathbf{r}} \cdot \mathbf{j}(\mathbf{r}, t), \quad (4.42)$$

where the electric field contribution vanishes as a surface term due to the Gaussian theorem. In order to make statements about the susceptibility of our system, we derive equations of motion for the current density from Eq. (4.36) by multiplying the microscopic dynamical equation (4.36) with the velocity and summing over all momenta. Using $\sum_{\mathbf{k}} \mathbf{v}_{\mathbf{k}} \otimes \nabla_{\mathbf{k}} f_{\mathbf{k}}(\mathbf{r}, t) = -\frac{\hbar}{m} \rho(\mathbf{r}, t) \mathbb{1}$, we obtain

$$\partial_t \mathbf{j}(\mathbf{r}, t) = -\nabla_{\mathbf{r}} \cdot \mathbb{P}(\mathbf{r}, t) - \frac{e}{m} \mathbf{E}(\mathbf{r}, t) \rho(\mathbf{r}, t) - \gamma \mathbf{j}(\mathbf{r}, t). \quad (4.43)$$

The first term on the right-hand side is the divergence of the second-order momentum in the factorization procedure of the Wigner function, which is the Cauchy stress tensor $\mathbb{P}(\mathbf{r}, t)$, defined in Eq. (4.35c). In agreement with common calculations for the hydrodynamic model [406], we now want to identify a pressure-like term, which is usually introduced via a gradient term of an energy-density functional associated with the density-dependent total energy of the electron gas. It is this pressure-like term that introduces the quantum mechanics of the electron system into the semi-classical equations of motion, as we described in Sec. 2.3.4. Therefore, we closely study our stress tensor term. Here, the pressure contributions can only arise from fluctuations of the velocity. Accordingly, we distinguish averages and fluctuations and decompose the velocity $\mathbf{v}_{\mathbf{k}} = \mathbf{v} + \delta \mathbf{v}_{\mathbf{k}}$ in a momentum-independent mean-field contribution $\mathbf{v}$ and a correction $\delta \mathbf{v}_{\mathbf{k}}$. Accordingly, the Cauchy stress tensor in Eq. (4.35c) reveals two contributions,

$$\mathbb{P} = -\frac{e}{V} \mathbf{v} \otimes \mathbf{v} \sum_{\mathbf{k}} f_{\mathbf{k}} - \frac{e}{V} \sum_{\mathbf{k}} \delta \mathbf{v}_{\mathbf{k}} \otimes \delta \mathbf{v}_{\mathbf{k}} f_{\mathbf{k}} = \mathbf{v} \otimes \mathbf{v} \rho + \hat{\mathbb{P}} \quad (4.44)$$

the linear term vanishes from symmetry considerations. The first kinetic term is a tensor product of the mean-field velocity with itself, the second one arises as a correction to the second-order momenta of the Wigner function, which we identify as the pressure contribution, $\hat{\mathbb{P}}$. This way, the velocity is promoted to a velocity field, $\mathbf{v}(\mathbf{r}, t)$, which allows us to factorize the macroscopic current density $\mathbf{j}(\mathbf{r}, t) = \rho(\mathbf{r}, t) \mathbf{v}(\mathbf{r}, t)$ into electron density $\rho(\mathbf{r}, t)$ and velocity field $\mathbf{v}(\mathbf{r}, t)$ of the electrons. Applying this decomposition to the continuity equation, Eq. (4.42), and the Euler equation, Eq. (4.43) we obtain, after some algebraic transformations, the final set of continuity equation and Euler equations

$$\partial_t \rho(\mathbf{r}, t) + \nabla \cdot (\rho(\mathbf{r}, t) \mathbf{v}(\mathbf{r}, t)) = 0, \quad (4.45a)$$

$$\rho(\mathbf{r}, t) (\partial_t + \mathbf{v}(\mathbf{r}, t) \cdot \nabla) \mathbf{v}(\mathbf{r}, t) = -\nabla \cdot \hat{\mathbb{P}}(\mathbf{r}, t) - \frac{e}{m} \mathbf{E}(\mathbf{r}, t) \rho(\mathbf{r}, t) - \gamma \rho(\mathbf{r}, t) \mathbf{v}(\mathbf{r}, t). \quad (4.45b)$$

In the following, we make the assumption that the non-equilibrium carrier distribution induced by optical excitation is thermalized through orientational carrier relaxation via electron-electron scattering [244, 245, 374]. On mesoscopic time scales, this thermalization process is assumed to be fast, which allows us to establish a local equilibrium description for the electrons. As a result, we can define a local equation of state for the pressure contribution in Eq. (4.45b). To achieve this, we utilize the Thomas-Fermi model [407, 408] and express the electron pressure as [246, 250, 251, 259, 405, 408, 408, 409]

$$\hat{\mathbb{P}} = \frac{e}{m} \mathbb{1} p_{\text{Fermi}} = \frac{1}{m e^{2/3}} \kappa \rho^{5/3}(\mathbf{r}, t) \mathbb{1}, \quad \kappa = \frac{\hbar^2}{5m} (3\pi^2)^{2/3}, \quad (4.46)$$

where the proportionality is adapted from the typical Fermi gas constant [246, 258] to our calculations in terms of the electron charge density. This equation can be solved using well-documented methods, as seen in Refs. [149, 151, 251–253, 261, 264, 410]. Starting from Eq. (4.5.2), we can apply a similar approach as in Sec. 4.5.1, perform an expansion in orders of the electric field, and identify the polarization. For detailed derivations, we refer to Ref. [411]. With this, we obtain the following equation for the polarization in linear order,

$$\frac{\beta^2}{\omega^2 + i\gamma\omega} \nabla(\nabla \cdot \mathbf{P}) + \mathbf{P} = -\frac{\varepsilon_0 \omega_p^2}{\omega^2 + i\gamma\omega} \mathbf{E}. \quad (4.47)$$

This equation resembles the standard Drude model derived in Sec. 4.5.1 and includes a correction resulting from the inclusion of nonlocal effects, expressed in terms of spatial gradients. Here, we defined $\beta^2 \equiv \frac{5\kappa\rho_0^{2/3}}{3me^{2/3}} = \frac{3}{5}v_F^2$ with the Fermi velocity v_F . The parameter β is usually understood as the speed of sound in the considered material.

From Eq. (4.47), one can typically obtain the permittivity, $\varepsilon_{\mathbf{Q}}(\omega)$, by distinguishing between the longitudinal and transverse components [147, 250, 253, 259],

$$\varepsilon_{\mathbf{Q}}^L(\omega) = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + i\gamma\omega - \beta^2|\mathbf{Q}|^2}, \quad (4.48a)$$

$$\varepsilon_{\mathbf{Q}}^T(\omega) = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}. \quad (4.48b)$$

This means that the electron pressure contribution affects the $\mathbf{Q}$ -modes in a generalized nonlocal optical response (GNOR) theory [151], which influences only the longitudinal component while leaving the transverse component invariant. The inclusion of these terms becomes prominent for small particles with a large surface-to-volume ratio, where a blue shift of the nanoparticle resonance can be observed [264]. In Sec. 5.5, we will further extend this formalism to include a strong quasi-static THz pump field.

4.6. Geometrical Effects at the Microscopic Level: Hartree Mean-Field Contribution

In general, the optical response of material systems is primarily determined by their material properties. In plasmonic systems, however, the importance of geometry becomes apparent in the derivation of the localized surface plasmon resonance (LSPR) and its pronounced resonance scaling with aspect ratio discussed in Sec. 2.4.1. This property is taken to its extreme in the lightning rod effect. The importance of geometrical effects also contributes significantly to the success of the surface response formalism, as discussed in Sec. 2.3.5.

In light of this, the aim of this section is to present an approach to incorporating geometric information directly into the microscopic equations, thus enabling the study of the optical response of metallic systems with diverse geometric shapes.

4.6.1. Coulomb Potential on the Microscopic Level

Previous approaches, as discussed in Sec. 2.4.1, generally followed a common procedure. They initially established a geometry-independent material model for a bulk material, and subsequently considered the geometrical effects on a macroscopic level by solving Maxwell's/Poisson's equations and applying boundary conditions to the field components defined by the specific geometry. Through this process, an effective polarizability was derived as a solution within the framework of classical Maxwell's theory, mostly up to dipole order. Here, we follow a different approach and use a geometry-resolved solution for the Coulomb potential [201, 351]. This Coulomb potential is introduced on the microscopic level in the microscopic scattering equation for the electronic Wigner distribution, Eq. (4.31). Including Hartree-Fock contributions and neglecting the scattering contributions, the full dynamical equation can be given as

$$\begin{aligned} \partial_t f_{\mathbf{k}}(\mathbf{r}) = & - \left(\mathbf{v}_{\mathbf{k}} - \frac{1}{\hbar} \sum_{\mathbf{k}'} (\nabla_{\mathbf{k}} V_{\mathbf{k}'-\mathbf{k}}) f_{\mathbf{k}'}(\mathbf{r}) \right) \cdot \nabla_{\mathbf{r}} f_{\mathbf{k}}(\mathbf{r}) \\ & + \frac{e}{\hbar} \left[\mathbf{E}^{\text{ext}}(\mathbf{r}) - \nabla_{\mathbf{r}} \Phi^{\text{H}}(\mathbf{r}) - \frac{1}{e} \sum_{\mathbf{k}'} V_{\mathbf{k}'-\mathbf{k}} \nabla_{\mathbf{r}} f_{\mathbf{k}'}(\mathbf{r}) \right] \cdot \nabla_{\mathbf{k}} f_{\mathbf{k}}(\mathbf{r}) , \end{aligned} \quad (4.49)$$

with the definition of the Hartree potential in Eq. (4.18a). The novelty of this approach will now be to include potential geometrical effects on the level of the Coulomb interaction as a solution to Poisson's equation [376]. Therefore, we expand the Coulomb potential in spherical harmonics as given in Refs. [201, 351], which is given for both $\mathbf{r}$ and $\mathbf{r}'$ inside

the nanoparticle as

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \frac{4\pi}{2\ell+1} \left[\frac{1}{\varepsilon_{\infty}} W_{\ell}^0(r, r') + \left(\frac{2\ell+1}{(\ell+1)\varepsilon_{\text{out}} + \ell\varepsilon_{\infty}} - \frac{1}{\varepsilon_{\infty}} \right) \frac{(rr')^{\ell}}{a^{2\ell+1}} \right] \times Y_{\ell m}(\Omega) Y_{\ell m}^*(\Omega'), \quad (4.50)$$

where

$$W_{\ell}^0(r, r') = \frac{r_{<}^{\ell}}{r_{>}^{\ell+1}}, \quad (4.51)$$

with $r_{<} = \min(r, r')$ and $r_{>} = \max(r, r')$. In this form, the respective modes can be approximated in the multipole order of interest. For our purposes, we will restrict ourselves to the dipole mode to compare to the classical dipole case, a generalization will be demanding but straightforward. In the following, the Fock contributions in Eq. (4.49) will be neglected as quantum corrections. However, these should also lead to nonlocal corrections similar to the discussion in Sec. 4.5.2.

4.6.2. Hartree Mean-Field and Oscillator Equation

From Eq. (4.49), we proceed similarly to the derivations of the Drude model where we used the mesoscopic definition of the current density in Eq. (4.35b) and linearize in order of the electric field so that we obtain a second order ordinary differential equation for the current density that reads

$$(\partial_t^2 + \gamma\partial_t)\mathbf{j}^1(\mathbf{r}, t) = \varepsilon_0\omega_p^2\partial_t\mathbf{E}^{\text{tot}}(\mathbf{r}, t). \quad (4.52)$$

In this equation, the total field $\mathbf{E}^{\text{tot}}(\mathbf{r}, t)$ was defined to include the external field, screened by the background contribution to the permittivity ε_0 , as well as the Hartree contribution,

$$\mathbf{E}^{\text{tot}}(\mathbf{r}, t) = \frac{3\varepsilon_{\text{out}}}{2\varepsilon_{\text{out}} + \varepsilon_{\infty}} \mathbf{E}^{\text{ext}}(\mathbf{r}, t) - \nabla_{\mathbf{r}}\Phi^{\text{H}}(\mathbf{r}, t). \quad (4.53)$$

Here, the spherical boundary conditions are already included in the prefactor of the external field, $\mathbf{E}^{\text{ext}}$, which is renormalized to include the background contributions related to ε_{∞} via the Maxwell equations. Using this definition for the total electric field, the equation for the current density becomes

$$(\partial_t^2 + \gamma\partial_t)\mathbf{j}^1(\mathbf{r}, t) = 3\varepsilon_{\text{out}}\varepsilon_0\omega_{\text{LSP}}^2\partial_t\mathbf{E}^{\text{ext}}(\mathbf{r}, t) - \varepsilon_0\omega_p^2\partial_t\nabla_{\mathbf{r}}\Phi^{\text{H}}(\mathbf{r}, t). \quad (4.54)$$

Using the definition of the Hartree potential in Eq. (4.18a), the last term in Eq. (4.54) can be reformulated as

$$\partial_t\nabla_{\mathbf{r}}\Phi^{\text{H}}(\mathbf{r}, t) = \frac{1}{e^2} \left(\nabla_{\mathbf{r}} \otimes \int d\mathbf{r}' (\nabla_{\mathbf{r}'} V(\mathbf{r} - \mathbf{r}')) \right) \cdot \mathbf{j}^1(\mathbf{r}, t), \quad (4.55)$$

so that we find a partial integro-differential equation for the first-order current density,

$$(\partial_t^2 + \gamma\partial_t + \omega_p^2 \frac{\varepsilon_0}{e^2} \left(\nabla_{\mathbf{r}} \otimes \int d\mathbf{r}' (\nabla_{\mathbf{r}'} V(\mathbf{r} - \mathbf{r}')) \right) \cdot) \mathbf{j}^1(\mathbf{r}, t) = 3\varepsilon_{\text{out}}\varepsilon_0\omega_{\text{LSP}}^2\partial_t\mathbf{E}^{\text{ext}}(\mathbf{r}, t). \quad (4.56)$$

From a simplified perspective, Eq.(4.56) resembles the form of a damped harmonic oscillator equation, but it contains a complex tensorial integro-differential expression at the position of the oscillators' eigenfrequency, which depends on the Coulomb potential expanded in spherical harmonics, as given in Eq.(4.50). By evaluating this expression using the geometry-adapted Coulomb potential for a sphere up to dipole order, we obtain the well-known equation

$$(\partial_t^2 + \gamma\partial_t + \omega_{\text{LSP}}^2)\mathbf{j}^1(\mathbf{r}, t) = 3\varepsilon_{\text{out}}\varepsilon_0\omega_{\text{LSP}}^2\partial_t\mathbf{E}^{\text{ext}}(\mathbf{r}, t), \quad (4.57)$$

where we define the plasmon frequency

$$\omega_{\text{LSP}} = \frac{\omega_p}{\sqrt{\varepsilon_{\infty} + 2\varepsilon_{\text{out}}}}. \quad (4.58)$$

Details of the analytical calculations are given in App. G. It is not surprising that this result agrees with the results usually obtained from the Fröhlich condition $\text{Re}\{\varepsilon(\omega)\} = -2\varepsilon_{\text{out}}$ for the localized surface plasmon resonance in quasistatic Mie theory, as similar steps were taken, with the only difference in the order of the evaluation. Hence, this approach reveals that it is possible to include the geometrical information already on the level of the microscopic Wigner equation, similar to approaches using the Rytova-Keldysh type approaches to model the Coulomb interaction in 2D materials [22, 23]. In perspective, this allows including the geometrical effects induced by the Coulomb contributions already on the level of the dynamical equations and allows studying its influence on the electron dynamics.

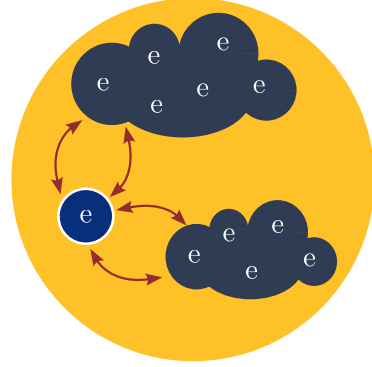


Figure 4.2.: **Illustration of Hartree Mean-Field.** Illustration of the interaction of a single electron with the Hartree mean-field, illustrated as an electron cloud.

4.7. Interband Transitions in Metals: A Microscopic Optical Response Model

Up to this point, we have focused on processes within the conduction band of the material under consideration. This is because the widely considered plasmon resonance is a collective excitation of conduction band electrons, cf. Sec. 2.3.2. However, as we elaborated in Sec. 2.3.6, it becomes necessary to include interband transitions in the material model above a certain energy to accurately model the optical response of metallic materials. For our material of choice, gold, this already becomes important in the visible range at approximately 2.4 eV.

To the best of our knowledge, the current description of interband contributions to the optical response in metals relies on rather phenomenological models with a significant number of fitting parameters [274–279] that do not take the microscopic structure of these materials into consideration. These models solely use the Lorentzian character of the interband transitions for fitting purposes to experimental data recorded in the late 20th century [272, 273]. In contrast to the semiconductor community, the derivation of a microscopic material model for interband transitions in metals has been challenging due to the non-symmetric band structure of metals [382, 383, 412]. Consequently, the

derivation of a comprehensive and accurate interband model for metals has remained elusive thus far and continues to be an ongoing endeavor [413].

In the forthcoming, inspired by the microscopic descriptions used in the semiconductor community, we employ the microscopic framework that we have developed in the previous section and describe our current approach towards a more sophisticated microscopic model for the interband transitions in metal, using the example of gold.

4.7.1. Microscopic Dynamics

To comprehensively describe interband transitions within the microscopic framework, we now extend our description to include multiple bands and transitions in between. Fortunately, the Hamiltonian presented in Sec. 4.1 already allows for an arbitrary number of electronic bands. Building upon the treatment of transition metal dichalcogenides (TMDCs) in Sec. 3, we further expand this approach using the Wigner function method introduced in Sec. 4.2 for two bands. Similar methodologies have been applied to semiconductors in Refs. [334, 376, 377, 379, 380, 401]. Recently, they have gained renewed interest in the context of exciton diffusion [364, 365]. To provide a mathematical description, we define

$$p_{\mathbf{k}}(\mathbf{r}, t) \equiv \sum_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{r}} \left\langle v_{\mathbf{k}-\mathbf{q}/2}^{\dagger} c_{\mathbf{k}+\mathbf{q}/2} \right\rangle, \quad (4.59a)$$

$$f_{\mathbf{k}}^c(\mathbf{r}, t) \equiv \sum_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{r}} \left\langle c_{\mathbf{k}-\mathbf{q}/2}^{\dagger} c_{\mathbf{k}+\mathbf{q}/2} \right\rangle, \quad (4.59b)$$

$$f_{\mathbf{k}}^v(\mathbf{r}, t) \equiv \sum_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{r}} \left\langle v_{\mathbf{k}-\mathbf{q}/2}^{\dagger} v_{\mathbf{k}+\mathbf{q}/2} \right\rangle. \quad (4.59c)$$

Here, in analogy to Ch. 3, these equations use the electron picture to describe the spatio-temporal electron density in the conduction and valence bands by $f_{\mathbf{k}}^c$ and $f_{\mathbf{k}}^v$, respectively.

From these definitions, it is rather straightforward to derive the spatio-temporal equations of motions for these three quantities, which is done in analogy to Sec. 4.3 and Sec. 3.3. Therefore, we assume a parabolic band structure for the individual bands that are separated by an energy gap E_G and assume that the photon momentum is small compared to the electron momentum, $\mathbf{k} \ll \mathbf{K}$ which is a good approximation due to the steep light dispersion compared to the electrons. With this, we obtain in a simplified model, only including the free Hamiltonian and the full electron-light interaction Hamiltonian, dynamical equations for the band occupations in agreement with Ref. [172],

$$\begin{aligned} \partial_t f_{\mathbf{k}}^v(\mathbf{r}, t) = & -\mathbf{v}_{\mathbf{k}}^v \cdot \nabla_{\mathbf{r}} f_{\mathbf{k}}^v(\mathbf{r}, t) + \frac{e}{\hbar} \mathbf{E}(\mathbf{r}, t) \cdot \nabla_{\mathbf{k}} f_{\mathbf{k}}^v(\mathbf{r}, t) \\ & - \frac{2}{\hbar} \mathbf{E}(\mathbf{r}) \cdot \text{Im} \left\{ \mathbf{d}_{\mathbf{k}}^{vc,*} p_{\mathbf{k}}(\mathbf{r}, t) \right\} + \partial_t f_{\mathbf{k}}^v(\mathbf{r}, t) \Big|_{\text{scat}}, \end{aligned} \quad (4.60a)$$

$$\begin{aligned} \partial_t f_{\mathbf{k}}^c(\mathbf{r}, t) = & -\mathbf{v}_{\mathbf{k}}^c \cdot \nabla_{\mathbf{r}} f_{\mathbf{k}}^c(\mathbf{r}, t) + \frac{e}{\hbar} \mathbf{E}(\mathbf{r}, t) \cdot \nabla_{\mathbf{k}} f_{\mathbf{k}}^c(\mathbf{r}, t) \\ & + \frac{2}{\hbar} \mathbf{E}(\mathbf{r}) \cdot \text{Im} \left\{ \mathbf{d}_{\mathbf{k}}^{vc,*} p_{\mathbf{k}}(\mathbf{r}, t) \right\} + \partial_t f_{\mathbf{k}}^c(\mathbf{r}, t) \Big|_{\text{scat}}, \end{aligned} \quad (4.60b)$$

and for the interband polarization,

$$\begin{aligned} \partial_t p_{\mathbf{k}}(\mathbf{r}, t) = & i \Delta\omega_{\mathbf{k}} p_{\mathbf{k}}(\mathbf{r}, t) - \mathbf{v}_{\mathbf{k}}^{vc} \cdot \nabla_{\mathbf{r}} p_{\mathbf{k}}(\mathbf{r}, t) + \frac{e}{\hbar} \mathbf{E}(\mathbf{r}, t) \cdot \nabla_{\mathbf{k}} p_{\mathbf{k}}(\mathbf{r}, t) \\ & - \frac{i}{\hbar} \mathbf{d}_{\mathbf{k}}^{vc} \cdot \mathbf{E}(\mathbf{r}, t) [f_{\mathbf{k}}^c(\mathbf{r}) - f_{\mathbf{k}}^v(\mathbf{r})] + \partial_t p_{\mathbf{k}}(\mathbf{r}, t) \Big|_{\text{scat}}. \end{aligned} \quad (4.61)$$

Here, we used the definition $\mathbf{v}_{\mathbf{k}}^{v(c)} = \nabla_{\mathbf{k}} \epsilon_{\mathbf{k}} / \hbar$ and define the average band velocity $\mathbf{v}_{\mathbf{k}}^{vc} = (\mathbf{v}_{\mathbf{k}}^v + \mathbf{v}_{\mathbf{k}}^c) / 2$ and the momentum-dependent energy difference between the valence and the conduction band $\Delta\omega_{\mathbf{k}} = (\epsilon_{\mathbf{k}}^c - \epsilon_{\mathbf{k}}^v) / \hbar$. In order to perform the Fourier transform of the band gap contribution, we employed the usual parabolic band approximation. The dipole matrix element, $\mathbf{d}_{\mathbf{k}}^{vc}$, is defined in Eq. (4.1e).

These equations form the foundation of various phenomena considered throughout this thesis and will be used in many instances in Chs. 5 and 6. Due to their spatio-temporal formulation depending on momentum and real space gradients, their solution becomes non-trivial and mostly only possible utilizing approximations.

4.7.2. Macroscopic Observables – Translationally Invariant Systems

For a first approach towards interband transitions in metals using this microscopic framework, we study translationally invariant bulk systems such that spatial gradients and the spatial dependence of the respective Wigner functions can be neglected. In addition, for an analytical approach towards the optical spectra of these systems, we will expand the equations in orders of the electric field,

$$p_{\mathbf{k}} = p_{\mathbf{k}}^1 + p_{\mathbf{k}}^2 + \mathcal{O}(E^3), \quad (4.62a)$$

$$f_{\mathbf{k}} = f_{\mathbf{k}}^0 + f_{\mathbf{k}}^1 + f_{\mathbf{k}}^2 + \mathcal{O}(E^3). \quad (4.62b)$$

With this, the microscopic equations in linear order become

$$f_{\mathbf{k}}^{1,c}(\mathbf{Q}, \omega) = \frac{e}{\hbar - i\omega + i\mathbf{v}_{\mathbf{k}}^c \cdot \mathbf{Q} + \gamma_{\mathbf{k}}} \cdot \nabla_{\mathbf{k}} f_{\mathbf{k}}^{0,c} \cdot \mathbf{E}_{\mathbf{Q}}(\omega), \quad (4.63a)$$

$$p_{\mathbf{k}}^1(\mathbf{Q}, \omega) = \frac{1}{\hbar \Delta\omega_{\mathbf{k}} - \omega + \mathbf{v}_{\mathbf{k}}^{vc} \cdot \mathbf{Q} - i\gamma'_{\mathbf{k}}} \cdot \mathbf{d}_{\mathbf{k}}^{vc} [f_{\mathbf{k}}^{0,v} - f_{\mathbf{k}}^{0,c}] \cdot \mathbf{E}_{\mathbf{Q}}(\omega). \quad (4.63b)$$

Here, we have used an effective momentum-resolved relaxation time approximation [171, 176] and introduced an intraband scattering rate $\gamma_{\mathbf{k}}$ and an interband scattering rate $\gamma'_{\mathbf{k}}$ for the scattering processes in Eq. (4.60) and (4.61).

Similar to the phenomenological material models [274, 277] and similar to the approaches using microscopic material models in Refs. [172, 334], we will consider the macroscopic polarization to be the sum of a microscopic and a macroscopic contribution

$$\mathbf{P}(\mathbf{r}; \omega) = \mathbf{P}^{\text{inter}}(\mathbf{r}; \omega) + \mathbf{P}^{\text{intra}}(\mathbf{r}; \omega). \quad (4.64)$$

The individual components are given in agreement with previous definitions in Eq. (3.12) and (4.35), where now provide general equations for the polarizations,

$$\mathbf{P}^{\text{inter}}(\mathbf{r}, t) = \frac{1}{V} \sum_{\mathbf{k}} \mathbf{d}_{\mathbf{k}}^{vc} p_{\mathbf{k}}(\mathbf{r}, t) + c.c., \quad (4.65a)$$

$$\mathbf{P}^{\text{intra}}(\mathbf{r}, t) = -\frac{ie}{\omega V} \sum_{\mathbf{k}\lambda} \mathbf{v}_{\mathbf{k}}^{\lambda} \cdot f_{\mathbf{k}}^{\lambda}(\mathbf{r}, t). \quad (4.65b)$$

Assuming the velocity field to be the first momentum gradient of the band structure, this approach can capture an arbitrary band structure. Using these definitions together with the solution of the linearized microscopic equations of motions, we find for the interband polarization,

$$\mathbf{P}_{\mathbf{Q}}^{\text{inter}}(\omega) = \frac{1}{\hbar V} \sum_{\mathbf{k}} \frac{[f_{\mathbf{k}}^{0,c} - f_{\mathbf{k}}^{0,v}] \mathbf{d}_{\mathbf{k}}^{vc,*} \otimes \mathbf{d}_{\mathbf{k}}^{vc}}{\Delta\omega_{\mathbf{k}} - \omega + \mathbf{v}_{\mathbf{k}}^{vc} \cdot \mathbf{Q} - i\gamma'_{\mathbf{k}}} \cdot \mathbf{E}_{\mathbf{Q}}(\omega) + c.c., \quad (4.66)$$

and for the intraband polarization,

$$\mathbf{P}_{\mathbf{Q}}^{\text{intra}}(\omega) = -\frac{e^2}{\hbar V} \sum_{\mathbf{k}\lambda} \frac{(\nabla_{\mathbf{k}} \mathbf{v}_{\mathbf{k}}^{\lambda}) f_{\mathbf{k}}^{0,\lambda}}{\omega^2 - i\omega \mathbf{v}_{\mathbf{k}}^{\lambda} \cdot \mathbf{Q} + i\gamma_{\mathbf{k}} \omega} \cdot \mathbf{E}_{\mathbf{Q}}(\omega). \quad (4.67)$$

The interband contribution resembles individual Lorentz oscillators that are placed throughout the Brillouin zone, with an individual oscillator strength $\mathbf{d}_{\mathbf{k}}^{vc,*}$. This scenario is equivalent to our findings in Ch. 3, where the dipole matrix element was approximated with its value at the K and K' points. Depending on the material complexity, these quantities can be derived in approximation, for example from tight-binding approaches [327, 414] for graphene, and can generally be obtained from calculations in density functional theory (DFT) [11, 381–383]. Having access to these quantities, would allow to significantly reduce the number of fitting parameters necessary to describe the optical response of metal nanostructures compared to current models [274, 277, 413]. Unfortunately, simple approximations fail to describe the complex, asymmetric band structure of gold quantitatively, so that we will, for the scope of this thesis, mostly limit ourselves to a qualitative discussion of the derived model and fit experimental data using a simplified model that we will derive from our complex momentum-resolved model in the following.

As we will be interested in a derivation of a pure material response, we will assume plane wave excitation. From this, one can derive the Drude model for the intraband contribution, as we have presented in Sec. 4.5.1. As we are lacking information about the dipole matrix elements, we need to transform our description to a discrete version, incorporating a finite number of interband transitions in the form of Lorentzian oscillators, similar to Sec. 2.3.6. This results in the simplified equation

$$\mathbf{P}(\omega) = \epsilon_0 \left(\frac{-\omega_p^2}{\omega^2 + i\gamma\omega} + \frac{1}{\hbar} \sum_j^N \frac{|d_j^{vc}|^2 (n_c - n_v)}{\Delta\omega_j - \omega - i\gamma'_j} \right) \mathbf{E}(\omega). \quad (4.68)$$

The first term describes the intraband motion of the electrons within the conduction band, a definition of the plasma frequency ω_p can be found in Sec. 4.5.1. As the valence band is fully occupied at equilibrium, there are no available states that electrons could scatter into, which is why we effectively neglect intraband contributions from the valence band. The second term describes interband processes with a transition energy $\hbar\Delta\omega_j$, an oscillator strength d_j^{vc} , and a line width γ'_j . These parameters will be used in Fig. 4.3 to fit the experimental data from Ref. [272]. The occurring densities are the conduction and valence band electron densities, n_c and n_v , respectively.

To model the microscopic response of our system, we include a background contribution ϵ_{∞} in analogy to the usual macroscopic material models, so that the full permittivity

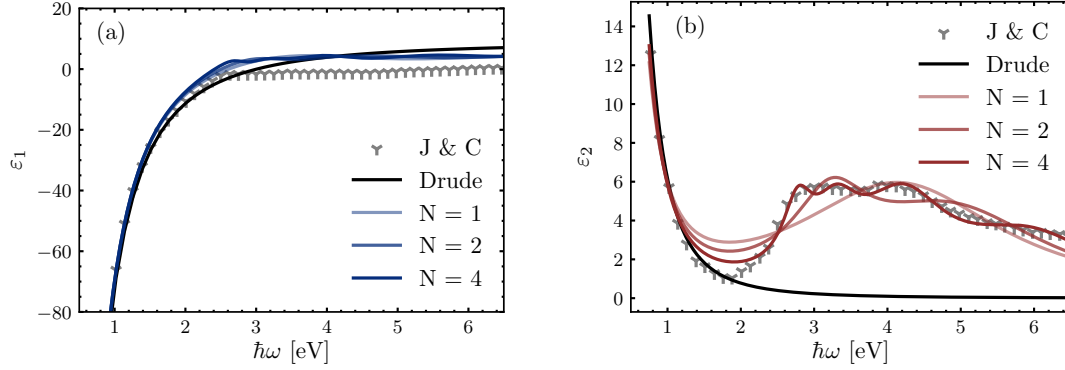


Figure 4.3.: **Microscopic Model Fitting to Johnson and Christy Data.** We perform a fitting analysis of the Johnson and Christy data (J & C) [272] using a standard Drude model and our microscopic permittivity $\epsilon_{\text{tot}}(\omega)$ from Eq. (4.69). The plot in (a) displays the real part of the permittivity, ϵ_1 , while in (b), we present the imaginary part, ϵ_2 .

becomes

$$\epsilon_{\text{tot}}(\omega) = \epsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} + \frac{1}{\hbar} \sum_j^N \frac{|d_j^{\text{vc}}|^2 (n_c - n_v)}{\Delta\omega_j - \omega - i\gamma_j'} \quad (4.69)$$

In Fig. 4.3, we see that a qualitatively good agreement with the experiment is already obtained by including a small number of interband transitions. These results are in good agreement with Ref. [275], where a qualitatively equivalent model is derived from a macroscopic perspective. However, due to the simplification we used in response to the missing DFT data regarding the optical dipole matrix elements, these results do not yet reveal the full strength of the microscopic approach as the number of fitting parameters is still on the same order as in the current literature [275, 277, 413]. The knowledge of these parameters would significantly improve the current description of the interplay of interband and intraband excitations in metals.

At this stage, it is important to acknowledge that the current treatment of the optical response is not yet fully self-consistent, since the electric field entering Eq. (4.68) still includes the field generated by the material itself. While solving the self-consistency problem has so far led to difficulties in accurately reproducing the characteristic Drude shape, it is worth noting that the current approach has successfully reproduced the macroscopic Drude model. It is important to note that the original derivation of the Drude model does not take self-consistency into account. For future studies on extended systems, a thorough investigation of this aspect will be crucial. To address these effects in more detail for metal nanoparticles, we will use the self-consistent treatment introduced in Sec. 2.4.4 in the following section.

4.7.3. Self-Consistent Optical Response of Metal Nanoparticles

When we want to describe the optical response of spatially extended systems, we have to take their depolarization into account self-consistently. This has been elaborated for the Drude model in Sec. 2.4.4 which we now extend to also include the interband terms

derived in the previous section. We again distinguish between the external field $\mathbf{E}_{\text{ext}}$, the background polarization of the sphere $\mathbf{P}_b$, and the Drude polarization $\mathbf{P}_d$, and now add the interband polarization $\mathbf{P}_{\text{inter}}$. The self-consistent total field $\mathbf{E}_{\text{tot}}$ within the nanoparticle then reads

$$\mathbf{E}_{\text{tot}}(\omega) = \mathbf{E}_{\text{ext}}(\omega) - \frac{1}{3\varepsilon_0\varepsilon_{\text{out}}}\mathbf{P}_b(\omega) - \frac{1}{3\varepsilon_0\varepsilon_{\text{out}}}\mathbf{P}_d(\omega) - \frac{1}{3\varepsilon_0\varepsilon_{\text{out}}}\mathbf{P}_{\text{inter}}(\omega). \quad (4.70)$$

Employing a similar treatment of the background field as in Sec. 2.4.4, we obtain an extension of Eq. (2.65), which can be expressed as

$$\mathbf{E}_{\text{tot}} = \frac{3\varepsilon_{\text{out}}}{\varepsilon_{\infty} + 2\varepsilon_{\text{out}}} \left[\mathbf{E}_{\text{ext}} - \frac{1}{3\varepsilon_0\varepsilon_{\text{out}}}(\mathbf{P}_d + \mathbf{P}_{\text{inter}}) \right]. \quad (4.71)$$

By combining this with the definition of the total polarization in response to the total field from Eq. (4.68), we can obtain a self-consistent solution for the optical response to the external electric field,

$$\mathbf{P}_{\text{tot}} = \mathbf{P}_d + \mathbf{P}_{\text{inter}} = \varepsilon_0\chi_{\text{tot}}(\omega)\mathbf{E}_{\text{ext}}, \quad (4.72a)$$

$$\chi_{\text{tot}} = -3\varepsilon_{\text{out}} \frac{\frac{\omega_{\text{LSP}}^2}{\omega^2 + i\gamma\omega} - \frac{m_e}{\hbar e^2} \sum_j^N \frac{\omega_{\text{LSP}}^2 |d_j^{vc}|^2}{\omega - \omega_j + i\gamma_j}}{1 - \frac{\omega_{\text{LSP}}^2}{\omega^2 + i\gamma\omega} + \frac{m_e}{\hbar e^2} \sum_j^N \frac{\omega_{\text{LSP}}^2 |d_j^{vc}|^2}{\omega - \omega_j + i\gamma_j}}. \quad (4.72b)$$

In the limit of vanishing interband contributions, $d_j^{vc} \rightarrow 0$, this approach reproduces the results obtained in Sec. 2.4.4 and 4.6. However, for non-vanishing d_j^{vc} , we not only obtain terms from interband and intraband contributions individually but also mixing terms. This is consistent with the usual Mie theory, where the contributions also mix via the Clausius-Mosotti factor. In Fig. 4.4, we utilize the proportionality of $\alpha(\omega) \propto \text{Im}\{\chi(\omega)\}$ [170, 171] to fit the experimental data we gratefully received from the group of Holger Lange [4].

In Fig. 4.4, we demonstrate that the combination of our microscopic approach with the self-consistent treatment of the total electric field can accurately describe the experimentally observed absorption of small gold nanoparticles. The accuracy of our approach strongly depends on the number of included interband transitions and related fitting parameters. However, it also highlights the potential of our approach when incorporating momentum-resolved dipole matrix elements $\mathbf{d}_{\mathbf{k}}^{vc}$ obtained from *ab initio* calculations. By including these dipole matrix elements, we can effectively reduce the number of fitting parameters to only include the damping terms. This refinement may eventually lead to a more precise and physically meaningful description of the optical response of metallic nanoparticles.

4.8. Conclusions

In this chapter, we have presented a comprehensive microscopic approach to study the electron and phonon dynamics in metals. In the Hamiltonian, we included the free electronic motion, light-matter interaction, Coulomb-mediated electron-electron interaction,

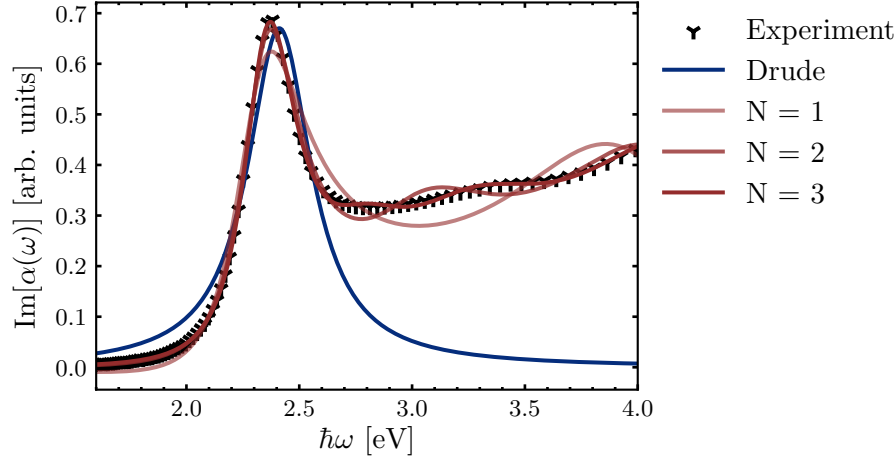


Figure 4.4.: **Fitting Total Susceptibility Function to UV-Vis Spectrum of AuNP Solution.** We conduct fitting analyses of the imaginary part of the susceptibility, as expressed in Eq. (4.72b), to absorption spectra collected experimentally from small gold nanoparticles (AuNPs) with an approximate diameter of 30 nm. These AuNPs are dispersed in hexadecyltrimethylammonium chloride (CTAC) solution.

and electron-phonon interaction. The resulting dynamical equations for the Wigner function provided a detailed description of the electron and phonon behavior in metals, as demonstrated in Sec. 4.3 and 4.4.

Through momentum expansion, we derived macroscopic equations for the electron density and electron current density in both local and nonlocal formulations, as discussed in Sec. 4.5. In the nonlocal regime, we successfully reproduce well-known hydrodynamical equations, thus validating the effectiveness of our framework.

Additionally, we have already provided two significant applications of our approach. In Sec. 4.6, we included geometrical effects through the Hartree mean-field. This allowed us to accurately reproduce the localized surface plasmon resonance in a metal sphere. Furthermore, we extended our approach to incorporate multi-band processes in Sec. 4.7, leading to a set of dynamical equations for a two-band model. These were used to model the optical response of gold structures and explicitly compared to experimental data for bulk gold and gold nanoparticles in solution. Our approach captures the full optical response in the optical regime.

The developed framework serves as a solid foundation for further investigations in subsequent chapters of this thesis. It provides a powerful tool to study complex interactions in metal systems and offers the potential for more accurate and physically meaningful descriptions of their optical response. In particular, the combination of our microscopic approach with *ab initio* calculations for dipole matrix elements promises to reduce the number of fitting parameters and improve the precision of our results. We will discuss this in more detail in the following section.

In conclusion, our framework work opens up exciting possibilities for studying various plasmonic phenomena and for understanding the behavior of metals in different geometric shapes and configurations.

4.9. Perspectives

In this chapter, we have utilized a parabolic dispersion model to describe electron motion, assuming free and undisturbed movement as suggested by the free electron model [258]. However, it is crucial to acknowledge that this model is an approximation that neglects the actual band structure of the system.

The parabolic approximation performs well for intraband processes in metals, effectively reproducing the characteristic plasmon peak observed in such systems. It also yields reasonably accurate results for interband transitions in semiconductors of a wide spectral range, in particular transition metal dichalcogenides with direct band gaps. However, in the case of metals, that possess a significantly more complex band structure, the parabolic approximation falls short in adequately describing interband transitions, especially in three dimensions.

Building upon the concepts discussed thus far, a potential avenue for progress is the integration of parameter-based dynamical calculations as presented in this chapter with density functional theory, which has emerged as a successful approach for calculating the electronic structure of atoms, molecules, and solids.

The proposed approach involves employing density functional theory to determine the electronic background upon which carriers move. Subsequently, we would use the dynamical Bloch equations to calculate their dynamics on this background. By incorporating the band structure and calculated dipole matrix elements, the number of fitting parameters to reproduce the optical spectra would be reduced to only include the background permittivity ε_∞ and damping rates. In an additional step, the microscopic scattering equations, describing electron-phonon scattering, we presented here could also be used for numerical calculations of the damping rates, further reducing the number of free parameters. It is important to note that this approach would be limited to the perturbative regime, where the back action of excitations on the band structure remains negligible. Therefore, it must be confined to the low excitation regime. In addition, careful consideration of interactions would be essential to avoid double counting.

In addition to its potential in accurately describing interband processes in metals, a microscopic understanding of the intra- and interband dynamics using this microscopic approach may also contribute to a more profound understanding of hot electron dynamics, which is of great interest in plasmon-assisted processes in chemical synthesis.

Overall, the integration of density functional theory with parameter-based dynamical calculations holds promise for improving our understanding of complex metal systems and providing a more physically meaningful description of their optical response.

5. Active Control of Plasmon Resonance: THz Pump-Optical Probe Signatures in Metal Nanoparticles

In the earlier chapters of this thesis, we extensively investigated plasmonic resonances of nanostructures at both macroscopic and microscopic levels. We discussed that the spectral position of the plasmon resonance is highly sensitive to the geometry of the nanostructure, as we have for example seen when changing the nanoparticle aspect ratio in Sec. 2.4.2. Furthermore, we have observed that the inclusion of hydrodynamic effects can explain a substantial shift in the plasmon resonance for small particles, cf. Sec. 2.4.3.

In this section, we will investigate the option of using this sensitivity to changes on the macroscopic and microscopic to actively tune the optical response of plasmonic nanostructures. In recent years, this has opened the subfield *Active plasmonics* that exploits the active control of surface plasmon resonance [101].

It is possible to divide active plasmonic structures into three categories according to the involved modulation mechanisms to actively tune the plasmon properties [101], as summarized in Fig. 5.1: First, the plasmon is a surface effect. Thus, changing the surface environment changes the plasmon properties. The second tuning option is the nanostructure geometry. Plasmons of proximal nanoparticles interact and form coupled modes, which can be exploited to tune the plasmon by modifying the interparticle distance. Third, as the plasmon is built up from electron oscillations, changing the amount of contributing electrons in the conduction band changes the properties of the plasmon.

Several experimental approaches have been developed to achieve plasmon tuning using one of the three mechanisms shown in Fig. 5.1, aiming to actively control and manipulate the optical properties of nanostructures: For example, changes in the surrounding medium have been achieved by chemical reactions, such as electrochemical doping of polymer films surrounding the gold nanostructures [415]. Tuning by distance control has been achieved through active substrates, for example by applying mechanical strain to the substrate [416], embedding plasmonic nanoparticles in liquid crystal [417], or thermo-responsive polymers [418]. Another approach was to use acoustic waves to actively tune the geometry of the plasmonic surface

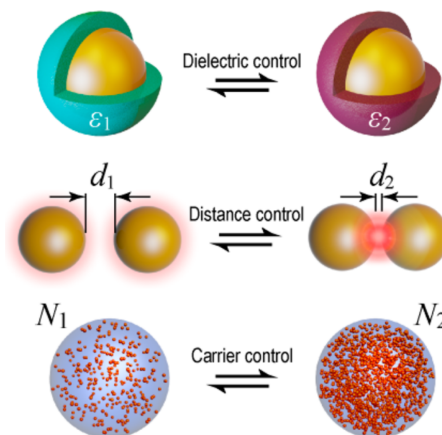


Figure 5.1.: Active Modulation Mechanisms for Tuning Plasmon Resonance. The mechanisms to tune the plasmon resonance can be divided into three categories: dielectric control, distance control, and carrier control [101]. Reprinted with permission from Ref. [101] Copyright (2018) American Chemical Society.

[419]. The third way to change the number of electrons contributing to the plasmon oscillation is achieved by electrochemical charging of gold nanoparticles [420]. Other interesting approaches to actively tune the plasmon resonance include active control of the incident light [421] or controlled melting of nanoparticles [422]. These approaches may find application in high-speed devices, in particular plasmonic modulators, where they have garnered interest due to the demand for high-speed modulators enabling Tbit/s communication. Various general concepts for plasmonic modulators have been introduced [84, 101, 423–426]. However, with most present methods, the achieved tuning occurs on timescales ranging from milliseconds to microseconds, which is still too slow and limits their practical applications. Interesting approach to combine optical and THz radiation for ultrafast plasmon modulation were discussed in Refs. [100, 427, 428].

Inspired by these approaches, we explore an experimental scenario where a strong THz electric field is used to perturb the electronic ground state of a metallic nanostructure. In particular, we focus on how the THz pulse affects the spatial density and kinetic distribution of the electrons, since these factors determine the plasmon frequency ω_{LSP} via the plasma frequency ω_p , as discussed in our microscopic derivation in Sec. 4.5.1. Consequently, changing the ground state electron distribution by the THz pulse leads to changes in the optical response of the nanoparticle, allowing to tune the plasmon resonance dynamically on the timescale of the THz pulse. The choice of using THz fields is motivated by the experimental ability to generate strong electric fields with peak intensities in the single-digit MV/cm range and durations of picoseconds.

This chapter addresses the situation described above by two different approaches. First, we describe the numerical tool that we are currently developing, which combines the microscopic Boltzmann scattering equations for the electronic Wigner function, as described in detail in Ch. 4, with a fully three-dimensional finite-difference time-domain solver. This combination enables us to couple multidimensional, k -resolved electron scattering processes to macroscopic solutions of Maxwell’s equations. As a result, the complete spatial dynamics of an electric field interacting with a metallic object of arbitrary shape can be studied, along with the electronic dynamics within these nanostructures. This approach enables a complete non-perturbative treatment of the spatio-temporal, non-equilibrium, nonlocal dynamics of electrons in metallic nanostructures. In addition, we have developed an analytical approach to study the influence of a non-perturbative THz field on the plasmon resonance of a spherical nanoparticle. This approach offers the possibility to analytically understand the physical processes that control the shift of the plasmon resonance.

Therefore, this chapter is structured as follows: before diving into the theoretical details, we present the initial experimental results that motivated this study in Sec. 5.1. In Sec. 5.2, we will describe the concept of our computational multiphysics approach that we are currently developing to efficiently couple three-dimensional codes for solving the macroscopic Maxwell equations with the microscopic Boltzmann scattering equations. We then provide the details of our implementation of our three-dimensional finite-difference time-domain (3D FDTD) code in Sec. 5.3.1, before discussing the details of the microscopic code in Sec. 5.4. In Sec. 5.5 we present the results of our analytical non-perturbative approach.

5.1. Experimental Motivation

This endeavor has primarily been motivated by the intriguing preliminary experimental results obtained in the group of Holger Lange at Universität Hamburg. In their research, they set up a THz-pump white-light-probe experiment to investigate the influence of a strong THz pulse on the optical absorption spectra of a periodic array of chemically synthesized plasmonic nanoparticles. Their experiment setup, conducted at CFEL, is schematically illustrated in Fig. 5.2(a), and the preliminary experimental results are depicted in Fig. 5.2(b).

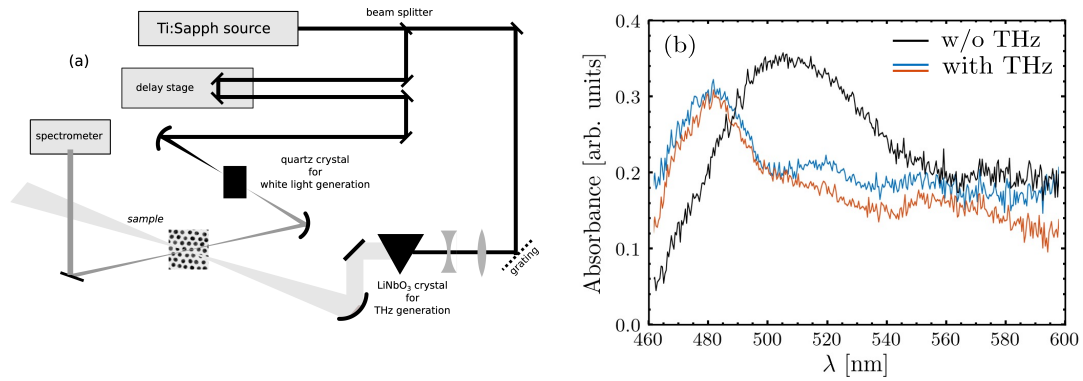


Figure 5.2.: **Experimental Setup and Preliminary Results.** (a) Experimental setup at CFEL illustrated schematically. (b) Gold nanoparticles array's response to white light absorption, with and without an overlapping THz pulse. The colors represent data from multiple experiment repetitions.

In the absence of a THz pulse, the absorption spectrum of the gold nanoparticle array exhibits the typical plasmon response, consistent with the discussions presented in the preceding sections. However, when the THz pulse is introduced, a notable blue-shift in the plasmon absorption peak is observed. To gain further insights, time-dependent studies are conducted to track the absorption change relative to the peak field of the THz pulse. Fascinatingly, the resonance of the plasmon absorption spectrum experiences a blue-shift during the peak of the THz pulse, allowing to observe the rise and recovery of this absorption change as the THz pulse propagates. Moreover, by varying the pump-probe delay, the onset and vanishing of the modulation are observed on picosecond timescales. Comparable changes in the plasmon resonance shift have to the best of our knowledge only been reported in response to variations in the geometrical dimensions of the system under study.

Despite these intriguing experimental findings, the exact origins of the observed shift remain unclear and necessitate a detailed theoretical treatment that accurately describes the pump-probe setup under consideration. The upcoming sections will focus on the theoretical description of this effect, aiming to shed light on the underlying mechanisms that govern the plasmon tuning with THz pulses on picosecond timescales.

5.2. Numerical Framework

To address the experimental situation theoretically, a self-consistent, space- and time-resolved treatment of the Maxwell equations and material equations governing the interaction of the nanoparticle with THz and optical fields is essential. Given the strong THz field, a treatment beyond the perturbative regime becomes necessary. In this context, we propose a computational multiphysics approach, coupling three-dimensional codes to solve the macroscopic Maxwell's equations with our developed microscopic momentum-resolved Boltzmann scattering equations, cf. Ch. 4.

Using the Wigner approach, we can describe the microscopic electron dynamics and incorporate nonlocal effects, including both intra- and interband transitions. By numerically solving the full microscopic Boltzmann scattering equations without any linearization, we can accurately describe the strong THz fields in the nonlinear regime. This approach will extend the work in Ref. [375], which couples a full solution of Maxwell's equations with microscopic energy-resolved scattering equations, to include a full 3D momentum-resolution to account for interband processes and band structure effects.

Consequently, our approach unites state-of-the-art numerical methods for simulating electromagnetic fields with a fully quantum mechanical nonlocal treatment of the many-particle kinetics of the carriers within the nanoparticle. This enables us to investigate the spatial dynamics of non-equilibrium processes in plasmonic nanostructures in the proposed THz pump-optical probe scenario. Accessing the momentum-resolved electron distribution provides a direct path towards multidimensional modeling of electron transport processes and allows studying the interplay of non-equilibrium thermal and propagation dynamics. In addition, the theory will describe the nonlinear response of the electrons/plasmons for plasmonic nanostructures of arbitrary shape to the THz pulse, encompassing dephasing and relaxation processes, while also accommodating nonlocal, multi-band processes eventually.

The conceptual idea of the numerical solver is depicted in Fig. 5.3 which follows the idea in Ref. [375].

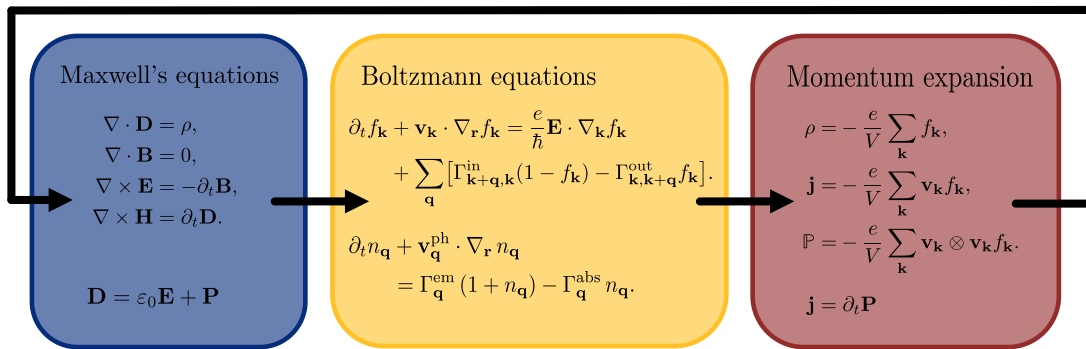


Figure 5.3.: **Illustration of Coupled Kinetic Maxwell-Boltzmann Solver.** We present the conceptual idea of our multi-physical computational approach that combines solution of three-dimensional macroscopic Maxwell's equations with a three-dimensional momentum-resolved microscopic Boltzmann scattering equation. The microscopic quantities are linked via a moment expansion of the electronic Wigner functions. For simplicity, we only illustrate the single-band case.

The proposed numerical scheme, as shown in Fig. 5.3, will iteratively solve Maxwell's equations in our geometry to compute the electric fields. These fields are then used as source terms in the microscopic scattering equations. Subsequently, the microscopic electron distribution will be momentum-expanded, analogous to Sec. 4.5, to obtain macroscopic quantities, specifically the polarization $\mathbf{P}$, which will in turn act as a source term in the macroscopic Maxwell's equations.

The iterative solution of both sets of equations facilitates the determination of electric fields, allowing to calculate cross sections or transmission and reflection of the nanostructure. In addition, this approach sheds light on the intricate microscopic electron dynamics within the material. It is important to note that this complex, effectively six-dimensional phase space solver is essential to incorporate the nonlinearity of the scattering equations and to effectively handle the potentially complex interactions between the THz and optical fields, especially when dealing with non-parallel polarizations or different angles of incidence.

The ultimate goal of this work is to gain a profound understanding of the microscopic dynamics in response to strong THz fields and their implications on the optical and THz responses in the linear regime. These insights can be compared to experimental results in the future and may allow exploring how these responses can be influenced by varying the size and shape of the nanoparticles.

To achieve this goal, in Sec. 5.3 we will first discuss the numerical simulation of the Maxwell equations using our self-developed finite-difference time-domain solver. Then, in Sec. 5.4, we will introduce the nonlocal quantum mechanical treatment of the microscopic dynamics. This lays a solid foundation for future investigations of the optical and THz responses of plasmonic systems.

5.3. Finite-Difference Time-Domain Solver

The first component of our combined solver is a classical finite-difference time-domain (FDTD) solver, enabling us to numerically solve Maxwell's equations. For this work, I have meticulously developed a 3D FDTD code in Python, which I will describe in more detail in the following sections. With the continuous increase in computational power, numerical investigations of intricate nanostructures have become indispensable. These structures, including complex metastructures with applications in beam steering, photonic crystals, active photonics, and quasi-normal mode studies, often exceed the analytical description's capacity. Consequently, the use of numerical methods, particularly finite-difference time domain (FDTD), finite-element methods (FEM), and boundary element method (BEM), has witnessed a remarkable surge with each possessing their individual strengths for certain scenarios. Notably, FEM, with COMSOL as a prominent commercial implementation, is the most powerful for time-periodic studies and is widely used for nanoscale material analysis.

However, since our experimental scenario inherently involves non time-periodic aspects, as we seek to model the interaction of two different pulses in the system, finite-difference time domain solutions are the natural and appropriate choice. This approach offers several advantages, including widespread use in the photonics community, ease of parallelization, broadband capabilities, and the ability to generate time-domain movies. Therefore, in the upcoming sections, we will introduce the essential concepts behind our FDTD implementation. As this explanation provides only a concise overview, read-

ers keen on exploring further details can refer to two comprehensive introductions in Refs. [131, 429].

We start to present our implementation of the fundamental Maxwell's equations using the Yee algorithm in Sec. 5.3.1. Next, we demonstrate how materials can be introduced into the simulation through an auxiliary differential equation in Sec. 5.3.2. We then introduce perfectly matched layers (PML) as boundary conditions and discuss the implementation of periodic boundary conditions in Sec. 5.3.3. The electric field is introduced either through a point dipole source or a plane-wave source employing the total-field scattered (TFSF) approach in Sec. 5.3.4. Lastly, in Sec. 5.3.5, we explore options for obtaining certain macroscopic observables from the simulation, such as the Purcell factor and scattering and absorption cross sections.

Our numerical implementation will be made available via git at Ref. [430].

5.3.1. Full 3D FDTD Implementation

The basic idea of FDTD is quite simple and easy to explain: it simply and elegantly takes Maxwell's equations in their differential form and implements the partial differential equation in a numerically efficient way. Accordingly, the governing equations are the curl Maxwell equations, which we express in the form

$$\frac{\partial \tilde{\mathbf{D}}(\mathbf{r}, t)}{\partial t} = c \nabla \times \mathbf{H}(\mathbf{r}, t), \quad (5.1a)$$

$$\frac{\partial \mathbf{H}(\mathbf{r}, t)}{\partial t} = -c \nabla \times \tilde{\mathbf{E}}(\mathbf{r}, t). \quad (5.1b)$$

We adopted the definition from Ref. [429], which employs rescaled electric fields, $\tilde{\mathbf{E}}(\mathbf{r}, t)$, and $\tilde{\mathbf{D}}(\mathbf{r}, t)$. These fields are related to the physical fields in SI units through the following relations

$$\tilde{\mathbf{E}} = \varepsilon_0 c \mathbf{E}, \quad \tilde{\mathbf{D}} = c \mathbf{D}, \quad \tilde{\mathbf{P}} = c \mathbf{P}. \quad (5.2)$$

In this definition, electric and magnetic fields have the same units, which can be seen by the vacuum impedance to be one $\eta_0 = 1$. This choice facilitates numerical stability due to similar orders of magnitude in the computation. In addition, we assume a non-magnetic material, so that material properties effectively enter only through the permittivity function $\varepsilon_r^*(\omega)$,

$$\tilde{\mathbf{D}}(\mathbf{r}, \omega) = \varepsilon_r^*(\omega) \cdot \tilde{\mathbf{E}}(\mathbf{r}, \omega). \quad (5.3)$$

The permittivity function incorporates essential system information regarding material properties, including the frequency dependence and spatial characteristics of the system. As discussed in Sec. 2.3.1, our implementation follows the widely used piecewise-constant approximation in classical electrodynamics, which does not inherently account for hydrodynamic effects. However, the FDTD method, with its inclusion of spatial derivatives, is well-suited for incorporating hydrodynamic effects in a formulation using spatial gradients [253], they only pose additional challenges for an advanced parallelized numerical implementation. Notably, a parallel FDTD implementation of the generalized nonlocal optical response (GNOR) has been achieved in Ref. [151, 431]. Other numerical hydrodynamical implementations using different computational electromagnetic methods, including the finite element method [432], the discontinuous Galerkin method [199, 433], and the boundary element method [434], also complement this development.

Yee Algorithm

Having stated the fundamental physical equations, it now becomes important how these are numerically implemented. In FDTD, the widely used Yee algorithm [435], proposed in 1966, proves to be remarkably robust. To solve electric and magnetic fields in space and time, they are placed on a so-called Yee cell. This arranges the electric field $\mathbf{E}$ and magnetic field components $\mathbf{H}$ in a leapfrog arrangement that places one electric field component within four circulating magnetic field components and vice versa, creating the beautiful picture of an intricate interlinking of Ampere's and Faraday's law in three-dimensional space [131]. Intuitively, this can be visualized as staggered fields in space and time, as shown in Fig. 5.4, where the staggered fields are typically placed half a Yee cell apart from each other. Notably, this approach achieves second-order accuracy while requiring the same number of function evaluations per step, in contrast to an Euler algorithm.

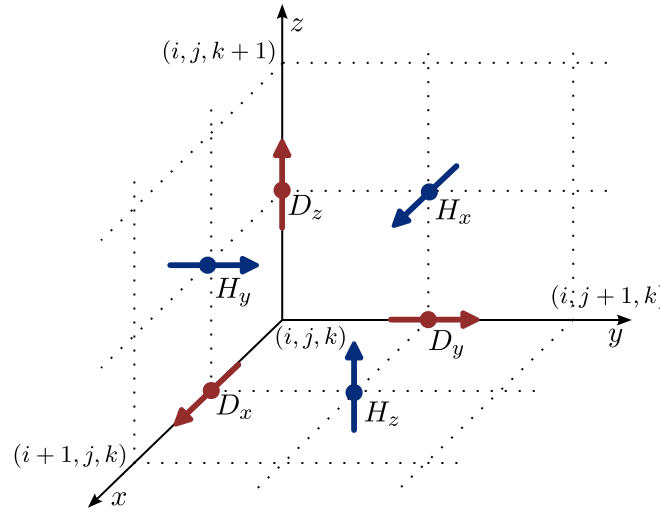


Figure 5.4.: **Illustration of a Yee Cell.** 3D Staggering of electric and magnetic fields. In addition to the spatial offset, they are reciprocally staggered in time.

To illustrate the general procedure, we employ the full Maxwell curl equations from Eq. (5.1), dividing them into individual components. This yields six scalar equations of the form

$$\frac{\partial D_x}{\partial t} = c \left(\frac{\partial H_z}{\partial y} - \frac{\partial H_y}{\partial z} \right), \quad \frac{\partial H_x}{\partial t} = c \left(\frac{\partial E_y}{\partial z} - \frac{\partial E_z}{\partial y} \right). \quad (5.4)$$

The other four equations can be obtained via circular permutation. In each of these equations, the temporal derivatives depend on the spatial derivatives of two other field quantities. By now employing, the Yee algorithm, cf. Fig. 5.4, we discretize space and place all the field components on staggered grid positions. The indices (i, j, k) correspond to the x, y, z direction, respectively. We illustrate this exemplarily for the x component

of the electric field,

$$D_x^{n+1/2}\left(i + \frac{1}{2}, j, k\right) = D_x^{n-1/2}\left(i + \frac{1}{2}, j, k\right) + S_c \left[H_z^n\left(i + \frac{1}{2}, j + \frac{1}{2}, k\right) - H_z^n\left(i + \frac{1}{2}, j - \frac{1}{2}, k\right) - H_y^n\left(i + \frac{1}{2}, j, k + \frac{1}{2}\right) + H_y^n\left(i + \frac{1}{2}, j, k - \frac{1}{2}\right) \right]. \quad (5.5)$$

The upper index n represents the position on the temporal grid, while the three arguments in the parenthesis correspond to the usual Cartesian position coordinates. These equations can be viewed as standard update equations, where the field at the updated time $n + 1/2$ depends on its value at a previous time step $n - 1/2$. Changes to the field value are incorporated through the influence of the surrounding magnetic fields, which are related via the curls in the Maxwell's equations, particularly Faraday's law in this case. The quantity S_c denotes the Courant number, defined as

$$S_c = \frac{c\Delta t}{\Delta x}. \quad (5.6)$$

This can be thought of the numerical increment, similar to the Euler algorithm. Importantly for FDTD calculations, the choice of S_c also determines the ratio of the temporal and the spatial resolution, meaning that a finer discretization in space inevitably leads to smaller time steps. For stability of the numerical implementation, there are natural bounds on S_c . A convergence condition is commonly derived from the Courant-Friedrichs-Lewy condition, which is a necessary condition for the convergence when numerically solving certain partial differential equations. Extensive testing and analysis of the growth factor for varying Courant numbers has been conducted and can be found in Ref. [131]. For a stable numerical implementation, the Courant stability bound typically becomes

$$S_c < \frac{1}{\sqrt{n}}. \quad (5.7)$$

Here, n is the dimensionality of the implementation. For our purposes, we have chosen $S_c = 0.5$ to fulfill this criterion for one-, two-, and three-dimensional systems. This choice allows us to transfer results from lower dimensions to the three-dimensional case.

5.3.2. Material Modeling

In the previous section, we described how the interplay of Maxwell's curl equations is numerically implemented using the Yee algorithm to integrate the fields over time. While this is sufficient to describe wave propagation in an infinitely extended vacuum, free space propagation is a rather trivial case that does not demand advanced numerical solutions, at least at that level of the description. The primary advantage of numerical FDTD implementation lies in describing complex geometries and their temporal dynamics. In this section, we will introduce our chosen method for modeling material properties, which involves employing an auxiliary differential equation to describe dispersive materials. Additionally, we will demonstrate how we introduce the geometry into the simulation, with particular emphasis on accurately treating the boundaries. For readers seeking more in-depth information on these topics or other models, we recommend referring to Refs. [131, 429].

Piecewise-Constant Permittivity

As a first example, we consider a non-dispersive, piecewise constant material. This can be visualized as a layered dielectric material with constant permittivity over the spectral range of interest, effectively making it non-dispersive. Thus, the permittivity only varies spatially but not spectrally. For simple layered cases, such problems can be addressed using the transfer matrix method. However, once complex geometry is introduced, as seen in photonic crystals, analytical solutions become demanding and may only be found in approximation. In contrast, these situations can be easily implemented in FDTD. The easiest way to approach this is through the *constitutive equation*,

$$\tilde{\mathbf{D}}(\mathbf{r}, t) = \varepsilon(\mathbf{r})\tilde{\mathbf{E}}(\mathbf{r}, t). \quad (5.8)$$

As explained in Sec. 2.3.1, this approximation effectively treats interactions as local and neglects the dispersive character of the material response, meaning that it does not depend on frequency or time. For numerical implementation, this allows for a straightforward update prescription for the $\mathbf{E}(\mathbf{r}, t)$ fields via

$$\tilde{E}_x(\mathbf{r}, t) = \varepsilon_x^{-1}(\mathbf{r}) \tilde{D}_x(\mathbf{r}, t), \quad \tilde{E}_y(\mathbf{r}, t) = \varepsilon_y^{-1}(\mathbf{r}) \tilde{D}_y(\mathbf{r}, t), \quad \tilde{E}_z(\mathbf{r}, t) = \varepsilon_z^{-1}(\mathbf{r}) \tilde{D}_z(\mathbf{r}, t). \quad (5.9)$$

Here, ε_i^{-1} represents the inverse permittivity. Notably, we distinguish the permittivity depending on the individual Cartesian coordinates, allowing for the description of anisotropic media. However, this distinction is primarily introduced due to the arrangement of fields in the Yee algorithm. As evident from Fig. 5.4, the electric fields are staggered in space, which necessitates consideration of their locations with potentially distinct effective permittivity. For bulk materials, this distinction may seem negligible. However, once we introduce geometries with structure sizes not much larger than the Yee cells and subsequently adopt a subgridding approach. This distinction becomes a vital part of the implementation.

Object Creation

Using the piecewise-constant approximation in Eq. (5.8), we automatically create the geometry of an object by varying the permittivity on a subset of the entire simulation space. In the algorithm, this is accomplished by determining whether each individual Yee cell surrounding each field component is inside or outside the material. As a result, they are assigned either ε_{in} or ε_{out} . In this manner, the object's geometry is explicitly defined within the simulation.

While this description is exact for objects adequately described in Cartesian coordinates, for other objects, such as spheres, the treatment of boundary cells that are only partially inside the sphere becomes non-trivial. A black or white approach would cause naturally smooth surfaces to become rough, leading to strong "staircasing" effects with local field enhancements due to the so-called "lightning rod" effect.

To counteract this and numerically smooth the particle surface, we employ a subgridding approach for cells at the boundary. If the Yee cell centered around the considered field quantity is only partially within the object, our implementation subdivides the cell into $f \times f \times f$ sub-cells and evaluates again if their individual centers are inside or outside the object. From this, we calculate a weighted average of the inside and outside

permittivity using the formula

$$\varepsilon_{\text{eff}} = \frac{n_{\text{in}} \varepsilon_{\text{in}} + n_{\text{out}} \varepsilon_{\text{out}}}{f^3}, \quad (5.10)$$

where n_{in} is the number of subcells inside the object and n_{out} the ones outside of it. This effectively covers the object's surface with a layer of intermediate permittivity, which can be chosen to significantly reduce staircasing compared to the rough black or white approach. As per the previous section, these quantities also need to be staggered in space to calculate the positional mismatch of the individual field components within the Yee cell accurately. A similar procedure will be adopted for the prefactors in the auxiliary differential equation.

Auxiliary Differential Equation (ADE)

So far, we have focused on non-dispersive systems, which describe materials with frequency-independent properties. This approximation is often reasonable, depending on the spectral range of interest. However, as extensively discussed throughout this work, we are interested in dispersive system that reveal a frequency-dependent response. Typically, these frequency-dependent materials are described in frequency space via their polarization,

$$\tilde{\mathbf{P}}(\omega) = \chi(\omega) \tilde{\mathbf{E}}(\omega). \quad (5.11)$$

To incorporate this frequency-based description into the time-domain-based FDTD method, the equations must be transferred to the time domain. Several approaches can achieve this, as discussed in Refs. [131, 436]. Here, we have chosen the auxiliary differential equation (ADE) approach due to its conceptual simplicity. In this approach, the susceptibility function is Fourier transformed to the time domain, where it is explicitly evaluated as an auxiliary differential equation of the material. In this section, we introduce this approach using the standard example of the Drude model, whose susceptibility is typically given in frequency space as

$$\chi(\omega) = -\frac{\omega_p^2}{\omega^2 + i\gamma\omega}. \quad (5.12)$$

For the Drude model, all dispersive contributions are contained in the susceptibility, while the frequency-independent background contribution to the permittivity, ε_∞ , as described in Eq. (2.36), will be introduced as a constant permittivity on the level of the piecewise-constant permittivity previously described in the section. In the time domain, the model for the Drude susceptibility can be reformulated in terms of temporal derivatives,

$$\partial_t^2 \tilde{\mathbf{P}} + \gamma \partial_t \tilde{\mathbf{P}} = \omega_p^2 \tilde{\mathbf{E}}. \quad (5.13)$$

This equation is what we label as the auxiliary differential equation and will be the equation we implement in addition to the FDTD update equations. Despite the staggered Yee cell, its implementation becomes rather intuitive because the polarization represents the electric response of the system and, as such, it will be placed at the same positions within the Yee cell as the electric fields. This simplifies the description significantly

because all equations are evaluated at the same Yee cell positions. This second-order differential equation requires the polarization at three positions in time for discretization, and it reads

$$\frac{\tilde{P}_i^{n+1} - 2\tilde{P}_i^n + \tilde{P}_i^{n-1}}{\Delta t^2} + \gamma \frac{\tilde{P}_i^{n+1} - \tilde{P}_i^{n-1}}{2\Delta t} = \omega_p^2 \tilde{E}_i^n. \quad (5.14)$$

The index i accounts for all three Cartesian coordinates. For numerical implementation, this needs to be reformulated in terms of an update equation, similar to the FDTD update equations in Eq. (5.5). After some algebraic work, this can be expressed schematically as the update equation for the auxiliary differential equation of the polarization,

$$\tilde{P}_i^{n+1} = D_1 \tilde{P}_i^n + D_2 \tilde{P}_i^{n-1} + D_3 \tilde{E}_i^n. \quad (5.15)$$

Here, we defined the prefactors as

$$D_1 = \frac{4}{2 + \gamma\Delta t}, \quad D_2 = \frac{\gamma\Delta t - 2}{2 + \gamma\Delta t}, \quad D_3 = \frac{2\omega_p^2\Delta t^2}{2 + \gamma\Delta t}. \quad (5.16)$$

This equation needs to be implemented for each spatial component and updated individually for all positions that are supposed to be contained in the considered object. Fortunately, the coefficients remain constant over time, making the implementation rather straightforward. Depending on the required accuracy and the temporal variation of the considered electric fields, it might be necessary to also consider the electric field at multiple time steps. However, for our considered temporal discretization with Δt in the single digit attosecond regime, the optical fields can be assumed to vary slowly, so that this implementation suffices for our purposes.

Implementation of this model for a gold slab gives excellent agreement with analytical predictions, as shown in Fig. 5.5. In Sec. 5.3.5, we show how these spectra can be obtained from the simulation.

Certainly, more complicated material models, such as the Drude-Lorentz model or even more advanced ones, can be included in the simulation. The numerical prescriptions for these models follow in analogy to the one we provided for the Drude model. However, as this topic will be covered in later sections, we refer the interested reader to Sec. 5.4 for further details and discussions.

Summarizing the advances up to this point, we have provided the key concepts for the standard update equations in FDTD implementation. A comprehensive overview is given in Fig. 5.6, where the numerical implementation of the described procedure is illustrated. We begin by using the auxiliary differential equation to calculate the polarization of the sphere, and then we update the $\mathbf{D}$ field accordingly. Subsequently, we use the updated $\mathbf{D}$ field and the polarization $\mathbf{P}$ to calculate the electric field $\mathbf{E}$, which, in turn, is needed to update the magnetic field $\mathbf{H}$. This procedure is repeated until the physical process of interest is over or until the field magnitudes no longer surpass a certain amplitude.

5.3.3. Boundary Conditions

Numerical solutions of Maxwell's equations, as well as general numerical simulations, face a significant limitation due to the constraints imposed by the finite computational space. In nature, when light impinges on an object, it gets scattered and propagates away, not returning unless specifically designed that way. Ideally, numerical models would

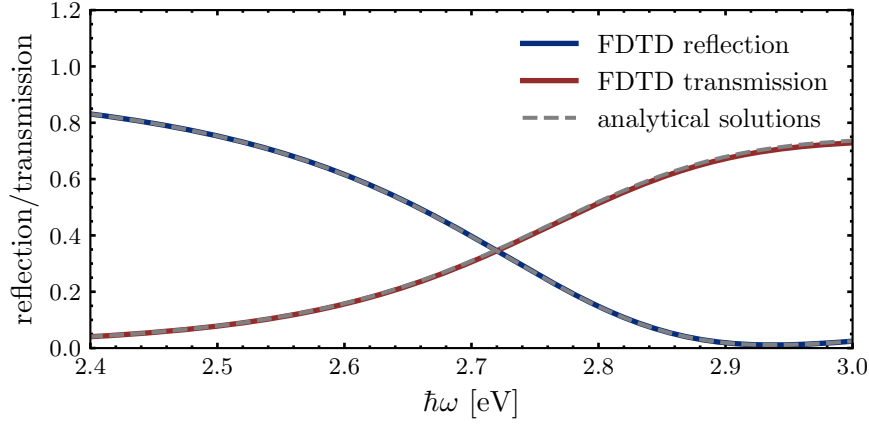


Figure 5.5.: **Benchmarking the 3D FDTD Code: Reflection and Transmission Spectra.** We perform an initial benchmark check of our full 3D FDTD code by comparing the reflection and transmission spectra to the analytical results for a 100 nm thick slab of gold modeled using Drude theory.

also cover such an infinitely large computational domain or at least one large enough to prevent outgoing waves from returning to the sample during the relevant time. However, this approach is usually unfeasible due to its high computational cost.

As a consequence, one is left with a finite computational domain, leading to the emergence of predominantly unphysical processes near the boundaries, primarily in the form of arbitrary reflections. To address this issue, the implementation of appropriate boundary conditions in the Finite-Difference Time-Domain (FDTD) method becomes crucial. The goal is to effectively mimic fully absorbing boundary conditions (ABC) so that waves leaving the physical volume of the computational domain do not return. This is usually achieved by separating the computational domain into a physical domain and an unphysical one, where unphysical equations are solved in a way that mimics the desired ABC. This establishes a computationally viable domain that exhibits physical behavior. In this study, we present two widely used approaches: Perfectly Matched Layers (PML) and Periodic Boundary Conditions (PBC). Additionally, prominent alternative boundary conditions, such as metallic and Bloch boundary conditions, are also available. Interested readers can find further details in Ref. [131].

Perfectly Matched Layers (PML)

As previously described, one of the challenges in FDTD simulations is the occurrence of unphysical reflections at the boundary, which can significantly influence the physical process within the simulation domain. A crucial aspect of the simulation is therefore to find a method to exclude these reflections at the boundary and ideally implement boundary conditions that perfectly absorb outgoing waves, preventing their return to the computational domain. To address this issue, we introduce the perfectly matched layer (PML) approach, developed by Ref. [437], which has become a widely used and effective technique for suppressing reflections in FDTD simulations, allowing for more accurate and reliable results when dealing with finite computational domains.

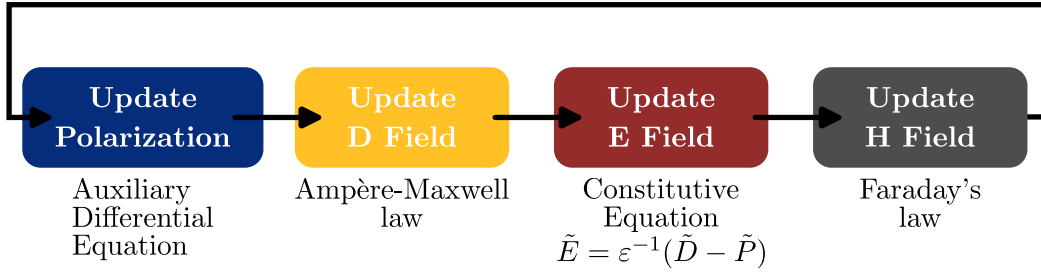


Figure 5.6.: **FDTD Method – Standard Iteration.** This figure illustrates the standard loop of the FDTD method. At each time step, the polarization is updated using an auxiliary differential equation. Next, the Ampère-Maxwell law is applied to update the $\tilde{\mathbf{D}}$ fields. This allows to update the $\tilde{\mathbf{E}}$ fields that are utilized to update the $\tilde{\mathbf{H}}$ fields. The process repeats for subsequent time steps.

The conceptual idea behind PML is based on the principle that when a wave propagates from medium A to medium B, the amount of reflection is determined by the intrinsic impedances of the two media, as described by the equation

$$\Gamma = \frac{\eta_B - \eta_A}{\eta_A + \eta_B}, \quad (5.17)$$

where Γ is the reflection coefficient and $\eta_{A/B}$ are the characteristic impedances of media A and B. It is evident that impedance-matched interfaces do not reflect electromagnetic radiation. However, for any choice of physical, non-magnetic materials, the impedance is defined as

$$\eta = \sqrt{\frac{\mu_0}{\varepsilon_r \varepsilon_0}}, \quad (5.18)$$

where ε_r is the relative permittivity of the material, which does not allow for perfect impedance matching at interfaces, leading to the presence of reflections. Fortunately, we are not limited to physical processes in the boundary layers; rather, our goal is to have them mimic the correct physics within what we now define as the physical domain. To accomplish this, we introduce the concept of perfectly matched layers (PML) – artificial, unphysical regions added to the boundaries of the computational domain. These PMLs are impedance-matched, which effectively eliminates reflections at the boundaries. In addition, the PML is designed to efficiently absorb electromagnetic waves within these layers. Even if waves are reflected at the boundary of the computational domain, they are sufficiently attenuated within the PML to have a negligible effect on the physical domain. This approach creates a seamless transition between the physical and nonphysical domains, effectively mimicking the behavior of perfectly absorbing boundary conditions. As a result, reflections are prevented from reaching the physical domain, significantly improving the accuracy and reliability of finite-difference time-domain (FDTD) simulations, even with finite computational domains.

On a technical level, this is done by introducing fictitious permittivities and permeabilities, denoted as ε_F^* and μ_F^* in the PML domain, respectively. These parameters are chosen to be impedance-matched and complex, introducing loss into the system.

The purpose is to attenuate the outgoing waves before they reach the boundary of the computational domain, where they are reflected.

In the frequency domain, the Maxwell curl equations for the PML region, Eqs. (5.1), take the following form for the z component

$$-i\omega\tilde{D}_z\varepsilon_{Fz}^*(x)\varepsilon_{Fz}^*(y)\varepsilon_{Fz}^*(z) = c\left(\frac{\partial H_y}{\partial x} - \frac{\partial H_x}{\partial y}\right), \quad (5.19a)$$

$$-i\omega H_z\mu_{Fz}^*(x)\mu_{Fz}^*(y)\mu_{Fz}^*(z) = c\left(\frac{\partial \tilde{E}_x}{\partial y} - \frac{\partial \tilde{E}_y}{\partial x}\right). \quad (5.19b)$$

The other components can be obtained by circular permutation. In the notation, the index of the permittivity or permeability refers to the field component to be attenuated, while the dependence refers to the direction of propagation. In the following, we will examine how these functions can be modeled to introduce the desired effect. It has been shown in Ref. [438] that two requirements must be met: The first, of course, is to match impedances to avoid reflections. Assuming that the objects in the physical domain are embedded in a vacuum, this condition becomes

$$\eta_0 = \eta_m = \sqrt{\frac{\mu_{Fx}^*(x)}{\varepsilon_{Fx}^*(x)}} = 1. \quad (5.20)$$

The last equivalence is due to our choice of rescaled units. The second, as shown in Ref. [438], is that in the direction perpendicular to the boundary, the fictitious quantities must be the inverse of those in the other directions. Assuming the boundary to be perpendicular to the x direction, this would mean

$$\varepsilon_{Fy}^* = \varepsilon_{Fz}^* = \frac{1}{\varepsilon_{Fx}^*}, \quad (5.21a)$$

$$\mu_{Fy}^* = \mu_{Fz}^* = \frac{1}{\mu_{Fx}^*}. \quad (5.21b)$$

To introduce the attenuation effects discussed earlier, we will assume that each of these quantities is a complex quantity of the form

$$\varepsilon_{Fm}^* = \varepsilon_{Fm} + \frac{\sigma_{Dm}}{i\omega\varepsilon_0}, \quad \mu_{Fm}^* = \mu_{Fm} + \frac{\sigma_{Dm}}{i\omega\mu_0}, \quad (5.22a)$$

for $m \in \{x, y, z\}$. In Ref. [439] it was shown that the criterion in Eq. (5.21) can be satisfied assuming for all m ,

$$\varepsilon_{Fm} = \mu_{Fm} = 1, \quad (5.23a)$$

$$\frac{\sigma_{Dm}}{\varepsilon_0} = \frac{\sigma_{Dm}}{\mu_0} = \frac{\sigma_D}{\varepsilon_0}. \quad (5.23b)$$

Using these definitions in Eq. (5.19), the fictitious permittivities and permeabilities can be given explicitly. As an example, we provide the equation for the $\tilde{D}_z$ component, which can be written as

$$-i\omega\left(1 + \frac{\sigma_D(x)}{i\omega\varepsilon_0}\right)\left(1 + \frac{\sigma_D(y)}{i\omega\varepsilon_0}\right)\left(1 + \frac{\sigma_D(z)}{i\omega\varepsilon_0}\right)^{-1} D_z = c\left(\frac{\partial H_y}{\partial x} - \frac{\partial H_x}{\partial y}\right). \quad (5.24)$$

All other components follow analogously and are given in App. H. This equation can be rewritten as

$$-i\omega \left(1 + \frac{\sigma_D(x)}{i\omega\varepsilon_0}\right) \left(1 + \frac{\sigma_D(y)}{i\omega\varepsilon_0}\right) D_z = \frac{c}{\Delta x} \left(\mathcal{C}_{yx}^H + \frac{\sigma_D(z)}{\varepsilon_0} \mathcal{I}_{Dz} \right), \quad (5.25)$$

where we have defined the following quantities

$$\mathcal{C}_{yx}^H \equiv \Delta H_y - \Delta H_x, \quad \mathcal{I}_{Dz} \equiv \frac{1}{i\omega} \mathcal{C}_{yx}^H. \quad (5.26)$$

In FDTD, we are used to time derivatives, as can be seen on the left side of Eq. (5.25), where the Fourier transform of $-i\omega \rightarrow \partial_t$ introduces a first-order time derivative. However, in the quantity $\mathcal{I}_{Dz}$ we observe a division by the frequency, which will lead to an integration in time in the numerical implementation.

Numerical Implementation In order to illustrate how this PML formalism is introduced numerically, we restrict ourselves for illustration purposes to a case with only one of the contributions on the left-hand side of Eq. (5.25). At the end of this section, we will touch upon the generalization of this approach. Using this reduced version of Eq. (5.25) and applying the Yee algorithm according to Fig. 5.4, the update equation for the electric field can be formulated as

$$\begin{aligned} D_z^{n+1/2} \left(i, j, k + \frac{1}{2} \right) &= \frac{1 - \sigma_D(i) \frac{\Delta t}{2\varepsilon_0}}{1 + \sigma_D(i) \frac{\Delta t}{2\varepsilon_0}} D_z^{n-1/2} \left(i, j, k + \frac{1}{2} \right) \\ &+ \frac{1}{1 + \sigma_D(i) \frac{\Delta t}{2\varepsilon_0}} \left[\mathcal{C}_{yx}^H(i, j, k + \frac{1}{2})/2 + \frac{\sigma_D(k + \frac{1}{2})\Delta t}{2\varepsilon_0} \mathcal{I}_{Dz}^{n+1/2} \left(i, j, k + \frac{1}{2} \right) \right]. \end{aligned} \quad (5.27)$$

Here, we used $S_c = 0.5$. The curl $\mathcal{C}_{yx}^H$ in its FDTD discretization reads, cf. Fig. 5.4,

$$\begin{aligned} \mathcal{C}_{yx}^{H,n}(i, j, k + 1/2) &= H_y^n(i + 1/2, j, k + 1/2) - H_y^n(i - 1/2, j, k + 1/2) \\ &- H_x^n(i, j + 1/2, k + 1/2) + H_x^n(i, j - 1/2, k + 1/2). \end{aligned} \quad (5.28)$$

The integral $\mathcal{I}_{Dz}$ incorporates a time integration scheme that is formulated recursively, enabling it to update itself at each time step and effectively reducing memory requirements. This can be expressed as

$$\mathcal{I}_{Dz}^{n+1/2}(i, j, k + 1/2) = \mathcal{I}_{Dz}^{n-1/2}(i, j, k + 1/2) + \mathcal{C}_{yx}^{H,n}(i, j, k + 1/2). \quad (5.29)$$

For the numerical implementation, we will follow the notation introduced in Ref. [439] that identifies abbreviations in Eq. (5.28) which will later be used to implement the PML. Using these, Eq. (5.28) can be given as

$$\begin{aligned} D_z^{n+1/2}(i, j, k + 1/2) &= g_{i3}(i) D_z^{n-1/2}(i, j, k + 1/2) \\ &+ g_{i2}(i) [\mathcal{C}_{yx}^H(i, j, k + 1/2) + g_{k1}(k) \mathcal{I}_{Dz}(i, j, k + 1/2)], \end{aligned} \quad (5.30)$$

where we defined the prefactors

$$g_{i2}(i) = \frac{1}{1 + \sigma_D(i) \frac{\Delta t}{2\varepsilon_0}}, \quad g_{i3}(i) = \frac{1 - \sigma_D(i) \frac{\Delta t}{2\varepsilon_0}}{1 + \sigma_D(i) \frac{\Delta t}{2\varepsilon_0}}, \quad g_{k1}(k) = \frac{\sigma_D(k) \Delta t}{2\varepsilon_0}. \quad (5.31)$$

The placement of PML layers is crucial for effectively attenuating the electric and magnetic fields before they reach the boundary. The fundamental idea is to divide the PML into multiple layers, and from layer to layer, the attenuation term σ_D gradually increases. This gradual increase in attenuation ensures that the fields are effectively damped, ideally before they reach the boundary.

Typically, a number of eight to twelve PML layers are used, depending on the specific simulation requirements. The goal is to design the PML layers in a way that the coefficients g_{i3} and g_{i2} in Eq. (5.30) decrease slowly, while g_{k1} increases gradually, starting from the boundary.

To achieve the required PML behavior, it was shown in Ref. [439] that it is not necessary to directly vary conductivities. Instead, an auxiliary parameter can be introduced,

$$\Gamma(i) = 0.333 \left(\frac{i}{\ell_{\text{PML}}} \right)^3, \quad i = 1, 2, \dots, \ell_{\text{PML}}, \quad (5.32)$$

where ℓ_{PML} is the number of PML layers. The parameter $\Gamma(i)$ is empirically identified with $\Gamma(i) = \frac{\sigma_D(i)\Delta t}{2\varepsilon_0}$. Using this auxiliary parameter, all the prefactors in Eq. (5.30) can be expressed in terms of $\Gamma(i)$,

$$g_{k1}(k) = \Gamma(k), \quad g_{i2}(i) = \frac{1}{1 + \Gamma(i)}, \quad g_{i3}(i) = \frac{1 - \Gamma(i)}{1 + \Gamma(i)}. \quad (5.33)$$

Since the PML is not a physical material, but an artificial layer introduced to mimic absorbing boundary conditions, its design and parameters are determined through numerical experimentation and optimization and as such derived purely empirically. The factors 0.333 and the cubic variation in the auxiliary parameter were found to be the most effective, as reported in Ref. [429].

The quantity in parentheses in Eq. (5.32) ranges between 0 and 1, leading to the following ranges for the other quantities

$$g_{k1}(k) \text{ from } 0 \text{ to } 0.333, \quad (5.34a)$$

$$g_{i2}(i) \text{ from } 1 \text{ to } 0.75, \quad (5.34b)$$

$$g_{i3}(i) \text{ from } 1 \text{ to } 0.5. \quad (5.34c)$$

These parameters are used for the numerical implementation. The remaining ones for a full 3D case are given in App. H.

Periodic Boundary Conditions

Periodic boundary conditions (PBCs) offer a powerful approach to simulate periodic structures, where components of the system exhibit discrete or continuous translational symmetry. For these systems, implementing PBCs can lead to a significant reduction in computational cost while still including supercell effects, where the individual object in the periodic structure effectively interacts with itself, yielding valuable insights into the behavior of the system.

For a numerical implementation, the choice of boundary conditions depends on the specific scenario of interest. The relevant case for us is modeling a plane wave impinging on a periodic structure. Here, periodic boundary conditions are applied in the directions perpendicular to the propagation direction of the incoming light. This is complemented

by a perfectly matched layer (PML) approach, as discussed in the previous section, in the direction of wave propagation to prevent unphysical reflections.

Implementing periodic boundary conditions is relatively straightforward; it only requires identifying all field components in the first and last cells such that

$$E_i[n] = E_i[0], \quad H_i[n] = H_i[0]. \quad (5.35)$$

This condition ensures that the fields can propagate freely across the periodic boundaries. A notable advantage of PBCs is that they allow for a more compact computational domain or an extended physical domain, as no PML layers are required along the identified periodic boundaries.

By using periodic boundary conditions, we can efficiently simulate periodic systems such as plasmonic supercrystals, allowing the calculation of absorption, transmission, and reflection spectra for infinitely extended structures. To ensure the versatility of our numerical implementation, the user can interchangeably use either the implementation of the full PML or the PBCs, allowing the calculation of scattering and absorption cross-sections or transmission and reflection spectra, depending on the specific case of interest.

5.3.4. Excitation Mechanisms

In the preceding section, we discussed the propagation of electromagnetic waves within our designated numerical domain. However, we have yet to address the methods and types of waves that can be introduced in our simulation. This section will focus on this aspect. Depending on the desired observable in our numerical implementation, we can employ various excitation mechanisms. In our code, we have implemented two fundamental mechanisms: a soft dipole source and the total-field scattered-field (TFSF) method, which allows for the simulation of a plane wave traveling along one Cartesian axis with polarization perpendicular to it.

In both cases, we utilize a Gaussian pulse

$$\mathbf{E}^{\text{pulse}}(t) = \mathbf{E}_0 \exp\left\{-\frac{(t - t_0)^2}{\sigma^2}\right\} \cos(\omega_{\text{LSP}}t), \quad (5.36)$$

as the pulse profile with the pulse amplitude $\mathbf{E}_0$, the pulse width σ , the temporal offset t_0 and the center frequency ω_{LSP} of the pulse.

In fully analytical calculations, especially when using the rotating wave approximation and moving to a rotating frame, the optical frequency and the actual pulse shape are generally not considered. However, in numerical simulations, including the oscillation frequency becomes crucial for obtaining the spectral response from a time-domain method like FDTD.

One of the key advantages of FDTD as a time-domain method is its ability to inherently probe the optical response of the system across a wide spectral range in a single simulation. This is a result of the pulses being Fourier-limited, which means that a short pulse in time corresponds to a wide pulse in the frequency domain, as illustrated in Fig. 5.7. This inherent property makes FDTD advantageous compared to frequency-based models, where separate calculations are required for each frequency. The shorter the pulse, the wider the spectral range that can be probed in a single simulation.

To ensure the validity of the obtained results, it is essential to ensure that the pulse bandwidth covers the entire spectral range of interest. In the subsequent sections, we will

describe how to implement the point source and the total-field scattered field (TFSF) approach, which are essential components for simulating electromagnetic interactions in FDTD simulations.

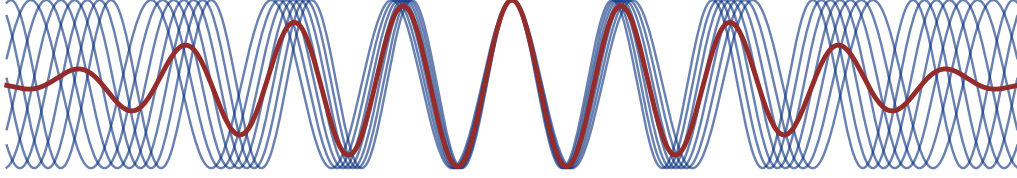


Figure 5.7.: **Fourier Decomposition of an Optical Pulse.** An optical pulse can be represented as a superposition of multiple waves, each having a different frequency. The combination of these waves generates the typical pulse shape. In this plot, we depict multiple sine waves (in blue) and their normalized sum (in red), which illustrates how they collectively form an optical pulse.

Point Dipole Source

Incorporating a point dipole source into the FDTD calculation can be achieved through a straightforward process. Two types of dipole sources are generally distinguished: soft and hard dipole sources. For this thesis, we focus on implementing the soft point dipole source.

In the case of the soft point dipole source, during each iteration when updating the electric field, the value of the pulse is simply added to the electric field at the source position

$$\mathbf{E}(\mathbf{r}_s, t) += \mathbf{E}^{\text{pulse}}(t). \quad (5.37)$$

This approach allows us to derive essential quantities such as the one- or two-point Green's functions, which are directly related to the local density of states (LDOS) and the Purcell factor. These derived quantities play a significant role in understanding the electromagnetic properties of individual systems. More details on these quantities and their applications will be discussed in Sec. 5.3.5.

Plane Wave Source – Total-Field Scattered-Field (TFSF) Approach

One highly successful approach to model plane waves in FDTD is the total-field scattered-field (TFSF) approach [131, 429], which we have implemented in our numerical code. In this framework, the physical domain is subdivided into two regions: the total field and the scattered field regions, as depicted in Fig. 5.8. The main purpose of this division is to minimize the load of the incident wave on the perfectly matched layers (PMLs). By reducing the interaction of the incident wave with the PML, we can effectively reduce the amount of reflected fields entering the physical domain, thus minimizing potential errors.

The conceptual idea behind the TFSF approach is to exploit the linearity of the electric field,

$$\mathbf{E}^{\text{total}} = \mathbf{E}^{\text{inc}} + \mathbf{E}^{\text{scat}}. \quad (5.38)$$

where $\mathbf{E}^{\text{total}}$ represents the total electric field, $\mathbf{E}^{\text{inc}}$ is the incident field, and $\mathbf{E}^{\text{scat}}$ denotes the scattered field. This is to be achieved by assuming that in the total field region the total field is stored in memory and in the scattered field region only the scattered field is stored. According to Eq. (5.38) this requires additional knowledge about the incident field $\mathbf{E}^{\text{inc}}$. However, since this is only a plane wave, it can be stored as an auxiliary one-dimensional array called the incident array. The propagation of the incident wave, as an effectively one-dimensional problem, can be easily modeled using a one-dimensional FDTD solver. Once this is done, it is only necessary to select a source position and add the field contribution at that point, which is then propagated in the three-dimensional FDTD simulation.

In the simulation, we effectively introduce the plane wave at a specific point, or more accurately, at a two-dimensional surface from which the wave propagates and interacts with the object under study. As the wave reaches the boundary of the total-field region, the contribution from the incident wave is removed, allowing only the fraction that is being scattered off the particle to continue propagating towards the PML. This strategic approach leads to a significant reduction in the field amplitude at the PML, effectively minimizing the amount of reflected light. Moreover, this technique allows us to focus solely on monitoring the light that is scattered by the object, which is typically the primary interest in many simulations.

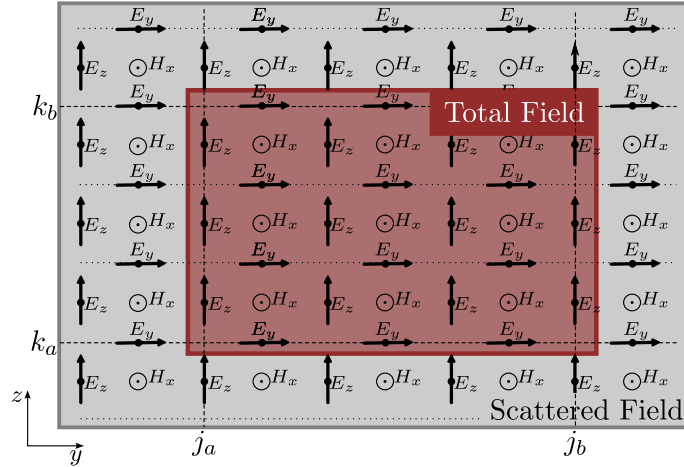


Figure 5.8.: **2D Illustration of the Total-Field Scattered-Field (TFSF) Method.** The cut in the $y - z$ direction displays H_x , E_y , and E_z components. At the boundary, the fields within each region depend on the fields in the other region due to the Yee algorithm. Ensuring consistency with the TFSF formulation, this dependency must be carefully considered in the numerical implementation.

The total-field and scattered-field regions are connected through a non-physical boundary, acting as the source for the plane wave. As depicted in Fig. 5.8, every point within the computational domain is assigned to either the total-field or scattered-field region, with no point lying directly on the boundary. In the Yee algorithm, each field component is updated using the values of four adjacent fields surrounding it. While at spatial positions far away from the boundary, all of these fields will be in the same region. However, closer to the boundary, some care must be taken to maintain consistency with the clear separation of the total field and scattered field.

To illustrate this point, let's consider an update equation

$$H_{x,\text{scat}}^{n+1}\left(i, j_a - \frac{1}{2}, k + \frac{1}{2}\right) = H_{x,\text{scat}}^n\left(i, j_a - \frac{1}{2}, k + \frac{1}{2}\right) + S_c \left[E_{z,\text{scat}}^{n+\frac{1}{2}}\left(i, j_a - 1, k + \frac{1}{2}\right) - E_{z,\text{total}}^{n+\frac{1}{2}}\left(i, j_a, k + \frac{1}{2}\right) \right]. \quad (5.39)$$

Here, we see that the update equation for a point in the scattered field uses points from both the scattered and total field regions to calculate the spatial derivatives. This must be corrected to ensure that only alike quantities are used.

To address this, we can make use of Eq. (5.38). Since the scattered field should only depend on scattered field quantities, we subtract the incident field contribution from the total field on the inside of the boundary to effectively obtain a scattered field contribution,

$$H_{x,\text{scat}}^{n+1}\left(i, j_a - \frac{1}{2}, k + \frac{1}{2}\right) = H_{x,\text{scat}}^n\left(i, j_a - \frac{1}{2}, k + \frac{1}{2}\right) + S_c \left[E_{z,\text{scat}}^{n+\frac{1}{2}}\left(i, j_a - 1, k + \frac{1}{2}\right) - \underbrace{E_{z,\text{total}}^{n+\frac{1}{2}}\left(i, j_a, k + \frac{1}{2}\right) + E_{z,\text{inc}}^{n+\frac{1}{2}}\left(i, j_a, k + \frac{1}{2}\right)}_{=-E_{z,\text{scat}}^{n+\frac{1}{2}}\left(i, j_a, k + \frac{1}{2}\right)} \right]. \quad (5.40)$$

Fortunately, there is no need to change the entire FDTD update loop. We can utilize the linearity of the fields again, cf. Eq. (5.38), and leave the main FDTD loop unchanged, making corrections in a subsequent loop,

$$H_x^{n+1}\left(i, j_a - \frac{1}{2}, k + \frac{1}{2}\right) = H_x^{n+1}\left(i, j_a - \frac{1}{2}, k + \frac{1}{2}\right) + S_c E_{z,\text{inc}}^{n+\frac{1}{2}}\left(i, j_a, k + \frac{1}{2}\right). \quad (5.41)$$

This process is repeated for the upper and lower boundaries, and similar corrections are performed for the other two coordinates perpendicular to the boundary. Due to the staggering, there are six faces of constant x , y , or z that have to be considered and corrected, depending on the direction of propagation for the plane wave or for an arbitrary TFSF setup. The collected update equations for a plane wave traveling in the y -direction with E_z and H_x components are given in App. H.

5.3.5. Observables – Post-Processing

To obtain information about the system from an FDTD calculation, monitors are typically placed at positions of interest to record and Fourier transform the monitored fields, since it is usually the frequency response that one is interested in. For an efficient FDTD implementation, one has the option of two monitor types: discrete Fourier transform (DFT) monitors, which record all places throughout space but only at one specific frequency, and point monitors, which record a single position but at all frequencies. While it is theoretically possible to have a monitor throughout space that records all frequencies, such an approach would consume an enormous amount of storage and significantly increase computational time, rendering it infeasible, as we will discuss further.

In our numerical implementation, we focus on three main observables: the Purcell factor, the scattering cross section, and the absorption cross-sections. The Purcell factor

is calculated using a point dipole source, cf. Sec. 5.3.4, and a point monitor. On the other hand, for the cross-sections, we utilize the TFSF approach, cf. Ref. 5.3.4, in combination with a set of DFT monitors. Detailed explanations will be provided in the following sections.

Point Monitors and Green's Functions

The implementation of a point monitor is fairly straightforward, as it simply involves recording the fields at certain positions of interest over time. Upon completion of the FDTD loop, as shown in Fig. 5.12, a Fast Fourier Transform (FFT) is used in the post-processing phase to identify the dominant frequencies within the system. In combination with the point sources, these point monitors allow the calculation of the Green's function for two points in space:

In general, the two-point Green's function connects the electric field at position $\mathbf{r}_a$ with the polarization at position $\mathbf{r}_b$,

$$E_i^{inh}(\mathbf{r}_a, \omega) = G_{ij}(\mathbf{r}_a, \mathbf{r}_b, \omega) P_j(\mathbf{r}_b, \omega). \quad (5.42)$$

This Green's function can be calculated numerically by recording the electric field at one position in space that is generated by a point dipole source at a second position. Choosing the same position, we can naturally obtain the one-point Green's function. This allows for an initial benchmark, as the 3D free space one-point Green's function can also be given analytically as [440]

$$\text{Im}[G_{ii}(\mathbf{r}_0, \mathbf{r}_0, \omega)] = \frac{n_b \omega^3}{6\pi c^3}, \quad (5.43)$$

with the refractive index of the background n_b . This is an excellent benchmark, in particular of the PML as for free space without any objects, potential reflects from the boundary become very prominent in the simulation. In Fig. 5.9(a), we provide the comparison of the simulation result and the analytical result and find excellent agreement with the analytical value. The z direction was chosen without loss of generality. Once we introduce objects to the computational domain, this Green's function will change substantially, as we discuss in the following.

Local Density of States (LDOS) and Purcell factor

From the Green's function, we can derive the Purcell factor (or normalized projected local density of states [441]) as the imaginary part of the Green's function renormalized by the free space Green's function,

$$PF_i(\mathbf{r}; \omega) = \frac{\text{Im}\{G_{ii}(\mathbf{r}, \mathbf{r}; \omega)\}}{\text{Im}\{G_{ii}^{\text{vac}}(\mathbf{r}, \mathbf{r}; \omega)\}}. \quad (5.44)$$

While the LDOS is equivalent to the power radiated by a unit dipole, the Purcell factor gives a measure of the enhanced spontaneous emission at the position under consideration. To numerically calculate the Purcell factor, we compute the one-point Green's function near an object of interest. The presence of the object influences the one-point Green's function in the way that the comparison to the vacuum Green's function, cf. Eq. (5.44), allows deriving the Purcell factor.

This illustrates one of the great advantages of FDTD, which intrinsically captures radiative processes, compared to other methods, e.g., Maxwell-Bloch equations, where great care has to be taken to introduce radiative correctly and self-consistently [442].

As an example calculation for the Purcell factor calculations, we provide the Purcell factor in Fig. 5.9(b) for a dipole source close to the surface of a gold nanoparticle of 100 nm radius for varying distances.

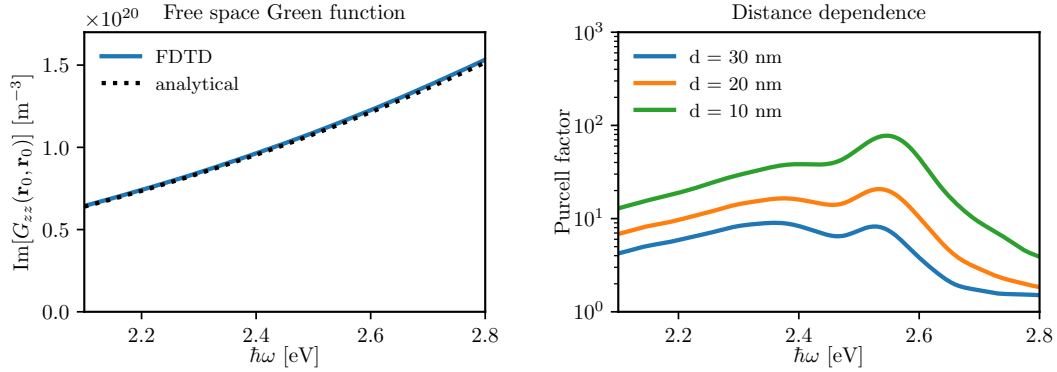


Figure 5.9.: **Results for One-Point Green's Function Calculation.** (a) A comparison of the simulated free space Green's function with the analytical solution exhibits excellent agreement between simulation and theory. (b) Simulation of the Purcell factor for varying distances of the source from the surface of a gold nanoparticle with 100 nm radius. We observe changes in the ratio between the dipole mode and higher-order modes depending on the distance from the nanoparticle.

In agreement with Ref. [441], we find that there exist multiple peaks that are associated with the localized plasmon dipole resonance and higher-order plasmon resonances. For short separations, the higher-order plasmon peaks dominate the spectrum, but they rapidly decay with the increasing distance so that the dipole mode becomes the dominant mode as expected for spherical nanoparticles under linearly polarization excitation. This method can be used to study the optical response of the nanoparticle, in particular when we want to study the changes induced by the non-perturbative THz pump.

Scattering and Absorption Cross Sections

The second observables of interest are the cross sections, here the scattering and absorption cross sections, σ_{scat} and σ_{abs} , from which one can also derive the extinction cross section σ_{ext} . For example, the definition of the scattering cross section is

$$\sigma_{\text{scat}} = \frac{W_{\text{scat}}}{I_{\text{inc}}}, \quad (5.45)$$

with the scattered energy flux W_{scat} and the incident field intensity I_{inc} . As their names indicate, the cross sections have units of area because the scattered energy flux W_{scat} describes the flow of energy per time and has units of Js^{-1} and the incident field intensity describes the energy flux per unit area and has units of $\text{Jm}^{-2}\text{s}^{-1}$. The general formula for the scattered energy flux is

$$W_{\text{scat}} = \int_A \langle \mathbf{S}_{\text{scat}} \rangle \cdot d\mathbf{A}, \quad (5.46)$$

where the surface element $d\mathbf{A}$ is chosen to point outwards. Here we define the time-averaged Poynting vectors, since we are interested in the time-averaged energy flux,

$$\langle \mathbf{S} \rangle = \frac{1}{T} \int_0^T S(t) dt = \frac{1}{2} \text{Re}[\mathbf{E}_m \times \mathbf{H}_m^*], \quad (5.47)$$

where the m index in the fields indicates the fields in the frequency domain. The field intensity is calculated similarly as the absolute value of the Fourier transformed Poynting vector of the incident field at that frequency. This can be given as

$$I_{\text{inc}} = \langle \mathbf{S}_{\text{inc}} \rangle. \quad (5.48)$$

To determine the placement of the monitors in the physical domain of our simulation, we use the total field-scattered field (TFSF) approach, as discussed in Sec. 5.3.4 and visualized in Fig. 5.10. Within this subdivided space, the absorption monitor is placed in the total field region, while the scattering monitor is placed in the scattered field region.

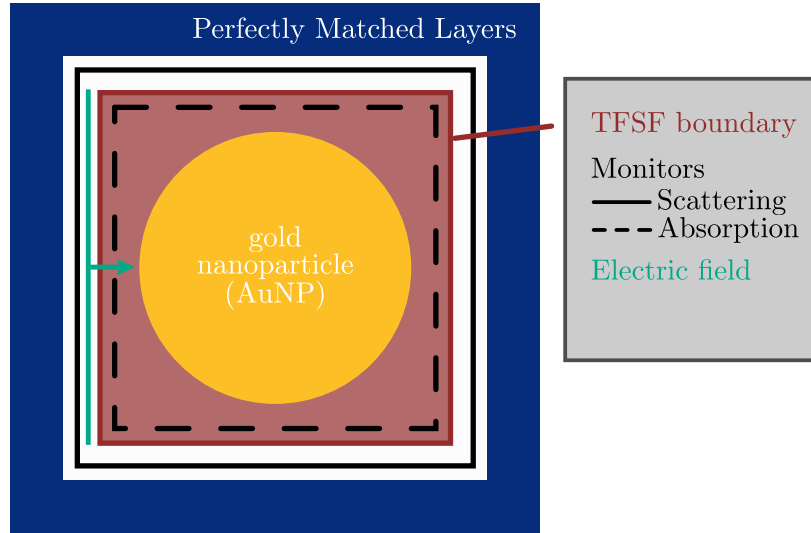


Figure 5.10.: **Computational Domain and Field Monitors for the FDTD Simulation.** The entire computational domain can be subdivided into the physical domain and the Perfectly Matched Layer (PML) boundary that surrounds the physical domain. The physical domain contains the object of interest, in this case a gold nanoparticle, and is divided into the total field domain (red) and the scattered field domain (white). For analysis, a scattered field monitor (solid black line) is placed within the scattered field region, while an absorption monitor (dashed black line) is placed within the total field region.

Our implementation uses six 2D monitors for each cross section monitor, two monitors per spatial direction. These monitors record the component of the Poynting vector perpendicular to them. Consequently, we can measure the energy flow through these monitors, which allows us to quantify the amount of energy absorbed or scattered by the nanoparticle.

In Fig. 5.11 we display the simulated scattering and absorption cross sections for particles with a radius of 50 nm excited by a plane wave. To benchmark our simulation, we compare the results of our custom FDTD code with those of the *miepython* implementation [443].

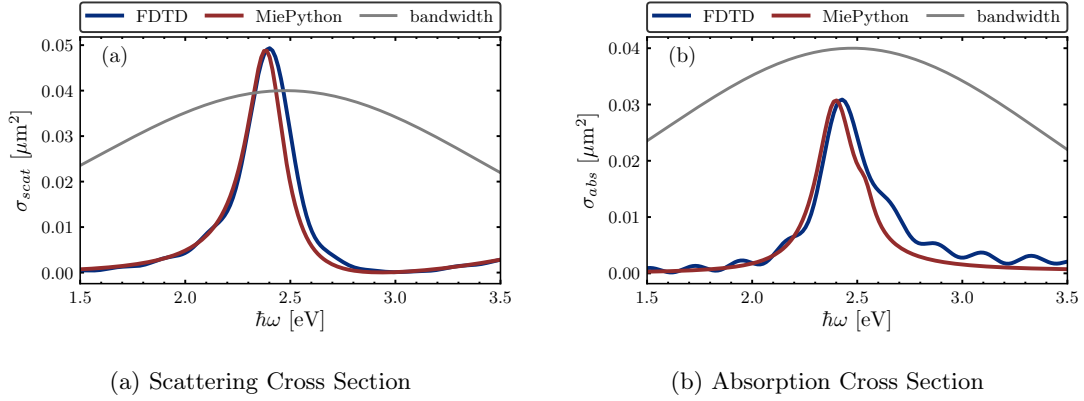


Figure 5.11.: **Benchmark of Scattering Cross Section Using FDTD Calculation.** The figure presents a benchmark comparison of the scattering cross section calculated from the FDTD method. The FDTD code is benchmarked against the MiePython scattering code for both the Johnson and Christy data and the same Drude model implemented in the code.

The agreement shown in Fig. 5.11 between our FDTD simulation and the *miepython* implementation is promising. The slight oscillations in the absorption cross section can be attributed to time integration constraints, but overall the agreement is striking given the complexity of our custom written FDTD code.

As we further develop and refine the microscopic code, these cross section calculations will provide a good benchmark to quantitatively compare the microscopic and macroscopic material models. This comparison will help us to analyze the validity and accuracy of our microscopic description, which will be introduced in Sec. 5.4.

Discrete Fourier Transformation (DFT)

In our simulations, the implementation of 2D monitors requires careful consideration, as an approach analogous to point monitors would lead to massive memory requirements and a significant increase in computational time, as continuous storage of field values would be required. To overcome this, we use a discrete Fourier transform, sometimes referred to as a running Fourier transform, which is integrated into the time loop as follows

$$\tilde{E}(\mathbf{r};, \omega_j) = \sum_k \Delta t e^{i\omega_j t_k} \tilde{E}(\mathbf{r}, t_k). \quad (5.49)$$

To implement this technique, a predetermined set of frequencies is selected, and for each frequency, the above equation is used to update the monitor at each spatial position and frequency. The advantage of this approach is that once the time loop is complete, the monitors are already evaluated. However, it is important to note that depending on the number of frequencies of interest, the computation time is significantly affected. This effect is already noticeable for two-dimensional monitors and becomes even more pronounced for three-dimensional DFT monitors. Careful consideration of the number of frequencies is essential to find a balance between computational efficiency and obtaining accurate results.

In combination with the periodic boundary conditions presented in Sec. 5.3.4, we have also implemented transmission and reflection monitors for plane wave excitation. This is realized using two 2D DFT monitors, one being placed in front of the object and another behind the object in the scattered field region.

5.3.6. Work Flow

To summarize our numerical FDTD implementation, we have successfully introduced all the necessary components for a comprehensive three-dimensional solution of Maxwell's equations. We have optimized the code for speed, utilized just-in-time compilation (jit) techniques, and are planning to incorporate full parallelization to further enhance computational efficiency.

The typical workflow for setting up a simulation involves defining the object of interest, which in our case is usually a sphere, but we have also considered effectively two-dimensional materials. Once the object is defined, appropriate boundary conditions are introduced, often employing full perfectly matched layers or periodic boundary conditions. Additionally, we have implemented options to include a field source, such as a point source or a plane wave, using the TFSF approach. The final step is to position monitors strategically to capture the fields of interest.

Once these initial steps are completed, the standard FDTD iteration begins. The simulation can start at any point in this loop, as it is crucial to ensure the approach's validity by slowly introducing interactions from an equilibrium situation. We chose to initiate the calculation of the polarization using an auxiliary differential equation. After updating the equations for the $\mathbf{D}$ field, we update the electric field, which, in turn, is used to update the $\mathbf{H}$ fields. Following each iteration, the individual monitors are updated, whether they are point monitors or DFT monitors.

Upon completion of the iteration, the obtained data is post-processed to extract relevant information, such as the Purcell factor from the recorded fields via Fourier transform or the cross sections from the evaluation of electric fields detected at the DFT monitors.

5.4. Coupled Kinetic Maxwell-Boltzmann Engine

As we have described in Sec. 5.2 and illustrated in Fig. 5.3, we aim to derive a self-consistent scheme to numerically solve the microscopic electron dynamics and the macroscopic Maxwell equations, which we treat using a self-written finite-difference time-domain implementation that we will introduce in Sec. 5.3.1 to model the optical response

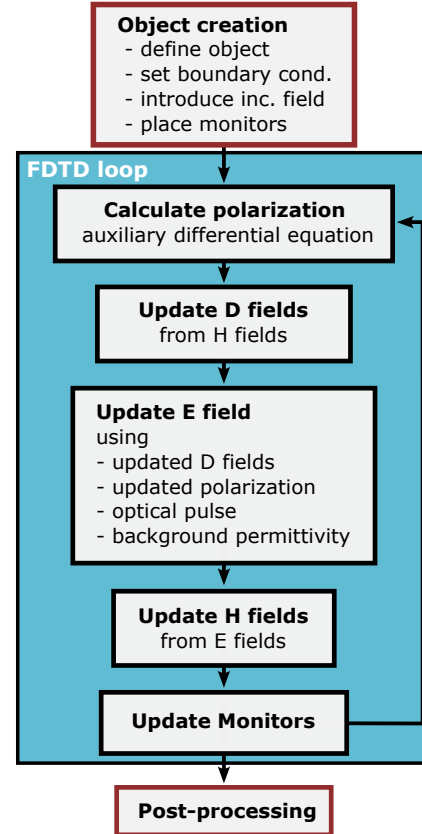


Figure 5.12.: Standard FDTD Iteration.

of the plasmonic nanoparticle in the described THz pump-optical probe setup. For the microscopic dynamics we start with a reduced version of the Boltzmann scattering equation for the electron and phonon Wigner functions, cf. Eqs. (4.31) and (4.33),

$$\begin{aligned} \partial_t f_{\mathbf{k}}(\mathbf{r}, t) = & -\mathbf{v}_{\mathbf{k}} \cdot \nabla_{\mathbf{r}} f_{\mathbf{k}}(\mathbf{r}, t) \\ & + \nabla_{\mathbf{k}} f_{\mathbf{k}}(\mathbf{r}, t) \cdot \left[\frac{e}{\hbar} (\mathbf{E}^{\text{opt}}(\mathbf{r}, t) + \mathbf{E}^{\text{THz}}(\mathbf{r}, t)) \right] \\ & + \sum_{\mathbf{q}} [\Gamma_{\mathbf{k}+\mathbf{q}, \mathbf{k}}^{\text{in}}(\mathbf{r}, t)(1 - f_{\mathbf{k}}(\mathbf{r}, t)) - \Gamma_{\mathbf{k}, \mathbf{k}+\mathbf{q}}^{\text{out}}(\mathbf{r}, t)f_{\mathbf{k}}(\mathbf{r}, t)], \end{aligned} \quad (5.50a)$$

$$\begin{aligned} \partial_t n_{\mathbf{q}}(\mathbf{r}, t) = & -\mathbf{v}_{\mathbf{q}}^{\text{ph}} \cdot \nabla_{\mathbf{r}} n_{\mathbf{q}}(\mathbf{r}, t) \\ & + \Gamma_{\mathbf{q}}^{\text{em}}(\mathbf{r}, t)(1 + n_{\mathbf{q}}(\mathbf{r}, t)) - \Gamma_{\mathbf{q}}^{\text{abs}}(\mathbf{r}, t)n_{\mathbf{q}}(\mathbf{r}, t), \end{aligned} \quad (5.50b)$$

in a single-band Wigner function approach that includes the intraband light-matter interaction and electron-phonon scattering. The scattering matrices are given in Eqs. (4.30) and (4.34). Here, the exciting electric field has been subdivided into one contribution from the optical field and one from the THz field. These equations have in our group successfully be implemented for 2D semiconductors and allowed for a derivation of the exciton linewidth [21, 176] or to study the competition between bosonic and fermionic behavior [178].

For the scope of this project, we have begun implementing Eqs. (5.50) to study nanospheres in three dimensions. Preliminary results from this implementation are shown in Fig. 5.13.

In this initial approach, we focus on solving the three-dimensional electronic dynamics described by Eq. (5.50a) while treating the phonon system as a bath. The electron-phonon interaction is implemented in analogy to Ref. [339], while the electron-light interaction is implemented using a finite element method. This means that we model the phonon contribution using a Bose-Einstein distribution at constant temperature. This model can be regarded as exact for low excitation powers that results in only minor changes in the lattice temperature and thus minor change in the Bose-Einstein distribution. In order to allow for an accurate treatment of the dynamics of the electron-phonon system for higher excitation powers, the current treatment will be extended to also feature the phonon dynamics according to Eqs. (4.33).

As shown in Fig. 5.13, we find in agreement with Ref. [375] that upon excitation, the electron contribution is brought out of equilibrium and returns to it on a picosecond timescale. For the electron-phonon interaction, we have adapted the parameters from Ref. [229]. For all scenarios already implemented, the electron distribution remains close to a thermal Fermi distribution.

As in initial benchmark, we have performed comparisons to the two-temperature model, cf. Sec. 2.3.3 and the standard parameters for the Drude model, cf. Sec. 2.3.1. Here, we currently find that the electron-phonon interaction is overestimated compared to the Drude parameters at room temperature, by about half an order of magnitude, but qualitatively reproduces the known results. The implementation of these equations was done by Jonas Grumm as part of his master thesis, more details can be found in Ref. [411]. The current version of the numerical implementation of the microscopic equations can be found at Ref. [444].

The results of the dynamical microscopic equations are transferred to the macroscopic level by the momentum expansion in Eq. (4.35). These quantities replace the auxiliary

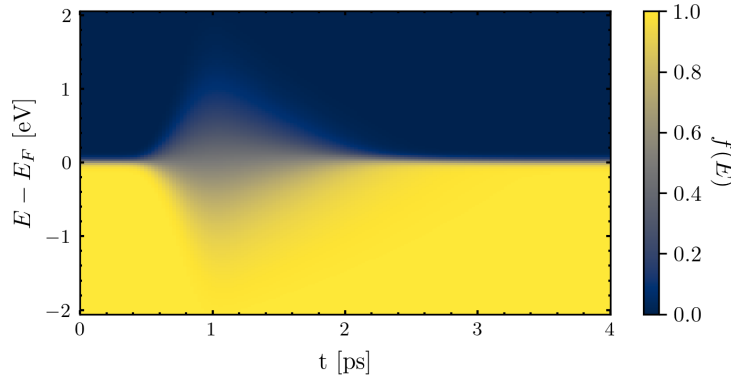


Figure 5.13.: **Time Evolution of the Electron Distribution after Optical Excitation.** Time evolution of the electron distribution after excitation with a 200 fs pulse with $5 \mu\text{J cm}^{-2}$.

differential equation in a three-dimensional finite-difference time-domain (3DFDTD) implementation, as described in Sec. 5.3.2. This leads to feedback between the electrons and the macroscopic fields, requiring an iterative solution of macroscopic Maxwell's equations and the microscopic Boltzmann transport equation, as shown in Fig. 5.3.

This combined approach effectively integrates a full solution of Maxwell's equations with a microscopic momentum-resolved study of electronic dynamics, including material dispersion and hydrodynamic effects. The solver operates in a six-dimensional space for material and field properties, making it an extension of the four-dimensional approach in Ref. [375], which assumed an isotropic momentum distribution in the electronic system (random-k approximation). Our goal is to improve this by considering the full anisotropic Wigner function representation.

Due to the complexity of this joint project, which involves a six-dimensional implementation based on the Wigner function phase space, it is still ongoing and does not yet provide quantitative results. The project is continuously being developed, and an updated version is available on git at Ref. [430].

5.5. Analytical Non-Perturbative Approach

In order to gain a more physical understanding of the processes involved in the THz pump – optical probe scenario, we develop in this section an analytical approach to study the situation that we have described fully numerically using the coupled kinetic Maxwell-Boltzmann engine in previous sections. Therefore, we will start again with the framework of spatio-temporal Boltzmann scattering equations that we developed in Ch. 4. Here we distinguish the THz field and the optical field and perform a momentum expansion similar to the purely hydrodynamic case in Sec. 2.3.4. The THz field is treated non-perturbatively so that it affects the electronic ground state, while the optical field is treated perturbatively as usual. This leads to updated effective equations for the permittivity in Sec. 5.5.1. Then the geometry of the system is introduced via boundary conditions similar to the standard quasi-static Mie solution in a sphere, cf. [201, 270], adapted to the hydrodynamical case, similar to Ref. [264], with the inclusion of the additional THz field in Sec. 5.3.3. This leads to a modified expression for the polarizability

of a metal nanoparticle in the dipole approximation, which we evaluate for experimentally feasible THz field strengths.

5.5.1. Hydrodynamic Equations

We start out with the microscopic equations we also derived in Sec. 4 for the microscopic Wigner function. We include the THz field as an additional field that contributes on the intraband level in the microscopic equations, accordingly, the microscopic Wigner functions reads

$$\partial_t f_{\mathbf{k}}(\mathbf{r}, t) + \mathbf{v}_{\mathbf{k}} \cdot \nabla_{\mathbf{r}} f_{\mathbf{k}}(\mathbf{r}, t) = \frac{e}{\hbar} \left[\mathbf{E}^{\text{opt}}(\mathbf{r}, t) + \mathbf{E}^{\text{THz}}(\mathbf{r}, t) \right] \cdot \nabla_{\mathbf{k}} f_{\mathbf{k}}(\mathbf{r}, t) + \partial_t f_{\mathbf{k}}(\mathbf{r}, t) \Big|_{\text{scat}}. \quad (5.51)$$

From this, we use the same momentum expansion technique from Eqs. (4.35) in order to obtain mesoscopic equations in terms of the electron density $\rho(\mathbf{r}, t)$ and the current density $\mathbf{j}(\mathbf{r}, t)$. From this, we factorize the current density $\mathbf{j} = \rho \mathbf{v}$ to obtain equations in terms of the electron density and the mean electron velocity $\mathbf{v}(\mathbf{r}, t)$. We find the same continuity equation as in Eq. (4.45a) and a modified Euler equation, cf. Eq. (4.45b), that reads

$$\rho(\mathbf{r}, t)(\partial_t + \mathbf{v}(\mathbf{r}, t) \cdot \nabla) \mathbf{v}(\mathbf{r}, t) = - \frac{\kappa}{m e^{2/3}} \nabla \rho^{5/3}(\mathbf{r}, t) - \gamma \rho(\mathbf{r}, t) \mathbf{v}(\mathbf{r}, t) - \frac{e}{m} \rho(\mathbf{r}, t) [\mathbf{E}^{\text{opt}}(\mathbf{r}, t) + \mathbf{E}^{\text{THz}}(\mathbf{r}, t)], \quad (5.52)$$

where we remind the reader of the definition $\kappa = \frac{\hbar^2}{5m} (3\pi^2)^{2/3}$. From here, we proceed in analogy to the expansion in orders of the electric field that we performed in Sec. 4.5. At this stage, it is crucial to treat the additional THz field appropriately to the situation under consideration: In our assumption, we assume a strong but temporally slow THz field that can no longer be seen as a perturbation to the ground state but actually effectively renormalizes the ground state of the system. Keeping this in mind, we assume that the THz field is zeroth order in the perturbation and the optical field first order, which we will express via

$$\mathbf{E}^{\text{THz}}(\mathbf{r}, t) = \mathbf{E}_0^{\text{THz}}, \quad \mathbf{E}^{\text{opt}}(\mathbf{r}, t) = \epsilon \mathbf{E}_1^{\text{opt}}(\mathbf{r}, t). \quad (5.53)$$

Here, ϵ describes is used as the expansion coefficient to expand in the individual orders. Accordingly, we find for the electron density and the electron velocity:

$$\rho(\mathbf{r}, t) = \rho_0(t) + \epsilon \rho_1(\mathbf{r}, t) + \epsilon^2 \rho_2(\mathbf{r}, t) + \mathcal{O}(\epsilon^3), \quad (5.54a)$$

$$\mathbf{v}(\mathbf{r}, t) = \mathbf{v}_0(t) + \epsilon \mathbf{v}_1(\mathbf{r}, t) + \epsilon^2 \mathbf{v}_2(\mathbf{r}, t) + \mathcal{O}(\epsilon^3), \quad (5.54b)$$

which implicitly means for the density contribution resulting from the pressure contribution

$$\rho^{5/3}(\mathbf{r}, t) = \rho_0^{5/3}(t) + \epsilon \frac{5}{3} \rho_0^{2/3} \rho_1(\mathbf{r}, t) + \epsilon^2 \frac{5}{9} \rho_0^{-1/3} \rho_1^2(\mathbf{r}, t) + \epsilon^2 \frac{5}{3} \rho_0^{2/3} \rho_2(\mathbf{r}, t) + \mathcal{O}(\epsilon^3). \quad (5.55)$$

Here, we made use of the fact that the THz wave length is on the order of micrometers and effectively neglect its spatial dependence. In classical quasi-static Mie theory, the

optical field is also assumed to be spatially constant within the material. However, to describe nonlocal hydrodynamic response of the electronic system in the optical regime, we allow for a spatial dependence in the optical field. As pointed out previously, the ground states ρ_0 and $\mathbf{v}_0$ are renormalized by the THz field and can no longer be assumed to be in equilibrium. In the following, we will assume that the two are spatially homogeneous, implying that the response with respect to the THz field is modeled using a Drude model rather than a full hydrodynamic model. Here, we make the assumption that the local response of the metal nanoparticle in response to the THz field is neglected due to its high field strength. This assumption is partly motivated by the fact that we are interested in the plasmonic response in the optical domain, which is clearly separate from the THz domain. Besides, it simplifies our analytical treatment substantially, as it avoids an additional self-consistency problem. Therefore, this assumption should be considered as a first approach to simplify the problem, and its validity requires further investigation in future studies. With this, we obtain a differential equation for the zeroth order electron velocity,

$$\rho_0 \partial_t \mathbf{v}_0 = -\frac{e}{m} \mathbf{E}^{\text{THz}} - \gamma_{\text{THz}} \mathbf{v}_0 \rho_0, \quad (5.56)$$

that results, as previously stated, in a Drude model for the zeroth order polarization in response to the THz excitation,

$$\mathbf{P}_0 = \frac{\rho_0 \mathbf{v}_0}{i\omega} = -\frac{\varepsilon_0 \omega_p^2}{\omega^2 + i\omega \gamma_{\text{THz}}} \mathbf{E}^{\text{THz}}. \quad (5.57)$$

Here, it is apparent that the zeroth order electron velocity will be with the frequency of the THz field so that we will later replace $\omega \rightarrow \omega_{\text{THz}}$. The damping term we find in this equation will be obtained from fits to experimental data in the THz regime, cf. Ref. [445]. Introducing the obtained equation for the zeroth order velocity into the first-order Euler equation, yields

$$\rho_0 \partial_t \mathbf{v}_1 + \rho_0 (\mathbf{v}_0 \cdot \nabla) \mathbf{v}_1 \rho_1 \partial_t \mathbf{v}_0 = -\beta^2 \nabla \rho_1 - \frac{e}{m} [\mathbf{E}^{\text{THz}} \rho_1 + \mathbf{E}^{\text{opt}} \rho_0] - \gamma [\rho_0 \mathbf{v}_1 - \rho_1 \mathbf{v}_0], \quad (5.58)$$

where we again define $\beta^2 \equiv \frac{5\kappa\rho_0^{2/3}}{3me^{2/3}}$ and obtain additional terms in the first-order Euler equation, compared to Sec. 4.5.2, namely a direct THz field contribution and one that couples through the first-order electron velocity. From the continuity equation that now also includes a zeroth order electron velocity, we can again identify the first-order electron velocity to be linked to the first order polarization via

$$\mathbf{v}_1 = \frac{1}{\rho_0} (\partial_t \mathbf{P}_1 + \mathbf{v}_0 (\nabla \cdot \mathbf{P}_1)). \quad (5.59)$$

Including these additional correction terms, we find that we first order polarization $\mathbf{P}_1$ can be linked to the electric field via

$$\frac{\tilde{\beta}^2}{\omega^2 + i\gamma\omega} [\nabla(\nabla \cdot \mathbf{P}) + \nu(\omega) \mathbf{E}^{\text{THz}} \nabla \cdot \mathbf{P}] + \mathbf{P} = -\frac{\varepsilon_0 \omega_p^2}{\omega^2 + i\gamma\omega} \mathbf{E}^{\text{opt}}. \quad (5.60)$$

Compared to the purely hydrodynamic case in Eq. (4.47), we obtain additional terms resulting from the inclusion of the THz field: the electron velocity is renormalized $\beta \rightarrow$

$\tilde{\beta}$, and we find an additional correction term that scales with the divergence of the polarization. Here, we defined

$$\tilde{\beta}^2 \equiv \beta^2 - |\mathbf{v}_0|^2, \quad \nu(\omega) \equiv \frac{e}{m\tilde{\beta}^2} \left(1 + 2 \frac{\omega}{\omega_{\text{THz}} + i\gamma_{\text{THz}}} \right). \quad (5.61)$$

Thus, the THz field acts on gradients in the electron density and must be treated similarly to the internal pressure of the electron gas. Here, ω is the optical frequency. The effect of the additional THz field is the renormalization of the electron velocity $\tilde{\beta}$ and the introduction of the term that scales linearly with the wave number $\mathbf{Q}$. The corresponding modes for $\mathbf{Q}$ have to be determined once a geometry is included, which we will do in the next section, where we consider a nonlocal Mie theory. In agreement with Sec. 4.5.2, the relation between $\mathbf{P}$ and $\mathbf{E}^{\text{opt}}$ for parallel polarization can be expressed in terms of the permittivity

$$\varepsilon_{\text{THz}}^L(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega + i\omega\gamma - \tilde{\beta}^2 \mathbf{Q}^2 + i\tilde{\beta}\nu(\omega) \mathbf{E}^{\text{THz}} \cdot \mathbf{Q}}, \quad (5.62a)$$

$$\varepsilon_{\text{THz}}^T(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}. \quad (5.62b)$$

Consistent with the existing literature, our findings indicate that both the hydrodynamic contributions and the THz modulation only affect the longitudinal component, leaving the transverse component unchanged. This observation aligns with the results obtained in the purely hydrodynamic case [147, 253] and leads to the hypothesis that the THz field can be regarded as an effective renormalization of the electron pressure.

5.5.2. THz Field in Nonlocal Mie Theory

Having defined the effective permittivity for the THz-pumped case, we proceed and derive the effective polarizability of small metal nanoparticle, similar to the derivation for the standard approach in local response approximation, cf. Ref. [270], and nonlocal theory, cf. Ref. [264]. This is done by solving an effective nonlocal Mie theory, that is extended to include the previously derived THz contributions. We start out with the equations for the optical electric field $\mathbf{E}^{\text{opt}}$ and the THz field $\mathbf{E}^{\text{THz}}$,

$$\nabla \cdot \mathbf{E}^{\text{opt}} = \frac{\rho}{\varepsilon_0 \varepsilon_\infty}, \quad \nabla \times \mathbf{E}^{\text{opt}} = 0, \quad (5.63a)$$

$$\nabla \cdot \mathbf{E}^{\text{THz}} = 0, \quad \nabla \times \mathbf{E}^{\text{THz}} = 0. \quad (5.63b)$$

As already mentioned in Sec. 5.5.1, the effects of the THz field will be introduced as a modification of the electronic ground state using a classical Drude theory. In doing so, we effectively disregard the self-interaction of the THz field with itself and include these effects on a different level. This allows us to neglect source terms in Eq. 5.63b to avoid self-consistency issues. We justify this approximation based on two main reasons.

Firstly, our primary focus lies in studying the far- and near-field behavior of the optical field. Secondly, we can assume that the THz field is much stronger than any material contributions induced by the THz field in the optical region. For an exact solution, one would have to set $\Delta\phi^{\text{THz}}(\mathbf{E}^{\text{THz}}) = -\rho(\mathbf{E}^{\text{THz}})/\varepsilon_0\varepsilon_\infty$ and solve an additional self-consistency problem. For a solution including the geometry, these governing equations for the electric field will be combined with the material equations, Eqs. (5.60) and (5.62).

Scalar Potentials

At this stage, in order to express the field quantities in terms of their gradients, one usually introduces scalar potentials in the hydrodynamic approach. We will proceed analogously after introducing an additional assumption necessary for our case: From Eq. (5.60) one can express the polarization in terms of a scalar potential if all fields are aligned $\mathbf{E}^{\text{THz}} \parallel \mathbf{E}^{\text{opt}} \parallel \mathbf{P}$. Otherwise, there would be vortices in the polarization field and the necessary introduction of a vector potential would increase the complexity of the problem. Since a parallel alignment of the fields is experimentally possible, and we intuitively expect the considered effect to be largest when the fields are aligned in parallel, we will proceed with this assumption throughout this study, leaving a generalization to later studies. Accordingly, we introduce the optical scalar potential ϕ^{opt} , the THz scalar potential ϕ^{THz} , and the polarization scalar potential ψ , defined in accordance with the standard hydrodynamic approach as

$$\mathbf{E}^{\text{opt}} = -\nabla\phi^{\text{opt}}, \quad \mathbf{E}^{\text{THz}} = -\nabla\phi^{\text{THz}}, \quad \mathbf{P} = -\nabla\psi. \quad (5.64)$$

By inserting these into our field equations, Eq. (5.63), and the material equations, Eq. (5.60), it can similarly to Ref. [264] be shown that the governing equations read

$$[\Delta - \nu(\omega)\mathbf{E}^{\text{THz}} \cdot \nabla + k^2(\omega)]\rho(\mathbf{r}; \omega) = 0, \quad (5.65a)$$

$$\Delta\phi^{\text{opt}} = -\frac{\rho}{\varepsilon_0\varepsilon_\infty}, \quad (5.65b)$$

$$\Delta\phi^{\text{THz}} = 0, \quad (5.65c)$$

$$\nabla\psi = -\frac{1}{\omega^2 + i\gamma\omega} \left(\beta^2 \nabla\rho + \varepsilon_0\omega_p^2 \nabla\phi^{\text{opt}} - \frac{e}{m} \mathbf{E}^{\text{THz}} \rho \right). \quad (5.65d)$$

We refer to the first of these equations, Eq. (5.65a), as the dispersive Helmholtz equation with the dispersion prefactor $\nu(\omega)$ introduced in Eq. (5.61), and the nonlocal, THz-pumped longitudinal wave vector $k^2(\omega) = (\omega^2 + i\gamma\omega - \omega_p^2/\varepsilon_\infty)/\tilde{\beta}^2$. The THz field introduces an additional first derivative in the standard Helmholtz equation for the charge density, cf. Ref. [264], and effectively breaks the spherical symmetry of the system. Accordingly, solutions are more complicated to obtain compared to the standard Helmholtz equation, since functions solving the dispersive Helmholtz equation are no longer eigenfunctions of the Helmholtz operator $(\Delta + k^2)$. Formally, they carry both the spherical symmetry of the MNP and the axial symmetry of the THz field. For vanishing THz field, Eq. (5.65a) approaches the standard Helmholtz equation without the dispersive term. In addition to the dispersive Helmholtz equation, we find Poisson's equation for the optical scalar potential in full agreement with Ref. [264] and Laplace's equation for the THz scalar potential, mainly resulting from the assumption of vanishing back-action of the charge densities on the THz field. In contrast to the common hydrodynamic model, the

scalar potential of the polarization field, ψ , cannot be calculated directly from the scalar potential of the optical field and the density, instead it has to be calculated as a solution of Eq. (5.65d). In the following, we will provide the details of our approach to the solution of Eqs. (5.65).

Solution of Differential Equations

We start a discussion of the dispersive Helmholtz equation, as the additional first-order derivative hinders us from using the standard spherical symmetric solutions. On a qualitative level, the additional THz field superimposes an additional axial symmetry in the direction of if field amplitude so that solutions are assumed to interpolate between spherical harmonics and Bessel functions. Without loss of generality, we will orient the THz field, and thus also the optical field, in the z direction, $\mathbf{E}^{\text{opt,THz}} = E_0^{\text{opt,THz}} \mathbf{e}_z$.

Due to the described symmetry induced by the external field, we solved the dispersive Helmholtz equation using a product ansatz in cylindrical coordinates, which were mapped back to spherical coordinates to allow incorporating the boundary conditions, defined on a sphere. Details on the calculation can be found in Ref. [411]. Using this approach, we obtain a solution of the dispersive Helmholtz equation that reads

$$\rho_{\text{in}}(r, \theta, \varphi) = e^{\nu E^{\text{THz}} r \cos(\theta)} \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} A_{\ell} j_{\ell}(kr) Y_{\ell}^m(\theta, \varphi), \quad \rho_{\text{out}} = 0. \quad (5.66)$$

This solution combines the spherical symmetry of the spherical harmonics Y_{ℓ}^m and the spherical Bessel functions $j_{\ell}(kr)$ with an additional distortion in the field direction in terms of the exponential prefactor. Hence, it covers all the aspects and in the limit of vanishing THz field reproduces the prescription given in Ref. [264]. We observe that the additional prefactor affects the motion depending on r and θ , while leaving the azimuthal motion, depending on φ unaltered. Here, we dropped the frequency dependencies of k and ν for brevity. As we will impose hard-wall boundary conditions, the densities outside the material vanish naturally.

For Laplace's equation in spherical coordinates, we make a standard ansatz using spherical harmonics,

$$\phi^{\text{THz}} = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} b_{\ell} r^{\ell} Y_{\ell}^m(\theta, \varphi). \quad (5.67)$$

Here, we already introduced the assumption of a finite potential within the sphere so that spatial dependencies with negative exponential vanish. The same ansatz can be made for the homogeneous solution of the optical scalar potential equation. In addition to the homogenous solution, we need to introduce a particular solution which can be done via

$$\phi^{\text{opt}} = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \left[B_{\ell} r^{\ell} + \frac{A_{\ell} j_{\ell}(kr) e^{\nu(\omega) E^{\text{THz}} r \cos(\theta)}}{\varepsilon_0 \varepsilon_{\infty} (k^2 - \nu(\omega)^2 E_{\text{THz}}^2)} \right] Y_{\ell}^m(\theta, \varphi). \quad (5.68)$$

A similar set of equations has been derived in Ref. [264] for the nonlocal case. These equations may now be used to derive an equation for the polarization scalar potential.

Solution of Scalar Potentials Equation with Boundary Conditions

Now it is time to introduce the spherical boundary conditions that are usually assumed to derive the polarizability of a sphere. For particles that are small compared to the wave length, this is usually via the quasi-static approximation, which allows employing the solution of a sphere in a static electric field [201, 270, 279]. Since no coupling to charge carrier densities occurs, the solution of the Laplace equation for the THz field is identical to the solution determined in classical local Mie theory. For the optical potential we proceed as done for the hydrodynamic model because Eq. (5.68) shares formal similarity with Eq. (8b) in Ref. [264]. We begin with the usual boundary condition that the fields at infinity are the applied fields only

$$\lim_{r \rightarrow \infty} \phi^{\text{THz}} = -E^{\text{THz}} r \cos(\theta), \quad \lim_{r \rightarrow \infty} \phi^{\text{opt}} = -E^{\text{opt}} r \cos(\theta). \quad (5.69)$$

In addition, we use the standard boundary conditions at interfaces that result from Maxwell's equations and require a continuous $\mathbf{E}$ field parallel to the surface and continuous $\mathbf{D}$ field perpendicular to the boundary. In terms of the potentials, this is written as

$$\varepsilon_{\infty} \partial_r \phi_{in}^{\text{opt, THz}}|_{r=a} = \varepsilon_{\text{out}} \partial_r \phi_{out}^{\text{opt, THz}}|_{r=a}, \quad (5.70a)$$

$$\partial_{\theta} \phi_{in}^{\text{opt, THz}}|_{r=a} = \partial_{\theta} \phi_{out}^{\text{opt, THz}}|_{r=a}. \quad (5.70b)$$

Due to the hydrodynamic character of the theory, which allows for longitudinal waves, we need to introduce an additional boundary condition, complementing the Maxwell boundary conditions. These can be derived unambiguously when explicitly neglecting electron spill-out in comparison with, e.g., Sec. 2.3.5. From this, one can find from the hydrodynamic equations, namely the continuity of the normal component of the electron current density $\mathbf{j}$ and thus in our formulation also of the polarization $\mathbf{P}$ that we formulate for our potential as [264, 446]

$$\partial_r \psi_{in}|_{r=a} = 0. \quad (5.71)$$

Having defined the boundary condition, we proceed to find expressions for the expansion coefficients, which in the standard approach [51, 264] allow introducing the polarizability of the sphere. In the derivation, some extra care is required in comparison with the standard spherical case, where the dipole order can be directly deduced from the order of the spherical harmonics. In comparison, due to the distortion resulting from the applied THz field, an expansion in cosine contributions becomes necessary to identify the dipole order. In doing so, we are able to recover an expression, similar to the one in nonlocal Mie theory, cf. Ref. [264] that can be given as

$$\alpha_{\text{THz}}(\omega, E_{\text{THz}}) = 4\pi\varepsilon_0\varepsilon_{\text{out}}a^3 \frac{\varepsilon_{\infty} - \varepsilon_{\text{out}}(1 + \Delta(\omega, E_{\text{THz}}))}{\varepsilon_{\infty} + 2\varepsilon_{\text{out}}(1 + \Delta(\omega, E_{\text{THz}}))}. \quad (5.72)$$

The only difference at this stage is that the additional THz field does not allow us to reproduce the version in terms of a rescaled background permittivity. However, for

vanishing THz field, we are able to recover the usual Clausius-Mosotti factor in the polarizability. For our case, the Delta factor with its full dependencies can be given as

$$\Delta(\omega, E_{\text{THz}}) = \frac{\omega_p^2}{\varepsilon_0 \tilde{\beta}^2} \frac{1 - \frac{j_1(ka)}{ka j_1'(ka)}}{k^2 - \nu^2(\omega) E_{\text{THz}}^2}. \quad (5.73)$$

Here, the prime denotes the derivative with respect to the full argument. Furthermore, the reader may be reminded of the definitions of

$$\tilde{\beta}^2 = \beta^2 + \frac{e^2}{m^2} \frac{E_{\text{THz}}^2}{\omega_{\text{THz}}^2 - \gamma_{\text{THz}}^2 + i\gamma_{\text{THz}}\omega_{\text{THz}}}, \quad (5.74a)$$

$$\nu(\omega) = \frac{e}{m\tilde{\beta}} \left[1 + \frac{2\omega}{\omega_{\text{THz}} + i\gamma_{\text{THz}}} \right], \quad (5.74b)$$

$$k^2(\omega) = \frac{\omega^2 + i\omega\gamma - \omega_p^2/\varepsilon_\infty}{\tilde{\beta}^2}, \quad (5.74c)$$

that we collect and restate at this stage to show the complexity of the dependencies, making it hard to analytically study the impact of an increased THz field. Therefore, in the following, we study the effect of a changing THz field on the plasmon resonance which we provide in Fig. 5.14.

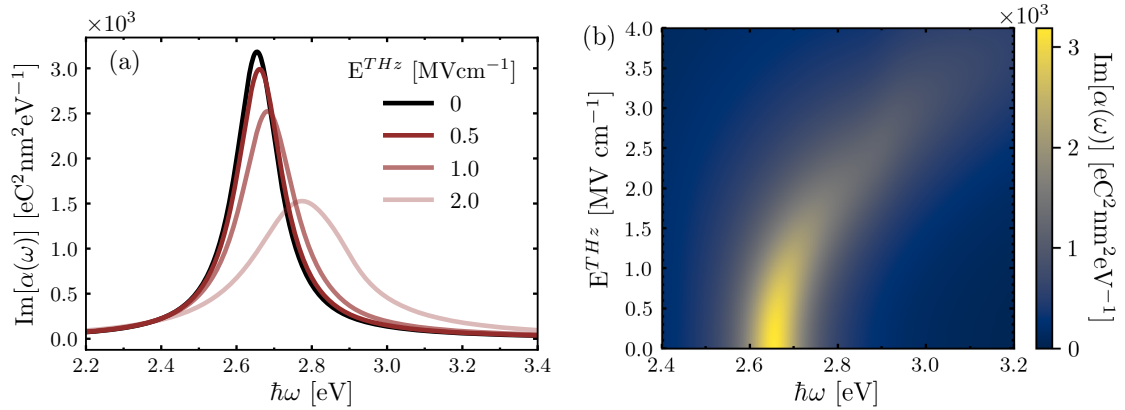


Figure 5.14.: **Polarizability of the Metal Nanoparticle under the Action of the Non-Perturbative THz Field.** This figure illustrates the impact of the non-perturbative THz field on the polarizability of a metal nanoparticle with 10 nm radius. For illustration purposes, we show discrete values of the THz peak field strength in panel (a) and continuous values in panel (b), as governed by Eq. (5.72).

Evaluating Eq. (5.72), we find that the additional THz pulse affects the resonance position of the gold nanoparticle and observe that it causes a blue shift of the resonance position. In addition, we observe a significant quenching of the resonance with increasing pulse strength. The spectra also show a slight dependence on the particle radius due to the behavior of the Bessel functions, similar to findings in Refs. [147, 264]. However, we won't discuss this aspect in detail here, and instead refer interested readers to Ref. [411] for further information.

As can be seen from Eq. (5.74), the ratio of ω_{THz} and γ_{THz} has a significant influence on the changes observed in $\tilde{\beta}$. Here, we focus on the physically meaningful case where $\omega_{\text{THz}} > \gamma_{\text{THz}}$. According to Eqs. (5.74), this condition results in an increase in $\tilde{\beta}$, leading to an enhanced blue shift compared to the pure hydrodynamic case.

Our findings are in good agreement with experimental data recorded by the group of Holger Lange, as presented in Sec. 5.1. To achieve shifts of a similar magnitude to those observed in the experiment, we predict that THz peak field strengths of approximately 0.75 MV/cm are required. As updated experimental data become available, we intend to validate our theory by comparing our calculations with them, with a special focus on the temperature dependence of the resonance shift, which according to Eq. (5.72) should be significantly influenced by γ_{THz} .

To investigate the effect of the additional THz field, similar to the changes in radius, we make a plot similar to Fig. 2.10 for the extinction cross section calculated using Eq. (2.62). As expected from the absorption results, we observe a blue shift in the resonance position and the same signatures from the spherical Bessel functions as shown in Fig. 2.10. Interestingly, the blue shift remains unaffected as the particle radius increases, and these signatures gradually diminish.

To comprehend the physical mechanisms responsible for the observed blue shift, we revisit Eqs. (5.72) and (5.74). The two effects present are the effective renormalization of the effective electron velocity, $\tilde{\beta}$ and the additional static polarization of the nanoparticle. The renormalization can be interpreted as an effective increase in the internal pressure of the electron gas induced by the THz field. Consequently, the strong THz field enhances the hydrodynamic character by increasing the internal pressure. The second contribution to the shift is the additional polarization, which disturbs the equilibrium of the electronic configuration. Since the shift is largely independent of size, and one would expect the pressure renormalization to show some size dependence, this effect is likely to be more dominant, at least for larger particles.

However, it is crucial to acknowledge that the approach presented in this study constitutes a preliminary, first-order approximation for the effects induced by external THz fields. While our findings align well with experimental observations, it is important to recognize that further refinements are essential. For instance, the inclusion of additional factors, such as the spatial dependence of the ground state electron density, and the performance of comprehensive studies that directly compare our theoretical predictions with experimental results are necessary.

5.6. Conclusions

In conclusion, this chapter has explored the potential of actively tuning the optical response of metal nanoparticles using a strong THz field, based on the theoretical framework developed in Ch. 4. The motivation for this study originated from experimental results suggesting significant resonance shifts using this method.

We have developed two distinct approaches to theoretically address this scenario. The first approach employs a fully numerical method that combines microscopic Boltzmann scattering equations for the electronic Wigner function, as described in detail in Ch. 4, with a three-dimensional finite-difference time-domain solver. Upon completion of the implementation, this combination will allow to couple multidimensional, momentum-resolved electron scattering processes with macroscopic solutions of Maxwell's equations.

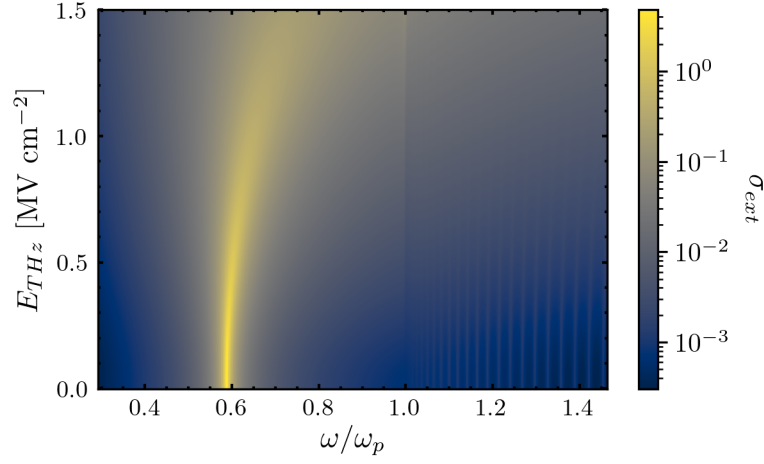


Figure 5.15.: **Impact of Non-Perturbative THz Field on Extinction Cross Section.** The figure demonstrates the effect of a non-perturbative THz field on the resonance of a nanoparticle with a radius of 5 nm. We observe a qualitatively similar result to the standard hydrodynamic model, cf. Fig. 2.10, with a blue shifting main resonance and additional resonances at higher energies. The extinction cross section is unitless, cf. Ref. 2.62.

As a result, our approach will enable a spatio-temporal treatment of microscopic dynamics, encompassing non-equilibrium, non-perturbative, and nonlocal phenomena. It will be applicable to arbitrary geometries and incorporate both intra- and interband transitions. This multiphysics approach builds upon existing work [375] but will additionally facilitate the inclusion of interband transitions and provide deeper insights into the microscopic dynamics of the nanoparticle.

Additionally, we have developed an analytical approach to study the influence of an additional non-perturbative THz field on the plasmon resonance of a spherical nanoparticle. This analytical method allows for a thorough understanding of the physical processes governing the factors contributing to the plasmon resonance shift. Our results reveal that the additional THz pulse effectively renormalizes the electronic ground state of the system by pressure renormalization of the electron gas inside the nanoparticle and, on the optical timescale, polarizes the nanoparticle quasi-statically. The combined effect of the two leads to a blue shift of the plasmon resonance. Importantly, these theoretical results show good agreement with preliminary experimental findings, suggesting that the THz pump optical-probe technique holds promise for actively tuning the plasmon resonance on picosecond timescales.

The combination of our numerical and analytical approaches establishes a robust foundation for further exploration of active tuning in plasmonic structures.

5.7. Perspectives

Once the numerical framework is sufficiently advanced, it will enable a comprehensive spatio-temporal treatment of microscopic, non-equilibrium, non-perturbative and nonlocal dynamics for arbitrary geometries, including intra- and interband transitions. This

will pave the way for a wide-ranging study of plasmonic devices, especially when combined with a DFT-based band structure to accurately describe interband transitions, as we have envisioned in Ch. 4. Such capabilities will allow the simultaneous study of microscopic dynamics and electric field evolution, facilitating the exploration of non-perturbative scenarios, as demonstrated in this chapter using strong THz fields. This may lead to new insights into light-induced active plasmonic effects.

Another intriguing possibility is to explore active plasmonics through different pump-probe scenarios in the optical regime, corresponding to the third tuning option shown in Fig. 5.1. This can be achieved by performing all-optical pump-probe experiments using the two-band framework developed in Ch. 4. By pumping the interband transitions of gold, the conduction band electron density can be tuned on the timescale of the interband lifetime, which is on the order of several picoseconds. An increased electron density would directly affect the resonance position of the nanoparticles, as seen from the definition of the plasma frequency, $\omega_p = \sqrt{\frac{ne^2}{m\varepsilon_0}}$, possibly leading to a blue shift of the plasmon resonance. Such experiments would provide a theoretically straightforward approach to actively tune the localized surface plasmon resonance of metal nanoparticles. However, it remains an open question whether the required field strengths are achievable and whether other processes, such as induced changes in the background permittivity ε_∞ , could compensate for the expected effect.

Furthermore, the analytical framework essentially predicts an additional polarization that manifests primarily at the surface of the nanoparticle. To characterize this additional polarization induced by the THz field, it may be beneficial to employ the surface response formalism described in Sec. 2.3.5. The projected dipole method [155] could then be used to study changes in the optical response of the nanoparticle induced by this additional polarization.

6. Radial Oscillations of Metal Nanoparticles

In the late 19th century, one focus of theoretical physics was the study of vibrations in elastic spheres, with Sir Horace Lamb providing the initial fundamental solutions that revealed the existence of tangential modes alongside simple breathing modes [447]. Over a century later, the observation of breathing modes in metal nanoparticles (MNPs) following optical excitation of localized surface plasmons confirmed Lamb’s calculations [71, 448–452]. These experiments demonstrated a precise match between the measured oscillation frequency and the theoretically predicted frequency [451].

However, despite these advances, the exact driving source responsible for these size oscillations has remained elusive due to experimental challenges in accessing their early onset, similar to the detection of coherent optical phonon modes in semiconductors where a distinction between impulsive stimulated Raman scattering (ISRS) and displacive excitation of coherent phonons (DECP) is non-trivial [453].

Traditionally, it has been assumed that the optically heated electron gas transfers its energy to the phonons in the nanoparticle, resulting in rapid expansion and serving as the dominant driving source for the size oscillations [448, 454, 455] following the plasmon decay. Currently, there is some discussion surrounding the details of this plasmon decay [71, 454–457]. It is now widely accepted that highly energetic “hot” electrons are generated, which are of significant interest for various applications, particularly in plasmon-enabled synthesis. These non-equilibrium carriers undergo thermalization through electron-electron scattering and subsequently couple to lattice phonons. The excess energy is eventually dissipated by the excited lattice into the surrounding environment [71, 454–457].

Recent advancements in experimental techniques, in particular femtosecond X-ray sources, have provided an opportunity for more precise investigation of the temporal onset of nanoparticle oscillations unaffected from electron temperature effects, down to femtosecond timescales [458–463]. These experiments have revealed that the radial oscillations begin before the expected timescales of lattice heating, suggesting that the conventional sequence of events (absorption, heating, oscillation) may not dominate in the early stages after excitation and leaving the actual driving source of the oscillations unidentified. Details on the experimental technique will be given in Sec. 6.1

Our objective in this study is to employ a microscopic framework that encompasses electron-phonon interaction and phonon-phonon interaction, enabling us to derive a comprehensive model to describe the onset of radial oscillations in MNPs. This approach draws inspiration from research conducted in the semiconductor community [380, 464–471].

One notable advantage of our approach compared to the existing classical model is its ability to distinguish coherent and incoherent phonon modes. The coherent phonon modes correspond to the radial vibrations of the macroscopic MNP, while the incoherent modes can be attributed to lattice temperature and, therefore, only contribute on the

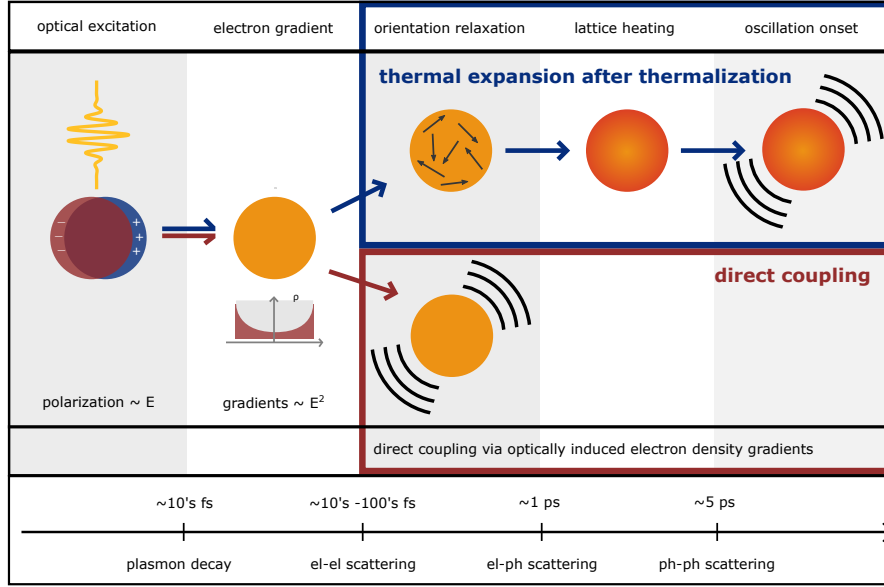


Figure 6.1.: **Schematic Illustration of the Relaxation Dynamics in Plasmonic Nanoparticles.** The optical pump causes a polarization of the electrons in the nanoparticle, which is accompanied by a density gradient. The blue path illustrates the thermal-driving mechanism of the breathing oscillations currently discussed in the literature: After Coulomb-driven orientation relaxation, electron-phonon scattering converts energy from the electrons to the lattice, which leads to an expansion of the particle. This initiates breathing oscillations. The red path demonstrates the coupling mechanism described in this study, where electron density gradients directly couple to the coherent phonon mode, initiating breathing oscillations impulsively.

thermal timescales of the electron-phonon system. By formulating our description in terms of a Hamiltonian, we achieve a consistent treatment of carrier-phonon coupling between all phonon modes and electrons.

Consequently, this formulation allows for a direct coupling between electrons and the breathing oscillation, which was not possible in the classical framework [448, 472], where oscillation onset is always mediated through a thermal process, as illustrated in Fig. 6.1. Some publications [448, 451, 473, 474] introduce a hot electron pressure term using the electronic Grüneisen parameter to match the experimentally observed oscillation phase. This additional term, derived from phenomenology, enables a more direct interaction between the hot electron system and the vibrational mode due to the rapid temperature rise of the electronic subsystem, initiating the onset of oscillation earlier than the interaction solely mediated by thermal phonons.

We obtain the spatially resolved direct electron-phonon coupling in nanoparticles by considering the dynamics of the Wigner distributions of electrons and phonons, which includes the coherent and incoherent processes following the optical excitation. Specifically, we employ the framework of Heisenberg equations of motion for the Wigner distributions to describe these dynamics in detail. To reduce complexity, we explore the hydrodynamic limit of these equations by coarse-graining to mesoscopic observables. This procedure allows us to retain coherent variables such as the optical field and coherent phonons, which interact with the macroscopic motion of charge density, current density, and temperature dynamics. By projecting our equations of motion onto the fundamental Lamb

modes [447, 475] of the elastic sphere under consideration, which are the fundamental vibrational eigenmodes, we can effectively perform an eigenmode expansion and explicitly calculate the electron and phonon dynamics following optical excitation.

The calculations yield two source terms for the lattice dynamics: The well-established thermal driving term via the lattice temperature [448, 451, 473, 474], and a new driving term arising from optically induced spatial gradients in the electron density. This latter term is identified as a more dominant source of the radial breathing oscillations compared to the time-delayed thermal heating process, primarily affecting the equilibrium position of the oscillation.

The electron gradients can arise from both intraband and interband processes, and we have focused on a pure single-band model in our investigation of silver [405], where intraband processes are dominant over a broad spectral range [476]. Additionally, we have studied interband contributions in a subsequent study for gold, where we compare our theory to experiments [4]. In this chapter, we comprehensively discuss and qualitatively compare both situations, addressing the dynamics of intraband and interband processes.

The dominance of the direct coupling between the displaced electrons and the lattice can have important consequences for applications harnessing hot electrons [477–481] and for the general understanding of nanoscale metal dynamics.

This chapter is organized as follows: We begin by briefly stating the current theoretical descriptions of the oscillation onset in Sec. 6.2.1 before we introduce some fundamentals like the distinction of coherent and incoherent phonons, Sec. 6.2.3, and the anharmonic Hamiltonian used to describe thermal expansion, Sec. 6.2.4.

We then derive the microscopic equations for the phonons, Sec. 6.3, and the electrons, Sec. 6.4 which are already coarse-grained to mesoscopic variables in these sections, leading to a closed set of coupled hydrodynamic equations. We employ a similar procedure for the intraband case, Sec. 6.4.1, and the interband case, Sec. 6.4.2, which begins by expansion up to second order in the excitation field and subsequent projection onto solutions of the vibrational Lamb modes in Sec. 6.5. In Sec. 6.6, we provide the numerical solutions for the coupled ordinary differential equations that arise, compare the qualitatively different source terms resulting from intraband and interband interaction and compare to experimental results. Finally, we conclude with a comparison of the influence of the individual driving terms on the nanoparticle oscillation in Sec. 6.7.

6.1. Experimental Motivation

This work has been inspired by experimental results that were obtained from our coworkers in the group of Holger Lange, which we also jointly published in Ref. [4]. In the experiment, the advance has been to use X-ray single particle imaging (SPI) instead of transient absorption (TA) as done in previous experiments to measure the temporal behavior of the oscillation.

Transient absorption (TA) experiments, as mentioned in Refs. [374, 456], rely on observing the temperature of the thermalized hot electron gas that is visible as a contrast in the optical measurements. The breathing oscillations of plasmonic nanoparticles manifest as periodic contrast modulations in the TA spectra [482–484]. However, TA experiments do not allow for a precise determination of the temporal onset of the breathing oscillations due to the dominating contrast from the initial electron dynamics. As a result, the

details of the oscillation were previously only extrapolated and as such only indirectly deduced.

In the new experimental technique, called transient small-angle X-ray scattering in a single-particle imaging scheme (tSAXS-SPI) [462, 485, 486], it becomes possible to access the entire oscillation, including the portion right after the optical pulse as it does not depend on the optical contrast dominated by electronic dynamics during the initial stages. A sketch of the experimental setup is shown in Fig. 6.2.

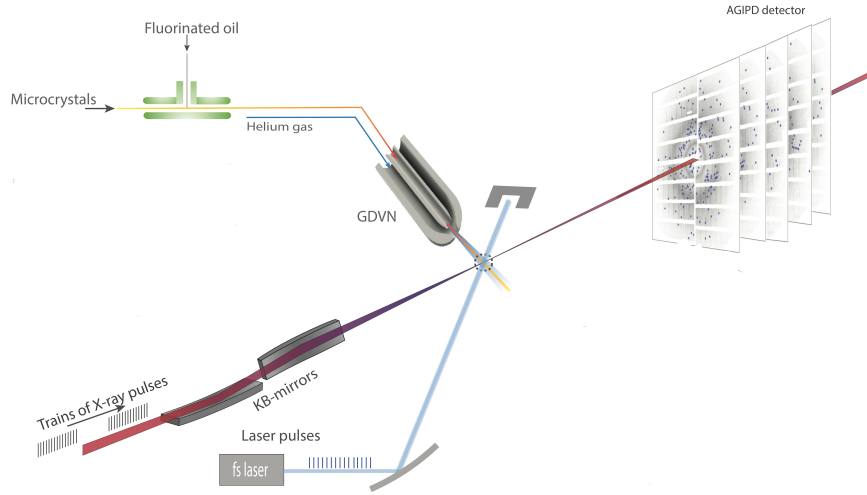


Figure 6.2.: **Transient Small-Angle X-ray Scattering in a Single-Particle Imaging Scheme (tSAXS-SPI).** This experimental technique is utilized to detect the oscillation of gold nanoparticles (AuNPs). A beam of individual AuNPs is precisely intersected with an optical laser pulse and an X-ray pulse. The laser pulse initiates the oscillation of the nanoparticles, while the X-ray pulse can be temporally adjusted to capture the nanoparticle’s diameter at a specific time after the optical pulse. Figure reproduced from Ref. [486] with permission from Springer Nature.

The tSAXS-SPI technique combines multiple diffraction patterns from individual particles to create a diffraction volume, which is then inverted to reconstruct the nanoparticle structure [462, 487]. A significant advantage of this technique is its ability to measure single-particle images. This is achieved by generating a beam of individual AuNPs, which are then accurately intersected with both the laser pulse and the X-ray pulse. This setup allows for the nanoparticle to be pumped by the laser pulse and subsequently observed at different time steps using the X-ray pulse. The single-particle imaging scheme not only enables the correction of sample inhomogeneity but also maintains statistical robustness through a serial measurement approach. By employing SPI data in a pump-probe fashion, a dynamic “movie” of the nanoparticle’s behavior can be obtained.

The experimentally obtained data that motivated our numerical studies will be presented in Sec. 6.6.4.

6.2. Prerequisites

This final major section of this thesis builds upon the concepts developed in the preceding sections, with particular emphasis on the utilization of the Wigner function approach,

as discussed in Sec. 4 and 5. However, to accurately describe the oscillations of the nanoparticle, further fundamental concepts are required, which are introduced in the subsequent discussion.

6.2.1. Current Theoretical Description

Over the past two decades, numerous experiments have observed nanoparticle oscillation, primarily in transient absorption [448–451, 458, 472, 474, 482, 488–490]. Some of these studies have proposed theoretical models to describe the onset of oscillation, particularly in Refs. [448, 451, 473, 474]. These descriptions share qualitative similarities, differing only in whether the initial temperature rise of the electron system is simulated or assumed to start from a specific initial electron temperature. However, as the rise in electron temperature resulting from excitation with femtosecond pulses is quasi-instantaneous on the timescale of the oscillation (picoseconds), all models can be considered quasi-equivalent. A brief overview is provided in App. I.1. In this study, we adopt the model proposed in Ref. [448], where changes in nanoparticle radius R are governed by the inhomogeneous ordinary differential equation,

$$\frac{\partial^2 R}{\partial t^2} + \frac{2}{\tau_d} \frac{\partial R}{\partial t} + \left(\frac{2\pi}{\Omega} \right)^2 \left[R - \left\{ R_0 + \frac{R_0 \alpha}{3} (T_\ell - T_0) \right\} \right] = 0. \quad (6.1)$$

This equation resembles a typical damped harmonic oscillator equation where τ_d represents the damping of the oscillation and is typically used as a fitting parameter. Ω denotes the period of oscillation, R_0 is the equilibrium radius at equilibrium temperature T_0 , T_ℓ is the temperature of the crystal lattice, and α is the coefficient of thermal expansion. Accordingly, it is apparent that changes in temperature affect the equilibrium position of the crystal lattice. Accordingly, for rapid changes of the lattice temperature, it is anticipated that the system undergoes transient oscillations until a new equilibrium is reached. In Fig. 6.3a, we reproduce the experimental data and the theory found in Ref. [448] which compares numerical solutions of Eq. (6.1) with data obtained from transient absorption measurements.

As illustrated in Fig. 6.3a, the temporal behavior of the oscillation and the general form are nicely reproduced. However, the author encounters a phase mismatch of the experimental data and the theory in the oscillation. This phase mismatch is typically attributed to the absence of contributions from hot electrons in Eq. (6.1), assuming that the electronic heat capacity C_e is much smaller than the lattice heat capacity C_ℓ , expressed as $C_e \ll C_\ell$, which holds under equilibrium conditions. However, for ultrafast experiments with femtosecond pulses, the electron temperature significantly exceeds the lattice temperature, resulting in $C_e \approx C_\ell$. This occurs because the electronic heat capacity scales approximately linearly with the temperature, while the lattice temperature can be approximated as constant over the temperature range of interest. To address this, the replacement

$$\frac{R_0 \alpha}{3} (T_\ell - T_0) \rightarrow \frac{R_0}{3B} \left(\gamma C_\ell (T_\ell - T_0) + \frac{2}{3} C_e (T_e) \cdot (T_e - T_0) \right) \quad (6.2)$$

was introduced. Here, γ represents the lattice Grüneisen parameter and B is the bulk modulus. Including this term accounts for contributions from hot electrons and becomes

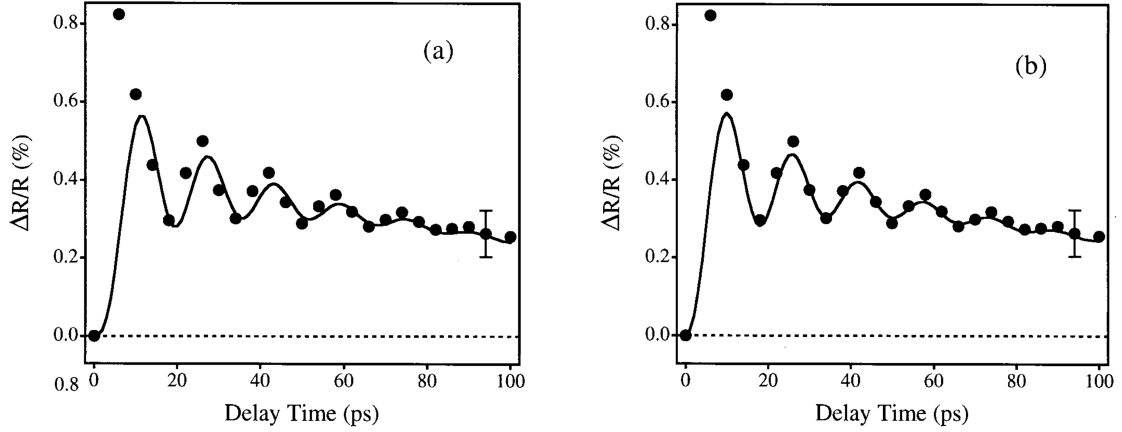


Figure 6.3.: **Comparison of Transient Absorption Data with Classical Theory.** The two plots compare experimental data with the theory developed in Ref. [448]. In (a) Eq. (6.1) is solved while hot electron contributions are neglected, which results in a phase mismatch of experiment and theory. In (b) hot electron contributions are introduced into the theory. This results in matching phases of experiment and theory. Both figures are reprinted from Ref. [448], with the permission of AIP Publishing.

relevant at early times when $T_e \gg T_\ell$. It effectively initiates oscillation earlier, shifting the observed phase towards earlier times and leading to qualitative agreement with the experimental data in Fig. 6.3. As mentioned earlier, similar approaches have also been adopted in Refs. [451, 473, 474].

At this stage, the shortcomings of TA experiments become clearly visible, as the data in the first picoseconds are dominated by the electronic response of the system and do not allow observing the actual oscillation onset. We will discuss this in more detail when we compare our theory with data from a new experimental method that we introduce in Sec. 6.6.4.

Furthermore, we want to point out that the very phenomenological introduction of hot electron contributions through Eq. (6.2) has motivated us to develop a theory on a microscopic level to describe the onset of these radial oscillations.

6.2.2. Two-Temperature Model

As we introduced in Sec. 2.3.3, the thermal dynamics in the electron-lattice system have been studied using the classical two-temperature model for the electron and lattice temperatures, T_e and T_ℓ [206, 207, 220, 448, 488]. Here, we employ the two-temperature model in the form,

$$C_e(T_e) \frac{\partial T_e}{\partial t} = -G(T_e - T_\ell) + \frac{W_0}{\sqrt{\pi}\sigma} \exp\{-t^2/\sigma^2\}, \quad (6.3a)$$

$$C_\ell \frac{\partial T_\ell}{\partial t} = G(T_e - T_\ell) - (T_\ell - T_0)/\tau_s. \quad (6.3b)$$

The thermal energy transfer between electrons and the lattice in this approach is modeled using the coupling constant G , which is associated with quantum mechanical electron-phonon coupling [220]. Experimental access to G has been demonstrated in Refs. [210, 399, 400, 491].

The optical excitation is characterized by the absorbed energy W_0 , which can be determined from optical experiments by measuring absorbance, pump fluence of the incident electric field, and the molar concentration of nanoparticles, which can be experimentally obtained from optical density measurements. A conceptual sketch of the derivation is presented in App. I.6 We assume well-established approximations for the heat capacities within the temperature ranges considered. The electron heat capacity $C_e(T_e)$ is approximated to scale linearly with the electron temperature T_e , denoted as $C_e(T_e) = \zeta T_e$ [168], while the lattice heat capacity C_ℓ is approximated as constant. The timescale τ_s for energy transfer from the lattice to the surroundings is listed in Tab. A.3 and is typically used as a fitting parameter to experimental results.

As discussed in Sec. 6.2.1, the temperature dynamics act as a source term for the nanoparticle oscillation, effectively displacing the equilibrium position of the oscillation. This process occurs when the electron and phonon systems are out of equilibrium, resulting in transient oscillations for rapid shifts in temperature. In Sec. 6.3, we illustrate how these thermal expansion effects are introduced microscopically through an anharmonic phonon-phonon Hamiltonian, Eq. 6.7.

6.2.3. Coherent and Incoherent Phonons

In the 90s, several experiments have revealed that ultrafast optical excitation of semiconductors causes oscillatory features in the temporal signal in reflection and transmission [492–494]. As the frequency of these oscillations matches one of the optical phonon modes, this was a strong indication that this phonon mode is coherently excited. Microscopic approaches towards these effects are derived in Refs. [464, 465] and have been widely and very successfully applied throughout the semiconductor community [453, 466, 469, 495, 496].

Coherent phonons are eigenstates of the annihilation operator, $b_{\mathbf{q}}$, leading to non-vanishing expectation values of the annihilation (creation) operator $b_{\mathbf{q}}^{(\dagger)}$. We define the microscopic coherent phonon operator,

$$s_{\mathbf{q}} \equiv \frac{1}{2} \left(\langle b_{\mathbf{q}} \rangle + \langle b_{-\mathbf{q}}^\dagger \rangle \right), \quad (6.4)$$

which describes the coherent phonon with momentum $\mathbf{q}$ [464]. This is based on the standard approach taken in many textbooks [165, 167, 168] to describe the lattice displacement,

$$\mathbf{u}(\mathbf{r}, t) = \sum_{\mathbf{q}} \sqrt{\frac{\hbar}{2MN\omega_{\mathbf{q}}}} \mathbf{e}_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{r}} \left(\langle b_{\mathbf{q}} \rangle + \langle b_{-\mathbf{q}}^\dagger \rangle \right). \quad (6.5)$$

Here, M is the ion mass in the unit cell, N is the ion number in the crystal and $\mathbf{e}_{\mathbf{q}}$ is the polarization vector of the phonon mode within the material.

For a later distinction of coherent and incoherent phonon dynamics, we define the incoherent phonon distribution in analogy to Refs. [380, 464],

$$\tilde{n}_{\mathbf{q}'}^c(\mathbf{q}) \equiv \langle b_{\mathbf{q}'-\mathbf{q}}^\dagger b_{\mathbf{q}'} \rangle - \langle b_{\mathbf{q}'-\mathbf{q}}^\dagger \rangle \langle b_{\mathbf{q}'} \rangle. \quad (6.6)$$

This can be seen from the cluster expansion that we presented in Sec. 2.1.1 [171].

6.2.4. Thermal Expansion

One of the effects, that we aim to describe microscopically, will be thermal expansion. Accordingly, we will have to describe expansion effects in our microscopic theory. As the formulation of second quantization is a generally harmonic theory which natively does not include these effects, we will have to consider anharmonic corrections to the harmonic phonon potential in order to describe thermal expansion. This is mostly done by inclusion of a thermal expansion term that in its most general formulation can be given by [205]

$$H_{\text{phph}} = \sum_{\substack{\mathbf{q}\mathbf{q}'\mathbf{q}'' \\ \alpha\alpha'\alpha''}} h_{\mathbf{q}\mathbf{q}'\mathbf{q}''}^{\alpha\alpha'\alpha''} (b_{\mathbf{q}\alpha} + b_{-\mathbf{q}\alpha}^\dagger) (b_{\mathbf{q}'\alpha'} + b_{-\mathbf{q}'\alpha'}^\dagger) (b_{\mathbf{q}''\alpha''} + b_{-\mathbf{q}''\alpha''}^\dagger). \quad (6.7)$$

This three phonon process includes three phonon modes $(\alpha, \alpha', \alpha'')$ with momenta $\mathbf{q}, \mathbf{q}', \mathbf{q}''$. The matrix element fulfills the condition $h_{\mathbf{q}\mathbf{q}'\mathbf{q}''}^{\alpha\alpha'\alpha''} = \delta_{\mathbf{q}+\mathbf{q}'+\mathbf{q}'',0} h_{\mathbf{q}\mathbf{q}'\mathbf{q}''}^{\alpha\alpha'\alpha''}$. As the different combinations of annihilation (creation) operators indicate, this Hamiltonian includes a variety of multi-phonon processes, one of the most conceptually prominent being a phonon decay process where one phonon decays into two phonons while conserving momentum and energy. A detailed description of the matrix element can be found in Ref. [205]. For the scope of this thesis, we limit ourselves to only including the longitudinal acoustic (LA) phonon branch, effectively dropping the branch index α in the following.

6.3. Coherent Phonon Dynamics

The full Hamiltonian that we consider for this part of the project combines the Hamiltonian given in Eq. (4.1a) with the phonon-phonon Hamiltonian, so that the full Hamiltonian reads

$$\begin{aligned} H = & \sum_{\mathbf{k}\lambda} \epsilon_{\mathbf{k}} \lambda_{\mathbf{k}}^\dagger \lambda_{\mathbf{k}} + \sum_{\mathbf{q}} \hbar \omega_{\mathbf{q}} b_{\mathbf{q}}^\dagger b_{\mathbf{q}} + \sum_{\mathbf{k}\mathbf{q}\lambda} g_{\mathbf{q}}^\lambda \lambda_{\mathbf{k}+\mathbf{q}}^\dagger \lambda_{\mathbf{k}} (b_{\mathbf{q}} + b_{-\mathbf{q}}^\dagger) + \frac{1}{2} \sum_{\substack{\mathbf{k}\mathbf{k}'\mathbf{q} \\ \lambda\lambda'}} V_{\mathbf{q}} \lambda_{\mathbf{k}+\mathbf{q}}^\dagger \lambda_{\mathbf{k}'-\mathbf{q}}^\dagger \lambda_{\mathbf{k}'} \lambda_{\mathbf{k}} \\ & + \frac{ie}{V} \sum_{\mathbf{k}, \mathbf{K}\lambda} \mathbf{E}_{-\mathbf{K}} \cdot \nabla_{\mathbf{K}} (\lambda_{\mathbf{k}}^\dagger \lambda_{\mathbf{k}+\mathbf{K}}) + \sum_{\mathbf{k}, \mathbf{K}\lambda} \mathbf{d}_{\mathbf{k}+\mathbf{K}, \mathbf{k}}^{\lambda\bar{\lambda}} \cdot \mathbf{E}_{-\mathbf{K}} (\lambda_{\mathbf{k}}^\dagger \bar{\lambda}_{\mathbf{k}+\mathbf{K}}) \\ & + \sum_{\substack{\mathbf{q}\mathbf{q}'\mathbf{q}'' \\ \alpha\alpha'\alpha''}} h_{\mathbf{q}\mathbf{q}'\mathbf{q}''}^{\alpha\alpha'\alpha''} (b_{\mathbf{q}\alpha} + b_{-\mathbf{q}\alpha}^\dagger) (b_{\mathbf{q}'\alpha'} + b_{-\mathbf{q}'\alpha'}^\dagger) (b_{\mathbf{q}''\alpha''} + b_{-\mathbf{q}''\alpha''}^\dagger). \end{aligned} \quad (6.8)$$

As mentioned earlier, the utilization of this Hamiltonian to construct a microscopic approach offers a significant advantage over currently available phenomenological models. In the classical model, illustrated in Fig. 6.4 with gray arrows, cf. Sec. 6.2.1, the interaction is solely mediated by incoherent (thermal) phonons, which are described in terms of the lattice temperature T_ℓ . However, this model does not include a direct interaction between electrons and the lattice oscillation.

In contrast, our Hamiltonian approach encompasses the interaction of all electron and phonon modes, as evidenced by the electron-phonon contribution with coupling strength $g_{\mathbf{k}}^\lambda$. This enables us to incorporate a direct coupling between optically induced electron density gradients and coherent phonon oscillations, depicted by red arrows in Figure 6.4.

We anticipate that this direct interaction term introduces an additional source term to the oscillator equation of the nanoparticle, potentially resulting in a more immediate oscillation onset.

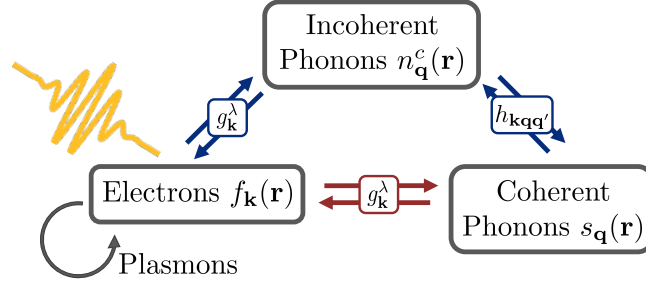


Figure 6.4.: **Direct Coupling Mechanism from Microscopic Theory.** Incident light excites the electrons that self-interact via a collective plasmon response. In all classical theories (blue arrows), the electrons couple to incoherent phonons, i.e., temperature, which transiently drive the coherent oscillations due to the spatial restriction (spherical particles). We study the possibility of a direct interaction of electrons and coherent phonons (red arrows).

We derive an equation of motion for the phonon annihilation (creation) operators $b_{\pm\mathbf{q}}^{(\dagger)}$ by utilizing the Heisenberg equation of motion with the Hamiltonian (Eq. 6.8),

$$(i\hbar\partial_t \mp \hbar\omega_{\pm\mathbf{q}}) b_{\pm\mathbf{q}}^{(\dagger)} = \pm \sum_{\mathbf{k}\lambda} g_{-\mathbf{q}}^{\lambda} \lambda_{\mathbf{k}-\mathbf{q}}^{\dagger} \lambda_{\mathbf{k}} \pm 3 \sum_{\mathbf{q}'} \tilde{h}_{\mathbf{q},\mathbf{q}',\mathbf{q}-\mathbf{q}'} [b_{\mathbf{q}'} + b_{-\mathbf{q}'}^{\dagger}] [b_{\mathbf{q}-\mathbf{q}'} + b_{-\mathbf{q}+\mathbf{q}'}^{\dagger}], \quad (6.9)$$

where the lower sign corresponds to creation and the upper sign to annihilation operators, respectively. In this expression, we have utilized momentum conservation, denoted as $\tilde{h}_{\mathbf{q},\mathbf{q}',\mathbf{q}''} = \hbar\mathbf{q},\mathbf{q}',\mathbf{q}''\delta_{\mathbf{q}+\mathbf{q}'+\mathbf{q}'',0}$. The left-hand side includes the dispersion of the phonons $\omega_{\mathbf{q}}$. The right-hand side contains the sources of the phonon amplitudes. The first term represents a momentum transfer from the electronic system to the phonons. The second term originates from phonon-phonon interaction. In the next step, we apply a time derivative to Eq. (6.9) which results in a second-order differential equation for the coherent phonon amplitude $s_{\mathbf{q}}$, cf. Eq. (6.4),

$$(\partial_t^2 + \omega_{\mathbf{q}}^2) s_{\mathbf{q}} = -\frac{\omega_{\mathbf{q}}}{\hbar} \sum_{\mathbf{k}\lambda} g_{-\mathbf{q}}^{\lambda} \tilde{f}_{\mathbf{k}}^{\lambda}(\mathbf{q}) - \frac{3\omega_{\mathbf{q}}}{\hbar} \sum_{\mathbf{q}'} \tilde{h}_{\mathbf{q},\mathbf{q}',\mathbf{q}-\mathbf{q}'} [2\tilde{n}_{\mathbf{q}'}^c(\mathbf{q}) + \delta_{\mathbf{q},0}] - \frac{3\omega_{\mathbf{q}}}{\hbar} \sum_{\mathbf{q}'} \tilde{h}_{\mathbf{q},\mathbf{q}',\mathbf{q}-\mathbf{q}'} [4s_{\mathbf{q}'}s_{\mathbf{q}-\mathbf{q}'} + \langle b_{\mathbf{q}'}b_{\mathbf{q}-\mathbf{q}'} \rangle^c + \langle b_{-\mathbf{q}'}^{\dagger}b_{-\mathbf{q}+\mathbf{q}'}^{\dagger} \rangle^c]. \quad (6.10)$$

On the right-hand side, we can identify two sources for the coherent phonon amplitude. The first term is the Fourier transform of the Wigner function of the electrons $\tilde{f}_{\mathbf{k}}(\mathbf{q}) = \langle \lambda_{\mathbf{k}-\mathbf{q}}^{\dagger} \lambda_{\mathbf{k}} \rangle$ [376]. The momentum- and real-space-dependent Wigner distribution is accordingly given by $f_{\mathbf{k}}^{\lambda}(\mathbf{r}) = \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} \tilde{f}_{\mathbf{k}}^{\lambda}(\mathbf{q})$. The second term considers driving of the coherent phonon amplitude from the incoherent phonon distribution $\tilde{n}_{\mathbf{q}'}^c(\mathbf{q}) \equiv \langle b_{\mathbf{q}'}^{\dagger}b_{-\mathbf{q}}b_{\mathbf{q}'} \rangle - \langle b_{\mathbf{q}'}^{\dagger}b_{-\mathbf{q}} \rangle \langle b_{\mathbf{q}'} \rangle$ [380, 464].

The final term in the first line represents a Kronecker symbol that arises from the commutation of the phonon creation (annihilation) operators into normal order. This term can be interpreted as a constant force acting on the oscillator, leading to a displacement of its equilibrium position due to phonon-phonon interactions. Moving to the second line, the first term corresponds to a self-interaction term that scales quadratically with the amplitude of the coherent phonon $s_{\mathbf{q}}$.

Since the equations of motion are not closed, we derive an equation of motion for the coherences in the last line of Eq.(6.10). This is accomplished following the approach described in Sec. 2.1.1. By employing a second-order correlation expansion and a Markov approximation, we find that they couple to phonon creation (annihilation) operators $b_{\mathbf{q}}^{(\dagger)}$. Further details are provided in App. I.2.1. The contributions of the correlated quantities resemble a dephasing of the coherent phonon mode, which can be written as

$$\begin{aligned} (\partial_t^2 + 2\gamma_{\mathbf{q}}\partial_t + \omega_{\mathbf{q}}^2)s_{\mathbf{q}} = & -\frac{\omega_{\mathbf{q}}}{\hbar} \sum_{\mathbf{k}\lambda} g_{-\mathbf{q}}^{\lambda} \tilde{f}_{\mathbf{k}}^{\lambda}(\mathbf{q}) \\ & - \frac{3\omega_{\mathbf{q}}}{\hbar} \sum_{\mathbf{q}'} \tilde{h}_{\mathbf{q},\mathbf{q}',\mathbf{q}-\mathbf{q}'} [2\tilde{n}_{\mathbf{q}'}^c(\mathbf{q}) + \delta_{\mathbf{q},0}]. \end{aligned} \quad (6.11)$$

This equation is formally equivalent to a classical damped oscillator equation for amplitudes $s_{\mathbf{q}}$. The left-hand side describes the oscillation of the coherent phonon amplitude with damping rate $\gamma_{\mathbf{q}}$ resulting from phonon-phonon interaction, which we provide in App. I.2.1, and the oscillator frequency $\omega_{\mathbf{q}}$. In Eq. (6.11) and in the following, non-linear terms in the coherent phonon amplitude $s_{\mathbf{q}}$ are suppressed since weak excitation is assumed.

From Eq. (6.11) for the coherent phonon amplitude, we obtain an equation of motion for the lattice displacement using its definition in Eq. (6.5),

$$\begin{aligned} [\partial_t^2 + 2\gamma_{\text{ph}}\partial_t - c_{LA}^2\nabla_{\mathbf{r}}^2]\mathbf{u}(\mathbf{r},t) = \\ \frac{1}{2M}\nabla_{\mathbf{r}} \sum_{\mathbf{k}\lambda} V_0^{\lambda} f_{\mathbf{k}}^{\lambda}(\mathbf{r},t) + \frac{6h}{\sqrt{2MN}\hbar} \frac{\mathbf{r}}{\ell} \sum_{\mathbf{q}} \frac{1}{\omega_{\mathbf{q}}} n_{\mathbf{q}}^c(\mathbf{r},t). \end{aligned} \quad (6.12)$$

At this stage, we assumed that the microscopic scattering term $\gamma_{\mathbf{q}}$ can be approximated by a macroscopic, overall momentum-independent term γ_{ph} . As the entire volume of the sphere is large in comparison to the size of a unit cell, we regard the lattice vectors $\mathbf{R}_n$ as continuous and replace them by the continuous space variable $\mathbf{r}$, i.e., $\mathbf{R}_n \rightarrow \mathbf{r}$. Furthermore, we have assumed that the major momentum dependence of the matrix element $\tilde{h}_{\mathbf{q}\mathbf{q}'\mathbf{q}''}$ is contained in the dispersion $\omega_{\mathbf{q}}$, such that it can be approximated as $\tilde{h}_{\mathbf{q}\mathbf{q}'\mathbf{q}''} \approx h/\sqrt{\omega_{\mathbf{q}}\omega_{\mathbf{q}'}\omega_{\mathbf{q}''}}$ [205] with the momentum independent quantity h . In addition, we made use of the symmetry $\omega_{\mathbf{q}} = \omega_{-\mathbf{q}}$ of the dispersion relation. The left-hand side accounts for the wave propagation of the phonon with the velocity of sound c_{LA} and the phonon-phonon interaction induced damping term γ_{ph} [165]. The right-hand side accounts for the sources of the coherent oscillations, where we identify two different contributions. The first term accounts for the displacement of the lattice vectors via spatial gradients of the electron density, as defined in Eq. (4.35). The second term originates from the anharmonic phonon-phonon interaction, where we incorporated the constant term in Eq. (6.11) as an offset of the oscillator position. Here, the parameter ℓ is the binding length of the material. This parameter had to be included in the description

to account for the nature of the thermal expansion in Eq. (6.12) as an extensive quantity compared to the harmonic contribution of the electron-phonon interaction in the first source term in Eq. (6.12).

In the oscillation Eq. (6.12), we find that the thermal expansion contribution can be expressed in terms of the incoherent phonon distribution $n_{\mathbf{q}}^c(\mathbf{r})$,

$$\frac{6h}{\sqrt{2MN\hbar}} \frac{\mathbf{r}}{\ell} \sum_{\mathbf{q}} \frac{1}{\omega_{\mathbf{q}}} n_{\mathbf{q}}^c(\mathbf{r}) \approx \frac{18h\sqrt{N}}{\sqrt{2M\hbar^3}} \frac{\mathbf{r}}{\omega_D^2 \ell} k_B T_\ell. \quad (6.13)$$

Here, we assume the incoherent phonon distribution $n_{\mathbf{q}}^c(\mathbf{r})$ to be spatially homogeneous and to follow a Bose-Einstein distribution. The sum can be performed in Debye approximation by replacing the sum over the first Brillouin zone by an integral over a sphere with the radius, q_D , which is defined such that the number of states is equivalent to the number of atoms. Using the linear dispersion of the Debye approximation, the Debye momentum q_D can be replaced by the Debye frequency ω_D [388]. We argue that the temperature of the nanoparticle can be approximated as spatially homogeneous, as the particle is small compared to the optical wavelength and the momentum-relaxation process is fast compared to the pulse width in the hydrodynamic limit. As only deviations from the equilibrium temperature drive the nanoparticle oscillation, we use the definition from the previous and absorb the equilibrium position into the equilibrium position of the oscillator at equilibrium temperature T_0 . With this, the source term of the oscillation scales with deviations from equilibrium $\Delta T_\ell(t) = T_\ell(t) - T_0$.

Accordingly, we find the oscillator equation for the absolute lattice displacement, which is given by

$$[\partial_t^2 + 2\gamma_{\text{ph}}\partial_t - c_{LA}^2 \nabla_{\mathbf{r}}^2] \mathbf{u}(\mathbf{r}, t) = \sum_{\lambda} \beta^{\lambda} \nabla_{\mathbf{r}} \rho^{\lambda}(\mathbf{r}, t) + \boldsymbol{\xi} \Delta T_\ell(t), \quad (6.14)$$

with the definitions

$$\beta^{\lambda} \equiv \frac{V_0^{\lambda} \Omega}{2Me}, \quad \boldsymbol{\xi} \equiv \frac{18h\sqrt{N}}{\sqrt{2M\hbar^3}} \frac{\mathbf{r}}{\omega_D^2 \ell} k_B. \quad (6.15)$$

Here, we used the momentum expansion for the Wigner occupations of the type in Eq. (4.35) and Refs. [254, 403, 404] to identify the electron density which for the band-specific case reads

$$\rho^{\lambda}(\mathbf{r}, t) \equiv \frac{e}{\Omega} \sum_{\mathbf{k}} f_{\mathbf{k}}^{\lambda}(\mathbf{r}, t), \quad (6.16)$$

with the unit cell volume Ω . We find two driving terms with prefactors β^{λ} and $\boldsymbol{\xi}$ that characterize the macroscopic model and depend on the electron-phonon and phonon-phonon interaction, respectively. The first represents the newly found displacement source resulting from an optically induced gradient in the spatial electron distribution, $\rho^{\lambda}(\mathbf{r}, t)$ and its behavior will be modeled in Sec. 6.4 using the spatio-temporal Wigner

function approach that we developed in Sec. 4. The second term occurs via the temperature difference as source and is found in agreement with previous thermal models, cf. Refs. [448, 451, 473, 474, 488]. The electronic driving term β scales linearly with the screened Coulomb potential, V_0^λ , and the thermal driving factor ξ is proportional to the anharmonic phonon-phonon potential h , cf. Eq. 6.15. For the scope of this thesis, the temperature changes are modeled using a two temperature model in agreement with previous literature [448, 451, 473, 474, 488].

Thomas-Fermi Theory for Strong Screening

In deriving the oscillator equation in Sec. 6.3, we assumed that the electron-phonon potential is strongly screened, which is a good approximation for most metals [165, 388]. This allows to use an effective electron-phonon coupling that is independent of the phonon momentum $\mathbf{q}$ [168],

$$V_0^\lambda = \frac{Z^{\text{eff},\lambda} e^2}{\epsilon_0 \Omega k_s^2}, \quad (6.17)$$

with an effective inverse screening length k_s and an effective nuclear charge $Z^{\text{eff},\lambda}$. For the intraband theory, the value for the 6s band [497] is used for $Z^{\text{eff},\lambda}$, since it is the only band that is only partially filled in gold. For silver, one would use the value for the 5s band instead. In the subsequent calculation, this inverse screening length is approximated by the Thomas-Fermi wave vector k_{TF} , which is given by

$$k_{\text{TF}}^2 = \frac{e^2 m}{\epsilon_0 \hbar^2 \pi^2} (3\pi^2 n)^{1/3}, \quad (6.18)$$

with the electron density n . Combining this with the definition of the potential, one can simplify the driving term β in Eq. (6.15) of the breathing oscillation due to electron gradients to

$$\beta^\lambda = \frac{Z^{\text{eff},\lambda} \hbar^2 \pi^2}{2mMe} (3\pi^2 n)^{-1/3}, \quad (6.19)$$

which depends entirely on the intrinsic quantities of electron density n , effective electron mass m , and unit cell mass M for the case of strong screening.

6.4. Mesoscopic Electron Dynamics in the Hydrodynamic Limit

As the electron Wigner function $\tilde{f}_{\mathbf{k}}^\lambda(\mathbf{q})$ acts as a driving term in the coherent phonon oscillation Eq. (6.11) through its occurrence in the definition of the electron density $\rho(\mathbf{r}, t)$, this section will be devoted to studying the electron dynamics within our system under the action of the Hamiltonian defined in Eq. (6.8). As discussed in detail in Sec. 2.3.6, metals exhibit strong signatures of both interband and intraband processes, depending on the spectral range of interest. Here, we introduce a theory that distinguishes between the purely intraband plasmon response and the predominantly interband excitation process, shedding light on their distinct pathways for exciting the coherent nanoparticle oscillation. By examining these qualitatively different excitation pathways, we can compare them with experimental data to determine the dominant excitation mechanism.

6.4.1. Intraband Case

As a purely intraband effect, the plasmonic response can be described using the Wigner approach in a single band, cf. Sec. 4.5, we consider in agreement with Sec. 4 the electronic Wigner function $f_{\mathbf{k}}(\mathbf{r}, t)$ for the full Hamiltonian in Eq. (6.8) within the gradient expansion [240, 376] and obtain similar to Ref. [401],

$$\begin{aligned} & \partial_t f_{\mathbf{k}}(\mathbf{r}, t) + \nabla_{\mathbf{r}} f_{\mathbf{k}}(\mathbf{r}, t) \cdot \left[\mathbf{v}_{\mathbf{k}} + \frac{e}{\hbar} \nabla_{\mathbf{k}} \Phi_{\mathbf{k}}^F(\mathbf{r}) \right] \\ &= \nabla_{\mathbf{k}} f_{\mathbf{k}}(\mathbf{r}, t) \cdot \left[\frac{e}{\hbar} (\mathbf{E}(\mathbf{r}, t) - \partial_{\mathbf{r}} \Phi^H(\mathbf{r}) + \partial_{\mathbf{r}} \Phi_{\mathbf{k}}^F(\mathbf{r})) + \frac{i}{\hbar} \sum_{\mathbf{q}} g_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{r}} \mathbf{q} s_{\mathbf{q}}(t) \right] \\ &+ \sum_{\mathbf{q}} [\Gamma_{\mathbf{k}+\mathbf{q}, \mathbf{k}}^{\text{in}}(\mathbf{r}, t)(1 - f_{\mathbf{k}}(\mathbf{r}, t)) - \Gamma_{\mathbf{k}, \mathbf{k}+\mathbf{q}}^{\text{out}}(\mathbf{r}, t)f_{\mathbf{k}}(\mathbf{r}, t)] \\ &+ \sum_{\mathbf{q}} [\mathcal{W}_{\mathbf{k}+\mathbf{q}, \mathbf{k}}^{\text{in}}(\mathbf{r}, t)(1 - f_{\mathbf{k}}(\mathbf{r}, t)) - \mathcal{W}_{\mathbf{k}, \mathbf{k}+\mathbf{q}}^{\text{out}}(\mathbf{r}, t)f_{\mathbf{k}}(\mathbf{r}, t)]. \end{aligned} \quad (6.20)$$

The left-hand side considers the drift of the electronic Wigner function with group velocity $\mathbf{v}_{\mathbf{k}} = \nabla_{\mathbf{k}} \epsilon_{\mathbf{k}}$ under the effect of the Fock potential $\phi_{\mathbf{k}}^F(\mathbf{r})$ that is given in Eq. (4.18b). The first term on the right-hand side accounts for the acceleration of electrons in the external optical driving field, screened by background contributions, $\mathbf{E}(\mathbf{r}, t) = \frac{3\epsilon_{\text{out}}}{\epsilon_{\infty} + 2\epsilon_{\text{out}}} \mathbf{E}^{\text{ext}}$ under the additional Hartree $\Phi^H(\mathbf{r})$ and Fock potentials $\Phi_{\mathbf{k}}^F(\mathbf{r})$, defined in Eqs. (4.18a) and (4.18b), respectively. They result from the inclusion of the Coulomb contribution in the Hamiltonian and are derived using the mean-field approximation and the gradient approximation, as outlined in Sec. 4.6.1. The third term on the right-hand side describes the acceleration of electrons due to interaction with coherent phonons $s_{\mathbf{q}}(\mathbf{r}, t)$. The Fock contributions are included here for completeness, but will be neglected in the following, since they represent quantum corrections to a semiclassical hydrodynamic model. These corrections are small compared to the total field $\tilde{\mathbf{E}}$, which is a combination of the external field $\mathbf{E}$ and the Hartree corrections of the internal field $-\partial_{\mathbf{r}} \Phi^H$. The total field is given by $\tilde{\mathbf{E}} \equiv \frac{3\epsilon_{\text{out}}}{\epsilon_{\infty} + 2\epsilon_{\text{out}}} \mathbf{E}^{\text{ext}} - \partial_{\mathbf{r}} \Phi^H$. The last two lines account for electron-phonon and electron-electron scattering and are derived using a second-order Born-Markov approximation. Details can be found in Sec. 4.3.4 and 4.3.3.

To derive an equation of motion for the electron density, we sum Eq. (6.20) over momenta $\mathbf{k}$ in the spirit of the hydrodynamic approach in Sec. 4.5. As scattering terms conserve the local electronic density in the gradient approximation, they vanish under the momentum sum. This results in a continuity equation for the electron density $\rho(\mathbf{r}, t)$ and the current density $\mathbf{j}(\mathbf{r}, t)$,

$$\partial_t \rho(\mathbf{r}, t) + \nabla \cdot \mathbf{j}(\mathbf{r}, t) = 0. \quad (6.21)$$

The appearing current density $\mathbf{j}(\mathbf{r}, t)$ is defined in Eq. (4.35b). To obtain a closed set of equations, we derive an equation of motion for the current density from Eq. (6.20) by multiplying the microscopic dynamical equation (6.20) with the velocity and summing over all momenta. We find a generalized Euler equation that also includes coherent phonon oscillations as source terms for the electron current density in the metal nanoparticle,

$$\begin{aligned} \partial_t \mathbf{j}(\mathbf{r}, t) &= -\gamma_v(T, \rho) \mathbf{j}(\mathbf{r}, t) - \nabla \cdot \mathbb{P}(\mathbf{r}, t) \\ &- \rho(\mathbf{r}, t) \left(\frac{e}{m} \tilde{\mathbf{E}}(\mathbf{r}, t) - \frac{V_0 N}{m} \nabla \otimes \nabla \cdot \mathbf{u}(\mathbf{r}, t) \right). \end{aligned} \quad (6.22)$$

The first term accounts for the decay of the macroscopic current density. Here, we have introduced the decay constant $\gamma_v(T, \rho)$ which has to be determined from the electron-phonon scattering contribution to Eq. (6.20) as the effective relaxation time of the current density [388]. It depends on the temperature as well as on the electron density itself. For weak excitation as discussed here, only the temperature dependence is relevant. The second term is the divergence of the second-order momentum in the factorization procedure of the Wigner function, which is the Cauchy stress tensor $\mathbb{P} \equiv \frac{e}{\Omega} \sum_{\mathbf{q}} \mathbf{v}_{\mathbf{q}} \otimes \mathbf{v}_{\mathbf{q}} f_{\mathbf{q}}(\mathbf{r}, t)$ as defined in Sec. 4.5.2. The second line accounts for the acceleration of the electrons in the total electric field $\tilde{\mathbf{E}}$ or via the lattice displacement field $\mathbf{u}$, respectively.

In the next step, we decompose the velocity $\mathbf{v}_{\mathbf{q}} = \mathbf{v} + \delta\mathbf{v}_{\mathbf{q}}$ into a momentum-independent mean-field contribution and a correction in agreement with Sec. 4.5.2 which yields two contributions in terms of the mean-field velocity $\mathbf{v}$ and the pressure contribution $\hat{\mathbb{P}} \equiv \frac{e}{\Omega} \sum_{\mathbf{q}} \delta\mathbf{v}_{\mathbf{q}} \otimes \delta\mathbf{v}_{\mathbf{q}} f_{\mathbf{q}}(\mathbf{r}, t)$. This way, the velocity is promoted to a velocity field, $\mathbf{v}(\mathbf{r}, t)$ which allows factorizing the macroscopic current density $\mathbf{j}(\mathbf{r}, t) = \rho(\mathbf{r}, t) \mathbf{v}(\mathbf{r}, t)$ into electron density $\rho(\mathbf{r}, t)$ and velocity field $\mathbf{v}(\mathbf{r}, t)$ of the electrons. Applying this decomposition to the continuity and Euler equations and performing some algebraic transformations, we obtain the final set of continuity equation,

$$\partial_t \rho(\mathbf{r}, t) + \nabla \cdot (\rho(\mathbf{r}, t) \mathbf{v}(\mathbf{r}, t)) = 0, \quad (6.23)$$

and Euler equations,

$$\begin{aligned} \left[\partial_t + \mathbf{v}(\mathbf{r}, t) \cdot \nabla \right] \mathbf{v}(\mathbf{r}, t) = & -\gamma_v(T, \rho) \mathbf{v}(\mathbf{r}, t) - \frac{\nabla \cdot \hat{\mathbb{P}}(\mathbf{r}, t)}{\rho(\mathbf{r}, t)} \\ & - \frac{e}{m} \tilde{\mathbf{E}}(\mathbf{r}, t) + \frac{V_0 N}{m} \nabla \otimes \nabla \cdot \mathbf{u}(\mathbf{r}, t). \end{aligned} \quad (6.24)$$

The left-hand side in Eq. (6.24) accounts for the substantial derivative of the velocity field. The first term on the right-hand side describes the decay of the velocity due to interaction with the phonons. The second term accounts for the source of the velocity in the presence of pressure. The pressure tensor will be expressed in terms of the scalar pressure function $p(\mathbf{r}, t)$ by $\hat{\mathbb{P}}(\mathbf{r}, t) = \frac{e}{m} p(\mathbf{r}, t) \mathbb{1}$ [498] in the following. The last line in Eq. (6.24) considers the acceleration of the electrons caused by the self-consistent near-field electric field $\tilde{\mathbf{E}}(\mathbf{r}, t)$ and the lattice displacement $\mathbf{u}(\mathbf{r}, t)$. In the remaining calculation, this latter term will be neglected, since we assume a dominant acceleration of the electrons by the electric field and the perturbation by $\mathbf{u}(\mathbf{r}, t)$ to contribute only in higher orders of the electric field $\tilde{\mathbf{E}}(\mathbf{r}, t)$. This way, the set of continuity and Euler equation, Eqs. 6.23 and 6.24, together with the oscillator equation, Eq. (6.14) forms a system of differential equations that we aim to solve self-consistently.

To approach Eq. (6.24) analytically, it will be coarse-grained in time: As the optical excitation leads to a non-equilibrium carrier distribution whose energy is thermalized by electron-electron scattering between electrons on very short time scales compared to the electron-phonon interaction [499]. On these short timescales, i.e., already during and shortly after the pulse, the density gradient $\nabla_{\mathbf{k}} f_{\mathbf{k}}$ builds up. The fast thermalization process allows us to find a local equilibrium description for the electrons on time scales of the electron-phonon coupling, which means that we can define a local equation of state with time-varying temperature $T(t)$ determined by the electron-phonon interaction. Therefore, similar as in Sec. 4.5.2, we assume an expression for the electron pressure in

terms of the equation of state for fermions: The pressure for a free Fermi gas can be given as [246, 251, 259]

$$p(\mathbf{r}, t) = \frac{\kappa}{e^{5/3}} \rho^{5/3}(\mathbf{r}, t), \quad (6.25)$$

where the proportionality constant $\kappa = \frac{\hbar^2}{5m} (3\pi^2)^{2/3}$ is adapted from the typical Fermi gas constant [246] to our calculations for the charge density.

In order to solve the nonlinear set of equations, Eqs. (6.23) and (6.24), and to use the results to determine the coherent phonon field $\mathbf{u}(\mathbf{r}, t)$ in Eq. (6.14), we expand the respective quantities in orders of the electric field [259]

$$\rho(\mathbf{r}, t) = \rho_0 + \rho_1(\mathbf{r}, t) + \rho_2(\mathbf{r}, t) + \mathcal{O}(\mathbf{E}^3), \quad (6.26a)$$

$$\mathbf{v}(\mathbf{r}, t) = \mathbf{v}_0 + \mathbf{v}_1(\mathbf{r}, t) + \mathbf{v}_2(\mathbf{r}, t) + \mathcal{O}(\mathbf{E}^3). \quad (6.26b)$$

For better readability, the spatial and temporal dependencies of the observables are suppressed from now on. The density dependence of the pressure term in Eq. (6.25) will be approximated in the same way, which results in [259]

$$\rho^{5/3} \approx \rho_0^{5/3} + \frac{5}{3} \rho_0^{2/3} \rho_1 + \frac{5}{9} \rho_0^{-1/3} \rho_1^2 + \frac{5}{3} \rho_0^{2/3} \rho_2. \quad (6.27)$$

Sorting in orders of the field, we find in zeroth order in the electric field, the standard equations of constant equilibrium density ρ_0 and vanishing equilibrium electron velocity $\mathbf{v}_0$,

$$\partial_t \rho_0 = 0, \quad (6.28a)$$

$$\mathbf{v}_0 = 0, \quad (6.28b)$$

In first order, we find the first-order equation of motion for the electron density,

$$\partial_t \rho_1 + \rho_0 \nabla \cdot \mathbf{v}_1 = 0, \quad (6.29)$$

which is analogous to the continuity equation, Eq. 6.23. The equation of motion for the first-order velocity is given as

$$\rho_0 (\partial_t + \gamma_v) \mathbf{v}_1 = -\frac{5\kappa}{3me^{2/3}} \rho_0^{2/3} \nabla \rho_1 - \frac{e}{m} \rho_0 \tilde{\mathbf{E}}. \quad (6.30)$$

Since the velocity scales linearly with the total electric field, it oscillates with the optical frequency and is typically too fast to be detected directly. Hence, a description in terms of first-order quantities is not sufficient and higher-order contributions have to be considered. Before we derive the second order contributions, i.e., the electron density oscillations, which determine the experimental signals, we introduce the geometrical constraints that renormalize the electric field inside the metal nanoparticle. This can be determined self-consistently and results in a resonance shift of the nanoparticle onto the plasmon resonance $\omega_{\text{LSP}} = \omega_p / \sqrt{\varepsilon_{\infty} + 2\varepsilon_{\text{out}}}$ [170] with the plasma frequency $\omega_p = (ne^2/m\varepsilon_0)^{1/2}$, the permittivity of the surrounding medium ε_{out} and the dielectric constant that accounts for the screening by bound charges ε_{out} inside the metal nanoparticle as we have discussed in more detail in Sec. 4. We find from Eq. (6.30),

$$\rho_0 (\partial_t + \gamma_v + i\omega_{\text{LSP}}) \mathbf{v}_1 = -\frac{5\kappa}{3me^{2/3}} \rho_0^{2/3} \nabla \rho_1 - 3\varepsilon_0 \varepsilon_{\text{out}} \omega_{\text{LSP}}^2 \mathbf{E}_0, \quad (6.31)$$

where, in addition to the plasmon frequency ω_{LSP} , the renormalized total electric field $\tilde{\mathbf{E}}$ was expressed in terms of the screened externally applied field: $\tilde{\mathbf{E}} \rightarrow 3\varepsilon_{\text{out}}/(\varepsilon_{\infty} + 2\varepsilon_{\text{out}}) \mathbf{E}_0$ which is equivalent to the equation we derived in Sec. 2.4.4. Accordingly, we apply the notation $\tilde{\mathbf{E}} \equiv 3\varepsilon_{\text{out}}/(\varepsilon_{\infty} + 2\varepsilon_{\text{out}}) \mathbf{E}_0$, when deriving second order quantities in the following. The time evolution of the second-order electron density is given by

$$\partial_t \rho_2 + \rho_0 \nabla \cdot \mathbf{v}_2 = -\nabla \cdot (\rho_1 \mathbf{v}_1), \quad (6.32)$$

and the equation of motion for the second-order velocity is

$$\begin{aligned} \rho_0 \partial_t \mathbf{v}_2 + \gamma_v \rho_0 \mathbf{v}_2 + \frac{5\kappa}{3me^{2/3}} \rho_0^{2/3} \nabla \rho_2 \\ = -\rho_1 \partial_t \mathbf{v}_1 - \rho_0 (\mathbf{v}_1 \cdot \nabla) \mathbf{v}_1 - \frac{5\kappa}{9me^{2/3}} \rho_0^{-1/3} \nabla \rho_1^2 + \frac{e}{m} \rho_1 \tilde{\mathbf{E}} - \gamma_v \rho_1 \mathbf{v}_1. \end{aligned} \quad (6.33)$$

In the following, we assume the carrier frequency ω_{opt} of the total electric field $\tilde{\mathbf{E}}$ to be in resonance with the plasmon frequency ω_{LSP} . To extract the signals relevant for the optical detection that are proportional to the cycle-averaged intensity, we separate the slowly varying components $\tilde{\mathbf{E}}^{\pm}(\mathbf{r}, t)$ from the fast oscillation by

$$\tilde{\mathbf{E}}(\mathbf{r}, t) = \frac{1}{2} [\tilde{\mathbf{E}}^+(\mathbf{r}, t) e^{i\omega_{\text{opt}} t} + \tilde{\mathbf{E}}^-(\mathbf{r}, t) e^{-i\omega_{\text{opt}} t}], \quad (6.34a)$$

$$\rho_1(\mathbf{r}, t) = \frac{1}{2} [\tilde{\rho}_1^+(\mathbf{r}, t) e^{i\omega_{\text{opt}} t} + \tilde{\rho}_1^-(\mathbf{r}, t) e^{-i\omega_{\text{opt}} t}], \quad (6.34b)$$

$$\mathbf{v}_1(\mathbf{r}, t) = \frac{1}{2} [\tilde{\mathbf{v}}_1^+(\mathbf{r}, t) e^{i\omega_{\text{opt}} t} + \tilde{\mathbf{v}}_1^-(\mathbf{r}, t) e^{-i\omega_{\text{opt}} t}]. \quad (6.34c)$$

This allows to move to a rotating frame and separate the slowly varying quantities in Eq. (6.33). We obtain

$$\begin{aligned} \left[\partial_t - \frac{5}{3} \frac{\kappa}{\gamma_v} \frac{\rho_0^{2/3}}{me^{2/3}} \nabla^2 \right] \tilde{\rho}_2 \\ = \frac{1}{2} \nabla \cdot \left\{ \frac{\rho_0}{\gamma_v} [(\tilde{\mathbf{v}}_1^+ \cdot \nabla) \tilde{\mathbf{v}}_1^- + (\tilde{\mathbf{v}}_1^- \cdot \nabla) \tilde{\mathbf{v}}_1^+] - \frac{e}{m\gamma_v} (\tilde{\rho}_1^+ \tilde{\mathbf{E}}^- + \tilde{\rho}_1^- \tilde{\mathbf{E}}^+) \right. \\ \left. + \frac{1}{\gamma_v} \tilde{\rho}_1^+ (\partial_t - i\omega_{\text{opt}}) \tilde{\mathbf{v}}_1^- + \frac{1}{\gamma_v} \tilde{\rho}_1^- (\partial_t + i\omega_{\text{opt}}) \tilde{\mathbf{v}}_1^+ \right. \\ \left. + \frac{10}{9me^{2/3}} \frac{\kappa}{\gamma_v} \rho_0^{-1/3} (\tilde{\rho}_1^+ \nabla \tilde{\rho}_1^- + \tilde{\rho}_1^- \nabla \tilde{\rho}_1^+) \right\}. \end{aligned} \quad (6.35)$$

We focus on the dominant driving contribution by making use of the relation $\gamma_v \ll \omega_{\text{LSP}}$. With the additional assumption that left- and right-handed quantities are equivalent in magnitude, i.e., $\tilde{\mathbf{E}}^+ = \tilde{\mathbf{E}}^- = \hat{\mathbf{E}}$, we are left with

$$[\partial_t - D \nabla^2] \tilde{\rho}_2 = K \nabla \cdot [(\hat{\mathbf{E}} \cdot \nabla) \hat{\mathbf{E}}]. \quad (6.36)$$

Hence, we have identified a diffusion equation for the second-order electron density distribution that is driven by spatial gradients of the electric field intensity similar to the ponderomotive force. The prefactors are defined as

$$D = \frac{5\kappa\rho_0^{2/3}}{3\gamma_v}, \quad K = \frac{e^2\rho_0}{\gamma_v^3 m^2}. \quad (6.37)$$

Here, we interpret D as the diffusion constant and K as the coupling constant of the electric field to the second-order electron density.

6.4.2. Interband Case

In comparison to the previous section, we will be concerned with the excitation pathway via interband transitions in this section. In gold, the interband transitions occur between the initially occupied $5d$ and the initially only partially occupied $6s$ band [500] that are below (above) the Fermi level, respectively. For simplicity of the notation, we will label them as v for valence and c for conduction band. The equation of motion for the phonon mode amplitude $s_{\mathbf{q}}(t)$ from Eq. (6.11) reads

$$\begin{aligned} (\partial_t^2 + 2\gamma_{\mathbf{q}}\partial_t + \omega_{\mathbf{q}}^2) s_{\mathbf{q}}(t) = & -\frac{\omega_{\mathbf{q}}}{\hbar} \sum_{\mathbf{k}} (g_{-\mathbf{q}}^c - g_{-\mathbf{q}}^v) \tilde{f}_{\mathbf{k}}^c(\mathbf{q}, t) \\ & - \frac{3\omega_{\mathbf{q}}}{\hbar} \sum_{\mathbf{q}'} \tilde{h}_{\mathbf{q}, \mathbf{q}', \mathbf{q}-\mathbf{q}'} [2\tilde{n}_{\mathbf{q}'}^c(\mathbf{q}) + \delta_{\mathbf{q}, 0}]. \end{aligned} \quad (6.38)$$

This equation describes the dynamics of a classical damped oscillator equation with mode index $\mathbf{q}$. The left-hand side is equivalent to Eq. (6.11) and describes the oscillation of the coherent phonon amplitude $s_{\mathbf{q}}$ with a damping rate $\gamma_{\mathbf{q}}$ [448] resulting from phonon-phonon interactions [405], that we again treat as a constant. On the right-hand side, we identify similar sources to the intraband case: the first term is determined by the dynamics of the Fourier transform of the Wigner function for the band occupations, $\tilde{f}_{\mathbf{k}}^{\lambda}(\mathbf{q}) = \langle \lambda_{\mathbf{k}-\mathbf{q}}^{\dagger} \lambda_{\mathbf{k}} \rangle$. For the two-band model, the temporal evolutions of $\tilde{f}_{\mathbf{k}}^c(\mathbf{q}, t)$ and $\tilde{f}_{\mathbf{k}}^v(\mathbf{q}, t)$ are complementary, so the source term of the oscillation that we found in Eq. (6.11) can be expressed by one of them. The prefactor scales with the difference $(g_{-\mathbf{q}}^c - g_{-\mathbf{q}}^v)$ of the electron-phonon coupling element of conduction and valence band. The second source of the coherent phonon amplitude results from thermal effects of the change of the incoherent phonon mode occupation caused by heat transfer from the electronic system. This will be treated in the same way as for the intraband case.

As the Wigner occupations $f_{\mathbf{k}}^{\lambda}(\mathbf{r})$ act as sources of the coherent phonon amplitude Eq. (6.38), we also derive an equation of motion for a two band model within the gradient expansion [376] and obtain

$$\partial_t f_{\mathbf{k}}^v(\mathbf{r}) = -\mathbf{v}_{\mathbf{k}}^v \cdot \nabla_{\mathbf{r}} f_{\mathbf{k}}^v(\mathbf{r}) - 2 \operatorname{Im} \left\{ \frac{\mathbf{d}^{vc} \cdot \mathbf{E}(\mathbf{r}, t)}{\hbar} p_{\mathbf{k}}(\mathbf{r}) \right\} - \frac{1}{\tau} (f_{\mathbf{k}}^v(\mathbf{r}) - f_{\mathbf{k}}^{v,0}(\mathbf{r})), \quad (6.39a)$$

$$\partial_t f_{\mathbf{k}}^c(\mathbf{r}) = -\mathbf{v}_{\mathbf{k}}^c \cdot \nabla_{\mathbf{r}} f_{\mathbf{k}}^c(\mathbf{r}) + 2 \operatorname{Im} \left\{ \frac{\mathbf{d}^{vc} \cdot \mathbf{E}(\mathbf{r}, t)}{\hbar} p_{\mathbf{k}}(\mathbf{r}) \right\} - \frac{1}{\tau} (f_{\mathbf{k}}^c(\mathbf{r}) - f_{\mathbf{k}}^{c,0}(\mathbf{r})), \quad (6.39b)$$

$$\partial_t p_{\mathbf{k}}(\mathbf{r}) = \left[-\frac{i}{\hbar} (\epsilon_{\mathbf{k}}^c - \epsilon_{\mathbf{k}}^v) - \gamma - \mathbf{v}_{\mathbf{k}}^{vc} \cdot \nabla_{\mathbf{r}} \right] p_{\mathbf{k}}(\mathbf{r}) + i \frac{\mathbf{d}^{cv} \cdot \mathbf{E}(\mathbf{r}, t)}{\hbar} [f_{\mathbf{k}}^v(\mathbf{r}) - f_{\mathbf{k}}^c(\mathbf{r})], \quad (6.39c)$$

where we remind the reader of the definition of the interband polarization $p_{\mathbf{k}}(\mathbf{r}, t) = \sum_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{r}} \langle v_{\mathbf{k}-\mathbf{q}}^{\dagger} c_{\mathbf{k}} \rangle(t)$ from Eq. (4.59a). In Eqs. (6.39a) and (6.39b), we identify the

group velocity $\mathbf{v}_{\mathbf{k}}^\lambda = \nabla_{\mathbf{k}} \epsilon_{\mathbf{k}}^\lambda / \hbar$ for the band $\lambda \in \{v, c\}$ that considers the drift of the electronic Wigner occupation, which we combined into the average group velocity $\mathbf{v}_{\mathbf{k}}^{vc} = (\mathbf{v}_{\mathbf{k}}^v + \mathbf{v}_{\mathbf{k}}^c)/2$. The term on the right-hand side in Eqs. (6.39a) and (6.39b) accounts for the optical source via the full electric field $\mathbf{E}(\mathbf{r}, t)$ that includes the external field as well as polarization contributions. In Eq. (6.39c), the interband polarization oscillates with the band gap $(\epsilon_{\mathbf{k}}^c - \epsilon_{\mathbf{k}}^v)$ and is also driven by the external optical driving field $\mathbf{E}(\mathbf{r}, t)$. γ is the electron-electron scattering induced damping term of the order of few femtoseconds [277] for the interband transition and was added phenomenologically. The decay of the excited electron density ρ_2^c is included by an overall relaxation rate τ that, we assume, can be approximated via the electron-phonon coupling time: $\tau \approx \tau_{el-ph} \approx 3$ ps [210, 235, 399, 400, 491].

In the following we proceed similarly to the intraband case and expand the individual Wigner functions in orders of the electric field $f_{\mathbf{k}}^\lambda(\mathbf{r}, t) = f_{\mathbf{k}}^{0,\lambda}(\mathbf{r}) + f_{\mathbf{k}}^{1,\lambda}(\mathbf{r}, t) + f_{\mathbf{k}}^{2,\lambda}(\mathbf{r}, t) + \mathcal{O}(\mathbf{E}^3)$ and $p_{\mathbf{k}}(\mathbf{r}, t) = p_{\mathbf{k}}^1(\mathbf{r}, t) + p_{\mathbf{k}}^2(\mathbf{r}, t) + \mathcal{O}(\mathbf{E}^3)$, cf. Eqs. (6.26), enter a rotating frame $\mathbf{E}(\mathbf{r}, t) = \tilde{\mathbf{E}}^+ e^{i\omega_{\text{opt}} t} + \tilde{\mathbf{E}}^- e^{-i\omega_{\text{opt}} t}$ and $p_{\mathbf{k}}(\mathbf{r}, t) = \tilde{p}_{\mathbf{k}}(\mathbf{r}, t) e^{-i\omega_{\text{opt}} t}$, cf. Eq. (6.34) and apply a rotating wave approximation. Assuming a fast dephasing γ , we solve the equation for the interband coherence adiabatically and also neglect the transport terms in Eqs. (6.39), as they are also small compared to the individual time dynamics. Since the spatial gradients needed to evaluate the displacement Eq. (6.14) are mainly determined by the dielectric, off-resonant contribution, we replace the full self-consistent field by the field $\hat{\mathbf{E}}$ formed by the dielectric background. In addition, a radiation self energy correction will be absorbed in the frequency $\omega_{\mathbf{k}} \equiv (\epsilon_{\mathbf{k}}^c - \epsilon_{\mathbf{k}}^v) \hbar \rightarrow \tilde{\omega}_{\mathbf{k}}$ and the dephasing $\gamma \rightarrow \tilde{\gamma}$. Thus, the governing equations for the band occupations read

$$\partial_t f_{\mathbf{k}}^{c,2}(\mathbf{r}, t) = \left| \frac{\mathbf{d}^{vc} \cdot \hat{\mathbf{E}}(\mathbf{r}, t)}{\hbar} \right|^2 \frac{2\tilde{\gamma}}{\tilde{\gamma}^2 + (\tilde{\omega}_{\mathbf{k}} - \omega_{\text{opt}})^2} \left[f_{\mathbf{k}}^{v,0}(\mathbf{r}) - f_{\mathbf{k}}^{c,0}(\mathbf{r}) \right] - \frac{1}{\tau} f_{\mathbf{k}}^{c,2}(\mathbf{r}), \quad (6.40a)$$

$$\partial_t f_{\mathbf{k}}^{v,2}(\mathbf{r}, t) = - \left| \frac{\mathbf{d}^{vc} \cdot \hat{\mathbf{E}}(\mathbf{r}, t)}{\hbar} \right|^2 \frac{2\tilde{\gamma}}{\tilde{\gamma}^2 + (\tilde{\omega}_{\mathbf{k}} - \omega_{\text{opt}})^2} \left[f_{\mathbf{k}}^{v,0}(\mathbf{r}) - f_{\mathbf{k}}^{c,0}(\mathbf{r}) \right] - \frac{1}{\tau} f_{\mathbf{k}}^{v,2}(\mathbf{r}). \quad (6.40b)$$

In the following, we apply a coarse-graining procedure using the macroscopic definition of the lattice displacement, Eq. (6.5) and a momentum expansion for the Wigner occupations of the type in Eq. (4.35) [254, 403, 404]. This allows to identify the contribution of the interband transitions in Eqs. (6.40) via the macroscopic interband susceptibility

$$\chi^{\text{inter}}(\omega) = - \frac{|d|^2}{\hbar \epsilon_0 \Omega} \sum_{\mathbf{k}} \frac{f_{\mathbf{k}}^{v,0}(\mathbf{r}) - f_{\mathbf{k}}^{c,0}(\mathbf{r})}{\omega - \tilde{\omega}_{\mathbf{k}} + i\tilde{\gamma}}, \quad (6.41)$$

with the unit cell volume Ω . This allows to identify macroscopic equations for the carrier densities,

$$\partial_t \rho_2^v(\mathbf{r}, t) = - \frac{2e\epsilon_0}{\hbar} \left| \hat{\mathbf{E}}(\mathbf{r}, t) \right|^2 \text{Im} \{ \chi^{\text{inter}}(\omega_{\text{opt}}) \} - \frac{1}{\tau} \rho_2^v(\mathbf{r}, t), \quad (6.42a)$$

$$\partial_t \rho_2^c(\mathbf{r}, t) = \frac{2e\epsilon_0}{\hbar} \left| \hat{\mathbf{E}}(\mathbf{r}, t) \right|^2 \text{Im} \{ \chi^{\text{inter}}(\omega_{\text{opt}}) \} - \frac{1}{\tau} \rho_2^c(\mathbf{r}, t). \quad (6.42b)$$

These equations describe the occupation dynamics for the individual bands, with a source term that creates or annihilates density in the respective band due to the presence of an external field $\tilde{\mathbf{E}}_0(\mathbf{r}, t)$.

6.4.3. Qualitative Comparison

After obtaining the coupled set of oscillator equations, as given by Eq. (6.14), and the electron equations for both the intraband case, Eq. (6.36), and the interband case, Eq. (6.42), we can now discuss the implications of our findings in comparison to previous models and the qualitative differences in the driving terms.

Our set of equations represents a generalization of previous models, such as those described in [448, 451, 473, 474]. Notably, our model introduces a novel source term that contributes to the initiation of vibrational breathing modes. This term arises from optically induced gradients in the electron density, $\rho(\mathbf{r}, t)$, and exhibits a quadratic scaling with the electric field, suggesting that it should be thought similarly to the ponderomotive force. In addition to the previously known thermal expansion, which is influenced by changes in lattice temperature, $\Delta T_\ell(t)$, this new driving term enhances the understanding of the oscillation onset. We highlight that our microscopic approach provides a reliable reproduction of the thermal driving term, thus establishing a microscopic foundation for the previous understanding.

We anticipate qualitative differences between the two driving terms in their contributions to the oscillation onset. The intraband terms represent excitations within the same electronic band, which, according to existing literature, are assumed to have short lifetimes due to fast scattering processes. Conversely, the interband process involves the promotion of carriers between two electronic bands, resulting in significantly longer lifetimes for the electronic densities to persist. These distinct temporal behaviors will be further discussed and evaluated individually in Sec. 6.6.

6.5. Vibrational Eigenmodes - Lamb Modes

To approach the coupled set of partial differential equations for the lattice displacement $\mathbf{u}(\mathbf{r}, t)$ and the second order electron density $\rho(\mathbf{r}, t)$ (for the intraband and the interband case respectively), we expand the equations into vibrational eigenmodes of the MNP, which describe the spatial properties of the spheres. These free oscillations of a sphere were first described in Ref. [447] solving for the modes of the vibrational equation for the continuum field $\mathbf{u}(\mathbf{r}, t)$,

$$(\lambda + \mu)\nabla(\nabla \cdot \mathbf{u}) + \mu\nabla^2\mathbf{u} = \rho\partial_t^2\mathbf{u}, \quad (6.43)$$

where μ and λ are the Lamé constants that are related to the elasticity tensor [447, 475]. The equation can be solved using three so-called Helmholtz potentials that satisfy Helmholtz equations, a full discussion can be found in App. I.5. In our initial approach, we focus on the Helmholtz potential $\phi_{nlm}(\mathbf{r})$, which predominantly describes radial motion, aligning with the observations of most experiments [4, 450, 476, 501, 502]. This allows us to express the displacement $\mathbf{u}(\mathbf{r})$ as a gradient,

$$\mathbf{u}_{nlm}(\mathbf{r}) = \nabla\phi_{nlm}(\mathbf{r}), \quad (6.44a)$$

$$\text{with } \phi_{nlm}(\mathbf{r}) = j_\ell(k_n r)P_\ell^m(\cos\theta)\exp\{im\varphi\}. \quad (6.44b)$$

The radial dependence is given by the spherical Bessel functions $j_\ell(k_n r)$, where k_n are the radial wave numbers that are determined by the boundary condition. Implementing stress-free boundary conditions, k_n is the n^{th} solution of the boundary conditions, Eq. 6.45, that is given in terms of the unitless frequency η [447, 448],

$$\eta \cot \eta = 1 - \frac{\eta^2}{4\delta^2}. \quad (6.45)$$

Here, δ is the ratio of transverse and longitudinal speed of sound $c_{\text{TA}}/c_{\text{LA}}$. The frequency ω is connected to the unitless frequency η by the relation $\omega_n = c_{\text{LA}} \eta_n / R$ where R is the radius of the sphere. To discuss purely radial modes as observed in experiment, we focus on the $\ell = 0$ case. Introducing units similar to Eq. (6.5) in the homogeneous equation (6.43), we find

$$\phi_n(r) = \left(\frac{\hbar}{2M\omega_n} \right)^{\frac{1}{2}} \frac{1}{k_n} j_0(k_n r), \quad (6.46a)$$

$$\mathbf{u}_n(r) = \left(\frac{\hbar}{2M\omega_n} \right)^{\frac{1}{2}} \frac{1}{k_n} \partial_r(j_0(k_n r)) \mathbf{e}_r. \quad (6.46b)$$

Since the wave numbers k_n arise from the stress-free boundary conditions imposed by Eq. (6.45), the spherical Bessel functions are not orthogonal, making a standard mapping to the fundamental modes infeasible. Thus, to approach the complex system of partial differential equations, we expand the displacement $\mathbf{u}(\mathbf{r}, t)$, and the Helmholtz potential $\phi(\mathbf{r}, t)$ in terms of the fundamental modes $\mathbf{u}_0(\mathbf{r})$ and $\phi_0(\mathbf{r})$ of the system related to the first root of the boundary equation, Eq. (6.45),

$$\rho(\mathbf{r}, t) = \rho(t) \phi_0(\mathbf{r}), \quad (6.47a)$$

$$\mathbf{u}(\mathbf{r}, t) = u(t) \mathbf{u}_0(\mathbf{r}). \quad (6.47b)$$

This expansion effectively assumes that only the fundamental mode of the system is excited. This is in good agreement with experimental observations [4, 448, 449, 451, 473, 474], where the period of the oscillation is well reproduced from the unitless frequency. In the following, we will use the definitions of the overlap functions,

$$A_0 \equiv \int \mathbf{u}_0^*(\mathbf{r}) \cdot \mathbf{u}_0(\mathbf{r}) d^3r, \quad B_0 \equiv \int \phi_0^*(\mathbf{r}) \phi_0(\mathbf{r}) d^3r. \quad (6.48)$$

Mapping the oscillator on the fundamental modes, $\mathbf{u}_0(\mathbf{r})$ and $\phi_0(\mathbf{r})$, allows discovering a dynamical equation for its expansion coefficient $u(t)$,

$$[\partial_t^2 + 2\gamma_{\text{ph}}\partial_t + \omega_{\text{LSP}}^2]u(t) = \beta\rho(t) + \xi\Delta T(t), \quad (6.49)$$

with the definition of the scalar thermal overlap,

$$\xi = \frac{1}{A_0} \int \mathbf{u}_0^* \cdot \boldsymbol{\xi} d^3r. \quad (6.50)$$

In doing so, we have simplified the complex dynamics of our system to the dynamics of its fundamental mode, resulting in a basic system of coupled first-order differential equations. The dynamics of the density expansion coefficient, along with their electric field overlaps, will be examined separately in the subsequent subsections.

6.5.1. Thermal Expansion

Since the contribution of the anharmonic potential to the Hamiltonian, Eq. 6.7, describes the macroscopic process of thermal expansion, we will approximate the corresponding prefactor in Eq. (6.50) by the classical linear expansion coefficient α_{cl} . This allows to compare our oscillator equation with the classical description [448, 488]. In our notation, the linear expansion coefficient is given by

$$\frac{u_r(\mathbf{R}, t)}{|\mathbf{R}|} = \alpha_{\text{cl}} \Delta T, \quad (6.51)$$

with the fraction of the radial projection of the lattice displacement $\mathbf{u}(\mathbf{R}, t) = u_r(\mathbf{R}, t)\mathbf{e}_r$ to the total particle radius $|\mathbf{R}|$, where $\mathbf{R}$ is chosen to be on the surface of the nanoparticle. Our calculated quantity $\mathbf{u}(\mathbf{R}, t)$ is a measure of the absolute radial displacement at a certain lattice position. Comparison of the thermal driving term in Eq. (6.49) with the classical equivalent in Eq. (6.51) reveals that by expanding in the fundamental Lamb mode $\mathbf{u}(\mathbf{r}, t) = \mathbf{u}_0(\mathbf{r})u(t)$, we find

$$u(t) = \frac{\alpha_{\text{cl}} R \Delta T(t)}{A_0} \int d^3r u_r^*(\mathbf{r}), \quad (6.52)$$

so that the coupling constant, describing the interaction with temperature changes in Eq. (6.49) can be approximated using the linear expansion coefficient α_{cl} as

$$\xi \equiv \alpha_{\text{cl}} \frac{\omega_{\text{LSP}}^2 R \int d^3r u_r^*(\mathbf{r})}{A_0}. \quad (6.53)$$

This calculation leads to a similar thermal drive term as given in the oscillation equation in Refs. [448, 451, 473, 474]. Therefore, it is expected that the models agree for purely thermal drive and lead to a similar oscillation behavior.

6.5.2. Electric Field Overlap

After presenting the expansion of the oscillator equation, which resulted in the scalar equation, Eq. (6.49), we now extend this expansion, Eq. (6.47), to the electronic equations. This will be done for the intra- and interband cases, cf. Eqs. (6.36) and (6.42) that will be treated separately in the subsequent sections.

To a good approximation, we will use the local Mie theory, cf. Sec. 2.4.1, to describe the electric field inside and outside the nanoparticle. The nanoparticle is much smaller in size compared to the wavelength of the incident light, making a quasistatic approximation applicable. Moreover, the nanoparticle is large enough that nonlocal effects can be neglected. We can then use a Heaviside Theta function $\Theta(\mathbf{r})$ to combine the standard Mie field terms [1, 201] into a single expression:

$$\mathbf{E}(\mathbf{r}) = \Theta(r - R) \mathbf{E}_{\text{out}} + \Theta(R - r) \mathbf{E}_{\text{in}}, \quad (6.54)$$

where the individual contributions inside and outside the nanoparticle can be expressed using the individual definitions [1, 201, 270],

$$\mathbf{E}_{\text{in}} = \frac{3\varepsilon_{\text{out}}}{\varepsilon(\omega) + 2\varepsilon_{\text{out}}} \mathbf{E}_0, \quad (6.55a)$$

$$\mathbf{E}_{\text{out}} = \mathbf{E}_0 + \frac{3\mathbf{n}(\mathbf{n} \cdot \mathbf{p}) - \mathbf{p}}{4\pi\varepsilon_0\varepsilon_{\text{out}}r^3}. \quad (6.55b)$$

This is illustrated in Fig. 6.5. The dipole moment $\mathbf{p}$ is given by $\mathbf{p} = \alpha(\omega)\mathbf{E}$, where $\alpha(\omega)$ is the polarizability of the MNP that we defined in Eq. (2.55). Here, we will use in a standard Drude model in first approximation, cf. Sec. 2.4.1. where the frequency-dependent material permittivity is given by the Drude model.

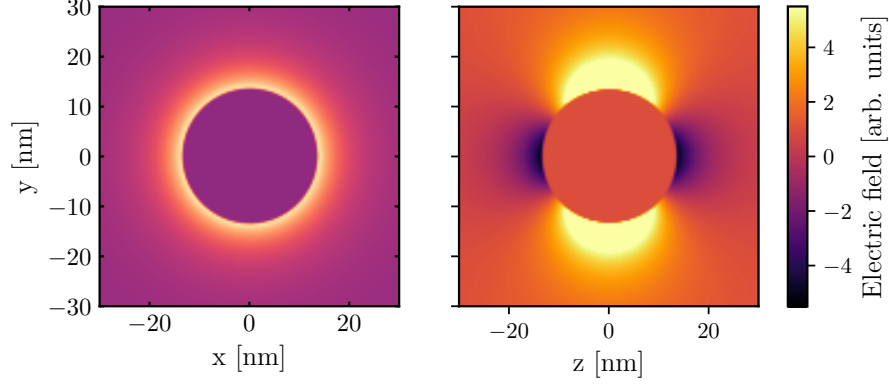


Figure 6.5.: **Electric Field of a Spherical Metal Nanoparticle.** For a z -aligned incident electric field, the resulting z component is illustrated on the left for the xy -plane. To the right, we see the x component illustrated for the xz -plane.

Intraband Case

Using the expansion for the intraband electron density from Eq. (6.36), we find

$$\partial_t \rho(t) + D \frac{\omega_{\text{LSP}}^2}{c_1^2} \rho(t) = -\frac{K}{B_0} \int \mathbf{u}_0^*(\mathbf{r}) \cdot \left[(\hat{\mathbf{E}} \cdot \nabla) \hat{\mathbf{E}} \right] d^3\mathbf{r}. \quad (6.56)$$

The overlap integral is taken over the volume of the nanosphere and can be evaluated using the definition of the electric field in Mie theory, cf. Eq. (6.54),

$$\begin{aligned} & \int \mathbf{u}_0^*(\mathbf{r}) \cdot \left[(\hat{\mathbf{E}}(\mathbf{r}, t) \cdot \nabla) \hat{\mathbf{E}}(\mathbf{r}, t) \right] d^3r \\ &= \frac{4\pi}{3} \left(\frac{\hbar}{2m\omega_{\text{LSP}}} \right)^{1/2} \hat{E}^2 \left[\frac{\partial_r j_0(k_0 R)}{k_0} \left((1-b^2)R^2 + \frac{4\alpha(\omega_{\text{opt}})\tilde{k}}{R} + \frac{4\alpha^2(\omega_{\text{opt}})\tilde{k}^2}{R^4} \right) \right] e^{-2t^2/\sigma^2}, \end{aligned} \quad (6.57)$$

with the definitions $\tilde{k} = 1/4\pi\epsilon_0\epsilon_{\text{out}}$ and $b = 3\epsilon_{\infty}/(\epsilon(\omega_{\text{opt}}) + \epsilon_{\text{out}})$. This provides the driving term for the electron gradient in the metal nanoparticle. As Fig. 6.5 indicates, the main source of the electron density gradients that in turn drive the nanoparticle oscillation, originates from the boundary, where the electric field gradients are largest.

Interband case

In analogy to the intraband case, using the projection in Eq. (6.42), we derive a first-order differential equation in time for the second-order electron density in the conduction band,

$$\partial_t \rho_2^c(t) = \frac{2e\epsilon_0}{\hbar A_0} \text{Im}\{\chi^{\text{inter}}(\omega_{\text{opt}})\} \int_{V_s} d^3r \mathbf{u}_0^*(\mathbf{r}) \cdot \nabla \left| \hat{\mathbf{E}}(\mathbf{r}, t) \right|^2 - \frac{1}{\tau} \rho_2^c(t). \quad (6.58)$$

This equation can be numerically integrated after the overlap integral has been evaluated. Performing the integration over the volume of the nanosphere, the integral in the driving term can be calculated to be

$$\int \mathbf{u}_0^*(\mathbf{r}) \cdot \nabla \left| \hat{\mathbf{E}}(\mathbf{r}, t) \right|^2 d^3r \quad (6.59)$$

$$= \left(\frac{\hbar}{8m\omega_{\text{LSP}}} \right)^{\frac{1}{2}} \frac{1}{k_0} \partial_r(j_0(k_0 R)) \left[\left(1 + \frac{3\varepsilon_{\text{out}}}{\varepsilon(\omega_{\text{opt}}) + 2\varepsilon_{\text{out}}} \right)^2 + 2 \left(\frac{\alpha(\omega_{\text{opt}})}{4\pi\varepsilon_0\varepsilon_{\text{out}}R^3} \right)^2 \right] \hat{E}^2 e^{-2t^2/\sigma^2}.$$

Here, $\varepsilon(\omega)$ is the intraband response of the Drude system within the nanoparticle that is not incorporated in the interband susceptibility $\chi^{\text{inter}}(\omega)$.

6.6. Numerical Results

Now that we have projected our full dynamics on the fundamental mode of the system, we can numerically evaluate the coupled system of first order differential equations, which we will do using numerical integration using the Runge-Kutta method. In this section, we will start investigating the temporal dynamics of the spatial mode coefficient of the electron density and compare the intraband and interband case. Using these, we analyze their impact on the nanoparticle oscillation driven by an external electric field, also comparing the two cases. Lastly, the results will be compared to the experimental results that were obtained in collaboration with the group of Holger Lange in Hamburg and published in Ref. [4].

6.6.1. Temporal Density Behavior

Based on the preceding sections, we have identified two competing mechanisms within the nanostructure that give rise to electron density gradients, which in turn drive the onset of oscillations. In this section, we analyze their respective temporal behaviors after mapping them onto the Lamb potential discussed in Sec. 6.5. The results are presented in Fig. 6.6.

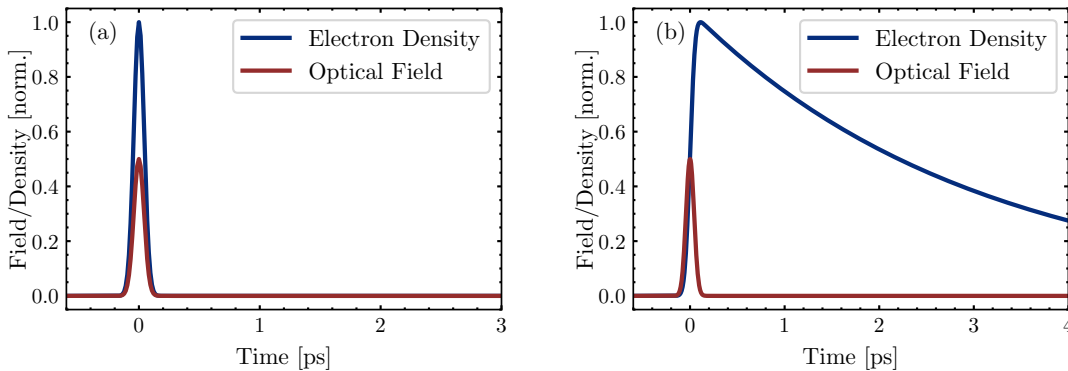


Figure 6.6.: Temporal Behavior of the Electron Density. The figure illustrates the temporal evolution of the expansion coefficient of the electron density (blue), as given by Eqs. (6.56) and (6.58), following optical excitation (blue). Panel (a) corresponds to the intraband case, while panel (b) represents the interband case.

Observing the figures, we note that the temporal behaviors are qualitatively distinct. In the case of intraband processes, cf. Fig. 6.6(a), the optical density follows the optical excitation and replicates the same shape as the optical pump profile. This is primarily due to the fast relaxation time associated with intraband processes in metals, characterized by a typical damping coefficient $\gamma \approx 100$ meV, corresponding to a lifetime of approximately 10 fs. As a result, this relaxation process is significantly shorter than the pulse width, leading to a reproduction of the shape of the electrical field envelope.

In contrast, occupations in other bands naturally possess much longer lifetimes compared to scattering processes within the same band. For metals, these processes have lifetimes on the order of a few picoseconds [399, 400, 491], which is considerably longer than the pulse width. Consequently, we observe a longer lifetime in Fig. 6.6(b).

Given that the temporal behavior of these electron density mechanisms directly influences the driving terms in the oscillator equation, it is evident that they will lead to different onset behaviors of the oscillations. In a simplified model, the intraband process can be envisioned as a Delta-like source, while the interband process resembles a step function. According to Landau's theory, this should result in an oscillation onset characterized by $\sin(\omega t)$ and $(1 - \cos(\omega t))$, respectively. The numerical results are presented in the subsequent section.

6.6.2. Oscillation Onset

We now turn to an investigation of the nanoparticle oscillation onset driven by the two different contributions in the electron density upon optical excitation. In Fig. 6.8, we provide the individual oscillation behaviors of the radial projection of the relative lattice displacement, $u^r(\mathbf{R}, t)/R$. Here, u^r is the projection of the oscillation vector on the radial unit vector, $u^r = \mathbf{e}_r^* \cdot \mathbf{u}$, which sufficiently characterizes the oscillation amplitude as a radial oscillation.

Looking at the onset of the oscillation in Fig. 6.7, we note that both driving terms indeed yield qualitatively quite distinct results. Here, we study the oscillation onset under the action of the electron density contribution term alone to understand their qualitative differences. We observe an immediate increase in the lattice displacement within the first 5 ps, the resulting oscillation behaves sinusoidal and can be described as a damped $\sin(\omega_{\text{LSP}} t)$ that starts right with the optical pulse. The immediate onset is mainly caused by the pulse being short compared to the period of the oscillation onset and accordingly, onsets the oscillation like a delta pulse, as we have seen the electron density behaves similarly in time, we obtain an effective delta source to the oscillation.

In contrast, the oscillation induced by interband transitions exhibits a qualitatively distinct temporal behavior compared to the intraband case. In this scenario, the oscillation onset is smoother and occurs later in time. This behavior can be attributed to the qualitative difference in the driving term, as depicted in Figure 6.6. The driving term associated with interband transitions persists for a longer duration compared to the optical pulse width. As a result, it can more likely be viewed as a step function driving the temporal behavior, in contrast to the instantaneous Delta-like term present in the intraband case.

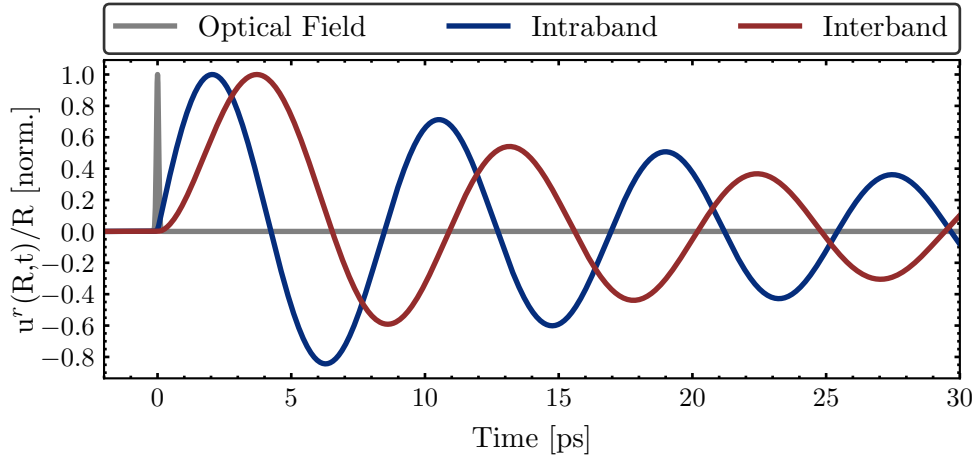


Figure 6.7.: **Electron Density Gradient Contributions to Onset of Radial Breathing Oscillations.** The figure presents the first picoseconds of the numerically determined relative lattice displacement at the surface of the nanoparticle, representing the relative change in nanoparticle size. Both figures study the isolated effect of the electron density gradients, disregarding thermal contributions. Panel (a) illustrates the onset of the intraband electron density contribution to the oscillation, while panel (b) displays the values for the dominant interband contributions to the oscillation.

6.6.3. Comparison to Current Theory

Until now, our analysis has focused solely on the pure contributions of the additional driving terms to study their respective temporal behavior. Now, we turn to the solution of the full oscillator equation and include both the electron density gradients and the classical thermal expansion source in the evaluation. The thermal expansion term is essential for accounting for the shift in the equilibrium position resulting from heating. However, we have not yet included this term, as evident from the fact that the oscillation is centered around zero once the electron density gradient contribution has dissipated.

By including the thermal terms, we can properly capture the combined effects of the driving forces and thermal expansion, allowing us to accurately describe the complete temporal behavior of the system.

In Fig. 6.8, we present a comparison of the oscillation onset resulting from the intra- and interband contributions, including the thermal driving term. Each figure also examines the individual contributions from purely thermal and direct interaction.

We observe in Fig. 6.8(a) the oscillation onset for resonant driving of the intraband plasmon resonance. We observe that the oscillation starts right with the optical pulse. For this case, the electronic source term leads to an immediate increase in the lattice displacement within the first 5 ps. Over the same period, the thermally driven part hardly changes its magnitude and needs more time to start the oscillation, so that with purely thermal interaction the first oscillation maximum is reached only after about 7 ps. The combined effect of both driving terms leads to an ultrafast oscillation onset directly with the optical excitation and a shift of the equilibrium position of the oscillation with increasing lattice temperature. We observe that the electron density contribution by far exceeds the thermal contribution in magnitude so that it dominates the oscillation

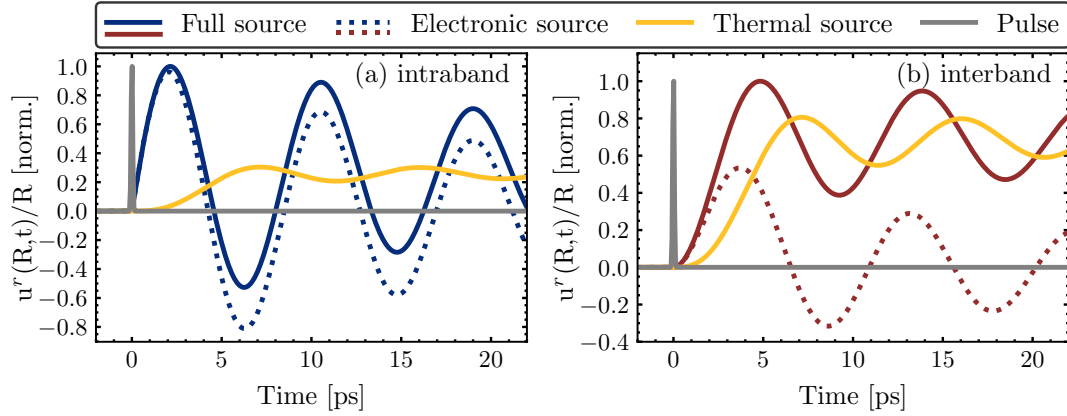


Figure 6.8.: **Onset of Radial Breathing Mode Oscillations.** The figure illustrates the first picoseconds of the numerically determined relative lattice displacement at the surface of the nanoparticle, which corresponds to the relative change in nanoparticle size. Panel (a) illustrates the onset for the intraband electron density, while panel (b) shows the values for dominant interband contributions to the oscillation.

onset in the combined onset. This causes the oscillation to also become negative, as the amplitude is larger than the change in equilibrium position.

Qualitatively, similar conclusions can be drawn from the interband case, illustrated in Fig. 6.8. However, its onset is not as immediate as for the intraband case, which leads to a phase shift of approximately $\pi/2$ in between the two. In addition, the absolute magnitude of the oscillation is smaller compared to the purely thermal case. As there is no band-specific electron-phonon coupling constant in the literature, we had to approximate the difference of valence and conduction band coupling constant in Eq. (6.38). We used this as a fitting parameter to the experimental data that we will present later in Sec. 6.6.4 and estimate as 8% of the individual valence band electron-phonon coupling elements. This is on the same order of magnitude as the estimations in [373] which are based on DOS averaged *ab initio* calculations. From this, we find electron density and thermal contribution to be similar in magnitude so that the effective oscillation onset begins on timescales between the two contributions. Having distinguished the individual contributions to the oscillation, we still have to compare to the current classical model [448, 451, 473, 474]. As discussed previously, these models are reproduced from our approach when only including the thermal source in the oscillator equation. Accordingly, the classical model coincides with the golden curves in Fig. 6.8. Accordingly, our model for the thermal source reproduces the temporal behavior observed in the classical model when the hot electron pressure contribution is not included.

In order to discuss the onset behavior of the individual models, we show the full oscillation onset from the full intraband, the full interband and the purely thermal/classical model in Fig. 6.9. We observe that the respective curves are shifted by approximately $\pi/2$, where the onset from the thermal contribution slightly depends on the excitation power and shifts to earlier times, and smaller magnitudes for lower excitation powers. The values used for the numerical implementation can be found in Tab. A.3. Apart from the phase, a qualitative difference is that the ratio of electron density gradient to thermal contribution is much more on the electron density side for the intraband case, which

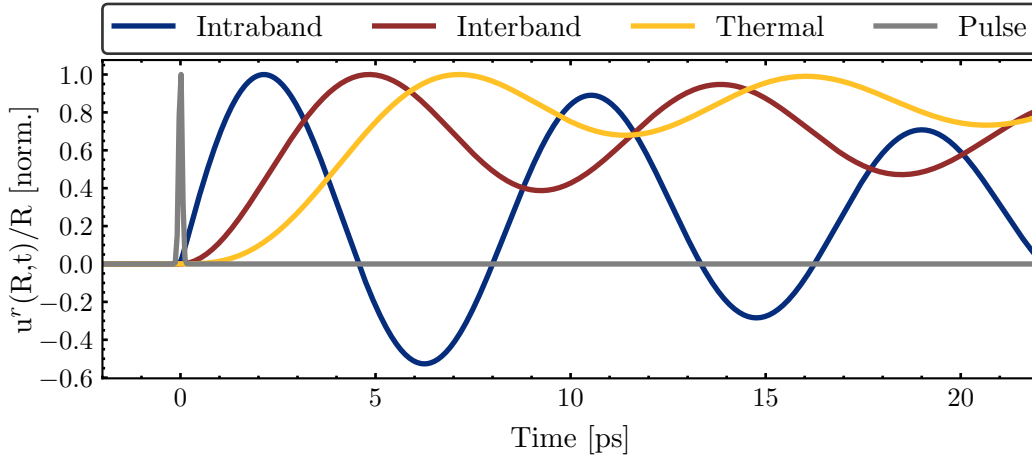


Figure 6.9.: **Phase Shift: Oscillation Onset Depending on the Coupling Model.** The onset behavior of the three models at hand is compared. Following the optical pulse (gray), the oscillation starts with different phases, depending on the interaction model. The most direct onset is caused by the intraband source (blue), followed by the interband source (red), and the purely thermal source (gold).

results in its value also becoming negative. At this stage, it would also be interesting to not only compare the oscillation onset for interband transitions with experimental data but also the one where the intraband plasmon is driven in resonance to see how strong this effect actually is.

6.6.4. Comparison to Experimental Results

In the following, we compare the results of our theory to experimental data that was recorded by our collaborators in Hamburg, which we also jointly published in Ref. [4]. In Sec. 6.1, we presented details of the experimental advance described in Ref. [4].

In Fig. 6.10, the experimental results from tSAXS-SPI and TA measurements are plotted and compared with the theoretical predictions we obtained previously, in particular, we show the relative lattice displacement $u^r(\mathbf{R}, t)/R$ for the individual influence of both, the electronic density gradient and the thermal contribution and for the combined effect of both, where u^r is the projection of the oscillation vector on the radial unit vector $u^r = \mathbf{e}_r^* \cdot \mathbf{u}$ which we have given in percent.

This comparison impressively demonstrates the advancements and capabilities of the tSAXS-SPI technique in capturing the complete oscillation dynamics, including the initial picosecond regime, which was previously inaccessible with TA experiments which can in this case only detect the second oscillation hump. In the experiment, an immediate increase in the lattice displacement by up to 0.5 % within the first 5 ps after the optical excitation pulse is observed and thus earlier than the excitation described using a purely thermal model (golden curve) which hardly changes its magnitude during the same time. A purely thermal source term needs more time to start the oscillation, so that with purely thermal interaction, the first oscillation maximum is reached only after about 7 ps. Hence, the oscillation onset occurs in the kinetic limit of the electron gas excitation, as we illustrated earlier in Fig. 6.1.

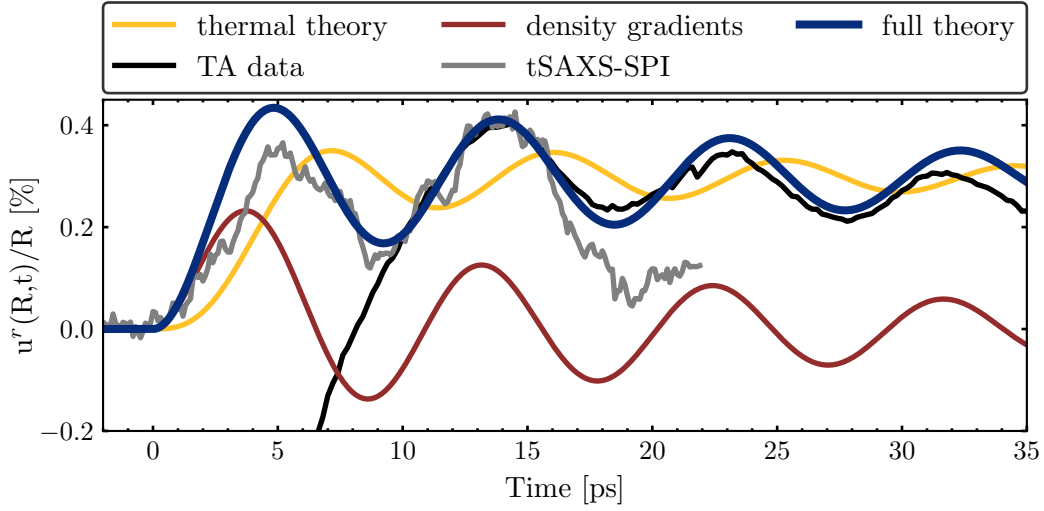


Figure 6.10.: **Experiment-Theory Comparison for Oscillation Onset.** Comparison of the temporal dynamics of the oscillation detected in the tSAXS-SPI and the TA measurement compared with the theoretical results for an oscillation onset caused by the thermal source, the interband electron density gradients and the combined action of the two previous. The TA data was scaled to match the data.

This oscillation onset is well captured by the additional driving term originating from spatial gradients in the electron density, which we have introduced in this chapter of the thesis. The combined effect of both driving terms leads to an ultrafast oscillation onset directly with the optical excitation and a shift of the equilibrium position of the oscillation with increasing lattice temperature. Accordingly, spatial electron gradients are identified as the dominating origin of the optically induced nanoparticle oscillations, since it can explain the onset of the oscillation. The thermal source acts via the lattice temperature change and causes an additional thermal expansion of the lattice, whose mayor impact is the shift of the equilibrium particle radius after the electron density has relaxed to its equilibrium position.

At this stage, we concluded that the effect observed in the experiment is caused by the interband coupling term as, firstly, it matches the phase of the onset of the oscillation and, secondly, coincides with the excitation wave length in the experiment which was $\lambda = 400$ nm and thus in the interband regime of gold.

6.7. Conclusions and Perspectives

In conclusion, our study has revealed important insights into the microscopic description of electron-phonon coupling in metal nanoparticles (MNPs) and its role in initiating radial oscillations. We have demonstrated that a direct interaction between optically induced spatial electron gradients and coherent phonons plays a crucial role in driving the oscillatory behavior of MNPs. This interaction term, beyond the thermal contributions, is incorporated into the oscillator equation for the lattice displacement and leads to an immediate onset of nanoparticle oscillation when subjected to optical excitation with sufficiently short pulse widths.

Our numerical evaluations have shown that the direct coupling between electrons and coherent phonons is the dominant source for the onset of radial oscillations on short time scales. In contrast, the thermal contribution primarily shifts the equilibrium position of the oscillation and cannot explain the immediate onset observed for short pulses. Additionally, we find that the indirect interaction via incoherent phonons does not play a dominant role in the early stages of the oscillation.

Furthermore, our experimental data obtained through time-resolved structural imaging of the breathing mode onset in gold nanoparticles (AuNPs) using single-particle imaging has provided strong confirmation of the requirement for two excitation sources for the breathing oscillations. This direct experimental evidence supports our theoretical framework and resolves previous uncertainties that were indicated indirectly through phase discrepancies. The combined analysis of time-resolved structural and optical data necessitated the inclusion of direct interactions between the electronic system and coherent phonons, which emerged as the dominant source term on short time scales, in addition to the thermal driving terms.

Our comprehensive theoretical model not only quantitatively explains all the experimental findings but also provides valuable insights into the plasmon-lattice interaction phenomenon. Moreover, the simultaneous coupling of the initial electron and lattice dynamics, arising from the immediate coupling of optically induced electron-density gradients and the breathing oscillation, has the potential for significant implications in energy transformations involving plasmonic hot carriers.

Overall, our study highlights the importance of considering direct electron-phonon interactions in understanding the initiation of radial oscillations in metal nanoparticles, paving the way for further exploration of plasmon-lattice interactions and their broader applications.

7. Conclusions and Perspectives

In summary, this work has led to the development of a comprehensive microscopic framework that describes spatio-temporal, momentum-resolved electron dynamics in Wigner phase space that is applicable to metal nanostructures. Various situations have been successfully investigated on a microscopic level, reproducing relevant macroscopic material models. Additionally, the current description of TMDC excitons has been extended to include hybrid metal-semiconductor nanostructures.

First, we derived momentum-resolved equations for exciton motion under the interaction with a single metal nanoparticle. This allowed us to identify a novel eigenvalue equation describing the center-of-mass motion of excitons in a plasmon-induced potential characterized by hybridized exciton-plasmon states. Our studies have shown that the existence of these hybridized states indicates strong coupling between plasmons and excitons, with excitons being spatially localized in the monolayer near the metal nanoparticle. The strong coupling occurred between the localized surface plasmon in the nanoparticle and momentum-dark excitons in the TMDC layer, observable in the electric near-field. Our findings suggest that metal nanoparticles can effectively localize excitons in two-dimensional TMDC layers, opening up potential applications in single-photon sources and making a microscopic description of surface plasmon polariton propagation possible.

The key achievement of this work is the successful development of a comprehensive microscopic approach for studying spatio-temporal, momentum-resolved electron and phonon dynamics in metals. This approach not only reproduces macroscopic equations in both local and nonlocal formulations, but also accurately incorporates geometrical effects and multi-band processes, allowing for a description of interband transitions based on microscopic parameters. Consequently, this framework lays a solid foundation for exploring complex interactions in metal systems and offers the potential for physically more meaningful insights compared to macroscopic fit models. By integrating *ab initio* calculations for dipole matrix elements, a substantial reduction in the number of fitting parameters is expected, significantly enhancing the model's accuracy and applicability.

The developed microscopic approach was used to investigate the potential of actively tuning the optical response of metal nanoparticles using strong THz fields. For this purpose, a fully numerical method combining the three-dimensional momentum-resolved microscopic Boltzmann scattering equations for the electronic Wigner function with a three-dimensional finite-difference time-domain solver was developed. This approach allows for a spatio-temporal treatment of microscopic dynamics, encompassing non-equilibrium, non-perturbative, and nonlocal phenomena, including interband transitions.

To study the influence of a strong THz field on the plasmon resonance of a spherical nanoparticle in more detail, we additionally derived an analytically model, treating the THz field non-perturbatively. This approach reveals that the additional THz pulse effectively renormalizes the electronic ground state of the system through pressure renormalization of the electron gas within the nanoparticle, leading to a blue shift of the plasmon resonance.

Finally, the framework was applied to study the onset of radial oscillations in spherical nanoparticles. The study highlighted the importance of considering direct electron-phonon interactions in understanding the onset of radial oscillations in metal nanoparticles. Spatial electron density gradients were identified as the dominant driving source for the onset of radial oscillations on short time scales beyond thermal contributions, explaining recent experimental results from our experimental collaborators.

Overall, the developed theory enables a microscopic treatment of electron dynamics in metals, allowing for the incorporation of interband transitions and intricate band structures in the theoretical description. This approach promises to capture ultrafast nonlinear, non-equilibrium, non-isotropic electron dynamics in metals and offers the exciting possibility of shedding light on fundamental processes in metal nanostructures from a microscopic perspective.

A. Parameters

The individual permittivity models are the Drude model $\varepsilon_D(\omega)$, the Drude-Lorentz model $\varepsilon_{DL}(\omega)$, and the critical point model $\varepsilon_{CP}(\omega)$,

$$\varepsilon_D(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega(\omega + i\gamma)}, \quad (\text{A.1a})$$

$$\varepsilon_{DL}(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega(\omega + i\gamma)} + \frac{\Delta\epsilon\Omega_L^2}{\Omega_L^2 - \omega^2 - i\gamma_L\omega}, \quad (\text{A.1b})$$

$$\varepsilon_{CP}(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega(\omega + i\gamma)} + \sum_{i=1,2} A_i \omega_i \left[\frac{e^{i\phi_i}}{\omega_i - \omega - i\gamma_i} + \frac{e^{-i\phi_i}}{\omega_i + \omega + i\gamma_i} \right]. \quad (\text{A.1c})$$

Table A.1.: Material parameters for gold permittivity

Parameter	Value	Unit	Reference
Drude Model from Ref. [274]			
ϵ_∞	9.0685		[274]
$\hbar\omega_p$	8.91236	eV	[274]
$\hbar\gamma_p$	0.07593	eV	[274]
Drude-Lorentz Model from Ref. [274]			
ϵ_∞	5.9673		[274]
$\hbar\omega_p$	8.74115	eV	[274]
$\hbar\gamma_p$	0.06584	eV	[274]
$\hbar\Omega_L$	2.68847	eV	[274]
$\hbar\Gamma_L$	0.43367	eV	[274]
$\hbar\Delta\epsilon$	1.09	eV	[274]
Critical Point Model from Ref. [277]			
ϵ_∞	1.53		[277]
$\hbar\omega_p$	8.55063	eV	[277]
$\hbar\gamma_p$	0.072932	eV	[277]
A_1	0.94		[277]
φ_1	$-\pi/4$		[277]
$\hbar\omega_1$	2.64923	eV	[277]
$\hbar\gamma_1$	0.53906	eV	[277]
A_2	1.36		[277]
φ_2	$-\pi/4$		[277]
$\hbar\omega_2$	3.74575	eV	[277]
$\hbar\gamma_2$	1.31898	eV	[277]

Appendix A. Parameters

Table A.2.: Material parameters for TMDC and geometry used in the numerical implementation for the hybrid structure

Parameter	Value	Unit	Reference
d	0.27	eC nm	[11]
M_{MoSe_2}	6.2535	fs ² eV nm ⁻²	[13]
$\hbar\gamma$ (300 K)	0.0269	eV	^b
φ_0	0.51	nm ⁻¹	^a
r_{xy}	8	nm	
r_z	4	nm	
z_{ex}	-1	nm	
z_{pl}	5	nm	
ε_1	4.5		
ε_2	1		

^a Calculated from Rytova approach for 4 layer system similar to Ref. [22]

^b Calculated by exploiting the method from Ref. [176]

Table A.3.: Material parameters for gold, used in the numerical implementation of radial oscillations

Parameter	Value	Unit	Reference
m	5.6856800	fs ² eV/nm ²	
M	$196.966569 \times 10439.60413$	fs ² eV/nm ²	[503]
c_{LA}	3.24×10^{-3}	nm fs ⁻¹	[504, 505]
c_{TA}	1.2×10^{-3}	nm fs ⁻¹	[504, 505]
γ_{el}	0.14099	fs ⁻¹	[111, 273]
γ_{ph}	4×10^{-5}	fs ⁻¹	^a
Z^{eff}	10.938		[497]
α_{cl}	14.2×10^{-6}	K ⁻¹	[504]
G	3.1×10^{11}	W K ⁻¹ mol ⁻¹	[472]
C_l	25.4	J K ⁻¹ mol ⁻¹	[504]
ζ	6.74×10^{-4}	J K ⁻² mol ⁻¹	[389]
τ_s	4×10^5	fs	^a

^aObtained from fits to data done in Ref. [448]

Table A.4.: **Universal constants** in semiconductor units.

e	1 eC	m_0	5.6856800 fs ² eV/nm ²
c	299.792458 nm fs ⁻¹	m_P	10439.60413 fs ² eV nm ⁻²
$\hbar$	0.658212196 eVfs	k_B	8.61745×10^{-5} eV K ⁻¹
ε_0	5.526308×10^{-2} eC ² eV ⁻¹ nm ⁻¹	π	3.14159265359
μ_0	$2.013384742 \times 10^{-4}$ eV fs ² eC ⁻² nm ⁻¹		

B. Fourier Transformation

The spatial Fourier transformations used in this work are

$$\mathbf{A}(\mathbf{r}, t) = \frac{1}{(2\pi)^3} \int d^3\mathbf{q} e^{i\mathbf{q}\cdot\mathbf{r}} \mathbf{A}(\mathbf{q}, t), \quad (\text{B.1a})$$

$$\mathbf{A}(\mathbf{q}, t) = \int d^3\mathbf{r} e^{-i\mathbf{q}\cdot\mathbf{r}} \mathbf{A}(\mathbf{r}, t). \quad (\text{B.1b})$$

The Fourier transform in time and frequency is given by

$$\mathbf{A}(t) = \frac{1}{2\pi} \int d\omega e^{-i\omega t} \mathbf{A}(\omega), \quad (\text{B.2a})$$

$$\mathbf{A}(\omega) = \int dt e^{i\omega t} \mathbf{A}(t). \quad (\text{B.2b})$$

C. Light-Matter Interaction Hamiltonian in r -E coupling

In nano-optics, we are interested in the interaction of electromagnetic radiation with different materials on the nanoscale. The dimensions of the considered materials are small and require a quantum description. The radiation could be described using a quantum theory too. Often, it turns out that the use of the wave picture is sufficient to describe the observed effects. This allows to describe optical radiation using classical field theory based on Maxwell's equation. Throughout this thesis, we will work in this framework of semi-classical theory that employs a classical picture for the radiation fields and a quantum theory of matter [332].

Generally, there are two equivalent formalisms that are used to describe the semi-classical light-matter interaction [333]. The options of pA and rE coupling differ in the fact which field quantity couples to which matter quantity. We decide to use the rE Hamiltonian that couples the position $\mathbf{r}$ to the electric field $\mathbf{E}$. The Hamiltonian in rE coupling can be derived using various methods. The interested reader may be referred to the great derivation in Ref. [333].

Both approaches yield a similar definition of the second quantization Hamiltonian, only differing in the matrix element. In first quantization, the rE Hamiltonian reads

$$H^{(1)} = -q \mathbf{r} \cdot \mathbf{E}(\mathbf{r}, t), \quad (\text{C.1})$$

which quantifies the classical dipole energy in an external field. Applying the quantization formalism for one particle quantities presented in Sec. 2.1, we obtain

$$\hat{H}^{(2)} = -q \sum_{\substack{\lambda\lambda' \\ \mathbf{k}\mathbf{k}'}} \int d^2\mathbf{r}_{\parallel} \phi_{\mathbf{k}\lambda}^*(\mathbf{r}) \mathbf{r} \cdot \mathbf{E}(\mathbf{r}) \phi_{\mathbf{k}'\lambda'}(\mathbf{r}) \lambda_{\mathbf{k}}^{\dagger} \lambda'_{\mathbf{k}'}, \quad (\text{C.2})$$

where we once again made use of the abbreviated notation for annihilation and creation operators. Expanding the wave function in lattice periodic Bloch functions

$$\phi_{\mathbf{k}\lambda}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k} \cdot \mathbf{r}} u_{\lambda\mathbf{k}}(\mathbf{r}), \quad (\text{C.3})$$

with V being the volume used to ensure normalization, yields

$$\hat{H}^{(2)} = -\frac{q}{V} \sum_{\substack{\lambda\lambda' \\ \mathbf{k}\mathbf{k}'}} \int d^2\mathbf{r}_{\parallel} e^{-i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}} u_{\lambda\mathbf{k}}^*(\mathbf{r}) \mathbf{r} \cdot \mathbf{E}(\mathbf{r}) u_{\lambda'\mathbf{k}'}(\mathbf{r}) \lambda_{\mathbf{k}}^{\dagger} \lambda'_{\mathbf{k}'}. \quad (\text{C.4})$$

We can express the electric field in terms of its Fourier transform for the in-plane component

$$\hat{H}^{(2)} = -\frac{q}{V^2} \sum_{\substack{\lambda\lambda' \\ \mathbf{k}\mathbf{k}'}} \int d^2\mathbf{r}_{\parallel} e^{-i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}} u_{\lambda\mathbf{k}}^*(\mathbf{r}) \mathbf{r} \cdot \sum_{\mathbf{Q}} e^{i\mathbf{Q} \cdot \mathbf{r}} \mathbf{E}_{\mathbf{Q}} u_{\lambda'\mathbf{k}'}(\mathbf{r}) \lambda_{\mathbf{k}}^{\dagger} \lambda'_{\mathbf{k}'}, \quad (\text{C.5})$$

and replace $\mathbf{r} \rightarrow \mathbf{R}_n + \mathbf{r}$ and the overall integral by a sum over individual integrals in the unit cells, which allows us to make use of the periodicity of the Bloch functions

$$\begin{aligned} \hat{H}^{(2)} = & -\frac{q}{V^2} \sum_{\substack{\lambda\lambda' \\ \mathbf{k}\mathbf{k}' \\ \mathbf{Q}}} \sum_{\mathbf{R}^n} e^{-i(\mathbf{k}-\mathbf{k}'-\mathbf{Q})\cdot\mathbf{R}^n} \times \\ & \times \int_{\text{UC}} d^2\mathbf{r}_{\parallel} e^{-i(\mathbf{k}-\mathbf{k}'-\mathbf{Q})\mathbf{r}} u_{\lambda\mathbf{k}}^*(\mathbf{r}) (\mathbf{r} + \mathbf{R}^n) \cdot \mathbf{E}_{\mathbf{Q}} u_{\lambda'\mathbf{k}'}(\mathbf{r}) \lambda_{\mathbf{k}}^\dagger \lambda_{\mathbf{k}'}. \end{aligned} \quad (\text{C.6})$$

C.1. Interband Light-Matter Interaction

If we restrict our calculations to interband transitions $\lambda' = \bar{\lambda}$, with $\bar{\lambda}$ being the opposite of λ , we can evaluate the λ' sum and neglect the $\mathbf{R}_{\parallel}^n$ contribution to the integral due to the orthogonality of the Bloch functions. In addition, we will approximate the electric field to be constant throughout the unit cell in z direction.

$$\hat{H}^{(2)} = -\frac{q}{A^2} \sum_{\substack{\mathbf{k}\mathbf{k}' \\ \lambda\bar{\lambda}}} \sum_{\mathbf{R}^n} \overbrace{e^{-i(\mathbf{k}-\mathbf{k}'-\mathbf{Q})\cdot\mathbf{R}^n}}^{N\delta_{\mathbf{k}-\mathbf{k}'-\mathbf{Q},0}} \times \quad (\text{C.7})$$

$$\times \int_{\text{UC}} d^2\mathbf{r}_{\parallel} e^{-i(\mathbf{k}-\mathbf{k}'-\mathbf{Q})\mathbf{r}} u_{\lambda\mathbf{k}}^*(\mathbf{r}) \mathbf{r} \cdot \mathbf{E}(\mathbf{Q}, z_0) u_{\bar{\lambda}\mathbf{k}'}(\mathbf{r}) \lambda_{\mathbf{k}}^\dagger \bar{\lambda}_{\mathbf{k}'}. \quad (\text{C.8})$$

We chose to restrict to the first Brillouin zone such that the Kronecker delta equates the momentum to zero. Evaluating it yields

$$\hat{H}^{(2)} = -\frac{q}{V} \underbrace{\sum_{\substack{\mathbf{k}\mathbf{Q} \\ \lambda}}}_{\equiv \frac{1}{\Omega}} \int_{\text{UC}} d^2\mathbf{r}_{\parallel} u_{\lambda\mathbf{k}}^*(\mathbf{r}) \mathbf{r} \cdot \mathbf{E}(\mathbf{Q}, z_0) u_{\bar{\lambda}\mathbf{k}-\mathbf{Q}}(\mathbf{r}) \lambda_{\mathbf{k}}^\dagger \bar{\lambda}_{\mathbf{k}-\mathbf{Q}}. \quad (\text{C.9})$$

Here, Ω is the volume of the first Brillouin zone. As our final definition of the carrier-light Hamiltonian in rE coupling, we find

$$\hat{H}^{(2)} = -\frac{1}{V} \sum_{\substack{\mathbf{k}, \mathbf{Q} \\ \lambda}} \mathbf{d}_{\mathbf{k}, \mathbf{k}-\mathbf{Q}}^{\lambda\bar{\lambda}} \cdot \mathbf{E}(\mathbf{Q}, z_0) \lambda_{\mathbf{k}}^\dagger \bar{\lambda}_{\mathbf{k}-\mathbf{Q}}, \quad (\text{C.10})$$

where we defined a dipole element in analogy to the classical case as

$$\mathbf{d}_{\mathbf{k}, \mathbf{k}-\mathbf{Q}}^{\lambda\bar{\lambda}} = \frac{1}{\Omega} \int_{\text{UC}} d^2\mathbf{r}_{\parallel} u_{\lambda\mathbf{k}}^*(\mathbf{r}) q \mathbf{r} u_{\bar{\lambda}\mathbf{k}-\mathbf{Q}}(\mathbf{r}). \quad (\text{C.11})$$

C.2. Intraband Light-Matter Interaction

Restricting to the same band from Eq. (C.6), we find

$$\hat{H}^{(2)} = -\frac{q}{V^2} \sum_{\substack{\mathbf{k}\mathbf{k}' \\ \mathbf{Q}\lambda}} \sum_{\mathbf{R}^n} \int_{\text{UC}} d^2\mathbf{r}_{\parallel} e^{-i(\mathbf{k}-\mathbf{k}'-\mathbf{Q})(\mathbf{r}+\mathbf{R}^n)} u_{\lambda\mathbf{k}}^*(\mathbf{r}) (\mathbf{r} + \mathbf{R}^n) \cdot \mathbf{E}_{\mathbf{Q}} u_{\lambda\mathbf{k}'}(\mathbf{r}) \lambda_{\mathbf{k}}^\dagger \lambda_{\mathbf{k}'}. \quad (\text{C.12})$$

Here, now use the identity

$$\mathbf{r} e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} = -i\nabla_{\mathbf{k}} e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}, \quad (\text{C.13})$$

and obtain

$$\hat{H}^{(2)} = -\frac{q}{V^2} \sum_{\mathbf{k}\mathbf{k}'} \sum_{\mathbf{R}^n} \int_{\text{UC}} d^2\mathbf{r}_{\parallel} u_{\lambda\mathbf{k}}^*(\mathbf{r}) \left(-i\nabla_{\mathbf{k}'} e^{-i(\mathbf{k}-\mathbf{k}'-\mathbf{Q})(\mathbf{r}+\mathbf{R}^n)} \right) \cdot \mathbf{E}_{\mathbf{Q}} u_{\lambda\mathbf{k}'}(\mathbf{r}) \lambda_{\mathbf{k}}^{\dagger} \lambda_{\mathbf{k}'}. \quad (\text{C.14})$$

From this, we obtain from integration by parts, where the surface contributions are assumed to vanish an expression that reads

$$\begin{aligned} \hat{H}^{(2)} = & -\frac{iq}{V^2} \sum_{\mathbf{k}\mathbf{k}'} \sum_{\lambda} \mathbf{E}(\mathbf{R}_n) e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}^n} \times \\ & \times \int_{\text{UC}} d^2\mathbf{r}_{\parallel} u_{\lambda\mathbf{k}}^*(\mathbf{r}) \left((\nabla_{\mathbf{k}'} u_{\lambda\mathbf{k}'}(\mathbf{r})) \lambda_{\mathbf{k}}^{\dagger} \lambda_{\mathbf{k}'} + u_{\lambda\mathbf{k}'}(\mathbf{r}) \lambda_{\mathbf{k}}^{\dagger} \nabla_{\mathbf{k}'} \lambda_{\mathbf{k}'} \right). \end{aligned} \quad (\text{C.15})$$

The first term can be identified with a pure interband term and such vanishes for this description, an insightful discussion can be found in Ref. [506]. Hence, after using the orthonormality of the Bloch factors, we find for the intraband Hamiltonian

$$\hat{H}^{(2)} = -\frac{iq}{V} \sum_{\mathbf{k}\mathbf{Q}\lambda} \mathbf{E}_{\mathbf{Q}} u_{\lambda\mathbf{k}}(\mathbf{r}) \lambda_{\mathbf{k}}^{\dagger} \nabla_{\mathbf{k}} \lambda_{\mathbf{k}+\mathbf{Q}}. \quad (\text{C.16})$$

D. Exciton-Plasmon Hybridization

D.1. Complex Contour Integration

In the following, we provide our solution of the wave equation:

$$\left(\nabla^2 - \frac{\varepsilon(z)}{c^2} \frac{\partial^2}{\partial t^2}\right) \mathbf{E}(\mathbf{r}, t) = \frac{1}{\varepsilon_0 c^2} \frac{\partial^2}{\partial t^2} \mathbf{P}(\mathbf{r}, t) - \frac{1}{\varepsilon(z) \varepsilon_0} \nabla(\nabla \cdot \mathbf{P}(\mathbf{r}, t)), \quad (\text{D.1})$$

which we will solve using the Green's method. Considering the right-hand side of Eq. (D.1) as inhomogeneity, the wave equation can be written as

$$\left(\nabla^2 - \frac{\varepsilon}{c^2} \frac{\partial^2}{\partial t^2}\right) \mathbf{E}(\mathbf{r}, t) = \mathbf{S}(\mathbf{r}, t), \quad (\text{D.2})$$

The equation that defines the Green's function is given by

$$\left(\nabla^2 - \frac{\varepsilon}{c^2} \frac{\partial^2}{\partial t^2}\right) \mathbf{G}(\mathbf{r} - \mathbf{r}', t - t') = \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'). \quad (\text{D.3})$$

To find the Green's function, we consider Eq. (D.2) and use Fourier transform to find an expression for the wave equation in momentum and frequency space as

$$\mathbf{E}_{\mathbf{Q}}(\omega) = \frac{1}{\frac{\varepsilon \omega^2}{c^2} - Q^2} \mathbf{S}_{\mathbf{Q}}(\omega). \quad (\text{D.4})$$

From this equation, it is straightforward to identify the Green's function in Fourier space because the convolution of Green's function and inhomogeneity in real space turns into a product in Fourier space. We find for the Green's function

$$G_{\mathbf{Q}}(\omega) = \left(\frac{\varepsilon \omega^2}{c^2} - Q^2\right)^{-1}. \quad (\text{D.5})$$

From this, it is easy to provide a solution for the electric field solely depending on momentum and frequency

$$\mathbf{E}_{\mathbf{Q}}(\omega) = \left(\frac{\varepsilon \omega^2}{c^2} - Q^2\right)^{-1} \left(-\frac{\omega^2}{\varepsilon_0 c^2} \mathbf{P}_{\mathbf{Q}}(\omega) + \frac{1}{\varepsilon \varepsilon_0} \mathbf{Q}(\mathbf{Q} \cdot \mathbf{P}_{\mathbf{Q}}(\omega))\right). \quad (\text{D.6})$$

However, we want to employ the inherent cylindrical symmetry of our system to find the electric field and its dependencies on $\mathbf{Q}_{\parallel}$ which governs the in-plane dynamics of the excitons while being located at the spatial position of the TMDC. Thus, we need the electric field

$$\mathbf{E}_{\mathbf{Q}_{\parallel}}(z) = \int dz' G_{\mathbf{Q}_{\parallel}}(z - z'; \omega) \mathbf{S}_{\mathbf{Q}_{\parallel}}(z'). \quad (\text{D.7})$$

which is given by a one dimensional convolution of Green's function and inhomogeneity. Transforming the inhomogeneity can be done by a straightforward convolution, and thus we are left with finding the Green's function with these dependencies. This can be done by an inverse Fourier transform of the Green's function in Eq. (D.5)

$$G_{\mathbf{Q}_{\parallel}}(z - z', \omega) = \frac{1}{2\pi} \int dQ_z e^{iQ_z(z-z')} \frac{1}{\frac{\varepsilon\omega^2}{c^2} - Q_{\parallel}^2 - Q_z^2}. \quad (\text{D.8})$$

Abbreviating $k_{\mathbf{Q}_{\parallel}} = \sqrt{\frac{\varepsilon\omega^2}{c^2} - Q_{\parallel}^2}$, this equation can be simplified to

$$G_{\mathbf{Q}_{\parallel}}(z - z', \omega) = -\frac{1}{2\pi} \int dQ_z e^{iQ_z(z-z')} \frac{1}{(Q_z + k_{\mathbf{Q}_{\parallel}})(Q_z - k_{\mathbf{Q}_{\parallel}})}. \quad (\text{D.9})$$

The exponential factor vanishes for either $Q_z \rightarrow \pm i\infty$. This allows to add a semicircle at either $\pm i\infty$ to the integration path, as it does not contribute. Hence, the integral along the real axis can be replaced by a complex integral along a closed contour γ . This contour integral can then be solved by using the residue theorem

$$\oint_{\gamma} f(z) = 2\pi i \sum_{a_k} \text{Res}[f, a_k], \quad (\text{D.10})$$

that equates the contour integral to the sum of all residues. For didactic reasons, we assume $z - z' > 0$ in the following. However, the case for $z - z' < 0$ works analogously. As illustrated in Fig. D.1, there are several distinct options for the choice of contour. Along the real axis we need to move the contour either above or below the singularities as the integrand diverges right at the singularity. For the general case, we could also assume to skip both singularities, either below or above. This is mostly done for temporal integrals that need to obey causality and lead to retarded or advanced Green's functions. However, as we perform a spatial integral, we are interested in symmetric solutions. Thus, we need to make sure to include at least one singularity in the contour, irrespective of the half plane that is chosen for the closure of the contour. This leaves us with the three options given in Fig. D.1, each of which only includes one singularity.

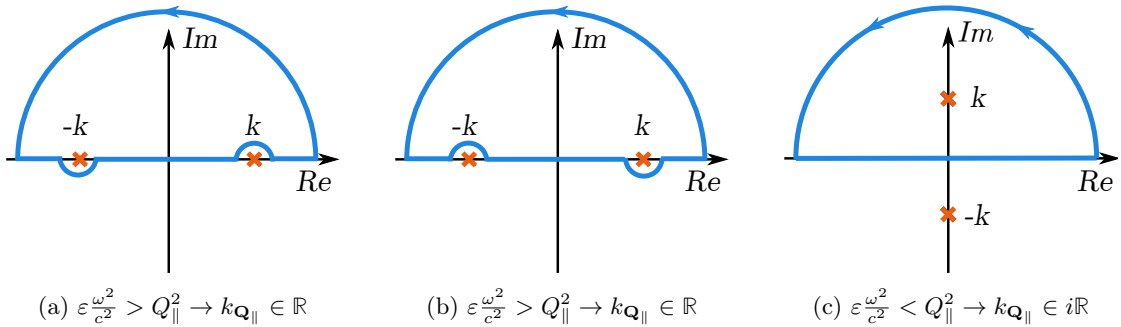


Figure D.1.: **Contour Integral: Different Contour Closures.** The figure illustrates the contour integral, showcasing various options for closing the contour based on different starting conditions.

The contours from Fig. D.1a/D.1b only differ in the singularity that is included. The Green's functions obtained from the individual calculations differ by an overall sign and

the sign of the exponent. Thus, the respective solutions either correspond to exponential damping or amplification (or ingoing or outgoing waves). We choose the physical solution that is damped for large $Q_{\parallel}$ and find the Green's function

$$G_{\mathbf{Q}_{\parallel}}(z - z'; \omega) = -\frac{i}{2k_{\mathbf{Q}_{\parallel}}} e^{ik_{\mathbf{Q}_{\parallel}}|z-z'|}. \quad (\text{D.11})$$

This will be used in the main text to find a solution for our specific geometry. For the geometry in Ch. 2, one can find

$$G_{\mathbf{Q}_{\parallel}}^{\text{st}}(z, z') = \begin{cases} -\frac{1}{2Q_{\parallel}} e^{-Q_{\parallel}|z-z'|} - \frac{1}{2Q_{\parallel}} \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} e^{-Q_{\parallel}|z+z'|} & , \quad z, z' > 0 \\ -\frac{1}{Q_{\parallel}} \frac{\varepsilon(z)}{\varepsilon_1 + \varepsilon_2} e^{-Q_{\parallel}|z-z'|} & , \quad \text{sgn}(z) \neq \text{sgn}(z') \\ -\frac{1}{2Q_{\parallel}} e^{-Q_{\parallel}|z-z'|} - \frac{1}{2Q_{\parallel}} \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1 + \varepsilon_2} e^{-Q_{\parallel}|z+z'|} & , \quad z, z' < 0, \end{cases} \quad (\text{D.12})$$

D.2. Numerical Solution of the Plexcitonic Equation

In Ch. 3, we solve the Wannier equation as well as the plexcitonic eigenvalue equation by numerical eigendecomposition. A great instruction on the numerical implementation of the Wannier equation can be found in Ref. [507]. Here, we employ the same formalism and apply it to the plexcitonic eigenvalue equation, Eq. (3.42),

$$\left[\frac{\hbar^2 \mathbf{Q}_{\parallel}^2}{2M} + X_{\mathbf{Q}_{\parallel}}(z_{\text{ex}}) \right] \Psi_{\mathbf{Q}_{\parallel}}^{\text{R},\lambda} - \frac{1}{(2\pi)^2} \int d^2 \mathbf{Q}'_{\parallel} V_{\mathbf{Q}_{\parallel} \mathbf{Q}'_{\parallel}}(z_{\text{ex}}, z_{\text{pl}}; \omega) \Psi_{\mathbf{Q}'_{\parallel}}^{\text{R},\lambda} = E^{\lambda} \Psi_{\mathbf{Q}_{\parallel}}^{\text{R},\lambda}, \quad (\text{D.13})$$

To solve this using numerical eigendecomposition, we discretize the integral to express it as a matrix product. With this, the first two terms provide contributions to the diagonal elements only, while the integral gives diagonal and off-diagonal contributions. The sum is performed over all momenta, including the two degrees of freedom $Q_{\parallel}$ and φ' . Hence, the plexcitonic eigenvalue equation is approximated as

$$\begin{pmatrix} \underline{B}_{0,0} & \underline{B}_{0,dQ_{\parallel}} & \cdots \\ \underline{B}_{dQ_{\parallel},0} & \underline{B}_{dQ_{\parallel},dQ_{\parallel}} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} \psi_{0,0}^{\text{R},\lambda} \\ \psi_{0,d\varphi}^{\text{R},\lambda} \\ \vdots \\ \psi_{dQ_{\parallel},0}^{\text{R},\lambda} \\ \vdots \end{pmatrix} = E^{\lambda} \begin{pmatrix} \psi_{0,0}^{\text{R},\lambda} \\ \psi_{0,d\varphi}^{\text{R},\lambda} \\ \vdots \\ \psi_{dQ_{\parallel},0}^{\text{R},\lambda} \\ \vdots \end{pmatrix}, \quad (\text{D.14})$$

with

$$\underline{B}_{Q_{\parallel},Q'_{\parallel}} = \begin{pmatrix} W_{Q_{\parallel},Q'_{\parallel}}^{0,0} & W_{Q_{\parallel},Q'_{\parallel}}^{0,d\varphi} & \cdots \\ W_{Q_{\parallel},Q'_{\parallel}}^{d\varphi,0} & W_{Q_{\parallel},Q'_{\parallel}}^{d\varphi,d\varphi} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}, \quad (\text{D.15})$$

and

$$W_{Q_{\parallel},Q'_{\parallel}}^{\varphi,\varphi'} = \delta_{Q_{\parallel},Q'_{\parallel}} \left[\frac{\hbar^2 Q_{\parallel}^2}{2M} + X_{\mathbf{Q}_{\parallel}}(z_{\text{ex}}) \right] - dQ'_{\parallel} Q'_{\parallel} d\varphi' V_{Q_{\parallel},\varphi,Q'_{\parallel},\varphi'}(z_{\text{ex}}, z_{\text{pl}}; \omega). \quad (\text{D.16})$$

The prefactors of the second term originate from careful consideration of the Jacobian determinant in polar coordinates.

E. Screened Coulomb Potential in Multilayer Systems

In multiple projects throughout my PhD thesis, we needed to calculate the Coulomb potential as a solution for of Poisson's equation for layered systems of arbitrary number of layers and varying thicknesses. In particular, for hybrid systems, consisting either of TMDC heterostructures or hybrid inorganic-organic system, the computation of 5 layers was crucial. For the AuNP on TMDC project, we presented in Chap. 3, a four layer system was employed. Here, we will start describing a 5 layer system and later show how we can generalize this to a system containing N layers of thickness d_i .

E.1. Coulomb Potential for 5-Layer System

Assuming a system as illustrated in Fig. E.1, we have to solve the Poisson equation [22] which read in the individual layers,

$$\frac{\partial^2 V_k^1(z, z')}{\partial z^2} - k^2 V_k^1(z, z') = 0, \quad (\text{E.1a})$$

$$\frac{\partial^2 V_k^2(z, z')}{\partial z^2} - k^2 V_k^2(z, z') = 0, \quad (\text{E.1b})$$

$$\frac{\partial^2 V_k^3(z, z')}{\partial z^2} - k^2 V_k^3(z, z') = 0, \quad (\text{E.1c})$$

$$\frac{\partial^2 V_k^4(z, z')}{\partial z^2} - k^2 V_k^4(z, z') = -\frac{q}{\varepsilon_0 \varepsilon_4} \delta(z - z'), \quad (\text{E.1d})$$

$$\frac{\partial^2 V_k^5(z, z')}{\partial z^2} - k^2 V_k^5(z, z') = 0, \quad (\text{E.1e})$$

and match the boundary conditions specified at the respective z position,

$$z = -R - L_1 : \quad V_k^1 = V_k^2 \quad \text{and} \quad \epsilon_1 \frac{\partial V_k^1}{\partial z} = \epsilon_2 \frac{\partial V_k^2}{\partial z}, \quad (\text{E.2a})$$

$$z = -R : \quad V_k^2 = V_k^3 \quad \text{and} \quad \epsilon_2 \frac{\partial V_k^2}{\partial z} = \epsilon_3 \frac{\partial V_k^3}{\partial z}, \quad (\text{E.2b})$$

$$z = 0 : \quad V_k^3 = V_k^4 \quad \text{and} \quad \epsilon_3 \frac{\partial V_k^3}{\partial z} = \epsilon_4 \frac{\partial V_k^4}{\partial z}, \quad (\text{E.2c})$$

$$z = L_2 : \quad V_k^4 = V_k^5 \quad \text{and} \quad \epsilon_4 \frac{\partial V_k^4}{\partial z} = \epsilon_5 \frac{\partial V_k^5}{\partial z}. \quad (\text{E.2d})$$

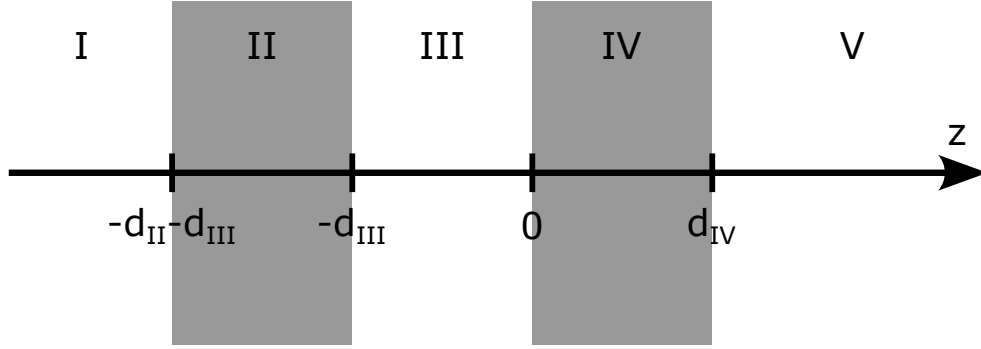


Figure E.1.: **Geometry Illustration of the 5-Layer System.** The figure depicts the dimensional geometry of the 5-layer system, where each section has a width d_i . Our particular interest lies in the Coulomb potential within the fourth layer.

The Poisson equations in Eqs. (E.1) are solved using the Ansatz

$$V_k^1 = a_1 e^{k(z-z')}, \quad (\text{E.3a})$$

$$V_k^2 = b_1 e^{k(z-z')} + b_2 e^{-k(z-z')}, \quad (\text{E.3b})$$

$$V_k^3 = c_1 e^{k(z-z')} + c_2 e^{-k(z-z')}, \quad (\text{E.3c})$$

$$V_k^4 = \frac{q}{2\varepsilon_0 \varepsilon_4 k} \left(e^{-k|z-z'|} + d_1 e^{k(z-z')} + d_2 e^{-k(z-z')} \right), \quad (\text{E.3d})$$

$$V_k^5 = f_2 e^{-k(z-z')}. \quad (\text{E.3e})$$

From this, we find for the 5 layer case

$$V_k^4 = \frac{q}{2\varepsilon_0 \varepsilon_4 k} \left\{ e^{-k|z-z'|} + \frac{1}{e^{2kd} - \delta_{45} \delta_{41}} \times \left[2\delta_{41} \delta_{45} \cosh k(z-z') + e^{kd} \left(\delta_{45} e^{k(z+z'-d)} + \delta_{41} e^{-k(z+z'-d)} \right) \right] \right\} \quad (\text{E.4})$$

where we define,

$$\delta_{41} = \frac{\varepsilon_4 - \varepsilon_3 \Delta_{31}}{\varepsilon_4 + \varepsilon_3 \Delta_{31}}, \quad \Delta_{31} = \frac{e^{2kd_3} - \delta_{31}}{e^{2kd_3} + \delta_{31}}, \quad (\text{E.5a})$$

$$\delta_{31} = \frac{\varepsilon_3 - \varepsilon_2 \Delta_{21}}{\varepsilon_3 + \varepsilon_2 \Delta_{21}}, \quad \Delta_{21} = \frac{e^{2kd_2} - \delta_{21}}{e^{2kd_2} + \delta_{21}}, \quad (\text{E.5b})$$

$$\delta_{21} = \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1 + \varepsilon_2}, \quad \delta_{45} = \frac{\varepsilon_4 - \varepsilon_5}{\varepsilon_4 + \varepsilon_5}. \quad (\text{E.5c})$$

E.2. Extension to N-layer System

Closer inspection of Eqs. (E.4) and (E.5) reveals that there exists a straightforward approach to generalize Eq. (E.4) for a system consisting of N layers of thickness d_i as depicted in Fig. E.2.

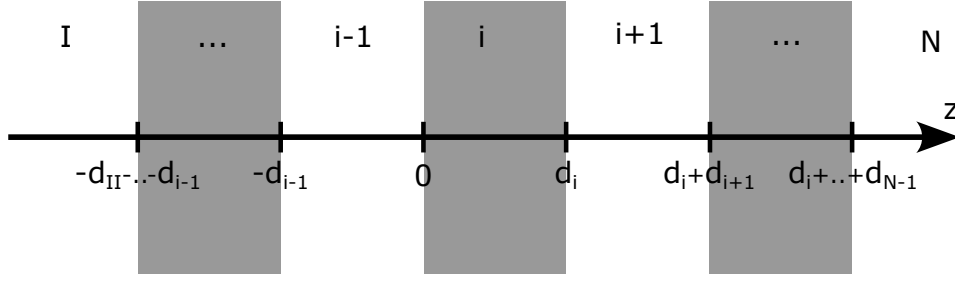


Figure E.2.: **Sketch of N-Layer System.** The figure illustrates the generalization to an N-layer system, where each section has a width d_i . Our specific focus centers on the Coulomb potential within the i th layer.

Assuming the charge to be in the i th layer, we can derive an expression for the potential in the i th layer that reads

$$V_k^i = \frac{q}{2\varepsilon_0\varepsilon_i k} \left\{ e^{-k|z-z'|} + \frac{1}{e^{2kd_i} - \delta_{in}\delta_{i1}} \times \left[2\delta_{i1}\delta_{in} \cosh k(z-z') + e^{kd_i} \left(\delta_{in} e^{k(z+z'-d_i)} + \delta_{i1} e^{-k(z+z'-d_i)} \right) \right] \right\} \quad (\text{E.6})$$

where we find a recursive formula to express the appearing δ -relations,

$$\delta_{i1} = \frac{\varepsilon_i - \varepsilon_{i-1}\Delta_{i-1,1}}{\varepsilon_i + \varepsilon_{i-1}\Delta_{i-1,1}}, \quad \Delta_{i1} = \frac{e^{2kd_i} - \delta_{i1}}{e^{2kd_i} + \delta_{i1}}, \quad (\text{E.7a})$$

$$\delta_{in} = \frac{\varepsilon_i - \varepsilon_{i+1}\Delta_{i+1,N}}{\varepsilon_i + \varepsilon_{i+1}\Delta_{i+1,N}}, \quad \Delta_{in} = \frac{e^{2kd_i} - \delta_{in}}{e^{2kd_i} + \delta_{in}}, \quad (\text{E.7b})$$

$$\delta_{21} = \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1 + \varepsilon_2}, \quad \delta_{N-1,N} = \frac{\varepsilon_{N-1} - \varepsilon_N}{\varepsilon_{N-1} + \varepsilon_N}. \quad (\text{E.7c})$$

The terms in Eq. (E.7c) end the recursive description. In the limit of $N \rightarrow 3$ with $\varepsilon_1 = 1 = \varepsilon_3$, $\varepsilon_2 = \varepsilon$, and $d_i = d$, the formula for the potential reproduces the typical Rytova potential given in Ref. [22],

$$V_{\mathbf{k}} = \frac{q}{2\varepsilon_0\varepsilon k} \left[e^{-k|z-z'|} + \frac{2\delta}{e^{2kd} - \delta^2} \left\{ \delta \cosh k(z-z') + e^{kd} \cosh k(z+z'-d) \right\} \right] \quad (\text{E.8})$$

F. Microscopic Spatio-Temporal Electron Description

Here, we provide details on the derivation of dynamical equations in the spatio-temporal framework. We start with the equations for the single bands before we continue using the definition for multiple bands.

F.1. Microscopic Dynamics in Single-Band Description

In the following subsection, we provide some detail on how we calculate the the microscopic scattering equations for the electronic Wigner function,

$$f_{\mathbf{k}}(\mathbf{r}, t) = \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} \left\langle a_{\mathbf{k}-\mathbf{q}/2}^{\dagger} a_{\mathbf{k}+\mathbf{q}/2} \right\rangle (t), \quad (\text{F.1})$$

We include the free electron contribution, electron-light, electron-phonon and Coulomb-mediated electron-electron interaction.

F.1.1. Free Electronic Motion

For the undisturbed contribution, it becomes straightforward to derive the equations of motion. As we know from most semiconductor equations, we find for

$$\partial_t f_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} \partial_t \left\langle a_{\mathbf{k}-\frac{\mathbf{q}}{2}}^{\dagger} a_{\mathbf{k}+\frac{\mathbf{q}}{2}} \right\rangle \quad (\text{F.2})$$

$$= -\frac{i}{\hbar} \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} \left\langle \left[a_{\mathbf{k}-\frac{\mathbf{q}}{2}}^{\dagger} a_{\mathbf{k}+\frac{\mathbf{q}}{2}}, \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}} \right]_- \right\rangle \quad (\text{F.3})$$

$$= \frac{i}{\hbar} \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} \left(\epsilon_{\mathbf{k}-\frac{\mathbf{q}}{2}} - \epsilon_{\mathbf{k}+\frac{\mathbf{q}}{2}} \right) \left\langle a_{\mathbf{k}-\frac{\mathbf{q}}{2}}^{\dagger} a_{\mathbf{k}+\frac{\mathbf{q}}{2}} \right\rangle \quad (\text{F.4})$$

At this stage, we can now use two methods to approach this problem. One can either use the parabolic approximation for the dispersion and effectively find

$$\partial_t f_{\mathbf{k}}(\mathbf{r}, t) = -i \sum_{\mathbf{q}} \mathbf{v}_{\mathbf{k}} \cdot \mathbf{q} e^{i\mathbf{q}\cdot\mathbf{r}} \left\langle a_{\mathbf{k}-\frac{\mathbf{q}}{2}}^{\dagger} a_{\mathbf{k}+\frac{\mathbf{q}}{2}} \right\rangle \quad (\text{F.5})$$

$$= - \sum_{\mathbf{q}} \mathbf{v}_{\mathbf{k}} \nabla_{\mathbf{r}} e^{i\mathbf{q}\cdot\mathbf{r}} \left\langle a_{\mathbf{k}-\frac{\mathbf{q}}{2}}^{\dagger} a_{\mathbf{k}+\frac{\mathbf{q}}{2}} \right\rangle \quad (\text{F.6})$$

$$= -\mathbf{v}_{\mathbf{k}} \cdot \nabla_{\mathbf{r}} f_{\mathbf{k}}(\mathbf{r}, t) \quad (\text{F.7})$$

where we use $\mathbf{v}_{\mathbf{k}} = \nabla_{\mathbf{k}} \epsilon_{\mathbf{k}} / \hbar = \hbar \mathbf{k} / m$ for the electron group velocity. The other one is the use of the convolution theorem, followed by a gradient expansion. The latter will not be discussed in detail here.

F.1.2. Electron-Light Interaction

For a single-band model, we only consider intraband transitions in the Hamiltonian in Eq. (4.1d)

$$\partial_t f_{\mathbf{k}}(\mathbf{r}, t) = -\frac{i}{\hbar} \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} \left\langle \left[a_{\mathbf{k}-\frac{\mathbf{q}}{2}}^\dagger a_{\mathbf{k}+\frac{\mathbf{q}}{2}}, \frac{ie}{V} \sum_{\mathbf{k}, \mathbf{K}, \lambda} \mathbf{E}_{-\mathbf{K}} \cdot \nabla_{\mathbf{K}} (\lambda_{\mathbf{k}}^\dagger \lambda_{\mathbf{k}+\mathbf{K}}) \right]_- \right\rangle \quad (\text{F.8})$$

$$= \frac{ie}{V} \sum_{\mathbf{q}, \mathbf{K}} e^{i\mathbf{q}\cdot\mathbf{r}} \mathbf{E}_{-\mathbf{K}} \cdot \nabla_{\mathbf{K}} \left(f_{\mathbf{k}-\frac{\mathbf{q}}{2}, \mathbf{k}+\frac{\mathbf{q}}{2}+\mathbf{K}} - f_{\mathbf{k}-\frac{\mathbf{q}}{2}-\mathbf{K}, \mathbf{k}+\frac{\mathbf{q}}{2}} \right) \quad (\text{F.9})$$

$$= \frac{ie}{V} \sum_{\mathbf{q}, \mathbf{K}} e^{i\mathbf{q}\cdot\mathbf{r}} \mathbf{E}_{-\mathbf{K}} \cdot \nabla_{\mathbf{K}} \left(f_{\mathbf{k}-\frac{\mathbf{q}}{2}, \underline{\mathbf{k}+\frac{\mathbf{q}}{2}+\mathbf{K}}} + f_{\underline{\mathbf{k}-\frac{\mathbf{q}}{2}-\mathbf{K}}, \mathbf{k}+\frac{\mathbf{q}}{2}} \right) \quad (\text{F.10})$$

$$= \frac{ie}{V} \sum_{\mathbf{q}, \mathbf{K}} e^{i\mathbf{q}\cdot\mathbf{r}} e^{-i\mathbf{K}\cdot\mathbf{r}} \mathbf{E}_{-\mathbf{K}} \cdot \nabla_{\mathbf{K}} \left(f_{\mathbf{k}-\frac{\mathbf{q}}{2}+\frac{\mathbf{K}}{2}, \underline{\mathbf{k}+\frac{\mathbf{q}}{2}+\frac{\mathbf{K}}{2}}} + f_{\underline{\mathbf{k}-\frac{\mathbf{q}}{2}-\frac{\mathbf{K}}{2}}, \mathbf{k}-\frac{\mathbf{K}}{2}+\frac{\mathbf{q}}{2}} \right) \quad (\text{F.11})$$

In the last line, the underlines refer to the component of the Wigner function that the derivative acts upon. At this stage, it is usually assumed that the momentum of the light is much smaller compared to the electron momentum, $\mathbf{k} \ll \mathbf{K}$, which is a good assumption due to the comparatively steep light dispersion. Thus, we find:

$$\partial_t f_{\mathbf{k}}(\mathbf{r}, t) = ie \underbrace{\frac{1}{V} \sum_{\mathbf{K}} \mathbf{E}_{-\mathbf{K}} e^{-i\mathbf{K}\cdot\mathbf{r}}}_{=\mathbf{E}(\mathbf{r})} \cdot \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} \nabla_{\mathbf{K}} f_{\mathbf{k}-\frac{\mathbf{q}}{2}, \mathbf{k}+\frac{\mathbf{q}}{2}} \quad (\text{F.12})$$

$$= ie \mathbf{E}(\mathbf{r}, t) \cdot \nabla_{\mathbf{K}} f_{\mathbf{k}}(\mathbf{r}, t). \quad (\text{F.13})$$

This will be the general formula that we employ to describe intraband transitions.

F.1.3. Electron-Phonon Interaction

As electron-phonon interaction provides the dominant dephasing mechanism in metals [399, 400], we will derive microscopic electron-phonon scattering equations. In the semiconductor community, these equations have allowed to numerically calculate the linewidth of radiative and non-radiative processes [19, 176, 180, 243]. To derive the electron-phonon scattering contributions, we follow a similar derivation as previously for the electron-electron scattering processes.

From the electron-phonon Hamiltonian in Eq. (4.1c), we find

$$\begin{aligned} \partial_t f_{\mathbf{k}}(\mathbf{r}) \Big|_{\text{el-ph}} &= -\frac{i}{\hbar} \sum_{\mathbf{q}, \mathbf{q}'} e^{i\mathbf{q}\cdot\mathbf{r}} g_{\mathbf{q}'} \left[\left\langle b_{-\mathbf{q}'}^\dagger a_{\mathbf{k}-\mathbf{q}/2}^\dagger a_{\mathbf{k}-\mathbf{q}'+\mathbf{q}/2} \right\rangle - \left\langle b_{-\mathbf{q}'}^\dagger a_{\mathbf{k}+\mathbf{q}'-\mathbf{q}/2}^\dagger a_{\mathbf{k}+\mathbf{q}/2} \right\rangle \right. \\ &\quad \left. + \left\langle b_{\mathbf{q}'} a_{\mathbf{k}-\mathbf{q}/2}^\dagger a_{\mathbf{k}-\mathbf{q}'+\mathbf{q}/2} \right\rangle - \left\langle b_{\mathbf{q}'} a_{\mathbf{k}+\mathbf{q}'-\mathbf{q}/2}^\dagger a_{\mathbf{k}+\mathbf{q}/2} \right\rangle \right]. \end{aligned} \quad (\text{F.14})$$

Here, the Wigner function is coupled to three operator quantities, namely $\langle b_{\mathbf{q}_1}^\dagger a_{\mathbf{k}_1}^\dagger a_{\mathbf{q}_1} \rangle$, which represent phonon-assisted intraband transitions. Since we neglect coherent phonons at this stage, i.e. $\langle b_{\mathbf{q}}^{(\dagger)} \rangle$, the singlet factorization vanishes and the expectation values

become correlations. These correlations are treated similarly to the electron-electron correlations. By considering the contributions to the dynamics from the free particle Hamiltonian and the electron-phonon Hamiltonian to be dominant, we derive equations of motion for the phonon assisted intraband transitions,

$$\begin{aligned} \partial_t \langle b_{\mathbf{q}_1}^\dagger a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_2} \rangle &= -\frac{i}{\hbar} (\epsilon_{\mathbf{k}_2} - \epsilon_{\mathbf{k}_1} - \hbar\omega_{\mathbf{q}_1}) \langle b_{\mathbf{q}_1}^\dagger a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_2} \rangle \\ &\quad - \frac{i}{\hbar} \sum_{\mathbf{q}} \left(\langle b_{\mathbf{q}_1}^\dagger b_{\mathbf{q}} a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_2-\mathbf{q}} \rangle - \langle b_{\mathbf{q}_1}^\dagger b_{\mathbf{q}} a_{\mathbf{k}_1+\mathbf{q}}^\dagger a_{\mathbf{k}_2} \rangle \right) \\ &\quad + \frac{i}{\hbar} g_{\mathbf{q}_1} \langle a_{\mathbf{k}_1+\mathbf{q}_1}^\dagger a_{\mathbf{k}_2} \rangle - \frac{i}{\hbar} \sum_{\mathbf{k}} g_{\mathbf{q}_1} \langle a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}+\mathbf{q}_1}^\dagger a_{\mathbf{k}} a_{\mathbf{k}_2} \rangle. \end{aligned} \quad (\text{F.15})$$

Now, we transform to the rotating frame,

$$b_{\mathbf{q}} = \tilde{b}_{\mathbf{q}} e^{-i\omega_{\mathbf{q}} t}, \quad a_{\mathbf{k}} = \tilde{a}_{\mathbf{k}} e^{-i\epsilon_{\mathbf{k}} t/\hbar}, \quad (\text{F.16})$$

where the transformation for the creation operators is obtained via complex conjugation. From this, we can use the formal integration technique, including the Markov approximation from Sec. 2.1.2 and obtain

$$\begin{aligned} \langle b_{\mathbf{q}_1}^\dagger a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_2} \rangle(t) &= \frac{i\pi}{\hbar} \sum_{\mathbf{q}} g_{\mathbf{q}} \left[\langle b_{\mathbf{q}_1}^\dagger b_{\mathbf{q}} a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_2-\mathbf{q}} \rangle \delta(\epsilon_{\mathbf{k}_2} - \epsilon_{\mathbf{k}_2-\mathbf{q}} - \hbar\omega_{\mathbf{q}}) \right. \\ &\quad \left. - \langle b_{\mathbf{q}_1}^\dagger b_{\mathbf{q}} a_{\mathbf{k}_1+\mathbf{q}}^\dagger a_{\mathbf{k}_2} \rangle \delta(\epsilon_{\mathbf{k}_1+\mathbf{q}} - \epsilon_{\mathbf{k}_1} - \hbar\omega_{\mathbf{q}}) \right] \\ &\quad - \frac{i\pi}{\hbar} g_{\mathbf{q}_1} \langle a_{\mathbf{k}_1+\mathbf{q}_1}^\dagger a_{\mathbf{k}_2} \rangle \delta(\epsilon_{\mathbf{k}_1+\mathbf{q}_1} - \epsilon_{\mathbf{k}_1} - \hbar\omega_{\mathbf{q}_1}) \\ &\quad + \frac{i\pi}{\hbar} g_{\mathbf{q}_1} \sum_{\mathbf{k}} \langle a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}+\mathbf{q}_1}^\dagger a_{\mathbf{k}} a_{\mathbf{k}_2} \rangle \delta(\epsilon_{\mathbf{k}+\mathbf{q}_1} - \epsilon_{\mathbf{k}} - \hbar\omega_{\mathbf{q}_1}). \end{aligned} \quad (\text{F.17})$$

We immediately rediscover the typical Hierarchy problem. To truncate the hierarchy, we make use of the cluster expansion [171] and truncate at the two-operator (one-particle) level, while neglecting coherent phonons. Following the usual second-order Born-Markov approximation, we find

$$\begin{aligned} \langle b_{\mathbf{q}_1}^\dagger a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_2} \rangle(t) &= \frac{i\pi}{\hbar} \sum_{\mathbf{q}} g_{\mathbf{q}} \langle b_{\mathbf{q}_1}^\dagger b_{\mathbf{q}} \rangle \left[\langle a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_2-\mathbf{q}} \rangle \delta(\epsilon_{\mathbf{k}_2} - \epsilon_{\mathbf{k}_2-\mathbf{q}} - \hbar\omega_{\mathbf{q}}) \right. \\ &\quad \left. - \langle a_{\mathbf{k}_1+\mathbf{q}}^\dagger a_{\mathbf{k}_2} \rangle \delta(\epsilon_{\mathbf{k}_1+\mathbf{q}} - \epsilon_{\mathbf{k}_1} - \hbar\omega_{\mathbf{q}}) \right] \\ &\quad - \frac{i\pi}{\hbar} g_{\mathbf{q}_1} \langle a_{\mathbf{k}_1+\mathbf{q}_1}^\dagger a_{\mathbf{k}_2} \rangle \delta(\epsilon_{\mathbf{k}_1+\mathbf{q}_1} - \epsilon_{\mathbf{k}_1} - \hbar\omega_{\mathbf{q}_1}) \\ &\quad + \frac{i\pi}{\hbar} g_{\mathbf{q}_1} \sum_{\mathbf{k}} \left[\langle a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_2} \rangle \langle a_{\mathbf{k}+\mathbf{q}_1}^\dagger a_{\mathbf{k}} \rangle - \langle a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}} \rangle \langle a_{\mathbf{k}+\mathbf{q}_1}^\dagger a_{\mathbf{k}_2} \rangle \right] \\ &\quad \times \delta(\epsilon_{\mathbf{k}+\mathbf{q}_1} - \epsilon_{\mathbf{k}} - \hbar\omega_{\mathbf{q}_1}). \end{aligned} \quad (\text{F.18})$$

The equations of motion of the other three-operator expectation values in Eq. (F.14) yields similar equations. After a Fourier transform and a gradient expansion, we find for the influence of the phonons of on the dynamics of the electronic Wigner function

$$\partial_t f_{\mathbf{k}}(\mathbf{r}, t) \Big|_{\text{el-ph}} = \sum_{\mathbf{q}} [\Gamma_{\mathbf{k}+\mathbf{q}, \mathbf{k}}^{\text{in}}(\mathbf{r}, t)(1 - f_{\mathbf{k}}(\mathbf{r}, t)) - \Gamma_{\mathbf{k}, \mathbf{k}+\mathbf{q}}^{\text{out}}(\mathbf{r}, t)f_{\mathbf{k}}(\mathbf{r}, t)]. \quad (\text{F.19})$$

The electron-phonon scattering terms also depend on the occupation of the initial state of the scattering event, i.e., in the case of in-scattering, on the electron occupation terms $f_{\mathbf{k}}$, and in the case of out-scattering, on the hole occupation terms $(1 - f_{\mathbf{k}})$. The electron-phonon scattering rates are given by [19, 376, 398, 401]

$$\Gamma_{\mathbf{k}+\mathbf{q},\mathbf{k}}^{\text{in}}(\mathbf{r},t) = \frac{2\pi}{\hbar^2} \sum_{\pm} |g_{\mathbf{q}}|^2 f_{\mathbf{k}+\mathbf{q}}(\mathbf{r},t) \times \quad (\text{F.20a})$$

$$\times \left(\frac{1}{2} \pm \frac{1}{2} + n_{\mathbf{q}}(\mathbf{r},t) \right) \delta(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}} \pm \hbar\omega_{\mathbf{q}}),$$

$$\Gamma_{\mathbf{k},\mathbf{k}+\mathbf{q}}^{\text{out}}(\mathbf{r},t) = \frac{2\pi}{\hbar^2} \sum_{\pm} |g_{\mathbf{q}}|^2 ((1 - f_{\mathbf{k}+\mathbf{q}}(\mathbf{r},t)) \times \quad (\text{F.20b})$$

$$\times \left(\frac{1}{2} \pm \frac{1}{2} + n_{\mathbf{q}}(\mathbf{r},t) \right) \delta(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}} \mp \hbar\omega_{\mathbf{q}}).$$

In the limit $\mathbf{q} = 0$, this spatio-temporal Boltzmann equation reproduces the well-known Boltzmann equations for electronic densities.

G. Hartree Mean-Field on Microscopic Level

The calculations, we present in the following, were performed by Jonas Grumm as part of our joint research. I only reproduce them here to enable an understanding of Sec. 4.6 as these calculations can not yet be found elsewhere.

As we have shown in Sec. 4.6, the linearized equation of motion of the current density can be brought in the form

$$(\partial_t^2 + \gamma \partial_t) \mathbf{j}^1(\mathbf{r}, t) = 3\varepsilon_{\text{out}} \varepsilon_0 \omega_0^2 \dot{\mathbf{E}}_{\text{ext}}(\mathbf{r}, t) - \varepsilon_0 \omega_p^2 \nabla_{\mathbf{r}} \dot{\phi}^H(\mathbf{r}, t) \quad (\text{G.1})$$

with the definition of the Hartree potential

$$\phi^H(\mathbf{r}, t) = -\frac{1}{eV} \int d\mathbf{r}' V(\mathbf{r} - \mathbf{r}') \sum_{\mathbf{k}'} f_{\mathbf{k}'}(\mathbf{r}', t) . \quad (\text{G.2})$$

As required in Eq. (G.1), the time derivative of the spatial gradient of the Hartree potential can be given by

$$\nabla_{\mathbf{r}} \dot{\phi}^H(\mathbf{r}, t) = -\frac{1}{eV} \nabla_{\mathbf{r}} \int d\mathbf{r}' V(\mathbf{r} - \mathbf{r}') \sum_{\mathbf{k}'} \dot{f}_{\mathbf{k}'}(\mathbf{r}', t) . \quad (\text{G.3})$$

To find a solution of this equation, we substitute the free equation of motion for the first derivative of the electronic Wigner function. With this, we obtain

$$\begin{aligned} \nabla_{\mathbf{r}} \dot{\phi}^H(\mathbf{r}, t) &= \frac{1}{eV} \nabla_{\mathbf{r}} \int d\mathbf{r}' V(\mathbf{r} - \mathbf{r}') \sum_{\mathbf{k}'} \mathbf{v}_{\mathbf{k}'}' \cdot \nabla_{\mathbf{r}'} f_{\mathbf{k}'}(\mathbf{r}', t) \\ &= -\frac{1}{eV} \nabla_{\mathbf{r}} \otimes \int d\mathbf{r}' (\nabla_{\mathbf{r}'} V(\mathbf{r} - \mathbf{r}')) \sum_{\mathbf{k}'} \mathbf{v}_{\mathbf{k}'}' f_{\mathbf{k}'}(\mathbf{r}', t) \\ &= \frac{1}{e^2} \nabla_{\mathbf{r}} \otimes \int d\mathbf{r}' (\nabla_{\mathbf{r}'} V(\mathbf{r} - \mathbf{r}')) \mathbf{j}(\mathbf{r}', t) \\ &= \frac{1}{e^2} \left(\nabla_{\mathbf{r}} \otimes \int d\mathbf{r}' (\nabla_{\mathbf{r}'} V(\mathbf{r} - \mathbf{r}')) \right) \cdot \mathbf{j}^1(\mathbf{r}, t) \end{aligned} \quad (\text{G.4})$$

The 0th order of $\mathbf{j}$ vanishes for reasons of symmetry.

G.1. Hartree Mean-Field with Spherical Boundary Conditions

To evaluate the impact of Hartree potential on the equation of motion, we explicitly evaluate the term in parentheses in Eq. (G.4). Therefore, we employ the Coulomb potential

in a sphere [351],

$$V(\mathbf{r}, \mathbf{r}') = \frac{e^2}{4\pi\epsilon_0} \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \frac{4\pi}{2\ell+1} \left[\frac{1}{\epsilon_{\infty}} \frac{r_{<}^{\ell}}{r_{>}^{\ell+1}} + \left(\frac{2\ell+1}{\ell\epsilon_{\infty} + (\ell+1)\epsilon_{\text{out}}} - \frac{1}{\epsilon_{\infty}} \right) \frac{(rr')^{\ell}}{a^{2\ell+1}} \right] \times Y_{\ell m}(\Omega) Y_{\ell m}^*(\Omega'), \quad (\text{G.5})$$

where

$$W_{\ell}^0(r, r') = \frac{r_{<}^{\ell}}{r_{>}^{\ell+1}}, \quad (\text{G.6})$$

with $r_{<} = \min(r, r')$ and $r_{>} = \max(r, r')$ and the radius of the sphere a . We begin to evaluate the monopole order with $\ell = 0$. In this order, the spherical harmonic $Y_{00} = \sqrt{\frac{1}{4\pi}}$ is constant and the potential is given by

$$V(\mathbf{r}, \mathbf{r}') = \frac{e^2}{4\pi\epsilon_0} \left[\frac{1}{\epsilon_{\infty}} \frac{1}{r_{>}} + \left(\frac{1}{\epsilon_{\text{out}}} - \frac{1}{\epsilon_{\infty}} \right) \frac{1}{a} \right]. \quad (\text{G.7})$$

From this, one can find that the monopole contribution to the integro-differential expression vanishes,

$$\nabla_{\mathbf{r}} \otimes \int d\mathbf{r}' (\nabla_{\mathbf{r}'} V(\mathbf{r}, \mathbf{r}'))|_{\ell=0} = 0, \quad (\text{G.8})$$

for both cases $r_{>} = r$ and $r_{>} = r'$. In dipole order $\ell = 1$, the expression can be written a

$$\frac{e^2}{4\pi\epsilon_0} \nabla_{\mathbf{r}} \otimes \int d\mathbf{r}' (\nabla_{\mathbf{r}'} \sum_{m=-1}^1 \frac{4\pi}{3} \left[\frac{1}{\epsilon_{\infty}} \frac{r_{<}}{r_{>}^2} + \left(\frac{3}{2\epsilon_{\text{out}} + \epsilon_{\infty}} - \frac{1}{\epsilon_{\infty}} \right) \frac{rr'}{a^3} \right] Y_{1m}(\Omega) Y_{1m}^*(\Omega')) . \quad (\text{G.9})$$

For the subsequent calculation, we need to distinguish between two cases: (i) $r' < r$ and (ii) $r' > r$. We set the integral limits for the radial contribution accordingly, i.e., $r' \in [0, r]$ for case (i) and $r' \in [r, a]$ for case (ii). We use the abbreviation

$$\frac{3}{2\epsilon_{\text{out}} + \epsilon_{\infty}} - \frac{1}{\epsilon_{\infty}} = \frac{2}{\epsilon_{\infty}} \frac{\epsilon_{\infty} - \epsilon_{\text{out}}}{\epsilon_{\infty} + 2\epsilon_{\text{out}}} = \frac{2}{\epsilon_{\infty}} \tilde{\epsilon}. \quad (\text{G.10})$$

$\ell = 1, m = 0$

In this case, the spherical harmonics can be evaluated to be

$$Y_{1,0}(\theta, \varphi) = \sqrt{\frac{3}{4\pi}} \cos(\theta). \quad (\text{G.11})$$

(i): $r' < r$

We start by calculating the gradient in spherical coordinates,

$$\begin{aligned}
 & \nabla_{\mathbf{r}'} \frac{e^2}{4\pi\epsilon_0\epsilon_\infty} \left(\frac{r'}{r^2} + 2\tilde{\epsilon} \frac{rr'}{a^3} \right) \cos(\theta) \cos(\theta') \\
 &= \frac{e^2}{4\pi\epsilon_0\epsilon_\infty} \cos(\theta) \left(\mathbf{e}_{\mathbf{r}'} \partial_{r'} + \frac{1}{r'} \mathbf{e}_{\theta'} \partial_{\theta'} + \frac{1}{r' \sin(\theta')} \mathbf{e}_{\varphi'} \partial_{\varphi'} \right) \cos(\theta') \left(\frac{r'}{r^2} + 2\tilde{\epsilon} \frac{rr'}{a^3} \right) \\
 &= \frac{e^2}{4\pi\epsilon_0\epsilon_\infty} \cos(\theta) \left[\cos(\theta') \mathbf{e}_{\mathbf{r}'} - \sin(\theta') \mathbf{e}_{\theta'} \right] \left(\frac{1}{r^2} + 2\tilde{\epsilon} \frac{r}{a^3} \right) \\
 &= \frac{e^2}{4\pi\epsilon_0\epsilon_\infty} \cos(\theta) \left(\frac{1}{r^2} + 2\tilde{\epsilon} \frac{r}{a^3} \right) \mathbf{e}_{\mathbf{z}}. \tag{G.12}
 \end{aligned}$$

The next step is the calculation of the integral over the sphere,

$$\begin{aligned}
 & \int d\mathbf{r}' \frac{e^2}{4\pi\epsilon_0\epsilon_\infty} \cos(\theta) \left(\frac{1}{r^2} + 2\tilde{\epsilon} \frac{r}{a^3} \right) \mathbf{e}_{\mathbf{z}} \\
 &= \frac{e^2}{4\pi\epsilon_0\epsilon_\infty} \cos(\theta) \left(\frac{1}{r^2} + 2\tilde{\epsilon} \frac{r}{a^3} \right) \mathbf{e}_{\mathbf{z}} \int_0^r dr' r'^2 \int_0^\pi d\theta' \sin(\theta') \int_0^{2\pi} d\varphi' \\
 &= \frac{e^2}{4\pi\epsilon_0\epsilon_\infty} \cos(\theta) \left(\frac{1}{r^2} + 2\tilde{\epsilon} \frac{r}{a^3} \right) \mathbf{e}_{\mathbf{z}} \frac{4\pi r^3}{3} \\
 &= \frac{e^2}{3\epsilon_0\epsilon_\infty} \cos(\theta) \left(r + 2\tilde{\epsilon} \frac{r^4}{a^3} \right) \mathbf{e}_{\mathbf{z}}. \tag{G.13}
 \end{aligned}$$

Finally, the gradient over $\mathbf{r}$ as a dyadic product reads

$$\begin{aligned}
 & \nabla_{\mathbf{r}} \otimes \frac{e^2}{3\epsilon_0\epsilon_\infty} \cos(\theta) \left(r + 2\tilde{\epsilon} \frac{r^4}{a^3} \right) \mathbf{e}_{\mathbf{z}} \\
 &= \frac{e^2}{3\epsilon_0\epsilon_\infty} \left(\mathbf{e}_{\mathbf{r}} \partial_r + \frac{1}{r} \mathbf{e}_{\theta} \partial_\theta + \frac{1}{r \sin(\theta)} \mathbf{e}_{\varphi} \partial_\varphi \right) \otimes \mathbf{e}_{\mathbf{z}} \cos(\theta) \left(r + 2\tilde{\epsilon} \frac{r^4}{a^3} \right) \\
 &= \frac{e^2}{3\epsilon_0\epsilon_\infty} \left(\begin{array}{c} \left(\sin(\theta) \cos(\theta) (1 + 8\tilde{\epsilon} \frac{r^3}{a^3}) - \sin(\theta) \cos(\theta) (1 + 2\tilde{\epsilon} \frac{r^3}{a^3}) \right) \cos(\varphi) \\ \left(\sin(\theta) \cos(\theta) (1 + 8\tilde{\epsilon} \frac{r^3}{a^3}) - \sin(\theta) \cos(\theta) (1 + 2\tilde{\epsilon} \frac{r^3}{a^3}) \right) \sin(\varphi) \\ \cos^2(\theta) (1 + 8\tilde{\epsilon} \frac{r^3}{a^3}) + \sin^2(\theta) (1 + 2\tilde{\epsilon} \frac{r^3}{a^3}) \end{array} \right) \otimes \mathbf{e}_{\mathbf{z}} \\
 &= \frac{e^2}{3\epsilon_0\epsilon_\infty} \begin{pmatrix} 0 & 0 & 6\tilde{\epsilon} \frac{r^3}{a^3} \sin(\theta) \cos(\theta) \cos(\varphi) \\ 0 & 0 & 6\tilde{\epsilon} \frac{r^3}{a^3} \sin(\theta) \cos(\theta) \sin(\varphi) \\ 0 & 0 & 1 + 2\tilde{\epsilon} \frac{r^3}{a^3} + 6\tilde{\epsilon} \frac{r^3}{a^3} \cos^2(\theta) \end{pmatrix} \tag{G.14}
 \end{aligned}$$

(ii): $r' > r$

In this case, the same steps have to be taken as before, we start by differentiating,

$$\begin{aligned}
 & \nabla_{\mathbf{r}'} \frac{e^2}{4\pi\epsilon_0\epsilon_\infty} \left(\frac{r}{r'^2} + 2\tilde{\epsilon} \frac{rr'}{a^3} \right) \cos(\theta) \cos(\theta') \\
 &= \frac{e^2}{4\pi\epsilon_0\epsilon_\infty} \left(\mathbf{e}_{\mathbf{r}'} \partial_{r'} + \frac{1}{r'} \mathbf{e}_{\theta'} \partial_{\theta'} + \frac{1}{r' \sin(\theta')} \mathbf{e}_{\varphi'} \partial_{\varphi'} \right) \left(\frac{r}{r'^2} + 2\tilde{\epsilon} \frac{rr'}{a^3} \right) \cos(\theta) \cos(\theta') \\
 &= \frac{e^2}{4\pi\epsilon_0\epsilon_\infty} \cos(\theta) \left[\left(2\tilde{\epsilon} \frac{r}{a^3} + \frac{r}{r'^3} \right) \mathbf{e}_{\mathbf{z}} - 3 \frac{r}{r'^3} \cos(\theta') \mathbf{e}_{\mathbf{r}'} \right], \tag{G.15}
 \end{aligned}$$

which is again followed by an integration,

$$\begin{aligned}
 & \int d\mathbf{r}' \frac{e^2}{4\pi\epsilon_0\epsilon_\infty} \cos(\theta) \left[\left(2\tilde{\epsilon} \frac{r}{a^3} + \frac{r}{r'^3} \right) \mathbf{e}_z - 3 \frac{r}{r'^3} \cos(\theta') \mathbf{e}_{\mathbf{r}'} \right] \\
 &= \frac{e^2}{4\pi\epsilon_0\epsilon_\infty} \cos(\theta) \int_r^a dr' r'^2 \int_0^\pi d\theta' \sin(\theta') \int_0^{2\pi} d\varphi' \left[\left(2\tilde{\epsilon} \frac{r}{a^3} + \frac{r}{r'^3} \right) \mathbf{e}_z - 3 \frac{r}{r'^3} \cos(\theta') \mathbf{e}_{\mathbf{r}'} \right] \\
 &= \frac{e^2}{4\pi\epsilon_0\epsilon_\infty} \cos(\theta) \left[\left(\frac{8\pi}{3} \tilde{\epsilon} \frac{r(a^3 - r^3)}{a^3} + 4\pi r \int_r^a dr' \frac{1}{r'} \right) \mathbf{e}_z \right. \\
 &\quad \left. - 3r \int_r^a dr' \frac{1}{r'} \int_0^\pi d\theta' \sin(\theta') \cos(\theta') \int_0^{2\pi} d\varphi' \mathbf{e}_{\mathbf{r}'} \right] \tag{G.16}
 \end{aligned}$$

Here, we use

$$\int_r^a dr' \frac{1}{r'} = \log(a) - \log(r) = \frac{1}{3} \log\left(\frac{a^3}{r^3}\right). \tag{G.17}$$

Further with the full integral:

$$\begin{aligned}
 &= \frac{e^2}{4\pi\epsilon_0\epsilon_\infty} \cos(\theta) \left[\frac{8\pi}{3} \tilde{\epsilon} \left(r - \frac{r^4}{a^3} \right) \mathbf{e}_z + \frac{4\pi}{3} r \log\left(\frac{a^3}{r^3}\right) \mathbf{e}_z - \frac{4\pi}{3} r \log\left(\frac{a^3}{r^3}\right) \mathbf{e}_z \right] \\
 &= \frac{2e^2}{3\epsilon_0\epsilon_\infty} \cos(\theta) \tilde{\epsilon} \left(r - \frac{r^4}{a^3} \right) \mathbf{e}_z \tag{G.18}
 \end{aligned}$$

Gradient over $\mathbf{r}$ as dyadic product:

$$\begin{aligned}
 & \nabla_{\mathbf{r}} \otimes \frac{2e^2}{3\epsilon_0\epsilon_\infty} \cos(\theta) \tilde{\epsilon} \left(r - \frac{r^4}{a^3} \right) \mathbf{e}_z \\
 &= \frac{2e^2}{3\epsilon_0\epsilon_\infty} \left(\mathbf{e}_r \partial_r + \frac{1}{r} \mathbf{e}_\theta \partial_\theta + \frac{1}{r \sin(\theta)} \mathbf{e}_\varphi \partial_\varphi \right) \otimes \mathbf{e}_z \cos(\theta) \tilde{\epsilon} \left(r - \frac{r^4}{a^3} \right) \\
 &= \frac{2e^2}{3\epsilon_0\epsilon_\infty} \tilde{\epsilon} \begin{pmatrix} \left(\sin(\theta) \cos(\theta) \left(1 - 4 \frac{r^3}{a^3} \right) - \sin(\theta) \cos(\theta) \left(1 - \frac{r^3}{a^3} \right) \right) \cos(\varphi) \\ \left(\sin(\theta) \cos(\theta) \left(1 - 4 \frac{r^3}{a^3} \right) - \sin(\theta) \cos(\theta) \left(1 - \frac{r^3}{a^3} \right) \right) \sin(\varphi) \\ \cos^2(\theta) \left(1 - 4 \frac{r^3}{a^3} \right) + \sin^2(\theta) \left(1 - \frac{r^3}{a^3} \right) \end{pmatrix} \otimes \mathbf{e}_z \\
 &= \frac{2e^2}{3\epsilon_0\epsilon_\infty} \tilde{\epsilon} \begin{pmatrix} 0 & 0 & -6 \frac{r^3}{a^3} \sin(\theta) \cos(\theta) \cos(\varphi) \\ 0 & 0 & -6 \frac{r^3}{a^3} \sin(\theta) \cos(\theta) \sin(\varphi) \\ 0 & 0 & 2 - 2 \frac{r^3}{a^3} - 6 \frac{r^3}{a^3} \cos^2(\theta) \end{pmatrix} \tag{G.19}
 \end{aligned}$$

Finally, we can add our result from (i) and (ii) and obtain

$$\begin{aligned}
 & \nabla_{\mathbf{r}} \otimes \int d\mathbf{r}' (\nabla_{\mathbf{r}'} V(\mathbf{r}, \mathbf{r}'))|_{\ell=1, m=0} = \text{(i)} + \text{(ii)} \\
 &= \frac{e^2}{3\epsilon_0\epsilon_\infty} \left[\tilde{\epsilon} \begin{pmatrix} 0 & 0 & 6 \frac{r^3}{a^3} \sin(\theta) \cos(\theta) \cos(\varphi) - 6 \frac{r^3}{a^3} \sin(\theta) \cos(\theta) \cos(\varphi) \\ 0 & 0 & 6 \frac{r^3}{a^3} \sin(\theta) \cos(\theta) \sin(\varphi) - 6 \frac{r^3}{a^3} \sin(\theta) \cos(\theta) \sin(\varphi) \\ 0 & 0 & 2 + 2 \frac{r^3}{a^3} - 2 \frac{r^3}{a^3} + 6 \frac{r^3}{a^3} \cos^2(\theta) - 6 \frac{r^3}{a^3} \cos^2(\theta) \end{pmatrix} + \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \right] \\
 &= \frac{e^2}{3\epsilon_0\epsilon_\infty} (2\tilde{\epsilon} + 1) \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \frac{e^2}{\epsilon_0} \frac{1}{2\epsilon_{\text{out}} + \epsilon_\infty} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{G.20}
 \end{aligned}$$

To no surprise, we find that the factor $\frac{1}{2\epsilon_{\text{out}} + \epsilon_\infty}$ agrees with the one in the macroscopic approach. In the following, we will investigate the other dipole contributions $m = \pm 1$ and discover the remaining diagonal components.

$\ell = 1, m \pm 1$

The spherical harmonics is given by

$$Y_{1,\pm 1}(\theta, \varphi) = \mp \sqrt{\frac{3}{8\pi}} \sin(\theta) e^{\pm i\varphi}. \quad (\text{G.21})$$

We again distinguish the individual cases:

(i): $r' < r$

We start by calculating the gradient in spherical coordinates,

$$\begin{aligned} \nabla_{\mathbf{r}'} \frac{e^2}{8\pi\epsilon_0\epsilon_\infty} \left(\frac{r'}{r^2} + 2\tilde{\epsilon} \frac{rr'}{a^3} \right) \sin(\theta) \sin(\theta') e^{\pm i\varphi} e^{\mp i\varphi'} \\ = \frac{e^2}{8\pi\epsilon_0\epsilon_\infty} \sin(\theta) e^{\pm i\varphi} \left(\mathbf{e}_{\mathbf{r}'} \partial_{r'} + \frac{1}{r'} \mathbf{e}_{\theta'} \partial_{\theta'} + \frac{1}{r' \sin(\theta')} \mathbf{e}_{\varphi'} \partial_{\varphi'} \right) \sin(\theta') e^{\mp i\varphi'} \left(\frac{r'}{r^2} + 2\tilde{\epsilon} \frac{rr'}{a^3} \right) \\ = \frac{e^2}{8\pi\epsilon_0\epsilon_\infty} \sin(\theta) e^{\pm i\varphi} \left[\sin(\theta') \mathbf{e}_{\mathbf{r}'} + \cos(\theta') \mathbf{e}_{\theta'} \mp i \mathbf{e}_{\varphi'} \right] \left(\frac{1}{r^2} + 2\tilde{\epsilon} \frac{r}{a^3} \right) e^{\mp i\varphi'} \\ = \frac{e^2}{8\pi\epsilon_0\epsilon_\infty} \sin(\theta) e^{\pm i\varphi} \left(\frac{1}{r^2} + 2\tilde{\epsilon} \frac{r}{a^3} \right) \begin{pmatrix} \cos(\varphi') \pm i \sin(\varphi') \\ \sin(\varphi') \mp i \cos(\varphi') \\ 0 \end{pmatrix} e^{\mp i\varphi'} \\ = \frac{e^2}{8\pi\epsilon_0\epsilon_\infty} \sin(\theta) e^{\pm i\varphi} \left(\frac{1}{r^2} + 2\tilde{\epsilon} \frac{r}{a^3} \right) \begin{pmatrix} 1 \\ \mp i \\ 0 \end{pmatrix}. \end{aligned} \quad (\text{G.22})$$

The next step is the calculation of the integral over the sphere,

$$\begin{aligned} \int d\mathbf{r}' \frac{e^2}{8\pi\epsilon_0\epsilon_\infty} \sin(\theta) e^{\pm i\varphi} \left(\frac{1}{r^2} + 2\tilde{\epsilon} \frac{r}{a^3} \right) \begin{pmatrix} 1 \\ \mp i \\ 0 \end{pmatrix} \\ = \frac{e^2}{8\pi\epsilon_0\epsilon_\infty} \sin(\theta) e^{\pm i\varphi} \left(\frac{1}{r^2} + 2\tilde{\epsilon} \frac{r}{a^3} \right) \begin{pmatrix} 1 \\ \mp i \\ 0 \end{pmatrix} \int_0^r dr' r'^2 \int_0^\pi d\theta' \sin(\theta') \int_0^{2\pi} d\varphi' \\ = \frac{e^2}{6\epsilon_0\epsilon_\infty} \sin(\theta) e^{\pm i\varphi} \left(r + 2\tilde{\epsilon} \frac{r^4}{a^3} \right) \begin{pmatrix} 1 \\ \mp i \\ 0 \end{pmatrix}. \end{aligned} \quad (\text{G.23})$$

Finally, the gradient over $\mathbf{r}$ as dyadic product

$$\begin{aligned} \nabla_{\mathbf{r}} \otimes \frac{e^2}{6\epsilon_0\epsilon_\infty} \sin(\theta) e^{\pm i\varphi} \left(r + 2\tilde{\epsilon} \frac{r^4}{a^3} \right) \begin{pmatrix} 1 \\ \mp i \\ 0 \end{pmatrix} \\ = \frac{e^2}{6\epsilon_0\epsilon_\infty} e^{\pm i\varphi} \begin{pmatrix} (\sin^2(\theta)(1 + 8\tilde{\epsilon} \frac{r^3}{a^3}) + \cos^2(\theta)(1 + 2\tilde{\epsilon} \frac{r^3}{a^3})) \cos(\varphi) \mp i \sin(\varphi)(1 + 2\tilde{\epsilon} \frac{r^3}{a^3}) \\ (\sin^2(\theta)(1 + 8\tilde{\epsilon} \frac{r^3}{a^3}) + \cos^2(\theta)(1 + 2\tilde{\epsilon} \frac{r^3}{a^3})) \sin(\varphi) \pm i \cos(\varphi)(1 + 2\tilde{\epsilon} \frac{r^3}{a^3}) \\ \cos(\theta) \sin(\theta)(1 + 8\tilde{\epsilon} \frac{r^3}{a^3}) - \sin(\theta) \cos(\theta)(1 + 2\tilde{\epsilon} \frac{r^3}{a^3}) \end{pmatrix} \otimes \begin{pmatrix} 1 \\ \mp i \\ 0 \end{pmatrix} \\ = \frac{e^2}{\epsilon_0\epsilon_\infty} \tilde{\epsilon} \frac{r^3}{a^3} \sin(\theta) e^{\pm i\varphi} \begin{pmatrix} \mathbf{e}_{\mathbf{r}} & \mp i \mathbf{e}_{\mathbf{r}} & \mathbf{0} \end{pmatrix} + \frac{e^2}{6\epsilon_0\epsilon_\infty} (1 + 2\tilde{\epsilon} \frac{r^3}{a^3}) \begin{pmatrix} 1 & \mp i & 0 \\ \pm i & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \end{aligned} \quad (\text{G.24})$$

(ii): $r' > r$

Now we have to do the same calculation for case (ii).

$$\begin{aligned}
 & \nabla_{\mathbf{r}'} \frac{e^2}{8\pi\epsilon_0\epsilon_\infty} \left(\frac{r}{r'^2} + 2\tilde{\epsilon} \frac{rr'}{a^3} \right) \sin(\theta) \sin(\theta') e^{\pm i\varphi} e^{\mp i\varphi'} \\
 &= \frac{e^2}{8\pi\epsilon_0\epsilon_\infty} \sin(\theta) e^{\pm i\varphi} \left(\mathbf{e}_{\mathbf{r}'} \partial_{r'} + \frac{1}{r'} \mathbf{e}_{\theta'} \partial_{\theta'} + \frac{1}{r' \sin(\theta')} \mathbf{e}_{\varphi'} \partial_{\varphi'} \right) \left(\frac{r}{r'^2} + 2\tilde{\epsilon} \frac{rr'}{a^3} \right) \sin(\theta') e^{\mp i\varphi'} \\
 &= \frac{e^2}{8\pi\epsilon_0\epsilon_\infty} \sin(\theta) e^{\pm i\varphi} \left[-3 \frac{r \sin(\theta')}{r'^3} e^{\mp i\varphi'} \mathbf{e}_{\mathbf{r}'} + \left(\frac{r}{r'^3} + 2\tilde{\epsilon} \frac{r}{a^3} \right) \begin{pmatrix} 1 \\ \mp i \\ 0 \end{pmatrix} \right] \quad (\text{G.25})
 \end{aligned}$$

Integrate:

$$\begin{aligned}
 & \int d\mathbf{r}' \frac{e^2}{8\pi\epsilon_0\epsilon_\infty} \sin(\theta) e^{\pm i\varphi} \left[-3 \frac{r \sin(\theta')}{r'^3} e^{\mp i\varphi'} \mathbf{e}_{\mathbf{r}'} + \left(\frac{r}{r'^3} + 2\tilde{\epsilon} \frac{r}{a^3} \right) \begin{pmatrix} 1 \\ \mp i \\ 0 \end{pmatrix} \right] \\
 &= \frac{e^2}{8\pi\epsilon_0\epsilon_\infty} \sin(\theta) e^{\pm i\varphi} \left[-3r \int_r^a dr' \frac{1}{r'} \int_0^\pi d\theta' \sin^2(\theta') \int_0^{2\pi} d\varphi' e^{\mp i\varphi'} \mathbf{e}_{\mathbf{r}'} \right. \\
 &\quad \left. + \left(4\pi r \int_r^a dr' \frac{1}{r'} + \frac{8\pi}{3} \tilde{\epsilon} \frac{r}{a^3} (a^3 - r^3) \right) \begin{pmatrix} 1 \\ \mp i \\ 0 \end{pmatrix} \right] \\
 &= \frac{e^2}{8\pi\epsilon_0\epsilon_\infty} \sin(\theta) e^{\pm i\varphi} \left[-r \log\left(\frac{a^3}{r^3}\right) \underbrace{\int_0^\pi d\theta' \sin^3(\theta')}_{=\frac{4}{3}} \begin{pmatrix} \pi \\ \mp i\pi \\ 0 \end{pmatrix} + \frac{4\pi}{3} r \log\left(\frac{a^3}{r^3}\right) \begin{pmatrix} 1 \\ \mp i \\ 0 \end{pmatrix} \right. \\
 &\quad \left. + \frac{8\pi}{3} \tilde{\epsilon} \left(r - \frac{r^4}{a^3} \right) \begin{pmatrix} 1 \\ \mp i \\ 0 \end{pmatrix} \right] \\
 &= \frac{e^2}{3\epsilon_0\epsilon_\infty} \tilde{\epsilon} \sin(\theta) e^{\pm i\varphi} \left(r - \frac{r^4}{a^3} \right) \begin{pmatrix} 1 \\ \mp i \\ 0 \end{pmatrix} \quad (\text{G.26})
 \end{aligned}$$

Gradient over $\mathbf{r}$ as dyadic product:

$$\begin{aligned}
 & \nabla_{\mathbf{r}} \otimes \frac{e^2}{3\epsilon_0\epsilon_\infty} \tilde{\epsilon} \sin(\theta) e^{\pm i\varphi} \left(r - \frac{r^4}{a^3} \right) \begin{pmatrix} 1 \\ \mp i \\ 0 \end{pmatrix} \\
 &= \frac{e^2}{3\epsilon_0\epsilon_\infty} \tilde{\epsilon} \left(\mathbf{e}_{\mathbf{r}} \partial_r + \frac{1}{r} \mathbf{e}_\theta \partial_\theta + \frac{1}{r \sin(\theta)} \mathbf{e}_\varphi \partial_\varphi \right) \otimes \begin{pmatrix} 1 \\ \mp i \\ 0 \end{pmatrix} \sin(\theta) e^{\pm i\varphi} \left(r - \frac{r^4}{a^3} \right) \\
 &= \frac{e^2}{3\epsilon_0\epsilon_\infty} \tilde{\epsilon} e^{\pm i\varphi} \left[\left(1 - \frac{r^3}{a^3} \right) e^{\mp i\varphi} \begin{pmatrix} 1 \\ \pm i \\ 0 \end{pmatrix} - 3 \frac{r^3}{a^3} \sin(\theta) \mathbf{e}_{\mathbf{r}} \right] \otimes \begin{pmatrix} 1 \\ \mp i \\ 0 \end{pmatrix} \\
 &= \frac{e^2}{\epsilon_0\epsilon_\infty} \tilde{\epsilon} \frac{r^3}{a^3} \sin(\theta) e^{\pm i\varphi} \begin{pmatrix} \mathbf{e}_{\mathbf{r}} & \mp i \mathbf{e}_{\mathbf{r}} & \mathbf{0} \end{pmatrix} + \frac{e^2}{3\epsilon_0\epsilon_\infty} \tilde{\epsilon} \left(1 - \frac{r^3}{a^3} \right) \begin{pmatrix} 1 & \mp i & 0 \\ \pm i & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (\text{G.27})
 \end{aligned}$$

Finally we can add our result from (i) and (ii) and get

$$\begin{aligned}
 \nabla_{\mathbf{r}} \otimes \int d\mathbf{r}' (\nabla_{\mathbf{r}'} V(\mathbf{r}, \mathbf{r}'))|_{l=1, m=\pm 1} &= \text{(i)} + \text{(ii)} \\
 &= (\mathbf{e}_{\mathbf{r}} \quad \mp i \mathbf{e}_{\mathbf{r}} \quad \mathbf{0}) \frac{e^2}{\varepsilon_0 \varepsilon_{\infty}} \tilde{\varepsilon} \frac{r^3}{a^3} \sin(\theta) e^{\pm i \varphi} (1 - 1) \\
 &+ \begin{pmatrix} 1 & \mp i & 0 \\ \pm i & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \frac{e^2}{3 \varepsilon_0 \varepsilon_{\infty}} \left(\tilde{\varepsilon} \left(1 - \frac{r^3}{a^3} \right) + \frac{1}{2} \left(1 + 2 \tilde{\varepsilon} \frac{r^3}{a^3} \right) \right) \\
 &= \frac{1}{2} \frac{e^2}{3 \varepsilon_0 \varepsilon_{\infty}} (1 + 2 \tilde{\varepsilon}) \begin{pmatrix} 1 & \mp i & 0 \\ \pm i & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} = \frac{1}{2} \frac{e^2}{\varepsilon_0} \frac{1}{2 \varepsilon_{\text{out}} + \varepsilon_{\infty}} \begin{pmatrix} 1 & \mp i & 0 \\ \pm i & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (\text{G.28})
 \end{aligned}$$

Now we can add all contributions of dipole and monopole order and obtain

$$\begin{aligned}
 \nabla_{\mathbf{r}} \otimes \int d\mathbf{r}' (\nabla_{\mathbf{r}'} V(\mathbf{r}, \mathbf{r}'))|_{\ell=0; \ell=1} &= \frac{e^2}{4\pi \varepsilon_0} \sum_{\ell=0}^1 \sum_{m=-\ell}^{\ell} \frac{4\pi}{2\ell+1} \nabla_{\mathbf{r}} \otimes \int d\mathbf{r}' \nabla_{\mathbf{r}'} \left[\frac{1}{\varepsilon_{\infty}} W_{\ell}^0(r, r') \right. \\
 &\quad \left. + \left(\frac{2\ell+1}{\ell \varepsilon_{\infty} + (\ell+1) \varepsilon_{\text{out}}} - \frac{1}{\varepsilon_{\infty}} \right) \frac{(rr')^{\ell}}{a^{2\ell+1}} \right] Y_{\ell m}(\Omega) Y_{\ell m}^*(\Omega') \\
 &= 0 + \frac{e^2}{\varepsilon_0} \frac{1}{2 \varepsilon_{\text{out}} + \varepsilon_{\infty}} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \frac{1}{2} \frac{e^2}{\varepsilon_0} \frac{1}{\varepsilon_{\infty} + 2 \varepsilon_{\text{out}}} \begin{pmatrix} 1 & +i & 0 \\ -i & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \\
 &\quad + \frac{1}{2} \frac{e^2}{\varepsilon_0} \frac{1}{\varepsilon_{\infty} + 2 \varepsilon_{\text{out}}} \begin{pmatrix} 1 & -i & 0 \\ +i & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \\
 &= \frac{e^2}{\varepsilon_0} \frac{1}{\varepsilon_{\infty} + 2 \varepsilon_{\text{out}}} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \frac{e^2}{\varepsilon_0} \frac{1}{\varepsilon_{\infty} + 2 \varepsilon_{\text{out}}} \mathbb{1}. \quad (\text{G.29})
 \end{aligned}$$

G.2. Implication on Equations of Motion

From the previous calculation, we identified

$$(\partial_t^2 + \gamma \partial_t + \omega_p^2 \frac{\varepsilon_0}{\varepsilon^2} (\nabla_{\mathbf{r}} \otimes \int d\mathbf{r}' (\nabla_{\mathbf{r}'} V(\mathbf{r} - \mathbf{r}')))) \cdot \mathbf{j}^1(\mathbf{r}, t) = 3 \varepsilon_{\text{out}} \varepsilon_0 \omega_0^2 \dot{\mathbf{E}}_{\text{ext}}(\mathbf{r}, t). \quad (\text{G.30})$$

Using the result from the evaluation of the integro-differential expression, we obtain

$$(\partial_t^2 + \gamma \partial_t + \frac{\omega_p^2}{2 \varepsilon_{\text{out}} + \varepsilon_{\infty}} \mathbb{1}) \cdot \mathbf{j}^1(\mathbf{r}, t) = 3 \varepsilon_{\text{out}} \varepsilon_0 \omega_0^2 \dot{\mathbf{E}}_{\text{ext}}(\mathbf{r}, t), \quad (\text{G.31})$$

$$(\partial_t^2 + \gamma \partial_t + \omega_0^2) \mathbf{j}^1(\mathbf{r}, t) = 3 \varepsilon_{\text{out}} \varepsilon_0 \omega_0^2 \dot{\mathbf{E}}_{\text{ext}}(\mathbf{r}, t). \quad (\text{G.32})$$

This equation is the same that one would obtain from a description using our self-consistent method from Sec. 2.4.4 or for example, the Fröhlich condition for the plasmon resonance. To obtain this, we evaluated the Hartree potential, originating from Coulomb

interaction within the sphere in dipole approximation. Accordingly, we presented a way how the geometrical resonance, usually obtained from macroscopic calculations, can be introduced in the microscopic calculations.

H. Finite-Difference Time-Domain (FDTD) Method

H.1. Freely Propagating Maxwell's equation

For free propagation, the Maxwell equations in components read

$$\frac{\partial D_x}{\partial t} = c \left(\frac{\partial H_z}{\partial y} - \frac{\partial H_y}{\partial z} \right), \quad \frac{\partial H_x}{\partial t} = c \left(\frac{\partial E_y}{\partial z} - \frac{\partial E_z}{\partial y} \right), \quad (\text{H.1})$$

$$\frac{\partial D_y}{\partial t} = c \left(\frac{\partial H_x}{\partial z} - \frac{\partial H_z}{\partial x} \right), \quad \frac{\partial H_y}{\partial t} = c \left(\frac{\partial E_z}{\partial x} - \frac{\partial E_x}{\partial z} \right), \quad (\text{H.2})$$

$$\frac{\partial D_z}{\partial t} = c \left(\frac{\partial H_y}{\partial x} - \frac{\partial H_x}{\partial y} \right), \quad \frac{\partial H_z}{\partial t} = c \left(\frac{\partial E_x}{\partial y} - \frac{\partial E_y}{\partial x} \right) \quad (\text{H.3})$$

Mapping onto the Yee cells, these can be written as

$$D_x^{n+1/2}(i + \frac{1}{2}, j, k) = D_x^{n-1/2}(i + \frac{1}{2}, j, k) \quad (\text{H.4})$$

$$+ 0.5 \left[H_z^n \left(i + \frac{1}{2}, j + \frac{1}{2}, k \right) - H_z^n \left(i + \frac{1}{2}, j - \frac{1}{2}, k \right) \right. \\ \left. - H_y^n \left(i + \frac{1}{2}, j, k + \frac{1}{2} \right) + H_y^n \left(i + \frac{1}{2}, j, k - \frac{1}{2} \right) \right]$$

$$D_y^{n+1/2}(i, j + \frac{1}{2}, k) = D_y^{n-1/2}(i, j + \frac{1}{2}, k) \quad (\text{H.5})$$

$$+ 0.5 \left[H_x^n \left(i, j + \frac{1}{2}, k + \frac{1}{2} \right) - H_x^n \left(i, j + \frac{1}{2}, k - \frac{1}{2} \right) \right. \\ \left. - H_z^n \left(i + \frac{1}{2}, j + \frac{1}{2}, k \right) + H_z^n \left(i - \frac{1}{2}, j + \frac{1}{2}, k \right) \right]$$

$$D_z^{n+1/2}(i, j, k + \frac{1}{2}) = D_z^{n-1/2}(i, j, k + \frac{1}{2}) \quad (\text{H.6})$$

$$+ 0.5 \left[H_y^n \left(i + \frac{1}{2}, j, k + \frac{1}{2} \right) - H_y^n \left(i - \frac{1}{2}, j, k + \frac{1}{2} \right) \right. \\ \left. - H_x^n \left(i, j + \frac{1}{2}, k + \frac{1}{2} \right) + H_x^n \left(i, j - \frac{1}{2}, k + \frac{1}{2} \right) \right]$$

and

$$H_x^{n+1}\left(i, j + \frac{1}{2}, k + \frac{1}{2}\right) = H_x^n\left(i, j + \frac{1}{2}, k + \frac{1}{2}\right) \quad (\text{H.7})$$

$$+ 0.5 \left[E_y^{n+1/2}\left(i, j + \frac{1}{2}, k + 1\right) - E_y^{n+1/2}\left(i, j + \frac{1}{2}, k\right) \right. \\ \left. - E_z^{n+1/2}\left(i, j + 1, k + \frac{1}{2}\right) + E_z^{n+1/2}\left(i, j, k + \frac{1}{2}\right) \right]$$

$$H_y^{n+1}\left(i + \frac{1}{2}, j, k + \frac{1}{2}\right) = H_y^n\left(i + \frac{1}{2}, j, k + \frac{1}{2}\right) \quad (\text{H.8})$$

$$+ 0.5 \left[E_z^{n+1/2}\left(i + 1, j, k + \frac{1}{2}\right) - E_z^{n+1/2}\left(i, j, k + \frac{1}{2}\right) \right. \\ \left. - E_x^{n+1/2}\left(i + \frac{1}{2}, j, k + 1\right) + E_x^{n+1/2}\left(i + \frac{1}{2}, j, k\right) \right]$$

$$H_z^{n+1}\left(i + \frac{1}{2}, j + \frac{1}{2}, k\right) = H_z^n\left(i + \frac{1}{2}, j + \frac{1}{2}, k\right) \quad (\text{H.9})$$

$$+ 0.5 \left[E_x^{n+1/2}\left(i + \frac{1}{2}, j + 1, k\right) - E_x^{n+1/2}\left(i + \frac{1}{2}, j, k\right) \right. \\ \left. - E_y^{n+1/2}\left(i + 1, j + \frac{1}{2}, k\right) + E_y^{n+1/2}\left(i, j + \frac{1}{2}, k\right) \right]$$

which reads for the simple 3D case as

```

1   dx[i,j,k] += 0.5 * ( hz[i,j,k] - hz[i,j-1,k] - hy[i,j,k] + hy[i,j,k
-1] )
2   dy[i,j,k] += 0.5 * ( hx[i,j,k] - hx[i,j,k-1] - hz[i,j,k] + hz[i-1,j,k
] )
3   dz[i,j,k] += 0.5 * ( hy[i,j,k] - hy[i-1,j,k] - hx[i,j,k] + hx[i,j-1,k
] )
4   hx[i,j,k] += 0.5 * ( ey[i,j,k+1] - ey[i,j,k] - ez[i,j+1,k] + ez[i,j,k
] )
5   hy[i,j,k] += 0.5 * ( ez[i+1,j,k] - ez[i,j,k] - ex[i,j,k+1] + ex[i,j,k
] )
6   hz[i,j,k] += 0.5 * ( ex[i,j+1,k] - ex[i,j,k] - ey[i+1,j,k] + ey[i,j,k
] )

```

H.2. Perfectly Matched Layers

Including the PML description, we have to update the curl equation. These updated equations are provided here

H.2.1. Analytical Expressions

The equations for the perfectly matched layers can be given as

$$\text{curl_H}^n = H_z^n\left(i + \frac{1}{2}, j + \frac{1}{2}, k\right) - H_z^n\left(i + \frac{1}{2}, j - \frac{1}{2}, k\right) \quad (\text{H.10}) \\ - H_y^n\left(i + \frac{1}{2}, j, k + \frac{1}{2}\right) + H_y^n\left(i + \frac{1}{2}, j, k - \frac{1}{2}\right)$$

$$I_{Dx}^{n+1/2}\left(i + \frac{1}{2}, j, k\right) = \text{curl}_- H^n + I_{Dx}^{n-1/2}\left(i + \frac{1}{2}, j, k\right) \quad (\text{H.11})$$

$$\begin{aligned} Dx^{n+1/2}\left(i + \frac{1}{2}, j, k\right) &= gj3(j)gk3(k)Dx^{n-1/2}\left(i + \frac{1}{2}, j, k\right) \\ &\quad + gj2(j)gk2(k)\left[0.5\text{curl}_- H^n + gi1\left(i + \frac{1}{2}\right)I_{Dx}^{n+1/2}\left(i + \frac{1}{2}, j, k\right)\right] \end{aligned} \quad (\text{H.12})$$

$$\begin{aligned} \text{curl}_- H^n &= H_x^n\left(i, j + \frac{1}{2}, k + \frac{1}{2}\right) - H_x^n\left(i, j + \frac{1}{2}, k - \frac{1}{2}\right) \\ &\quad - H_z^n\left(i + \frac{1}{2}, j + \frac{1}{2}, k\right) + H_z^n\left(i - \frac{1}{2}, j + \frac{1}{2}, k\right) \end{aligned} \quad (\text{H.13})$$

$$I_{Dy}^{n+1/2}\left(i, j + \frac{1}{2}, k\right) = \text{curl}_- H^n + I_{Dy}^{n-1/2}\left(i, j + \frac{1}{2}, k\right) \quad (\text{H.14})$$

$$\begin{aligned} Dy^{n+1/2}\left(i, j + \frac{1}{2}, k\right) &= gi3(i)gk3(k)Dy^{n-1/2}\left(i, j + \frac{1}{2}, k\right) \\ &\quad + gi2(i)gk2(k)\left[0.5\text{curl}_- H^n + gj1\left(j + \frac{1}{2}\right)I_{Dy}^{n+1/2}\left(i, j + \frac{1}{2}, k\right)\right] \end{aligned} \quad (\text{H.15})$$

$$\begin{aligned} \text{curl}_- H^n &= H_y^n\left(i + \frac{1}{2}, j, k + \frac{1}{2}\right) - H_y^n\left(i - \frac{1}{2}, j, k + \frac{1}{2}\right) \\ &\quad - H_x^n\left(i, j + \frac{1}{2}, k + \frac{1}{2}\right) + H_x^n\left(i, j - \frac{1}{2}, k + \frac{1}{2}\right) \end{aligned} \quad (\text{H.16})$$

$$I_{Dz}^{n+1/2}\left(i, j, k + \frac{1}{2}\right) = \text{curl}_- H^n + I_{Dz}^{n-1/2}\left(i, j, k + \frac{1}{2}\right) \quad (\text{H.17})$$

$$\begin{aligned} Dz^{n+1/2}\left(i, j, k + \frac{1}{2}\right) &= gi3(i)gj3(j)Dz^{n-1/2}\left(i, j, k + \frac{1}{2}\right) \\ &\quad + gi2(i)gj2(j)\left[0.5\text{curl}_- H^n + gk1\left(k + \frac{1}{2}\right)I_{Dz}^{n+1/2}\left(i, j, k + \frac{1}{2}\right)\right] \end{aligned} \quad (\text{H.18})$$

$$\begin{aligned} \text{curl}_- E^{n+1/2} &= E_y^{n+1/2}\left(i, j + \frac{1}{2}, k + 1\right) - E_y^{n+1/2}\left(i, j + \frac{1}{2}, k\right) \\ &\quad - E_z^{n+1/2}\left(i, j + 1, k + \frac{1}{2}\right) + E_z^{n+1/2}\left(i, j, k + \frac{1}{2}\right) \end{aligned} \quad (\text{H.19})$$

$$I_{Hx}^{n+1}\left(i, j + \frac{1}{2}, k + \frac{1}{2}\right) = \text{curl}_- E^{n+1/2} + I_{Hx}^n\left(i, j + \frac{1}{2}, k + \frac{1}{2}\right) \quad (\text{H.20})$$

$$\begin{aligned} H_x^{n+1}\left(i, j + \frac{1}{2}, k + \frac{1}{2}\right) &= fj3\left(j + \frac{1}{2}\right)fk3\left(k + \frac{1}{2}\right)H_x^n\left(i, j + \frac{1}{2}, k + \frac{1}{2}\right) \\ &\quad + fj2\left(j + \frac{1}{2}\right)fk2\left(k + \frac{1}{2}\right) \\ &\quad \times \left[0.5\text{curl}_- E^{n+1/2} + fi1(i)I_{Hx}^{n+1}\left(i, j + \frac{1}{2}, k + \frac{1}{2}\right)\right] \end{aligned} \quad (\text{H.21})$$

$$\begin{aligned} \text{curl}_- E^{n+1/2} = E_z^{n+1/2} \left(i+1, j, k + \frac{1}{2} \right) - E_z^{n+1/2} \left(i, j, k + \frac{1}{2} \right) \\ - E_x^{n+1/2} \left(i + \frac{1}{2}, j, k+1 \right) + E_x^{n+1/2} \left(i + \frac{1}{2}, j, k \right) \end{aligned} \quad (\text{H.22})$$

$$I_{Hy}^{n+1} \left(i + \frac{1}{2}, j, k + \frac{1}{2} \right) = \text{curl}_- E^{n+1/2} + I_{Hy}^n \left(i + \frac{1}{2}, j, k + \frac{1}{2} \right) \quad (\text{H.23})$$

$$\begin{aligned} H_y^{n+1} \left(i + \frac{1}{2}, j, k + \frac{1}{2} \right) = fi3 \left(i + \frac{1}{2} \right) fk3 \left(k + \frac{1}{2} \right) H_y^n \left(i + \frac{1}{2}, j, k + \frac{1}{2} \right) \\ + fi2 \left(i + \frac{1}{2} \right) fk2 \left(k + \frac{1}{2} \right) \\ \times \left[0.5 \text{curl}_- E^{n+1/2} + fj1(j) I_{Hy}^{n+1} \left(i + \frac{1}{2}, j, k + \frac{1}{2} \right) \right] \end{aligned} \quad (\text{H.24})$$

$$\begin{aligned} \text{curl}_- E^{n+1/2} = E_x^{n+1/2} \left(i + \frac{1}{2}, j+1, k \right) - E_x^{n+1/2} \left(i + \frac{1}{2}, j, k \right) \\ - E_y^{n+1/2} \left(i+1, j + \frac{1}{2}, k \right) + E_y^{n+1/2} \left(i, j + \frac{1}{2}, k \right) \end{aligned} \quad (\text{H.25})$$

$$I_{Hz}^{n+1} \left(i + \frac{1}{2}, j + \frac{1}{2}, k \right) = \text{curl}_- E^{n+1/2} + I_{Hz}^n \left(i + \frac{1}{2}, j + \frac{1}{2}, k \right) \quad (\text{H.26})$$

$$\begin{aligned} H_z^{n+1} \left(i + \frac{1}{2}, j + \frac{1}{2}, k \right) = fi3 \left(i + \frac{1}{2} \right) fj3 \left(j + \frac{1}{2} \right) H_z^n \left(i + \frac{1}{2}, j + \frac{1}{2}, k \right) \\ + fi2 \left(i + \frac{1}{2} \right) fj2 \left(j + \frac{1}{2} \right) \\ \times \left[0.5 \text{curl}_- E^{n+1/2} + fk1(k) I_{Hz}^{n+1} \left(i + \frac{1}{2}, j + \frac{1}{2}, k \right) \right] \end{aligned} \quad (\text{H.27})$$

with the respective definition of the factors,

$$fi1(i) = \text{xn}(i), \quad fj1(j) = \text{xn}(j), \quad fk1(k) = \text{xn}(k), \quad (\text{H.28a})$$

$$gi1(i) = \text{xn}(i), \quad gj1(j) = \text{xn}(j), \quad gk1(k) = \text{xn}(k), \quad (\text{H.28b})$$

$$fi2(i) = \frac{1}{1 + \text{xn}(i)}, \quad fj2(j) = \frac{1}{1 + \text{xn}(j)}, \quad fk2(k) = \frac{1}{1 + \text{xn}(k)}, \quad (\text{H.28c})$$

$$gi2(i) = \frac{1}{1 + \text{xn}(i)}, \quad gj2(j) = \frac{1}{1 + \text{xn}(j)}, \quad gk2(k) = \frac{1}{1 + \text{xn}(k)}, \quad (\text{H.28d})$$

$$fi3(i) = \frac{1 - \text{xn}(i)}{1 + \text{xn}(i)}, \quad fj3(j) = \frac{1 - \text{xn}(j)}{1 + \text{xn}(j)}, \quad fk3(k) = \frac{1 - \text{xn}(k)}{1 + \text{xn}(k)}, \quad (\text{H.28e})$$

$$gi3(i) = \frac{1 - \text{xn}(i)}{1 + \text{xn}(i)}, \quad gj3(j) = \frac{1 - \text{xn}(j)}{1 + \text{xn}(j)}, \quad gk3(k) = \frac{1 - \text{xn}(k)}{1 + \text{xn}(k)}, \quad (\text{H.28f})$$

where

$$\text{xn}(i) = 0.33 \left(\frac{i}{\text{npml}} \right)^{1/3} \quad (\text{H.29})$$

H.3. Update Equations for Perfectly Matched Layers

H.3.1. D-Fields

```

1 @numba.jit(nopython=True)
2 def calculate_dx_field(dims,dx,h,idx,pml):
3     for i in range(0,dims.x):
4         for j in range (1,dims.y):
5             for k in range (1,dims.z):
6                 curlH = h.z[i,j,k] - h.z[i,j-1,k] - \
7                     h.y[i,j,k] + h.y[i,j,k-1]
8                 idx[i,j,k] = curlH + idx[i,j,k]
9                 dx[i,j,k] = pml.gj3[j]*pml.gk3[k]*dx[i,j,k] + \
10                    pml.gj2[j]*pml.gk2[k]*(0.5 * curlH + pml.gi1[
11 i]*idx[i,j,k])
12     return dx,idx
13
14 @numba.jit(nopython=True)
15 def calculate_dy_field(dims,dy,h,idy,pml):
16     for i in range(1,dims.x):
17         for j in range (0,dims.y):
18             for k in range (1,dims.z):
19                 curlH = h.x[i,j,k] - h.x[i,j,k-1] - \
20                     h.z[i,j,k] + h.z[i-1,j,k]
21                 idy[i,j,k] = curlH + idy[i,j,k]
22                 dy[i,j,k] = pml.gi3[i]*pml.gk3[k]*dy[i,j,k] + \
23                    pml.gi2[i]*pml.gk2[k]*(0.5 * curlH + pml.gj1[
24 j]*idy[i,j,k])
25     return dy,idy
26
27 @numba.jit(nopython=True)
28 def calculate_dz_field(dims,dz,h,idz,pml):
29     for i in range(1,dims.x):
30         for j in range (1,dims.y):
31             for k in range (0,dims.z):
32                 curlH = h.y[i,j,k] - h.y[i-1,j,k] - \
33                     h.x[i,j,k] + h.x[i,j-1,k]
34                 idz[i,j,k] = curlH + idz[i,j,k]
35                 dz[i,j,k] = pml.gi3[i]*pml.gj3[j]*dz[i,j,k] + \
36                    pml.gi2[i]*pml.gj2[j]*(0.5 * curlH + pml.gk1[
37 k]*idz[i,j,k])
38     return dz,idz

```

H.3.2. E-Fields

```

1 @numba.jit(nopython=True)
2 def calculate_e_fields(dims,e,d,ga,p):
3     for i in range(0,dims.x):
4         for j in range (0,dims.y):
5             for k in range (0,dims.z):
6                 e.x[i,j,k]=ga.x[i,j,k]*(d.x[i,j,k]-p.x[i,j,k])
7                 e.y[i,j,k]=ga.y[i,j,k]*(d.y[i,j,k]-p.y[i,j,k])
8                 e.z[i,j,k]=ga.z[i,j,k]*(d.z[i,j,k]-p.z[i,j,k])
9     return e

```

H.3.3. H-Fields

```

1 @numba.jit(nopython=True)
2 def calculate_hx_field(dims,hx,e,ihx,pml):
3     for i in range(0,dims.x):
4         for j in range (0,dims.y-1):
5             for k in range (0,dims.z-1):
6                 curlE = (e.y[i,j,k+1] - e.y[i,j,k] -\
7                     e.z[i,j+1,k] + e.z[i,j,k])
8                 ihx[i,j,k] = curlE + ihx[i,j,k]
9                 hx[i,j,k] = pml.fj3[j]*pml.fk3[k]*hx[i,j,k] +\
10                     pml.fj2[j]*pml.fk2[k]*(0.5 * curlE + pml.fi1[
11 i]* ihx[i,j,k])
12     return hx,ihx
13
14 @numba.jit(nopython=True)
15 def calculate_hy_field(dims,hy,e,ihy,pml):
16     for i in range(0,dims.x-1):
17         for j in range (0,dims.y):
18             for k in range (0,dims.z-1):
19                 curlE = (e.z[i+1,j,k] - e.z[i,j,k] -\
20                     e.x[i,j,k+1] + e.x[i,j,k])
21                 ihy[i,j,k] = curlE + ihy[i,j,k]
22                 hy[i,j,k] = pml.fi3[i]*pml.fk3[k]*hy[i,j,k] +\
23                     pml.fi2[i]*pml.fk2[k]*(0.5 * curlE + pml.fj1[
24 j]* ihy[i,j,k])
25     return hy,ihy
26
27 @numba.jit(nopython=True)
28 def calculate_hz_field(dims,hz,e,ihz,pml):
29     for i in range(0,dims.x-1):
30         for j in range (0,dims.y-1):
31             for k in range (0,dims.z):
32                 curlE = (e.x[i,j+1,k] - e.x[i,j,k] -\
33                     e.y[i+1,j,k] + e.y[i,j,k])
34                 ihz[i,j,k] = curlE + ihz[i,j,k]
35                 hz[i,j,k] = pml.fi3[i]*pml.fj3[j]*hz[i,j,k] +\
36                     pml.fi2[i]*pml.fj2[j]*(0.5 * curlE + pml.fk1[
37 k]* ihz[i,j,k])
38     return hz,ihz

```

H.4. Update Equations for Periodic Boundary conditions

H.4.1. D-Fields

```

1 def calculate_dx_field_PBC(dims,dx,h,idx,pml):
2     for i in range(0,dims.x):
3         for j in range (1,dims.y):
4             curlH = h.z[i,j,0] - h.z[i,j-1,0] - \
5                 h.y[i,j,0] + h.y[i,j,-1]
6             idx[i,j,0] = curlH + idx[i,j,0]
7             dx[i,j,0] = pml.gj3[j]*pml.gk3[0]*dx[i,j,0] +\
8                 pml.gj2[j]*pml.gk2[0]*(0.5 * curlH + pml.gi1[i]*
9 idx[i,j,0])
10    return dx,idx

```

```

11 @numba.jit(nopython=True)
12 def calculate_dy_field_PBC(dims,dy,h,idy,pml):
13     for j in range (0,dims.y):
14         for i in range(1,dims.x):
15             curlH = h.x[i,j,0] - h.x[i,j,-1] - \
16                 h.z[i,j,0] + h.z[i-1,j,0]
17             idy[i,j,0] = curlH + idy[i,j,0]
18             dy[i,j,0] = pml.gi3[i]*pml.gk3[0]*dy[i,j,0] + \
19                 pml.gi2[i]*pml.gk2[0]*(0.5 * curlH + pml.gj1[
20 j]*idy[i,j,0])
21         for k in range (1,dims.z):
22             curlH = h.x[0,j,k] - h.x[0,j,k-1] - \
23                 h.z[0,j,k] + h.z[-1,j,k]
24             idy[0,j,k] = curlH + idy[0,j,k]
25             dy[0,j,k] = pml.gi3[0]*pml.gk3[k]*dy[0,j,k] + \
26                 pml.gi2[0]*pml.gk2[k]*(0.5 * curlH + pml.gj1[j]*
27 idy[0,j,k])
28     return dy,idy
29
30 @numba.jit(nopython=True)
31 def calculate_dz_field_PBC(dims,dz,h,idz,pml):
32     for j in range (1,dims.y):
33         for k in range (0,dims.z):
34             curlH = h.y[0,j,k] - h.y[-1,j,k] - \
35                 h.x[0,j,k] + h.x[0,j-1,k]
36             idz[0,j,k] = curlH + idz[0,j,k]
37             dz[0,j,k] = pml.gi3[0]*pml.gj3[j]*dz[0,j,k] + \
38                 pml.gi2[0]*pml.gj2[j]*(0.5 * curlH + pml.gk1[k]*
39 idz[0,j,k])
40     return dz,idz

```

H.4.2. H-Fields

```

1 @numba.jit(nopython=True)
2 def calculate_hx_field_PBC(dims,hx,e,ihx,pml):
3     for i in range(0,dims.x):
4         for j in range (0,dims.y-1):
5             curlE = (e.y[i,j,0] - e.y[i,j,dims.z-1] - \
6                 e.z[i,j+1,dims.z-1] + e.z[i,j,dims.z-1])
7             ihx[i,j,dims.z-1] = curlE + ihx[i,j,dims.z-1]
8             hx[i,j,dims.z-1] = pml.fj3[j]*pml.fk3[dims.z-1]*hx[i,j,
9 dims.z-1] + \
10                 pml.fj2[j]*pml.fk2[dims.z-1]*(0.5 * curlE
11 + pml.fi1[i]* ihx[i,j,dims.z-1])
12     return hx,ihx
13
14 @numba.jit(nopython=True)
15 def calculate_hy_field_PBC(dims,hy,e,ihy,pml):
16     for j in range (0,dims.y):
17         for i in range(0,dims.x-1):
18             curlE = (e.z[i+1,j,dims.z-1] - e.z[i,j,dims.z-1] - \
19                 e.x[i,j,0] + e.x[i,j,dims.z-1])
20             ihy[i,j,dims.z-1] = curlE + ihy[i,j,dims.z-1]
21             hy[i,j,dims.z-1] = pml.fi3[i]*pml.fk3[dims.z-1]*hy[i,j,dims.z
22 -1] + \
23                 pml.fi2[i]*pml.fk2[dims.z-1]*(0.5 * curlE + pml.
24 fj1[j]* ihy[i,j,dims.z-1])
25     for k in range (0,dims.z-1):

```

```

21         curlE = (e.z[0,j,k] - e.z[dims.x-1,j,k] -\
22                 e.x[dims.x-1,j,k+1] + e.x[dims.x-1,j,k])
23         ihy[dims.x-1,j,k] = curlE + ihy[dims.x-1,j,k]
24         hy[dims.x-1,j,k] = pml.fi3[dims.x-1]*pml.fk3[k]*hy[dims.x-1,j
,k] +\
25         pml.fi2[dims.x-1]*pml.fk2[k]*(0.5 * curlE + pml.
fj1[j]* ihy[dims.x-1,j,k])
26     return hy,ihy
27 @numba.jit(nopython=True)
28 def calculate_hz_field_PBC(dims,hz,e,ihz,pml):
29     for j in range(0,dims.y-1):
30         for k in range(0,dims.z):
31             curlE = (e.x[dims.x-1,j+1,k] - e.x[dims.x-1,j,k] -\
32                     e.y[0,j,k] + e.y[dims.x-1,j,k])
33             ihz[dims.x-1,j,k] = curlE + ihz[dims.x-1,j,k]
34             hz[dims.x-1,j,k] = pml.fi3[dims.x-1]*pml.fj3[j]*hz[dims.x-1,j
,k] +\
35             pml.fi2[dims.x-1]*pml.fj2[j]*(0.5 * curlE + pml.
fk1[k]* ihz[dims.x-1,j,k])
36     return hz,ihz
    
```

H.5. Total Field-Scattered Field (TFSF)

The collected update equations for a plane wave travelling in y direction with E_z and H_x components are given by:

```

1 @numba.jit(nopython=True)
2 def calculate_dy_inc_TFSF(tfsf,dy,hx_inc):
3     '''Corrects the Dy field for TFSF BC'''
4     for i in range(tfsf.x_min,tfsf.x_max+1):
5         for j in range(tfsf.y_min,tfsf.y_max):
6             dy[i,j,tfsf.z_min]= dy[i,j,tfsf.z_min]-0.5*hx_inc[j]
7             dy[i,j,tfsf.z_max+1]= dy[i,j,tfsf.z_max+1]+0.5*hx_inc[j]
8     return dy
9
10
11 @numba.jit(nopython=True)
12 def calculate_dz_inc_TFSF(tfsf,dz,hx_inc):
13     '''Corrects the Dz field for TFSF BC'''
14     for i in range(tfsf.x_min,tfsf.x_max+1):
15         for k in range(tfsf.z_min,tfsf.z_max+1):
16             dz[i,tfsf.y_min,k]= dz[i,tfsf.y_min,k]+0.5*hx_inc[tfsf.y_min
-1]
17             dz[i,tfsf.y_max,k]= dz[i,tfsf.y_max,k]-0.5*hx_inc[tfsf.y_max]
18     return dz
19
20 @numba.jit(nopython=True)
21 def calculate_hx_inc_TFSF(tfsf,hx,ez_inc):
22     '''Corrects the Hx field for TFSF BC'''
23     for i in range(tfsf.x_min,tfsf.x_max+1):
24         for k in range(tfsf.z_min,tfsf.z_max+1):
25             hx[i,tfsf.y_min-1,k]= hx[i,tfsf.y_min-1,k]+0.5*ez_inc[tfsf.
y_min]
26             hx[i,tfsf.y_max,k]= hx[i,tfsf.y_max,k]-0.5*ez_inc[tfsf.y_max]
27     return hx
28
29 @numba.jit(nopython=True)
    
```

```

30 def calculate_hy_inc_TFSF(tfsf,hy,ez_inc):
31     '''Corrects the Hy field for TFSF BC'''
32     for j in range(tfsf.y_min,tfsf.y_max+1):
33         for k in range(tfsf.z_min,tfsf.z_max+1):
34             hy[tfsf.x_min-1,j,k]= hy[tfsf.x_min-1,j,k]-0.5*ez_inc[j]
35             hy[tfsf.x_max,j,k]= hy[tfsf.x_max,j,k]+0.5*ez_inc[j]
36     return hy

```

This changes of course for different directions of propagations. The TFSF region was chosen such that the magnetic fields are just outside the region, while the electric fields are just inside. The same thing will apply to polarization as an electric contribution.

H.6. Monitors

Here, we exemplarily provide the absorption monitor

```

1  @numba.jit(nopython=True)
2  def DFT_abs_update(e_abs_x_min,e_abs_x_max,h_abs_x_min,h_abs_x_max,
3                    e_abs_y_min,e_abs_y_max,h_abs_y_min,h_abs_y_max,
4                    e_abs_z_min,e_abs_z_max,h_abs_z_min,h_abs_z_max,
5                    e,h,abs,iwmax,omegaDFT,t):
6
7      for om in range(0,iwmax+1):
8          exponent = np.exp(-1j*omegaDFT[om]*t)
9          #xnormal
10         e_abs_x_min.y[om,:,:] += exponent*e.y[abs.x_min,:,:]
11         e_abs_x_min.z[om,:,:] += exponent*e.z[abs.x_min,:,:]
12         h_abs_x_min.y[om,:,:] += exponent*h.y[abs.x_min,:,:]
13         h_abs_x_min.z[om,:,:] += exponent*h.z[abs.x_min,:,:]
14
15         e_abs_x_max.y[om,:,:] += exponent*e.y[abs.x_max,:,:]
16         e_abs_x_max.z[om,:,:] += exponent*e.z[abs.x_max,:,:]
17         h_abs_x_max.y[om,:,:] += exponent*h.y[abs.x_max,:,:]
18         h_abs_x_max.z[om,:,:] += exponent*h.z[abs.x_max,:,:]
19
20         #ynormal
21         e_abs_y_min.x[om,:,:] += exponent*e.x[:,abs.y_min,:]
22         e_abs_y_min.z[om,:,:] += exponent*e.z[:,abs.y_min,:]
23         h_abs_y_min.x[om,:,:] += exponent*h.x[:,abs.y_min,:]
24         h_abs_y_min.z[om,:,:] += exponent*h.z[:,abs.y_min,:]
25
26         e_abs_y_max.x[om,:,:] += exponent*e.x[:,abs.y_max,:]
27         e_abs_y_max.z[om,:,:] += exponent*e.z[:,abs.y_max,:]
28         h_abs_y_max.x[om,:,:] += exponent*h.x[:,abs.y_max,:]
29         h_abs_y_max.z[om,:,:] += exponent*h.z[:,abs.y_max,:]
30
31         #znormal
32         e_abs_z_min.x[om,:,:] += exponent*e.x[:,abs.z_min]
33         e_abs_z_min.y[om,:,:] += exponent*e.y[:,abs.z_min]
34         h_abs_z_min.x[om,:,:] += exponent*h.x[:,abs.z_min]
35         h_abs_z_min.y[om,:,:] += exponent*h.y[:,abs.z_min]
36
37         e_abs_z_max.x[om,:,:] += exponent*e.x[:,abs.z_max]
38         e_abs_z_max.y[om,:,:] += exponent*e.y[:,abs.z_max]
39         h_abs_z_max.x[om,:,:] += exponent*h.x[:,abs.z_max]
40         h_abs_z_max.y[om,:,:] += exponent*h.y[:,abs.z_max]
41

```

```
42     return e_abs_x_min,e_abs_x_max,h_abs_x_min,h_abs_x_max,\
43           e_abs_y_min,e_abs_y_max,h_abs_y_min,h_abs_y_max,\
44           e_abs_z_min,e_abs_z_max,h_abs_z_min,h_abs_z_max
```

I. Radial Oscillations

In this chapter of the appendix, we provide some additional detail regarding the calculation performed in the main part.

I.1. Phenomenological Models

Over the past two decades, numerous experiments have observed nanoparticle oscillation, primarily in transient absorption [448–451, 458, 472, 474, 482, 488–490]. Some of these studies have proposed theoretical models to describe the onset of oscillation, particularly in Refs. [448, 451, 473, 474]. These descriptions share qualitative similarities, differing only in whether the initial temperature rise of the electron system is simulated or assumed to start from a specific initial electron temperature. However, as the rise in electron temperature resulting from excitation with femtosecond pulses is quasi-instantaneous on the timescale of the oscillation (picoseconds), all models can be considered quasi-equivalent. Here, we present a brief overview of common models

Hartland Approach

In Ref. [448], the standard oscillator equation is provided as follows:

$$\frac{d^2 R}{dt^2} + \frac{2}{\tau_d} \frac{dR}{dt} + \left(\frac{2\pi}{\Omega} \right)^2 \left[R - \left\{ R_0 + \frac{R_0 \alpha}{3} (T_l - 298) \right\} \right] = 0 \quad (\text{I.1})$$

However, this only includes the action of the lattice and disregards hot electron effects. To fix this, they include a hot electron pressure by writing,

$$\alpha = \frac{1}{B} \left(\gamma C_l + \frac{2}{3} C_e(T_e) \right) \quad (\text{I.2})$$

with the bulk modulus B , the (lattice) Grüneisen parameter γ and the electron heat capacity. According to their finding, this shifts the oscillation onset to earlier times.

Perner Approach

In Ref. [473], the oscillator equation is formulated as

$$\frac{d^2 \Delta x}{dt^2} + 2\rho \frac{d\Delta x}{dt} + \omega_0^2 \Delta x = \frac{A\sigma}{m}, \quad (\text{I.3})$$

where the driving terms σ are defined as

$$\sigma_{L,e} = -\gamma_{L,e} \int_{T_R}^{T_{L,e}} C_{L,e} dT_{L,e}. \quad (\text{I.4})$$

Here, $\gamma_{L,e}$ are the Grüneisen parameters and the $C_{L,e}$'s are the heat capacities of the lattice and the electrons, respectively. Assuming that the C_l is constant and $C_e = \xi T_e$ scales linearly, the expressions can be expressed as

$$\sigma_L = -\gamma_L C_L (T_L - T_R), \quad (\text{I.5})$$

$$\sigma_e = -\gamma_e \int_{T_R}^{T_e} \xi T_e dT_e = -\frac{\gamma_e \xi}{2} (T_e^2 - T_R^2). \quad (\text{I.6})$$

With this assumption, the full oscillator equation reads

$$\frac{d^2 \Delta x}{dt^2} + 2\rho \frac{d\Delta x}{dt} + \omega_0^2 \Delta x = -\frac{A}{m} \left(\gamma_L C_L (T_L - T_R) + \frac{\gamma_e \xi}{2} (T_e^2 - T_R^2) \right) \quad (\text{I.7})$$

where A is the surface area of the particle and m its mass.

Crut Approach

Compared to the previous approaches, the oscillator equation in Ref. [451] is given by

$$\frac{d^2 A_q}{dt^2} + 2\gamma_q \frac{dA_q}{dt} + |\omega_q|^2 A_q = F_q(t). \quad (\text{I.8})$$

The driving term $F_q(t)$ consists of an electronic and a lattice contribution,

$$F_q^e(t) = \omega_q^2 A_{q0}^e \exp\{-t/\tau_{e-L}\}, \quad (\text{I.9})$$

$$F_q^L(t) = \omega_q^2 A_{q0}^L (1 - \exp\{-t/\tau_{e-L}\}). \quad (\text{I.10})$$

Compared to the previous approaches, this definition assumed an instantaneous onset of one of the driving terms and does not simulate the respective oscillation onset. As such, it is only applicable for situations where the pulse is short compared to the oscillation period.

Voisin Approach

In Ref. [474], the oscillator equation is modeled very similar to the previous approach,

$$\frac{d^2 x}{dt^2} + \frac{2}{\tau_h} \frac{dx}{dt} + \omega_0^2 x = F_D + F_I, \quad (\text{I.11})$$

where they label the direct (D) and indirect (I) driving terms which they provide to be:

$$F_D = \omega_0^2 x_0^D \exp\{-t/\tau_{e-ph}\}, \quad (\text{I.12})$$

$$F_I = \omega_0^2 x_0^I (1 - \exp\{-t/\tau_{e-ph}\}). \quad (\text{I.13})$$

Hence, this description is mathematically equivalent to the one in Ref. [451]. However, a conceptual distinction is that they do not explicitly comment on the lattice or electron processes but mention that the direct process is happening on the timescale of the electron-lattice interaction while the other one is a more indirect process.

I.2. Microscopic Dynamics of Coherent Phonon Modes

In order to describe the dynamics of the radial oscillation process, we once again employ the framework of Heisenberg equations of motion. This process yields the first order equation for the phonon annihilation (creation) operators $b_{\mathbf{q}}^{(\dagger)}$,

$$i\hbar\partial_t b_{\mathbf{q}} = \hbar\omega_{\mathbf{q}} b_{\mathbf{q}} + \sum_{\mathbf{k}} g_{-\mathbf{q}} a_{\mathbf{k}-\mathbf{q}}^\dagger a_{\mathbf{k}} + 3 \sum_{\mathbf{q}'} \tilde{h}_{\mathbf{q},\mathbf{q}',\mathbf{q}-\mathbf{q}'} (b_{\mathbf{q}'} + b_{-\mathbf{q}'}^\dagger) (b_{\mathbf{q}-\mathbf{q}'} + b_{-\mathbf{q}+\mathbf{q}'}^\dagger) \quad (\text{I.14})$$

$$i\hbar\partial_t b_{-\mathbf{q}}^\dagger = -\hbar\omega_{-\mathbf{q}} b_{-\mathbf{q}}^\dagger - \sum_{\mathbf{k}} g_{-\mathbf{q}} a_{\mathbf{k}-\mathbf{q}}^\dagger a_{\mathbf{k}} - 3 \sum_{\mathbf{q}'} \tilde{h}_{\mathbf{q},\mathbf{q}',\mathbf{q}-\mathbf{q}'} (b_{\mathbf{q}'} + b_{-\mathbf{q}'}^\dagger) (b_{\mathbf{q}-\mathbf{q}'} + b_{-\mathbf{q}+\mathbf{q}'}^\dagger) \quad (\text{I.15})$$

As the first order equations do not close, we derive dynamical equations in second-order for the phonon annihilation (creation) operators $b_{\mathbf{q}}^{(\dagger)}$. This is done by substituting the first order equation into itself. These equations can then be combined to derive an equation for the coherent phonon mode operator $s_{\mathbf{q}}$,

$$\begin{aligned} (\partial_t^2 + \omega_{\mathbf{q}}^2) s_{\mathbf{q}} = & -\frac{\omega_{\mathbf{q}} g_{-\mathbf{q}}}{\hbar} \sum_{\mathbf{k}} \tilde{f}_{\mathbf{k}}(\mathbf{q}) - \frac{3\omega_{\mathbf{q}}}{\hbar} \sum_{\mathbf{q}'} \tilde{h}_{\mathbf{q},\mathbf{q}',\mathbf{q}-\mathbf{q}'} [2\tilde{n}_{\mathbf{q}'}^c(\mathbf{q}) + \delta_{\mathbf{q},0}] \\ & - \frac{3\omega_{\mathbf{q}}}{\hbar} \sum_{\mathbf{q}'} \tilde{h}_{\mathbf{q},\mathbf{q}',\mathbf{q}-\mathbf{q}'} [4s_{\mathbf{q}'} s_{\mathbf{q}-\mathbf{q}'} + \langle b_{\mathbf{q}'} b_{\mathbf{q}-\mathbf{q}'} \rangle^c + \langle b_{-\mathbf{q}'}^\dagger b_{-\mathbf{q}+\mathbf{q}'}^\dagger \rangle^c] \end{aligned} \quad (\text{I.16})$$

where $\tilde{f}_{\mathbf{k}}(\mathbf{q})$ is the Fourier transformation of the Wigner function $f_{\mathbf{k}}(\mathbf{r})$. In the derivation, we made the assumption of a symmetric phonon dispersion $\omega_{\mathbf{q}} = \omega_{-\mathbf{q}}$, which is valid for the three acoustic phonon branches found in gold and should also hold for optical phonons.

I.2.1. Coherent Phonon Damping

To evaluate the effect of the coherences in the last line in Eq. (I.16), we again follow the approach presented in Sec. 2.1.1 and derive an equation of motion for them, performing a formal integration and a Markov approximation to obtain a closed equation. In order to do so, we use the phonon-phonon Hamiltonian in Eq. (6.7) in normal ordering,

$$\begin{aligned} H_{\text{phph}} = & \sum_{345} h_{345} (b_3 b_4 b_5 + b_{-3}^\dagger b_{-4}^\dagger b_{-5}^\dagger) \\ & + \tilde{h}_{345} b_{-3}^\dagger b_4 b_5 + \tilde{h}_{345} b_{-5}^\dagger b_{-4}^\dagger b_3 + \tilde{h}_{345} (b_3 + b_{-3}^\dagger) \delta_{4,-5} \end{aligned} \quad (\text{I.17})$$

which is necessary to use the cluster expansion technique from Ref. [171]. For the ease of reading, we changed the notation so that momenta are expressed in terms of their indices. In Eq. (I.17), we used the definition $\tilde{h}_{123} = h_{123} + h_{213} + h_{231}$, and will use in the following, that phonon-phonon scattering is momentum conserving, $\tilde{h}_{\mathbf{q},\mathbf{q}',\mathbf{q}''} =$

$\hat{h}_{\mathbf{q}, \mathbf{q}', \mathbf{q}''} \delta_{\mathbf{q} + \mathbf{q}' + \mathbf{q}'', 0}$. Computing the commutators explicitly, we find

$$\begin{aligned} [b_1^\dagger b_2^\dagger, H_{\text{phph}}] = & \\ & - \sum_{i=1,2} \sum_{3,4} \left\{ \tilde{h}_{\bar{i}34} b_i^\dagger b_3 b_4 + (\tilde{h}_{3\bar{i}4} + \tilde{h}_{34\bar{i}}) b_i^\dagger b_{-3}^\dagger b_4 + \tilde{h}_{\bar{i}34} b_i^\dagger b_{-3}^\dagger b_{-4}^\dagger \right\} \\ & - \sum_3 \left\{ (\tilde{h}_{312} + \tilde{h}_{321}) b_{-3}^\dagger + (\tilde{h}_{132} + \tilde{h}_{123}) b_3 + \tilde{h}_{23-3} b_1^\dagger + \tilde{h}_{13-3} b_2^\dagger \right\}, \quad (\text{I.18}) \end{aligned}$$

and

$$\begin{aligned} [b_1 b_2, H_{\text{phph}}] = & \\ & - \sum_{i=1,2} \sum_{3,4} \left\{ \tilde{h}_{-\bar{i}34} b_{-3}^\dagger b_{-4}^\dagger b_i + (\tilde{h}_{3-\bar{i}4} + \tilde{h}_{34-\bar{i}}) b_{-4}^\dagger b_i b_3 + \tilde{h}_{-\bar{i}34} b_i b_3 b_4 \right\} \\ & - \sum_3 \left\{ (\tilde{h}_{3-1-2} + \tilde{h}_{3-2-1}) b_3 + (\tilde{h}_{-2-13} + \tilde{h}_{-23-1}) b_{-3}^\dagger + \tilde{h}_{-23-3} b_1^\dagger + \tilde{h}_{-13-3} b_2^\dagger \right\}. \quad (\text{I.19}) \end{aligned}$$

For the ease of notation, we incorporated the i sum, and used a similar definition as in Ch. 3 that $\bar{i}$ is always the complement to i . From these terms, which are already in normal order, we can perform a cluster expansion, as given in Sec. 2.1.1 and in Ref. [171, Eq. (15.43)],

$$\begin{aligned} \partial_t \langle b_1^\dagger b_2^\dagger \rangle_{\text{phph}} = & \quad (\text{I.20}) \\ & \frac{i}{\hbar} \sum_{i=1,2} \langle b_i^\dagger \rangle \left[\sum_3 \tilde{h}_{\bar{i}3-3} + \sum_4 \left[(\tilde{h}_{3\bar{i}4} + \tilde{h}_{34\bar{i}}) \langle b_{-3}^\dagger b_4 \rangle + \tilde{h}_{\bar{i}34} (\langle b_3 b_4 \rangle + \langle b_{-3}^\dagger b_{-4}^\dagger \rangle) \right] \right] \\ & + \sum_3 \frac{i}{\hbar} \langle b_{-3}^\dagger \rangle \left[(\tilde{h}_{312} + \tilde{h}_{321}) + \sum_{i=1,2} \sum_4 \left[(\tilde{h}_{3\bar{i}4} + \tilde{h}_{34\bar{i}}) \langle b_i^\dagger b_4 \rangle + (\tilde{h}_{\bar{i}34} + \tilde{h}_{\bar{i}43}) \langle b_i^\dagger b_{-4}^\dagger \rangle \right] \right] \\ & + \frac{i}{\hbar} \sum_3 \langle b_3 \rangle \left[(\tilde{h}_{132} + \tilde{h}_{123}) + \sum_{i=1,2} \sum_4 \left[(\tilde{h}_{\bar{i}34} + \tilde{h}_{\bar{i}43}) \langle b_i^\dagger b_4 \rangle + (\tilde{h}_{4\bar{i}3} + \tilde{h}_{43\bar{i}}) \langle b_i^\dagger b_{-4}^\dagger \rangle \right] \right] \end{aligned}$$

and

$$\begin{aligned}
 \partial_t \langle b_1 b_2 \rangle_{\text{phph}} = & \quad (I.21) \\
 & -\frac{i}{\hbar} \sum_{i=1,2} \langle b_i \rangle \left[\sum_3 \tilde{h}_{-i3-3} + \sum_4 \left[\left(\tilde{h}_{3-i4} + \tilde{h}_{34-i} \right) \langle b_{-4}^\dagger b_3 \rangle + \tilde{h}_{-i34} \left(\langle b_3 b_4 \rangle + \langle b_{-3}^\dagger b_{-4}^\dagger \rangle \right) \right] \right] \\
 & -\frac{i}{\hbar} \sum_3 \langle b_3 \rangle \left[\left(\tilde{h}_{3-1-2} + \tilde{h}_{3-2-1} \right) \right. \\
 & \quad \left. + \sum_{i=1,2} \sum_4 \left[\left(\tilde{h}_{3-i4} + \tilde{h}_{34-i} \right) \langle b_{-4}^\dagger b_i \rangle + \left(\tilde{h}_{-i34} + \tilde{h}_{-i43} \right) \langle b_i b_4 \rangle \right] \right] \\
 & -\frac{i}{\hbar} \sum_3 \langle b_{-3}^\dagger \rangle \left[\left(\tilde{h}_{-2-13} + \tilde{h}_{-23-1} \right) \right. \\
 & \quad \left. + \sum_{i=1,2} \sum_4 \left[\left(\tilde{h}_{-i34} + \tilde{h}_{-i43} \right) \langle b_{-4}^\dagger b_i \rangle + \left(\tilde{h}_{4-i3} + \tilde{h}_{43-i} \right) \langle b_i b_4 \rangle \right] \right]
 \end{aligned}$$

To derive an equation of motion for the purely correlated quantities, one has to derive an equation for the quantities

$$\langle b_1^\dagger b_2^\dagger \rangle^c = \langle b_1^\dagger b_2^\dagger \rangle - \langle b_1^\dagger \rangle \langle b_2^\dagger \rangle, \quad (I.22)$$

$$\partial_t \langle b_1^\dagger b_2^\dagger \rangle^c = \partial_t \langle b_1^\dagger b_2^\dagger \rangle - \left[\partial_t \langle b_1^\dagger \rangle \langle b_2^\dagger \rangle - \langle b_1^\dagger \rangle \left[\partial_t \langle b_2^\dagger \rangle \right] \right]. \quad (I.23)$$

From this definition, we find,

$$\begin{aligned}
 \partial_t \langle b_1^\dagger b_2^\dagger \rangle_{\text{phph}}^c = & \quad (I.24) \\
 & \sum_3 \frac{i}{\hbar} \langle b_{-3}^\dagger \rangle \left[\left(\tilde{h}_{312} + \tilde{h}_{321} \right) + \sum_{i=1,2} \sum_4 \left[\left(\tilde{h}_{3i4} + \tilde{h}_{34i} \right) \langle b_i^\dagger b_4 \rangle + \left(\tilde{h}_{i34} + \tilde{h}_{i43} \right) \langle b_i^\dagger b_{-4}^\dagger \rangle \right] \right] \\
 & + \frac{i}{\hbar} \sum_3 \langle b_3 \rangle \left[\left(\tilde{h}_{132} + \tilde{h}_{123} \right) + \sum_{i=1,2} \sum_4 \left[\left(\tilde{h}_{i34} + \tilde{h}_{i43} \right) \langle b_i^\dagger b_4 \rangle + \left(\tilde{h}_{4i3} + \tilde{h}_{43i} \right) \langle b_i^\dagger b_{-4}^\dagger \rangle \right] \right],
 \end{aligned}$$

and

$$\begin{aligned}
 \partial_t \langle b_1 b_2 \rangle_{\text{phph}}^c = & \quad (I.25) \\
 & -\frac{i}{\hbar} \sum_3 \langle b_3 \rangle \left[\left(\tilde{h}_{3-1-2} + \tilde{h}_{3-2-1} \right) \right. \\
 & \quad \left. + \sum_{i=1,2} \sum_4 \left[\left(\tilde{h}_{3-i4} + \tilde{h}_{34-i} \right) \langle b_{-4}^\dagger b_i \rangle + \left(\tilde{h}_{-i34} + \tilde{h}_{-i43} \right) \langle b_i b_4 \rangle \right] \right] \\
 & -\frac{i}{\hbar} \sum_3 \langle b_{-3}^\dagger \rangle \left[\left(\tilde{h}_{-2-13} + \tilde{h}_{-23-1} \right) \right. \\
 & \quad \left. + \sum_{i=1,2} \sum_4 \left[\left(\tilde{h}_{-i34} + \tilde{h}_{-i43} \right) \langle b_{-4}^\dagger b_i \rangle + \left(\tilde{h}_{4-i3} + \tilde{h}_{43-i} \right) \langle b_i b_4 \rangle \right] \right].
 \end{aligned}$$

Formal Integration

This equation will be solved using via formal integration and Markov approximation, cf. Sec. 2.1.1. Here, we assume that the scattering processes only occur with occupations, which allows introducing an additional Delta function. Furthermore, we abbreviated $H_{123} = \tilde{h}_{123} + \tilde{h}_{132}$, using that the scattering process is momentum conserving so that $H_{123} = \hat{H}_{123}\delta_{3,-1-2}$ and defined $\mathcal{H}_{1,2}$ which is the sum of all permutations of $\hat{H}_{1,2,-1-2}$. From this, we find

$$\langle b_1^\dagger b_2^\dagger \rangle^c = \frac{i\pi}{\hbar} \mathcal{H}_{1,2} \langle b_{1+2}^\dagger \rangle \left[1 + \langle b_1^\dagger b_1 \rangle + \langle b_2^\dagger b_2 \rangle \right] \delta(\omega_1 + \omega_2 - \omega_{1+2}) \quad (\text{I.26})$$

$$\langle b_1 b_2 \rangle^c = -\frac{i\pi}{\hbar} \mathcal{H}_{-1,-2} \langle b_{1+2} \rangle \left[1 + \langle b_1^\dagger b_1 \rangle + \langle b_2^\dagger b_2 \rangle \right] \delta(\omega_1 + \omega_2 - \omega_{1+2}) \quad (\text{I.27})$$

Using this identity in the equation of motion for the the coherent phonons, one finds the equations

$$\begin{aligned} \partial_t \langle b_{\mathbf{q}} \rangle = & -i\omega_{\mathbf{q}} \langle b_{\mathbf{q}} \rangle - \gamma_{\mathbf{q}} \langle b_{\mathbf{q}} \rangle - \frac{ig_{-\mathbf{q}}}{\hbar} \sum_{\mathbf{k}} \langle a_{\mathbf{k}-\mathbf{q}}^\dagger a_{\mathbf{k}} \rangle \\ & - \frac{i}{\hbar} \sum_{\mathbf{k}} \hat{h}_{-\mathbf{q},\mathbf{k},\mathbf{q}-\mathbf{k}} \left(2 \langle b_{-\mathbf{q}+\mathbf{k}}^\dagger b_{\mathbf{k}} \rangle^c + \delta_{\mathbf{q},0} \right), \end{aligned} \quad (\text{I.28})$$

$$\begin{aligned} \partial_t \langle b_{-\mathbf{q}}^\dagger \rangle = & i\omega_{-\mathbf{q}} \langle b_{-\mathbf{q}}^\dagger \rangle - \gamma_{-\mathbf{q}} \langle b_{-\mathbf{q}}^\dagger \rangle + \frac{ig_{-\mathbf{q}}}{\hbar} \sum_{\mathbf{k}} \langle a_{\mathbf{k}-\mathbf{q}}^\dagger a_{\mathbf{k}} \rangle \\ & + \frac{i}{\hbar} \sum_{\mathbf{k}} \hat{h}_{-\mathbf{q},\mathbf{k},\mathbf{q}-\mathbf{k}} \left(2 \langle b_{-\mathbf{q}+\mathbf{k}}^\dagger b_{\mathbf{k}} \rangle^c + \delta_{\mathbf{q},0} \right). \end{aligned} \quad (\text{I.29})$$

At this stage, we introduce the microscopic damping rate of the coherent phonon amplitude given by

$$\begin{aligned} \gamma_{\mathbf{q}} \equiv & \frac{2\pi}{\hbar^2} \sum_{\mathbf{q}'} \left| \hat{h}_{-\mathbf{q},\mathbf{q}',\mathbf{q}-\mathbf{q}'} \right|^2 [1 + \tilde{n}_{\mathbf{q}'}^c + \tilde{n}_{\mathbf{q}-\mathbf{q}'}^c] \\ & \times \delta(\omega_{\mathbf{q}'} - \omega_{\mathbf{q}-\mathbf{q}'} - \omega_{\mathbf{q}}), \end{aligned} \quad (\text{I.30})$$

which results from phonon-phonon interaction. Here, we again want to point out that the phonon terms are actual occupations, off-diagonal terms are neglected as higher-order contributions. As the last term cancels once both terms are added (which is our case of interest), we will not consider them from now on. In order to close this equation for the coherent phonon operator, we take the second derivative of our oscillator equation and find

$$\begin{aligned} [\partial_t^2 + \gamma_{\mathbf{q}} \partial_t + \omega_{\mathbf{q}}^2] \langle b_{\mathbf{q}} \rangle = & +i\omega_{\mathbf{q}} \gamma_{\mathbf{q}} \langle b_{\mathbf{q}} \rangle - \frac{g_{-\mathbf{q}} \omega_{\mathbf{q}}}{\hbar} \sum_{\mathbf{k}} \langle a_{\mathbf{k}-\mathbf{q}}^\dagger a_{\mathbf{k}} \rangle \\ & - \frac{\omega_{\mathbf{q}}}{\hbar} \sum_{\mathbf{k}} \mathcal{H}_{\mathbf{q},\mathbf{k}} \left(2 \langle b_{-\mathbf{q}+\mathbf{k}}^\dagger b_{\mathbf{k}} \rangle^c + \delta_{\mathbf{q},0} \right), \end{aligned} \quad (\text{I.31})$$

$$\begin{aligned} [\partial_t^2 + \gamma_{-\mathbf{q}} \partial_t + \omega_{-\mathbf{q}}^2] \langle b_{-\mathbf{q}}^\dagger \rangle = & -i\omega_{-\mathbf{q}} \gamma_{-\mathbf{q}} \langle b_{-\mathbf{q}}^\dagger \rangle - \frac{g_{-\mathbf{q}} \omega_{-\mathbf{q}}}{\hbar} \sum_{\mathbf{k}} \langle a_{\mathbf{k}-\mathbf{q}}^\dagger a_{\mathbf{k}} \rangle \\ & - \frac{\omega_{-\mathbf{q}}}{\hbar} \sum_{\mathbf{k}} \hat{h}_{-\mathbf{q},\mathbf{k},\mathbf{q}-\mathbf{k}} \left(2 \langle b_{-\mathbf{q}+\mathbf{k}}^\dagger b_{\mathbf{k}} \rangle^c + \delta_{\mathbf{q},0} \right). \end{aligned} \quad (\text{I.32})$$

Hence, we obtain a damped harmonic oscillator equation for the respective phonon operator. The only issue arising at this stage is that we get an additional imaginary contribution to our equation, which is the inherent result of the second derivative framework. By combining the two equations, and neglecting the arising difference term, we find

$$(\partial_t^2 + 2\gamma_{\mathbf{q}}\partial_t + \omega_{\mathbf{q}}^2)s_{\mathbf{q}} = -\frac{\omega_{\mathbf{q}}}{\hbar} \sum_{\mathbf{k}\lambda} g_{-\mathbf{q}}^{\lambda} \tilde{f}_{\mathbf{k}}^{\lambda}(\mathbf{q}) - \frac{3\omega_{\mathbf{q}}}{\hbar} \sum_{\mathbf{q}'} \tilde{h}_{\mathbf{q},\mathbf{q}',\mathbf{q}-\mathbf{q}'} [2\tilde{n}_{\mathbf{q}'}^c(\mathbf{q}) + \delta_{\mathbf{q},0}]. \quad (\text{I.33})$$

which we will be the main oscillator equation, we use in the main part.

I.3. Momentum Closure of the Microscopic Equations

To promote the microscopic coherent phonon amplitude to a macroscopic level, we use the standard textbook definition of the lattice displacement. For the single band case, this reads

$$\mathbf{u}(\mathbf{R}_n) = \sum_{\mathbf{k}\alpha} \sqrt{\frac{\hbar}{2MN\omega_{\mathbf{k}}^{\alpha}}} \mathbf{e}_{\mathbf{k}}^{\alpha} e^{i\mathbf{k}\cdot\mathbf{R}_n} (b_{-\mathbf{k}\alpha}^{\dagger} + b_{\mathbf{k}\alpha}) = \sum_{\mathbf{k}\alpha} \sqrt{\frac{2\hbar}{MN\omega_{\mathbf{k}}^{\alpha}}} \mathbf{e}_{\mathbf{k}}^{\alpha} e^{i\mathbf{k}\cdot\mathbf{R}_n} s_{\mathbf{k}\alpha} \quad (\text{I.34})$$

$$g_{\mathbf{q}\alpha} = -i\sqrt{\frac{\hbar N}{2M\omega_{\alpha}(\mathbf{q})}} [\mathbf{e}_{\mathbf{q}}^{\alpha} \cdot \mathbf{q}] \Phi_{\mathbf{q}} \quad (\text{I.35})$$

To find a closed solution, we will need to assume a vanishing $\mathbf{k}$ dependence of the Fourier transformed Coulomb potential, which can be achieved by a Strong Screening assumption. In doing so, the momentum dependence of the Coulomb potential is replaced with the (Thomas-Fermi) screening length λ . Hence, the strongly screened Coulomb potential is given by

$$V_0 = \frac{e^2}{\Omega\epsilon_0\lambda^2}. \quad (\text{I.36})$$

From this, we update the definition of the electron-phonon matrix element

$$g_{\mathbf{q}} = -i\sqrt{\hbar N/2M\omega_{\mathbf{q}}} [\mathbf{e}_{\mathbf{q}} \cdot \mathbf{q}] V_0. \quad (\text{I.37})$$

From this, we can use the microscopic oscillator equation in Eq. (6.11),

$$(\partial_t^2 + 2\gamma_{\mathbf{q}}\partial_t + \omega_{\mathbf{q}}^2)s_{\mathbf{q}} = -\frac{\omega_{\mathbf{q}}g_{-\mathbf{q}}}{\hbar} \sum_{\mathbf{k}} \tilde{f}_{\mathbf{k}}(\mathbf{q}) - \frac{3\omega_{\mathbf{q}}}{\hbar} \sum_{\mathbf{q}'} \tilde{h}_{\mathbf{q},\mathbf{q}',\mathbf{q}-\mathbf{q}'} [2\tilde{n}_{\mathbf{q}'}^c(\mathbf{q}) + \delta_{\mathbf{q},0}]. \quad (\text{I.38})$$

and under neglecting the momentum dependencies of the phonon-phonon matrix element, $\tilde{h}_{\mathbf{q},\mathbf{q}',\mathbf{q}-\mathbf{q}'} \approx H$, find

$$(\partial_t^2 + 2\gamma_{\mathbf{q}}\partial_t + \omega_{\mathbf{q}}^2)s_{\mathbf{q}} = -i\sqrt{\frac{\omega_{\mathbf{q}}N}{2M\hbar}} [\mathbf{e}_{\mathbf{q}} \cdot \mathbf{q}] V_0 \sum_{\mathbf{k}} \tilde{f}_{\mathbf{k}}(\mathbf{q}) - \frac{3\omega_{\mathbf{q}}H}{\hbar} \sum_{\mathbf{q}'} [2\tilde{n}_{\mathbf{q}'}^c(\mathbf{q}) + \delta_{\mathbf{q},0}]. \quad (\text{I.39})$$

Now, using the identity in Eq. (I.34),

$$\begin{aligned} \sqrt{\frac{2\hbar}{MN\omega_{\mathbf{q}}}} \mathbf{e}_{\mathbf{q}} (\partial_t^2 + 2\gamma_{\mathbf{q}} \partial_t + \omega_{\mathbf{q}}^2) s_{\mathbf{q}} = & -\frac{iV_0}{M} \mathbf{e}_{\mathbf{q}} [\mathbf{e}_{\mathbf{q}} \cdot \mathbf{q}] \sum_{\mathbf{k}} \tilde{f}_{\mathbf{k}}(\mathbf{q}) \\ & - 3H \sqrt{\frac{2\omega_{\mathbf{q}}}{MN\hbar}} \mathbf{e}_{\mathbf{q}} \sum_{\mathbf{q}'} [2\tilde{n}_{\mathbf{q}'}^c(\mathbf{q}) + \delta_{\mathbf{q},0}]. \end{aligned} \quad (\text{I.40})$$

$$\begin{aligned} (\partial_t^2 + 2\gamma_{\mathbf{q}} \partial_t + \omega_{\mathbf{q}}^2) \mathbf{u}_{\mathbf{q}} = & -\frac{iV_0}{M} \mathbf{e}_{\mathbf{q}} [\mathbf{e}_{\mathbf{q}} \cdot \mathbf{q}] \sum_{\mathbf{k}} \tilde{f}_{\mathbf{k}}(\mathbf{q}) \\ & - 3H \sqrt{\frac{2\omega_{\mathbf{q}}}{MN\hbar}} \mathbf{e}_{\mathbf{q}} \sum_{\mathbf{q}'} [2\tilde{n}_{\mathbf{q}'}^c(\mathbf{q}) + \delta_{\mathbf{q},0}]. \end{aligned} \quad (\text{I.41})$$

According to Ref. [205], the definition of H contains three unit vectors. As we change the definition of the oscillation vector, we have to add the factor of $-i$ in order to get a real-valued quantity. Hence, we replace $H = -i\tilde{H}$;

$$(\partial_t^2 + 2\gamma_{\mathbf{q}} \partial_t + \omega_{\mathbf{q}}^2) \mathbf{u}_{\mathbf{q}} = +\frac{iV_0}{M} \mathbf{e}_{\mathbf{q}} [\mathbf{e}_{\mathbf{q}} \cdot \mathbf{q}] \sum_{\mathbf{k}} \tilde{f}_{\mathbf{k}}(\mathbf{q}) + 3i\tilde{H} \sqrt{\frac{2\omega_{\mathbf{q}}}{MN\hbar}} \mathbf{e}_{\mathbf{q}} \sum_{\mathbf{q}'} [2\tilde{n}_{\mathbf{q}'}^c(\mathbf{q}) + \delta_{\mathbf{q},0}]. \quad (\text{I.42})$$

$$(\partial_t^2 + 2\gamma_{\mathbf{q}} \partial_t + \omega_{\mathbf{q}}^2) \mathbf{u}_{\mathbf{q}} = \frac{iV_0}{M} \mathbf{q} \sum_{\mathbf{k}} \tilde{f}_{\mathbf{k}}(\mathbf{q}) - 3\tilde{H} \sqrt{\frac{2\omega_{\mathbf{q}}}{MN\hbar}} \frac{\mathbf{q}}{|\mathbf{q}|} \sum_{\mathbf{q}'} [2\tilde{n}_{\mathbf{q}'}^c(\mathbf{q}) + \delta_{\mathbf{q},0}]. \quad (\text{I.43})$$

Using a Fourier transformation, and absorbing the constant on the right-hand side into the equilibrium position of the oscillator equation, we find

$$(\partial_t^2 + 2\gamma_{\mathbf{q}} \partial_t + \omega_{\mathbf{q}}^2) \mathbf{u}(\mathbf{r}) = \frac{V_0}{M} \nabla_{\mathbf{r}} \sum_{\mathbf{k}} f_{\mathbf{k}}(\mathbf{r}) - 6\tilde{H} \sqrt{\frac{2\omega_{\mathbf{q}}}{MN\hbar}} \mathbf{e}_{\mathbf{r}} \sum_{\mathbf{q}'} n_{\mathbf{q}'}^c(\mathbf{r}). \quad (\text{I.44})$$

$$(\partial_t^2 + 2\gamma_{\mathbf{q}} \partial_t + \omega_{\mathbf{q}}^2) \mathbf{u}(\mathbf{r}) = \frac{V_0\Omega}{eM} \nabla_{\mathbf{r}} \rho(\mathbf{r}) - 6\tilde{H} \sqrt{\frac{2\omega_{\mathbf{q}}}{MN\hbar}} \mathbf{e}_{\mathbf{r}} \sum_{\mathbf{q}'} n_{\mathbf{q}'}^c(\mathbf{r}). \quad (\text{I.45})$$

Thus, our **final microscopic equations** at this stage are

$$(\partial_t^2 + 2\gamma_{\mathbf{q}} \partial_t + \omega_{\mathbf{q}}^2) \mathbf{u}(\mathbf{r}) = \frac{V_0\Omega}{eM} \nabla_{\mathbf{r}} \rho(\mathbf{r}) - 6\tilde{H} \sqrt{\frac{2\omega_{\mathbf{q}}}{MN\hbar}} \mathbf{e}_{\mathbf{r}} \sum_{\mathbf{q}'} n_{\mathbf{q}'}^c(\mathbf{r}). \quad (\text{I.46})$$

In summary, we find a second order differential equation in time and momentum space that we employ in the main part of this thesis, with the only correction that we need to incorporate the nature of thermal expansion as an extensive quantity. Details are provided in the main part.

I.4. Microscopic Temperature Equation

This is to be seen as an approach to obtain an equation for the temperature, which follows from energy conservation in hydrodynamics. We start with a simplified version

of our Wigner equation (no phonons, only electric fields), it reads

$$\partial_t f_{\mathbf{k}}(\mathbf{r}, t) + \mathbf{v}_{\mathbf{k}} \cdot \nabla_{\mathbf{r}} f_{\mathbf{k}}(\mathbf{r}, t) = \mathbf{E}(\mathbf{r}, t) \cdot \nabla_{\mathbf{k}} f_{\mathbf{k}}(\mathbf{r}, t). \quad (\text{I.47})$$

We will assume that the velocity can be written as $\mathbf{v}_{\mathbf{k}} = \mathbf{v} + \delta\mathbf{v}_{\mathbf{k}}$. We multiply the equation with $\delta\mathbf{v}_{\mathbf{k}} \otimes \delta\mathbf{v}_{\mathbf{k}}$ and sum over the momentum. One obtains

$$\partial_t \frac{e}{V} \sum_{\mathbf{q}} \delta\mathbf{v}_{\mathbf{k}} \otimes \delta\mathbf{v}_{\mathbf{k}} f_{\mathbf{k}} + \frac{e}{V} \sum_{\mathbf{q}} \delta\mathbf{v}_{\mathbf{k}} \otimes \delta\mathbf{v}_{\mathbf{k}} (\mathbf{v}_{\mathbf{k}} \cdot \nabla_{\mathbf{r}}) f_{\mathbf{k}} = \frac{e}{V} \sum_{\mathbf{q}} \delta\mathbf{v}_{\mathbf{k}} \otimes \delta\mathbf{v}_{\mathbf{k}} \mathbf{E} \cdot \nabla_{\mathbf{q}} f_{\mathbf{k}}. \quad (\text{I.48})$$

Employing integration by parts and that $\mathbf{v}_{\mathbf{k}}$ is not spatially dependent, one finds

$$\begin{aligned} \partial_t \frac{e}{V} \sum_{\mathbf{q}} \delta\mathbf{v}_{\mathbf{k}} \otimes \delta\mathbf{v}_{\mathbf{k}} f_{\mathbf{k}} = & -\nabla_{\mathbf{r}} \left[\frac{e}{V} \sum_{\mathbf{q}} \delta\mathbf{v}_{\mathbf{k}} \otimes \delta\mathbf{v}_{\mathbf{k}} \otimes (\mathbf{v} + \delta\mathbf{v}_{\mathbf{k}}) f_{\mathbf{k}} \right] \\ & - \frac{e}{V} \sum_{\mathbf{q}} \nabla_{\mathbf{q}} (\mathbf{v}_{\mathbf{k}} \otimes \mathbf{v}_{\mathbf{k}}) \otimes \mathbf{E} f_{\mathbf{k}}, \end{aligned} \quad (\text{I.49})$$

From this, we are able to identify

$$\partial_t \mathbf{P} = -\nabla_{\mathbf{r}} [\mathbf{P} \otimes \mathbf{v} + \mathbf{Q}] - \frac{2\hbar}{m} \rho \mathbf{v} \otimes \mathbf{E}, \quad (\text{I.50})$$

where we defined the pressure tensor $\mathbf{P}$ and the heat flux $\mathbf{Q}$

$$\mathbf{P} = \frac{e}{V} \sum_{\mathbf{q}} \delta\mathbf{v}_{\mathbf{k}} \otimes \delta\mathbf{v}_{\mathbf{k}} f_{\mathbf{k}}, \quad (\text{I.51})$$

$$\mathbf{Q} = \frac{e}{V} \sum_{\mathbf{q}} \delta\mathbf{v}_{\mathbf{k}} \otimes \delta\mathbf{v}_{\mathbf{k}} \otimes \delta\mathbf{v}_{\mathbf{k}} f_{\mathbf{k}}. \quad (\text{I.52})$$

Using the replacement $\mathbf{P} = \frac{3}{2} \frac{\rho}{m} k_B T$, one finds

$$\frac{3}{2} \partial_t \frac{\rho}{m} k_B T = -\nabla_{\mathbf{r}} \left[\frac{3}{2} \frac{\rho}{m} k_B T \otimes \mathbf{v} + \mathbf{Q} \right] - \frac{2\hbar}{m} \rho \mathbf{v} \otimes \mathbf{E}. \quad (\text{I.53})$$

Combining this with the continuity equation, and assuming isotropy to reduce the complexity of the tensor product, one finds

$$\frac{3}{2} \rho [\partial_t + \mathbf{v} \cdot \nabla_{\mathbf{r}}] k_B T = -m \nabla_{\mathbf{r}} \mathbf{Q} - 2\hbar \rho \mathbf{v} \cdot \mathbf{E} \quad (\text{I.54})$$

This equation effectively couples the temperature in the system with the heat flux, based on a microscopic calculation. However, the future has to judge if this additional equation yields reasonable results.

I.5. Lamb modes - Eigenmodes of a Traction-Free Sphere

In order to characterize in the eigenmodes of the oscillation and solve the spatial part of the partial differential equation, we will assume that our analysis lacks the treatment of

the bulk and shear modulo and hence needs to be extended to include those. Thus, we assume that the spatial contribution to the oscillation satisfies the equation

$$(\lambda + \mu)\nabla(\nabla \cdot \mathbf{u}) + \mu\nabla^2 \mathbf{u} = \rho\partial_t^2 \mathbf{u}. \quad (\text{I.55})$$

An overview of the analytical solution of this equation can be found in Refs. [447, 475, 501]. In summary, solutions of this equation can be given as

$$\mathbf{u} = \mathbf{L} + \mathbf{M} + \mathbf{N} \quad (\text{I.56})$$

with

$$\mathbf{L} = \nabla\phi \quad (\text{I.57a})$$

$$\mathbf{M} = \nabla \times (w\psi\mathbf{e}_3) \quad (\text{I.57b})$$

$$\mathbf{N} = \xi\nabla \times \nabla \times (w\chi\mathbf{e}_3) \quad (\text{I.57c})$$

The Helmholtz potentials can in our geometry, assuming a full sphere be written as

$$\phi = j_l(\alpha r)P_l^m(\cos\theta)\exp\{i(m\varphi - \omega t)\} \quad (\text{I.58a})$$

$$\psi = j_l(\beta r)P_l^m(\cos\theta)\exp\{i(m\varphi - \omega t)\} \quad (\text{I.58b})$$

$$\chi = j_l(\beta r)P_l^m(\cos\theta)\exp\{i(m\varphi - \omega t)\} \quad (\text{I.58c})$$

where $j_l(x)$ are the spherical Bessel functions and the wave numbers α and β differ depending on the longitudinal/transverse speed of sound

$$\alpha \equiv \omega/c_1, \quad \beta \equiv \omega/c_2, \quad (\text{I.59})$$

The resulting modes are named Lamb modes, due to the first works by Horace Lamb [447]. Due to symmetry considerations, we decided to focus on the first Helmholtz potential and also reduced to the $\ell = 0$ case, as we are interested in radial oscillations. These will be rescaled in order to match our prescription and allowing to connect them to the eigenmodes of our system. Using this simplification, the eigenmodes of our system can be given as

$$\phi_n(r) = \left(\frac{\hbar}{2M\omega}\right)^{\frac{1}{2}} \frac{1}{k_n} j_0(k_n r), \quad (\text{I.60})$$

$$\mathbf{u}_n(r) = \left(\frac{\hbar}{2M\omega}\right)^{\frac{1}{2}} \frac{1}{k_n} \partial_r(j_0(k_n r))\mathbf{e}_r. \quad (\text{I.61})$$

$$(\text{I.62})$$

The prefactor was chosen to match the units of length for the lattice displacement $\mathbf{u}(\mathbf{r})$. We will use these quantities to expand our vector and scalar-valued quantities in

$$\tilde{\rho}_2(\mathbf{r}, t) = \sum_n \phi_n(\mathbf{r})\rho_n(t), \quad \mathbf{u}(\mathbf{r}, t) = \sum_n \mathbf{u}_n(\mathbf{r})u_n(t). \quad (\text{I.63})$$

From this, we also define the overlap integrals

$$A_n = \int d^3r \mathbf{u}_n^*(\mathbf{r}) \cdot \mathbf{u}_n(\mathbf{r}) = \frac{\hbar}{2M\omega} \frac{4\pi}{k_n^2} \int_0^R r^2 (\partial_r(j_0(k_n r)))^2 dr, \quad (\text{I.64})$$

$$B_n = \int d^3r \phi_n^*(\mathbf{r})\phi_n(\mathbf{r}) = \frac{\hbar}{2M\omega} \frac{4\pi}{k_n^2} \int_0^R r^2 (j_0(k_n r))^2 dr \quad (\text{I.65})$$

I.5.1. Boundary Conditions

The remaining quantum number is related to the boundary condition that quantizes the α and β . In the literature, they are usually related to the unitless frequencies

$$\xi = \alpha a = \frac{\omega a}{c_1} = \frac{2a\pi\nu}{c_1}, \quad (\text{I.66a})$$

$$\eta = \beta a = \frac{\omega a}{c_2} = \frac{2a\pi\nu}{c_2}. \quad (\text{I.66b})$$

Here, c_1 is the longitudinal speed of sound in the medium and c_2 the transverse one. For radial modes $\ell = 0$, the stress-free boundary conditions are given by [449]

$$\eta \cot \eta = 1 - \frac{\eta^2}{4\delta^2} \quad (\text{I.67})$$

The original work on this can be found in Ref. [447] but more recent works have greatly contributed to a more profound understanding of these eigenmodes [449, 450, 501, 502].

I.5.2. Overlap Integrals

Here, we present our calculation of the overlap integrals. In Mie theory, the electric field is given by

$$\mathbf{E}_{\text{in}} = \frac{3\varepsilon_{\text{out}}}{\varepsilon_{\infty} + \varepsilon_{\text{out}}} \mathbf{E}_{\text{ext}}, \quad \mathbf{E}_{\text{out}} = \mathbf{E}_{\text{ext}} + \frac{3\mathbf{n}(\mathbf{n} \cdot \mathbf{p}) - \mathbf{p}}{4\pi\varepsilon_0\varepsilon_{\text{out}}r^3}. \quad (\text{I.68})$$

From this, we use a Heaviside Theta function to place them in a single expression,

$$\mathbf{E}(\mathbf{r}) = \Theta(r - R)\mathbf{E}_{\text{out}} + \Theta(R - r)\mathbf{E}_{\text{in}}. \quad (\text{I.69})$$

This allows us to compute the integral expression by integration by parts. Under the physical assumption that the material wave functions only exist within the sphere, the integrals on the outside of the sphere should vanish and one only integrates over the volume of the sphere.

When computing the overlap, we make use of the fact that the Lamb mode is the gradient of the first Helmholtz potential, as we restricted ourselves to the purely radial case,

$$\nabla\phi_n = \mathbf{u}_n(r) \approx \left(\frac{\hbar}{2m\omega}\right)^{\frac{1}{2}} \frac{1}{k_n} \partial_r(j_0(k_nr))\mathbf{e}_r \quad (\text{I.70})$$

From this, we discuss the individual cases of interband and intraband excitation in the following.

Intraband case

The equation for the densities reads

$$\partial_t \rho_n(t) + D \frac{\omega_n^2}{c_1^2} \rho_n(t) = -\frac{K}{B_n} \int \mathbf{u}_n^*(\mathbf{r}) \cdot [(\tilde{\mathbf{E}} \cdot \nabla) \tilde{\mathbf{E}}] d^3r. \quad (\text{I.71})$$

where we defined

$$D = \frac{5}{3} \frac{\kappa}{\gamma} \rho_0^{2/3}, \quad K = \frac{\rho_0}{\gamma^3} \left(\frac{e}{m} \right)^2 \quad (\text{I.72})$$

Performing the integral, we find

$$\begin{aligned} & -\frac{K}{B_n} \int \nabla \phi_n \cdot (\mathbf{E} \cdot \nabla) \mathbf{E} \\ &= -\frac{4\pi}{3} \left(\frac{\hbar}{2m\omega} \right)^{1/2} \frac{K}{B_n} E_0^2 \left[\frac{\partial_r j_l(k_n R)}{k_n} \left((1-b^2)R^2 + \frac{4\alpha\tilde{k}}{R} + \frac{4\alpha^2\tilde{k}^2}{R^4} \right) \right], \end{aligned} \quad (\text{I.73})$$

where we defined for simplicity

$$k = \tilde{k}/r^3, \quad \tilde{k} = \frac{1}{4\pi\epsilon_0\epsilon_{\text{out}}}. \quad (\text{I.74})$$

Interband case

The equation that we obtain for the electric field overlap is given by

$$\partial_t \rho_2^c(\mathbf{r}, t) = \frac{2e\epsilon_0}{\hbar} \left| \tilde{\mathbf{E}}_0(\mathbf{r}, t) \right|^2 \text{Im}\{\chi^{\text{inter}}(\omega_{\text{opt}})\}. \quad (\text{I.75})$$

We now decided to take the gradient of the density equation to expand it in the same Lamb mode as before,

$$\partial_t \nabla \rho_2^c(\mathbf{r}, t) = \frac{2e\epsilon_0}{\hbar} \nabla \left| \tilde{\mathbf{E}}_0(\mathbf{r}, t) \right|^2 \text{Im}\{\chi^{\text{inter}}(\omega_{\text{opt}})\}. \quad (\text{I.76})$$

as we used $\mathbf{u} = \nabla \phi$, this can be expanded in terms of the vector valued Lamb modes,

$$\partial_t \rho_2^c(t) = \frac{2e\epsilon_0}{\hbar A} \int d^3r \mathbf{u}_0^*(\mathbf{r}) \cdot \nabla \left| \tilde{\mathbf{E}}_0(\mathbf{r}, t) \right|^2 \text{Im}\{\chi^{\text{inter}}(\omega_{\text{opt}})\}. \quad (\text{I.77})$$

Making use of the field definition via the Theta functions, we can evaluate the integral explicitly and find

$$\begin{aligned} \partial_t \rho_2^c(t) &= \frac{8\pi e\epsilon_0}{\hbar A} u_0^*(R) \left[\left(1 + \frac{3\epsilon_{\text{out}}}{\epsilon_d + 2\epsilon_{\text{out}}} \right)^2 + 2 \left(\frac{\alpha}{4\pi\epsilon_0\epsilon_{\text{out}}R^3} \right)^2 \right] \\ &\quad \times E_0^2 \text{Im}\{\chi^{\text{inter}}(\omega_{\text{opt}})\} \exp\{-2t^2/\sigma^2\}, \end{aligned} \quad (\text{I.78})$$

where we assumed vacuum for the background and in the Drude permittivity, ϵ_d , we use the parameters from the critical point model [277] so that all interband contributions are contained in the susceptibility in the back while all Drude terms are used in these parameters.

I.6. Pump Fluence

Our electric field is defined to be

$$\mathbf{E}(t) = \mathbf{E}_0 e^{-2\ln(2)t^2\tau^2} \cos(\omega t) \quad (\text{I.79})$$

with the optical frequency, ω_0 which is large compared to the pulse length. The pulse length is defined as the full width at half maximum (FWHM) which means that it is the time difference of the two points where the exponential function reaches 1/2 for the intensity as we will check later on.

The intensity is defined as the time averaged electric field over one period

$$I(t) = c\varepsilon_0 n \frac{1}{T_0} \int_{t-T_0/2}^{t+T_0/2} \left[\mathbf{E}_0 e^{-2 \ln 2 t^2 / \tau^2} \cos(\omega_0 t') \right]^2 dt' \quad (\text{I.80})$$

assuming that the envelope varies slowly compared to the optical oscillation, one finds

$$I(t) = c\varepsilon_0 n \frac{1}{T_0} |\mathbf{E}_0|^2 e^{-4 \ln 2 t^2 / \tau^2} \int_{t-T_0/2}^{t+T_0/2} \cos^2(\omega_0 t') dt' = \frac{c\varepsilon_0 n}{2} |\mathbf{E}_0|^2 e^{-4 \ln 2 t^2 / \tau^2} \quad (\text{I.81})$$

At this stage, it is easy to see that the intensity falls off to 1/2 as t reaches $\tau/2$. Evaluating the time integral, results in the absolute energy contained in one pulse (pump fluence)

$$W = \frac{c\varepsilon_0 n}{2} |\mathbf{E}_0|^2 \int_{-\infty}^{\infty} e^{-4 \ln 2 t^2 / \tau^2} dt = \frac{c\varepsilon_0 n}{2} \sqrt{\frac{\pi}{\ln 2}} \frac{\tau}{2} |\mathbf{E}_0|^2, \quad (\text{I.82})$$

which allows transforming the electric field strength and the intensity into each other according to

$$E_0 = \sqrt{\frac{4}{c\varepsilon_0 n \tau}} \sqrt{\frac{\ln 2}{\pi}} W. \quad (\text{I.83})$$

At this stage, it feels important to check the units,

$$[W] = \frac{m}{s} \frac{As}{Vm} s \frac{V^2}{m^2} = \frac{As}{m^2} V = \frac{J}{m^2}. \quad (\text{I.84})$$

In addition, this allows to define an expression for the field intensity, depending on the pump fluence

$$I(t) = \frac{W}{\sigma} e^{-t^2 / \sigma^2}, \quad (\text{I.85})$$

where we defined $\sigma = \tau / \sqrt{4 \ln 2}$ as can be found Ref. [448].

Bibliography

- [1] G. Mie, Beiträge zur Optik trüber Medien, speziell kolloidaler Metallösungen, *Annalen der Physik* **330**, 377–445 (1908).
- [2] J. P. Dowling and G. J. Milburn, Quantum Technology: The Second Quantum Revolution, *Philosophical Transactions: Mathematical, Physical and Engineering Sciences* **361**, 1655–1674 (2003).
- [3] M. Kop, M. Aboy, E. De Jong, U. Gasser, T. Minssen, I. G. Cohen, M. Brongersma, T. Quintel, L. Floridi, and R. Laflamme, *Towards Responsible Quantum Technology*, Harvard Berkman Klein Center for Internet & Society Research Publication Series #2023-1 (Harvard University, 2023).
- [4] D. Hoeing, R. Salzwedel, L. Worbs, Y. Zhuang, A. K. Samanta, J. Lübke, A. D. Estillore, K. Dlugolecki, C. Passow, B. Erk, N. Ekanayake, D. Ramm, J. Correa, C. C. Papadopoulou, A. T. Noor, F. Schulz, M. Selig, A. Knorr, K. Ayer, J. Küpper, and H. Lange, Time-Resolved Single-Particle X-ray Scattering Reveals Electron-Density Gradients As Coherent Plasmonic-Nanoparticle-Oscillation Source, *Nano Letters* **23**, 5943–5950 (2023).
- [5] S. Manzeli, D. Ovchinnikov, D. Pasquier, O. V. Yazyev, and A. Kis, 2D transition metal dichalcogenides, *Nature Reviews Materials* **2**, 17033 (2017).
- [6] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, Electric field effect in atomically thin carbon films, *Science* **306**, 666–669 (2004).
- [7] K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, and A. K. Geim, Two-dimensional atomic crystals, *Proceedings of the National Academy of Sciences* **102**, 10451–10453 (2005).
- [8] K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, Atomically Thin MoS₂: A New Direct-Gap Semiconductor, *Physical Review Letters* **105**, 136805 (2010).
- [9] A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C.-Y. Chim, G. Galli, and F. Wang, Emerging photoluminescence in monolayer MoS₂, *Nano Letters* **10**, 1271–1275 (2010).
- [10] T. Cao, G. Wang, W. Han, H. Ye, C. Zhu, J. Shi, Q. Niu, P. Tan, E. Wang, and B. Liu, Valley-selective circular dichroism of monolayer molybdenum disulphide, *Nature Communications* **3**, 887 (2012).
- [11] D. Xiao, G.-B. Liu, W. Feng, X. Xu, and W. Yao, Coupled Spin and Valley Physics in Monolayers of MoS₂ and Other Group-VI Dichalcogenides, *Physical Review Letters* **108**, 196802 (2012).

- [12] K. Kořmider, J. W. Gonzalez, and J. Fernandez-Rossier, Large spin splitting in the conduction band of transition metal dichalcogenide monolayers, *Physical Review B* **88**, 245436 (2013).
- [13] A. Kormanyos, G. Burkard, M. Gmitra, J. Fabian, V. Zolyomi, N. D. Drummond, and V. Fal’ko, $\mathbf{K} \cdot \mathbf{p}$ theory for two-dimensional transition metal dichalcogenide semiconductors, *2D Materials* **2**, 022001 (2015).
- [14] K. F. Mak, K. L. McGill, J. Park, and P. L. McEuen, The valley Hall effect in MoS₂ transistors, *Science* **344**, 1489–1492 (2014).
- [15] P. Rivera, K. L. Seyler, H. Yu, J. R. Schaibley, J. Yan, D. G. Mandrus, W. Yao, and X. Xu, Valley-polarized exciton dynamics in a 2D semiconductor heterostructure, *Science* **351**, 688–691 (2016).
- [16] J. R. Schaibley, H. Yu, G. Clark, P. Rivera, J. S. Ross, K. L. Seyler, W. Yao, and X. Xu, Valleytronics in 2D materials, *Nature Reviews Materials* **1**, 16055 (2016).
- [17] A. Chernikov, T. C. Berkelbach, H. M. Hill, A. Rigosi, Y. Li, O. B. Aslan, D. R. Reichman, M. S. Hybertsen, and T. F. Heinz, Exciton Binding Energy and Nonhydrogenic Rydberg Series in Monolayer WS₂, *Physical Review Letters* **113**, 076802 (2014).
- [18] G. Wang, A. Chernikov, M. M. Glazov, T. F. Heinz, X. Marie, T. Amand, and B. Urbaszek, *Colloquium* : Excitons in atomically thin transition metal dichalcogenides, *Reviews of Modern Physics* **90**, 021001 (2018).
- [19] M. Selig, F. Katsch, S. Brem, G. F. Mkrtchian, E. Malic, and A. Knorr, Suppression of intervalley exchange coupling in the presence of momentum-dark states in transition metal dichalcogenides, *Physical Review Research* **2**, 023322 (2020).
- [20] A. Steinhoff, M. Florian, M. Rosner, G. Schonhoff, T. O. Wehling, and F. Jahnke, Exciton fission in monolayer transition metal dichalcogenide semiconductors, *Nature Communications* **8**, 1166 (2017).
- [21] F. Katsch, M. Selig, and A. Knorr, Exciton-Scattering-Induced Dephasing in Two-Dimensional Semiconductors, *Physical Review Letters* **124**, 257402 (2020).
- [22] N. S. Rytova, Screened potential of a point charge in a thin film, *Moscow University Physics Bulletin* **3**, 1–4 (1967).
- [23] L. V. Keldysh, Coulomb interaction in thin semiconductor and semimetal films, *JETPL* **29**, 658 (1979).
- [24] M. Feierabend, G. Berghauser, A. Knorr, and E. Malic, Proposal for dark exciton based chemical sensors, *Nature Communications* **8**, 14776 (2017).
- [25] K. Greben, S. Arora, M. G. Harats, and K. I. Bolotin, Intrinsic and extrinsic defect-related excitons in TMDCs, *Nano Letters* **20**, 2544–2550 (2020).
- [26] M. Rosner, C. Steinke, M. Lorke, C. Gies, F. Jahnke, and T. O. Wehling, Two-Dimensional Heterojunctions from Nonlocal Manipulations of the Interactions, *Nano Letters* **16**, 2322–2327 (2016).

-
- [27] O. Benson, Assembly of hybrid photonic architectures from nanophotonic constituents, *Nature* **480**, 193–199 (2011).
- [28] M. Katzer, S. Kovalchuk, K. Greben, K. I. Bolotin, M. Selig, and A. Knorr, Impact of dark excitons on Förster-type resonant energy transfer between dye molecules and atomically thin semiconductors, *Physical Review B* **107**, 035304 (2023).
- [29] D. Christiansen, M. Selig, M. Rossi, and A. Knorr, Optical classification of excitonic phases in molecular functionalized atomically-thin semiconductors, *Physical Review B* **107**, L041401 (2023).
- [30] J. J. P. Thompson, M. Gerhard, G. Witte, and E. Malic, Optical signatures of Förster-induced energy transfer in organic/TMD heterostructures, *npj 2D Materials and Applications* **7**, 69 (2023).
- [31] T. Pincelli, T. Vasileiadis, S. Dong, S. Beaulieu, M. Dendzik, D. Zahn, S.-E. Lee, H. Seiler, Y. Qi, R. P. Xian, J. Maklar, E. Coy, N. S. Mueller, Y. Okamura, S. Reich, M. Wolf, L. Rettig, and R. Ernstorfer, Observation of Multi-Directional Energy Transfer in a Hybrid Plasmonic–Excitonic Nanostructure, *Advanced Materials* **35**, 2209100 (2023).
- [32] N. S. Mueller and S. Reich, Microscopic theory of optical absorption in graphene enhanced by lattices of plasmonic nanoparticles, *Physical Review B* **97**, 235417 (2018).
- [33] P. Kusch, N. S. Mueller, M. T. Hartmann, and S. Reich, Strong light-matter coupling in MoS₂, *Physical Review B* **103**, 235409 (2021).
- [34] Z.-S. Deng, L.-Y. Li, C.-L. You, Y.-W. Lu, and J.-F. Liu, Effective Modes for a Strongly Coupled Quantum Emitter-MoS₂ Nanodisk System, *IEEE Photonics Journal* **15**, 1–7 (2023).
- [35] A. K. Geim and I. V. Grigorieva, Van der Waals heterostructures, *Nature* **499**, 419–425 (2013).
- [36] P. Rivera, J. R. Schaibley, A. M. Jones, J. S. Ross, S. Wu, G. Aivazian, P. Klement, K. Seyler, G. Clark, N. J. Ghimire, J. Yan, D. G. Mandrus, W. Yao, and X. Xu, Observation of long-lived interlayer excitons in monolayer MoSe₂–WSe₂ heterostructures, *Nature Communications* **6**, 6242 (2015).
- [37] S. Ovesen, S. Brem, C. Linderålv, M. Kuisma, T. Korn, P. Erhart, M. Selig, and E. Malic, Interlayer exciton dynamics in van der Waals heterostructures, *Communications Physics* **2**, 23 (2019).
- [38] C. Jin, E. C. Regan, A. Yan, M. Iqbal Bakti Utama, D. Wang, S. Zhao, Y. Qin, S. Yang, Z. Zheng, S. Shi, K. Watanabe, T. Taniguchi, S. Tongay, A. Zettl, and F. Wang, Observation of moiré excitons in WSe₂/WS₂ heterostructure superlattices, *Nature* **567**, 76–80 (2019).
- [39] S. Shabani, D. Halbertal, W. Wu, M. Chen, S. Liu, J. Hone, W. Yao, D. N. Basov, X. Zhu, and A. N. Pasupathy, Deep moiré potentials in twisted transition metal dichalcogenide bilayers, *Nature Physics* **17**, 720–725 (2021).

- [40] D. Schmitt, J. P. Bange, W. Bennecke, A. AlMutairi, G. Meneghini, K. Watanabe, T. Taniguchi, D. Steil, D. R. Luke, R. T. Weitz, S. Steil, G. S. M. Jansen, S. Brem, E. Malic, S. Hofmann, M. Reutzel, and S. Mathias, Formation of moiré interlayer excitons in space and time, *Nature* **608**, 499–503 (2022).
- [41] S. Y. Woo, A. Zobelli, R. Schneider, A. Arora, J. A. Preuß, B. J. Carey, S. Michaelis De Vasconcellos, M. Palummo, R. Bratschitsch, and L. H. G. Tizei, Excitonic absorption signatures of twisted bilayer WSe₂ by electron energy-loss spectroscopy, *Physical Review B* **107**, 155429 (2023).
- [42] F. Wu, T. Lovorn, and A. H. MacDonald, Topological Exciton Bands in Moiré Heterojunctions, *Physical Review Letters* **118**, 147401 (2017).
- [43] F. Wu, T. Lovorn, and A. H. MacDonald, Theory of optical absorption by interlayer excitons in transition metal dichalcogenide heterobilayers, *Physical Review B* **97**, 035306 (2018).
- [44] T. Mueller and E. Malic, Exciton physics and device application of two-dimensional transition metal dichalcogenide semiconductors, *npj 2D Materials and Applications* **2**, 29 (2018).
- [45] T. Gao, M. von Helversen, C. Antón-Solanas, C. Schneider, and T. Heindel, Atomically-thin single-photon sources for quantum communication, *npj 2D Materials and Applications* **7**, 4 (2023).
- [46] K. Barthelmi, J. Klein, A. Hötger, L. Sigl, F. Sigger, E. Mitterreiter, S. Rey, S. Gyger, M. Lorke, M. Florian, F. Jahnke, T. Taniguchi, K. Watanabe, V. Zwiller, K. D. Jöns, U. Wurstbauer, C. Kastl, A. Weber-Bargioni, J. J. Finley, K. Müller, and A. W. Holleitner, Atomistic defects as single-photon emitters in atomically thin MoS₂, *Applied Physics Letters* **117**, 070501 (2020).
- [47] P. Tonndorf, R. Schmidt, R. Schneider, J. Kern, M. Buscema, G. A. Steele, A. Castellanos-Gomez, H. S. J. van der Zant, S. Michaelis de Vasconcellos, and R. Bratschitsch, Single-photon emission from localized excitons in an atomically thin semiconductor, *Optica* **2**, 347–352 (2015).
- [48] Y.-M. He, G. Clark, J. R. Schaibley, Y. He, M.-C. Chen, Y.-J. Wei, X. Ding, Q. Zhang, W. Yao, X. Xu, C.-Y. Lu, and J.-W. Pan, Single quantum emitters in monolayer semiconductors, *Nature Nanotechnology* **10**, 497–502 (2015).
- [49] K. L. Seyler, P. Rivera, H. Yu, N. P. Wilson, E. L. Ray, D. G. Mandrus, J. Yan, W. Yao, and X. Xu, Signatures of moiré-trapped valley excitons in MoSe₂/WSe₂ heterobilayers, *Nature* **567**, 66–70 (2019).
- [50] F. Mahdikhany Sarvejahany, D. N. Shanks, M. Klein, Q. Wang, M. R. Koehler, D. G. Mandrus, T. Taniguchi, K. Watanabe, O. L. A. Monti, B. J. LeRoy, and J. R. Schaibley, Localized interlayer excitons in MoSe₂–WSe₂ heterostructures without a moiré potential, *Nature Communications* **13**, 5354 (2022).
- [51] S. A. Maier, *Plasmonics: Fundamentals and Applications* (Springer, New York, 2007).

-
- [52] N. J. Halas, Plasmonics: An Emerging Field Fostered by *Nano Letters*, *Nano Letters* **10**, 3816–3822 (2010).
- [53] V. Amendola, R. Pilot, M. Frasconi, O. M. Maragò, and M. A. Iatì, Surface plasmon resonance in gold nanoparticles: A review, *Journal of Physics: Condensed Matter* **29**, 203002 (2017).
- [54] M. I. Stockman, K. Kneipp, S. I. Bozhevolnyi, S. Saha, A. Dutta, J. Ndukaife, N. Kinsey, H. Reddy, U. Guler, V. M. Shalaev, A. Boltasseva, B. Gholipour, H. N. S. Krishnamoorthy, K. F. MacDonald, C. Soci, N. I. Zheludev, V. Savinov, R. Singh, P. Groß, C. Lienau, M. Vadai, M. L. Solomon, D. R. Barton, M. Lawrence, J. A. Dionne, S. V. Boriskina, R. Esteban, J. Aizpurua, X. Zhang, S. Yang, D. Wang, W. Wang, T. W. Odom, N. Accanto, P. M. de Roque, I. M. Hancu, L. Piatkowski, N. F. van Hulst, and M. F. Kling, Roadmap on plasmonics, *Journal of Optics* **20**, 043001 (2018).
- [55] J. Aizpurua, H. A. Atwater, J. J. Baumberg, S. I. Bozhevolnyi, M. L. Brongersma, J. A. Dionne, H. Giessen, N. Halas, Y. Kivshar, M. F. Kling, F. Krausz, S. Maier, S. V. Makarov, M. Mikkelsen, M. Moskovits, P. Nordlander, T. Odom, A. Polman, C. W. Qiu, M. Segev, V. M. Shalaev, P. Törmä, D. P. Tsai, E. Verhagen, A. Zayats, X. Zhang, and N. I. Zheludev, Mark Stockman: Evangelist for Plasmonics, *ACS Photonics* **8**, 683–698 (2021).
- [56] E. Hao and G. C. Schatz, Electromagnetic fields around silver nanoparticles and dimers, *The Journal of Chemical Physics* **120**, 357–366 (2004).
- [57] K. B. Crozier, A. Sundaramurthy, G. S. Kino, and C. F. Quate, Optical antennas: Resonators for local field enhancement, *Journal of Applied Physics* **94**, 4632–4642 (2003).
- [58] W. L. Barnes, A. Dereux, and T. W. Ebbesen, Surface plasmon subwavelength optics, *Nature* **424**, 824–830 (2003).
- [59] R. Alvarez-Puebla, L. M. Liz-Marzán, and F. J. García de Abajo, Light Concentration at the Nanometer Scale, *The Journal of Physical Chemistry Letters* **1**, 2428–2434 (2010).
- [60] D. K. and S. I. Bozhevolnyi, Plasmonics beyond the diffraction limit, *Nature Photonics* **4**, 83–91 (2010).
- [61] S. I. Bozhevolnyi, V. S. Volkov, E. Devaux, J.-Y. Laluet, and T. W. Ebbesen, Channel plasmon subwavelength waveguide components including interferometers and ring resonators, *Nature* **440**, 508–511 (2006).
- [62] M. E. Stewart, C. R. Anderton, L. B. Thompson, J. Maria, S. K. Gray, J. A. Rogers, and R. G. Nuzzo, Nanostructured Plasmonic Sensors, *Chemical Reviews* **108**, 494–521 (2008).
- [63] N. Yu, P. Genevet, M. A. Kats, F. Aieta, J.-P. Tetienne, F. Capasso, and Z. Gaburro, Light Propagation with Phase Discontinuities: Generalized Laws of Reflection and Refraction, *Science* **334**, 333–337 (2011).

- [64] T. Ellenbogen, K. Seo, and K. B. Crozier, Chromatic Plasmonic Polarizers for Active Visible Color Filtering and Polarimetry, *Nano Letters* **12**, 1026–1031 (2012).
- [65] A. Boltasseva and H. A. Atwater, Low-Loss Plasmonic Metamaterials, *Science* **331**, 290–291 (2011).
- [66] A. N. Grigorenko, M. Polini, and K. S. Novoselov, Graphene plasmonics, *Nature Photonics* **6**, 749–758 (2012).
- [67] H. A. Atwater and A. Polman, Plasmonics for improved photovoltaic devices, *Nature Materials* **9**, 205–213 (2010).
- [68] A. Polman and H. A. Atwater, Photonic design principles for ultrahigh-efficiency photovoltaics, *Nature Materials* **11**, 174–177 (2012).
- [69] H. A. Atwater, The promise of plasmonics, *Scientific American* **296**, 56–63 (2007).
- [70] S. A. Maier, Plasmonics: The promise of highly integrated optical devices, *IEEE Journal of Selected Topics in Quantum Electronics* **12**, 1671–1677 (2006).
- [71] M. Brongersma, N. Halas, and P. Nordlander, Plasmon-induced hot carrier science and technology, *Nature Nanotechnology* **10**, 25–34 (2015).
- [72] S. A. Maier and H. A. Atwater, Plasmonics: Localization and guiding of electromagnetic energy in metal/dielectric structures, *Journal of Applied Physics* **98**, 011101 (2005).
- [73] E. Cortés, W. Xie, J. Cambiasso, A. S. Jermyn, R. Sundararaman, P. Narang, S. Schlücker, and S. A. Maier, Plasmonic hot electron transport drives nanolocalized chemistry, *Nature Communications* **8**, 14880 (2017).
- [74] E. Cortés, L. V. Besteiro, A. Alabastri, A. Baldi, G. Tagliabue, A. Demetriadou, and P. Narang, Challenges in Plasmonic Catalysis, *ACS Nano* **14**, 16202–16219 (2020).
- [75] S. Ezendam, M. Herran, L. Nan, C. Gruber, Y. Kang, F. Gröbmeyer, R. Lin, J. Gargiulo, A. Sousa-Castillo, and E. Cortés, Hybrid Plasmonic Nanomaterials for Hydrogen Generation and Carbon Dioxide Reduction, *ACS Energy Letters* **7**, 778–815 (2022).
- [76] H. Fischer and O. J. F. Martin, Engineering the optical response of plasmonic nanoantennas, *Optics Express* **16**, 9144 (2008).
- [77] L. Novotny and N. Van Hulst, Antennas for light, *Nature Photonics* **5**, 83–90 (2011).
- [78] D. Lin, P. Fan, E. Hasman, and M. L. Brongersma, Dielectric gradient metasurface optical elements, *Science* **345**, 298–302 (2014).
- [79] A. M. Shaltout, V. M. Shalaev, and M. L. Brongersma, Spatiotemporal light control with active metasurfaces, *Science* **364**, eaat3100 (2019).
- [80] X. Ni, N. K. Emani, A. V. Kildishev, A. Boltasseva, and V. M. Shalaev, Broadband Light Bending with Plasmonic Nanoantennas, *Science* **335**, 427–427 (2012).

-
- [81] K. Li, M. I. Stockman, and D. J. Bergman, Self-Similar Chain of Metal Nanospheres as an Efficient Nanolens, *Physical Review Letters* **91**, 227402 (2003).
- [82] L. Verslegers, P. B. Catrysse, Z. Yu, J. S. White, E. S. Barnard, M. L. Brongersma, and S. Fan, Planar Lenses Based on Nanoscale Slit Arrays in a Metallic Film, *Nano Letters* **9**, 235–238 (2009).
- [83] W. Cai, J. S. White, and M. L. Brongersma, Compact, High-Speed and Power-Efficient Electrooptic Plasmonic Modulators, *Nano Letters* **9**, 4403–4411 (2009).
- [84] J. A. Dionne, K. Diest, L. A. Sweatlock, and H. A. Atwater, PlasMOStor: A Metal-Oxide-Si Field Effect Plasmonic Modulator, *Nano Letters* **9**, 897–902 (2009).
- [85] L. R. Hirsch, R. J. Stafford, J. A. Bankson, S. R. Sershen, B. Rivera, R. E. Price, J. D. Hazle, N. J. Halas, and J. L. West, Nanoshell-mediated near-infrared thermal therapy of tumors under magnetic resonance guidance, *Proceedings of the National Academy of Sciences* **100**, 13549–13554 (2003).
- [86] S. Lal, S. E. Clare, and N. J. Halas, Nanoshell-Enabled Photothermal Cancer Therapy: Impending Clinical Impact, *Accounts of Chemical Research* **41**, 1842–1851 (2008).
- [87] A. G. Brolo, Plasmonics for future biosensors, *Nature Photonics* **6**, 709–713 (2012).
- [88] N. Liu, M. Mesch, T. Weiss, M. Hentschel, and H. Giessen, Infrared Perfect Absorber and Its Application As Plasmonic Sensor, *Nano Letters* **10**, 2342–2348 (2010).
- [89] R. A. Pala, J. White, E. Barnard, J. Liu, and M. L. Brongersma, Design of Plasmonic Thin-Film Solar Cells with Broadband Absorption Enhancements, *Advanced Materials* **21**, 3504–3509 (2009).
- [90] I. Thomann, B. A. Pinaud, Z. Chen, B. M. Clemens, T. F. Jaramillo, and M. L. Brongersma, Plasmon Enhanced Solar-to-Fuel Energy Conversion, *Nano Letters* **11**, 3440–3446 (2011).
- [91] C. G. Biris and N. C. Panoiu, Second harmonic generation in metamaterials based on homogeneous centrosymmetric nanowires, *Physical Review B* **81**, 195102 (2010).
- [92] A. Hille, M. Moefertdt, C. Wolff, C. Matyssek, R. Rodríguez-Oliveros, C. Prohm, J. Niegemann, S. Grafström, L. M. Eng, and K. Busch, Second Harmonic Generation from Metal Nano-Particle Resonators: Numerical Analysis On the Basis of the Hydrodynamic Drude Model, *The Journal of Physical Chemistry C* **120**, 1163–1169 (2016).
- [93] M. Kauranen and A. V. Zayats, Nonlinear plasmonics, *Nature Photonics* **6**, 737–748 (2012).
- [94] N. C. Panoiu, W. E. I. Sha, D. Y. Lei, and G.-C. Li, Nonlinear optics in plasmonic nanostructures, *Journal of Optics* **20**, 083001 (2018).

- [95] Y. Zhang, N. K. Grady, C. Ayala-Orozco, and N. J. Halas, Three-Dimensional Nanostructures as Highly Efficient Generators of Second Harmonic Light, *Nano Letters* **11**, 5519–5523 (2011).
- [96] S. Mukherjee, F. Libisch, N. Large, O. Neumann, L. V. Brown, J. Cheng, J. B. Lassiter, E. A. Carter, P. Nordlander, and N. J. Halas, Hot Electrons Do the Impossible: Plasmon-Induced Dissociation of H₂ on Au, *Nano Letters* **13**, 240–247 (2013).
- [97] G. M. Akselrod, C. Argyropoulos, T. B. Hoang, C. Ciraci, C. Fang, J. Huang, D. R. Smith, and M. H. Mikkelsen, Probing the mechanisms of large Purcell enhancement in plasmonic nanoantennas, *Nature Photonics* **8**, 835–840 (2014).
- [98] C. Van Vlack, P. T. Kristensen, and S. Hughes, Spontaneous emission spectra and quantum light-matter interactions from a strongly coupled quantum dot metal-nanoparticle system, *Physical Review B* **85**, 075303 (2012).
- [99] P. Yao, C. Van Vlack, A. Reza, M. Patterson, M. M. Dignam, and S. Hughes, Ultrahigh Purcell factors and Lamb shifts in slow-light metamaterial waveguides, *Physical Review B* **80**, 195106 (2009).
- [100] K. F. MacDonald, Z. L. Sámsón, M. I. Stockman, and N. I. Zheludev, Ultrafast active plasmonics, *Nature Photonics* **3**, 55–58 (2009).
- [101] N. Jiang, X. Zhuo, and J. Wang, Active Plasmonics: Principles, Structures, and Applications, *Chemical Reviews* **118**, 3054–3099 (2018).
- [102] I. Ahmed, E. H. Khoo, O. Kurniawan, and E. P. Li, Modeling and simulation of active plasmonics with the FDTD method by using solid state and Lorentz–Drude dispersive model, *Journal of the Optical Society of America B* **28**, 352–359 (2011).
- [103] A. V. Krasavin and N. I. Zheludev, Active plasmonics: Controlling signals in Au/Ga waveguide using nanoscale structural transformations, *Applied Physics Letters* **84**, 1416–1418 (2004).
- [104] P. Pertsch, R. Kulkock, V. Gabriel, L. Zurak, M. Emmerling, and B. Hecht, Tunable Nanoplasmonic Photodetectors, *Nano Letters* **22**, 6982–6987 (2022).
- [105] H. Xu, E. J. Bjerneld, M. Käll, and L. Börjesson, Spectroscopy of Single Hemoglobin Molecules by Surface Enhanced Raman Scattering, *Physical Review Letters* **83**, 4357–4360 (1999).
- [106] C. Sönnichsen, B. M. Reinhard, J. Liphardt, and A. P. Alivisatos, A molecular ruler based on plasmon coupling of single gold and silver nanoparticles, *Nature Biotechnology* **23**, 741–745 (2005).
- [107] R. Zhang, Y. Zhang, Z. C. Dong, S. Jiang, C. Zhang, L. G. Chen, L. Zhang, Y. Liao, J. Aizpurua, Y. Luo, J. L. Yang, and J. G. Hou, Chemical mapping of a single molecule by plasmon-enhanced Raman scattering, *Nature* **498**, 82–86 (2013).

-
- [108] R. Chikkaraddy, B. de Nijs, F. Benz, S. J. Barrow, O. A. Scherman, E. Rosta, A. Demetriadou, P. Fox, O. Hess, and J. J. Baumberg, Single-molecule strong coupling at room temperature in plasmonic nanocavities, *Nature* **535**, 127–130 (2016).
- [109] A. Babaze, R. Esteban, A. G. Borisov, and J. Aizpurua, Electronic Exciton–Plasmon Coupling in a Nanocavity Beyond the Electromagnetic Interaction Picture, *Nano Letters* **21**, 8466–8473 (2021).
- [110] P. Törmä and W. L. Barnes, Strong coupling between surface plasmon polaritons and emitters: A review, *Reports on Progress in Physics* **78**, 013901 (2015).
- [111] C. Carlson, R. Salzwedel, M. Selig, A. Knorr, and S. Hughes, Strong coupling regime and hybrid quasinormal modes from a single plasmonic resonator coupled to a transition metal dichalcogenide monolayer, *Physical Review B* **104**, 125424 (2021).
- [112] R.-C. Ge, C. V. Vlack, P. Yao, J. F. Young, and S. Hughes, Accessing quantum nanoplasmonics in a hybrid quantum dot–metal nanosystem: Mollow triplet of a quantum dot near a metal nanoparticle, *Physical Review B* **87**, 205425 (2013).
- [113] J.-Y. Li, W. Li, J. Liu, J. Zhong, R. Liu, H. Chen, and X.-H. Wang, Room-Temperature Strong Coupling Between a Single Quantum Dot and a Single Plasmonic Nanoparticle, *Nano Letters* **22**, 4686–4693 (2022).
- [114] J. Lawless, C. Hrelescu, C. Elliott, L. Peters, N. McEvoy, and A. L. Bradley, Influence of Gold Nano-Bipyramid Dimensions on Strong Coupling with Excitons of Monolayer MoS₂, *ACS Applied Materials & Interfaces* **12**, 46406–46415 (2020).
- [115] E. Kokin, H. J. An, D. Koo, S. Han, K. Whang, T. Kang, I. Choi, and L. P. Lee, Quantum Electrodynamical Behavior of Chlorophyll in a Plasmonic Nanocavity, *Nano Letters* **22**, 9861–9868 (2022).
- [116] H. Groß, J. M. Hamm, T. Tufarelli, O. Hess, and B. Hecht, Near-field strong coupling of single quantum dots, *Science Advances* **4**, eaar4906 (2018).
- [117] D. Friedrich, J. Qin, B. Schurr, T. Tufarelli, H. Groß, and B. Hecht, Anticrossing of a plasmonic nanoresonator mode and a single quantum dot at room temperature (2023), [arxiv:2305.06909](https://arxiv.org/abs/2305.06909).
- [118] F. Stete, W. Koopman, C. Henkel, O. Benson, G. Kewes, and M. Bargheer, Optical Spectra of Plasmon–Exciton Core–Shell Nanoparticles: A Heuristic Quantum Approach, *ACS Photonics* **10**, 2511–2520 (2023).
- [119] P. Drude, Zur Elektronentheorie der Metalle, *Annalen der Physik* **306**, 566–613 (1900).
- [120] D. Bohm and D. Pines, A collective description of electron interactions. I. Magnetic interactions, *Physical Review* **82**, 625–634 (1951).
- [121] D. Pines and D. Bohm, A collective description of electron interactions: II. Collective vs individual particle aspects of the interactions, *Physical Review* **85**, 338–353 (1952).

- [122] D. Bohm and D. Pines, A collective description of electron interactions: III. Coulomb interactions in a degenerate electron gas, *Physical Review* **92**, 609–625 (1953).
- [123] D. Pines, A collective description of electron interactions: IV. Electron interaction in metals, *Physical Review* **92**, 626–636 (1953).
- [124] N. J. Halas, S. Lal, W.-S. Chang, S. Link, and P. Nordlander, Plasmons in Strongly Coupled Metallic Nanostructures, *Chemical Reviews* **111**, 3913–3961 (2011).
- [125] E. Prodan and P. Nordlander, Structural Tunability of the Plasmon Resonances in Metallic Nanoshells, *Nano Letters* **3**, 543–547 (2003).
- [126] R.-C. Ge, P. T. Kristensen, J. F. Young, and S. Hughes, Quasinormal mode approach to modelling light-emission and propagation in nanoplasmonics, *New Journal of Physics* **16**, 113048 (2014).
- [127] P. T. Kristensen, R.-C. Ge, and S. Hughes, Normalization of quasinormal modes in leaky optical cavities and plasmonic resonators, *Physical Review A* **92**, 053810 (2015).
- [128] S. Franke, S. Hughes, M. K. Dezfouli, P. T. Kristensen, K. Busch, A. Knorr, and M. Richter, Quantization of Quasinormal Modes for Open Cavities and Plasmonic Cavity Quantum Electrodynamics, *Physical Review Letters* **122**, 213901 (2019).
- [129] S. Franke, M. Richter, J. Ren, A. Knorr, and S. Hughes, Quantized quasinormal-mode description of nonlinear cavity-QED effects from coupled resonators with a Fano-like resonance, *Physical Review Research* **2**, 033456 (2020).
- [130] J. Ren, S. Franke, and S. Hughes, Quasinormal Modes, Local Density of States, and Classical Purcell Factors for Coupled Loss-Gain Resonators, *Physical Review X* **11**, 041020 (2021).
- [131] A. Taflov and S. C. Hagness, *Computational Electrodynamics: The Finite-Difference Time-Domain Method* (Artech House, Boston, 2005).
- [132] J.-M. Jin, *The Finite Element Method in Electromagnetics* (John Wiley & Sons, Hoboken, 2015).
- [133] F. J. García de Abajo and A. Howie, Retarded field calculation of electron energy loss in inhomogeneous dielectrics, *Physical Review B* **65**, 115418 (2002).
- [134] D. N. Basov, M. M. Fogler, and F. J. García de Abajo, Polaritons in van der Waals materials, *Science* **354**, aag1992 (2016).
- [135] P. A. D. Gonçalves and N. M. Peres, *An Introduction to Graphene Plasmonics* (World Scientific, Singapore, 2016).
- [136] T. Christensen, *From Classical to Quantum Plasmonics in Three and Two Dimensions*, Springer Theses (Springer, Cham, 2017).
- [137] A. Kavokin, ed., *Microcavities*, Series on Semiconductor Science and Technology (Oxford University Press, Oxford, 2017).

-
- [138] J. J. Baumberg, Picocavities: A Primer, *Nano Letters* **22**, 5859–5865 (2022).
- [139] N. Kongsuwan, A. Demetriadou, M. Horton, R. Chikkaraddy, J. J. Baumberg, and O. Hess, Plasmonic Nanocavity Modes: From Near-Field to Far-Field Radiation, *ACS Photonics* **7**, 463–471 (2020).
- [140] C. Ciracì, R. T. Hill, J. J. Mock, Y. Urzhumov, A. I. Fernández-Domínguez, S. A. Maier, J. B. Pendry, A. Chilkoti, and D. R. Smith, Probing the Ultimate Limits of Plasmonic Enhancement, *Science* **337**, 1072–1074 (2012).
- [141] M. S. Tame, K. R. McEnery, Ş. K. Özdemir, J. Lee, S. A. Maier, and M. S. Kim, Quantum Plasmonics, *Nature Physics* **9**, 329–340 (2013).
- [142] S. I. Bozhevolnyi, L. Martin-Moreno, and F. J. García-Vidal, eds., *Quantum Plasmonics*, Springer Series in Solid-State Sciences (Springer, Cham, 2017).
- [143] J. J. Baumberg, J. Aizpurua, M. H. Mikkelsen, and D. R. Smith, Extreme nanophotonics from ultrathin metallic gaps, *Nature Materials* **18**, 668–678 (2019).
- [144] S. I. Bozhevolnyi and N. A. Mortensen, Plasmonics for emerging quantum technologies, *Nanophotonics* **6**, 1185–1188 (2017).
- [145] P. Halevi, Hydrodynamic model for the degenerate free-electron gas: Generalization to arbitrary frequencies, *Physical Review B* **51**, 7497–7499 (1995).
- [146] F. J. García de Abajo, Nonlocal Effects in the Plasmons of Strongly Interacting Nanoparticles, Dimers, and Waveguides, *The Journal of Physical Chemistry C* **112**, 17983–17987 (2008).
- [147] J. M. McMahon, S. K. Gray, and G. C. Schatz, Nonlocal Optical Response of Metal Nanostructures with Arbitrary Shape, *Physical Review Letters* **103**, 097403 (2009).
- [148] S. A. Khan and M. Bonitz, Quantum Hydrodynamics, in *Complex Plasmas: Scientific Challenges and Technological Opportunities*, Springer Series on Atomic, Optical, and Plasma Physics (Springer, Cham, 2014).
- [149] G. Toscano, J. Straubel, A. Kwiatkowski, C. Rockstuhl, F. Evers, H. Xu, N. Asger Mortensen, and M. Wubs, Resonance shifts and spill-out effects in self-consistent hydrodynamic nanoplasmonics, *Nature Communications* **6**, 7132 (2015).
- [150] C. Ciracì and F. Della Sala, Quantum hydrodynamic theory for plasmonics: Impact of the electron density tail, *Physical Review B* **93**, 205405 (2016).
- [151] N. A. Mortensen, S. Raza, M. Wubs, T. Søndergaard, and S. I. Bozhevolnyi, A generalized non-local optical response theory for plasmonic nanostructures, *Nature Communications* **5**, 3809 (2014).
- [152] P. Ginzburg, A. V. Krasavin, G. A. Wurtz, and A. V. Zayats, Nonperturbative Hydrodynamic Model for Multiple Harmonics Generation in Metallic Nanostructures, *ACS Photonics* **2**, 8–13 (2015).
- [153] P. Feibelman, Surface electromagnetic fields, *Progress in Surface Science* **12**, 287–407 (1982).

- [154] Y. Yang, D. Zhu, W. Yan, A. Agarwal, M. Zheng, J. D. Joannopoulos, P. Lalanne, T. Christensen, K. K. Berggren, and M. Soljačić, A general theoretical and experimental framework for nanoscale electromagnetism, *Nature* **576**, 248–252 (2019).
- [155] W. Yan, M. Wubs, and N. Asger Mortensen, Projected Dipole Model for Quantum Plasmonics, *Physical Review Letters* **115**, 137403 (2015).
- [156] N. A. Mortensen, P. a. D. Gonçalves, F. A. Shuklin, J. D. Cox, C. Tserkezis, M. Ichikawa, and C. Wolff, Surface-response functions obtained from equilibrium electron-density profiles, *Nanophotonics* **10**, 3647–3657 (2021).
- [157] A. Manjavacas, F. J. García de Abajo, and P. Nordlander, Quantum Plexcitonics: Strongly Interacting Plasmons and Excitons, *Nano Letters* **11**, 2318–2323 (2011).
- [158] N. T. Fofang, T.-H. Park, O. Neumann, N. A. Mirin, P. Nordlander, and N. J. Halas, Plexcitonic Nanoparticles: Plasmon-Exciton Coupling in Nanoshell-J-Aggregate Complexes, *Nano Letters* **8**, 3481–3487 (2008).
- [159] R. Sáez-Blázquez, Á. Cuartero-González, J. Feist, F. J. García-Vidal, and A. I. Fernández-Domínguez, Plexcitonic Quantum Light Emission from Nanoparticle-on-Mirror Cavities, *Nano Letters* **22**, 2365–2373 (2022).
- [160] X. Xiong, N. Kongsuwan, Y. Lai, C. E. Png, L. Wu, and O. Hess, Room-temperature plexcitonic strong coupling: Ultrafast dynamics for quantum applications, *Applied Physics Letters* **118**, 130501 (2021).
- [161] W. Zhang, J.-B. You, J. Liu, X. Xiong, Z. Li, C. E. Png, L. Wu, C.-W. Qiu, and Z.-K. Zhou, Steering Room-Temperature Plexcitonic Strong Coupling: A Diexcitonic Perspective, *Nano Letters* **21**, 8979–8986 (2021).
- [162] A. I. Fernández-Domínguez, S. I. Bozhevolnyi, and N. A. Mortensen, Plasmon-Enhanced Generation of Nonclassical Light, *ACS Photonics* **5**, 3447–3451 (2018).
- [163] E. Schrödinger, An Undulatory Theory of the Mechanics of Atoms and Molecules, *Physical Review* **28**, 1049–1070 (1926).
- [164] W. Heisenberg, Über quantentheoretische Umdeutung kinematischer und mechanischer Beziehungen, *Zeitschrift für Physik* **33**, 879–893 (1925).
- [165] O. Madelung, *Introduction to Solid-State Theory* (Springer, Berlin Heidelberg, 1978).
- [166] C. Kittel, *Introduction to Solid State Physics* (Wiley, Hoboken, 2005).
- [167] G. Czycholl, *Theoretische Festkörperphysik. Band 1: Grundlagen: Phononen und Elektronen in Kristallen* (Springer, Berlin Heidelberg, 2016).
- [168] C. Kittel and C. Y. Fong, *Quantum Theory of Solids* (Wiley, New York, 1987).
- [169] P. Ehrenfest, Bemerkung über die angenäherte Gültigkeit der klassischen Mechanik innerhalb der Quantenmechanik, *Zeitschrift für Physik* **45**, 455–457 (1927).
- [170] H. Haug and S. W. Koch, *Quantum Theory of the Optical and Electronic Properties of Semiconductors* (World Scientific, Singapore, 2004).

-
- [171] M. Kira and S. W. Koch, *Semiconductor Quantum Optics* (Cambridge University Press, Cambridge, 2012).
 - [172] E. Malic, A. Knorr, and S. Winnerl, *Graphene and Carbon Nanotubes: Ultrafast Relaxation Dynamics and Optics* (Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2013).
 - [173] M. Lindberg and S. W. Koch, Effective Bloch equations for semiconductors, *Physical Review B* **38**, 3342–3350 (1988).
 - [174] S. Butscher, F. Milde, M. Hirtschulz, E. Malić, and A. Knorr, Hot electron relaxation and phonon dynamics in graphene, *Applied Physics Letters* **91**, 203103 (2007).
 - [175] T. Kuhn, Density matrix theory of coherent ultrafast dynamics, in *Theory of Transport Properties of Semiconductor Nanostructures*, edited by E. Schöll (Springer US, Boston, 1998).
 - [176] M. Selig, G. Berghäuser, A. Raja, P. Nagler, C. Schüller, T. F. Heinz, T. Korn, A. Chernikov, E. Malic, and A. Knorr, Excitonic linewidth and coherence lifetime in monolayer transition metal dichalcogenides, *Nature Communications* **7**, 13279 (2016).
 - [177] M. Katzer, *Excitons between bosonic and fermionic nature*, *Ph.D. thesis*, Technische Universität Berlin, Berlin (2023).
 - [178] M. Katzer, M. Selig, L. Sigl, M. Troue, J. Figueiredo, J. Kiemle, F. Sigger, U. Wurstbauer, A. W. Holleitner, and A. Knorr, Exciton-phonon scattering: Competition between the bosonic and fermionic nature of bound electron-hole pairs, *Physical Review B* **108**, L121102 (2023).
 - [179] F. Katsch, M. Selig, A. Carmele, and A. Knorr, Theory of Exciton–Exciton Interactions in Monolayer Transition Metal Dichalcogenides, *physica status solidi (b)* **255**, 1800185 (2018).
 - [180] D. Christiansen, M. Selig, G. Berghäuser, R. Schmidt, I. Niehues, R. Schneider, A. Arora, S. M. de Vasconcellos, R. Bratschitsch, E. Malic, and A. Knorr, Phonon Sidebands in Monolayer Transition Metal Dichalcogenides, *Physical Review Letters* **119**, 187402 (2017).
 - [181] I. N. Bronstein, J. Hromkovic, B. Luderer, H.-R. Schwarz, J. Blath, A. Schied, S. Dempe, G. Wanka, and S. Gottwald, *Taschenbuch Der Mathematik* (Springer-Verlag, Wiesbaden, 2012).
 - [182] W. Heitler, *The Quantum Theory of Radiation* (Clarendon Press, Oxford, 1984).
 - [183] I. Waldmüller, *Intersubband Dynamics in Semiconductor Quantum Wells – Linear and Nonlinear Response of Quantum Confined Electrons*, *Ph.D. thesis*, Technische Universität Berlin, Berlin (2005).
 - [184] R. A. Bromley, R. B. Murray, and A. D. Yoffe, The band structures of some transition metal dichalcogenides. III. Group VIA: Trigonal prism materials, *Journal of Physics C: Solid State Physics* **5**, 759–778 (1972).

- [185] G.-B. Liu, D. Xiao, Y. Yao, X. Xu, and W. Yao, Electronic structures and theoretical modelling of two-dimensional group-VIB transition metal dichalcogenides, [Chemical Society Reviews](#) **44**, 2643–2663 (2015).
- [186] J. A. Wilson and A. D. Yoffe, The transition metal dichalcogenides discussion and interpretation of the observed optical, electrical and structural properties, [Advances in Physics](#) **18**, 193–335 (1969).
- [187] G. L. Bir and G. E. Pikus, *Symmetry and Strain-Induced Effects in Semiconductors* (Wiley, New York, 1974).
- [188] A. Ramasubramaniam, Large excitonic effects in monolayers of molybdenum and tungsten dichalcogenides, [Physical Review B](#) **86**, 115409 (2012).
- [189] Z. Y. Zhu, Y. C. Cheng, and U. Schwingenschlögl, Giant spin-orbit-induced spin splitting in two-dimensional transition-metal dichalcogenide semiconductors, [Physical Review B](#) **84**, 153402 (2011).
- [190] T. Cheiwchanchamnangij and W. R. L. Lambrecht, Quasiparticle band structure calculation of monolayer, bilayer, and bulk MoS₂, [Physical Review B](#) **85**, 205302 (2012).
- [191] D. Y. Qiu, F. H. da Jornada, and S. G. Louie, Optical Spectrum of MoS₂ : Many-Body Effects and Diversity of Exciton States, [Physical Review Letters](#) **111**, 216805 (2013).
- [192] J. C. Maxwell, *A Treatise on Electricity and Magnetism* (Clarendon Press, Oxford, 1873).
- [193] O. Heaviside, *Electromagnetic Theory* (American Mathematical Society, Providence, 2003).
- [194] B. Gallinet, J. Butet, and O. J. F. Martin, Numerical methods for nanophotonics: Standard problems and future challenges, [Laser & Photonics Reviews](#) **9**, 577–603 (2015).
- [195] COMSOL Multiphysics®, COMSOL AB.
- [196] Lumerical Inc.
- [197] A. M. Kern and O. J. F. Martin, Surface integral formulation for 3D simulations of plasmonic and high permittivity nanostructures, [Journal of the Optical Society of America A](#) **26**, 732–740 (2009).
- [198] J. S. Hesthaven and T. Warburton, *Nodal Discontinuous Galerkin Methods: : Algorithms, Analysis, and Applications*, edited by J. E. Marsden, L. Sirovich, and S. S. Antman, Texts in Applied Mathematics (Springer Science & Business Media, New York, 2008).
- [199] K. Busch, M. König, and J. Niegemann, Discontinuous Galerkin methods in nanophotonics, [Laser & Photonics Reviews](#) **5**, 773–809 (2011).

- [200] O. J. F. Martin and N. B. Piller, Electromagnetic scattering in polarizable backgrounds, [Physical Review E](#) **58**, 3909–3915 (1998).
- [201] J. D. Jackson, *Classical Electrodynamics* (John Wiley & Sons, Hoboken, 1999).
- [202] P. A. D. Gonçalves, *Plasmonics and Light–Matter Interactions in Two-Dimensional Materials and in Metal Nanostructures: Classical and Quantum Considerations*, Springer Theses (Springer, Cham, 2020).
- [203] A. A. Maradudin, J. R. Sambles, and W. L. Barnes, *Modern Plasmonics*, Handbook of Surface Science (Elsevier, Amsterdam, 2014).
- [204] H. U. Yang, J. D’Archangel, M. L. Sundheimer, E. Tucker, G. D. Boreman, and M. B. Raschke, Optical dielectric function of silver, [Physical Review B](#) **91**, 235137 (2015).
- [205] E. K. U. Gross, E. Runge, and O. Heinonen, *Many-Particle Theory* (Adam Hilger, Bristol, 1986).
- [206] M. Kaganov, I. Lifshitz, and L. Tanatarov, Relaxation between Electrons and the Crystalline Lattice, *Soviet Physics JETP* **4**, 173–178 (1957).
- [207] S. I. Anisimov, B. L. Kapeliovich, and T. L. Perelman, Electron emission from metal surfaces exposed to ultrashort laser pulses, *Zh. Eksp. Teor. Fiz* **66**, 375–377 (1974).
- [208] J. G. Fujimoto, J. M. Liu, E. P. Ippen, and N. Bloembergen, Femtosecond Laser Interaction with Metallic Tungsten and Nonequilibrium Electron and Lattice Temperatures, [Physical Review Letters](#) **53**, 1837–1840 (1984).
- [209] H. E. Elsayed-Ali, T. B. Norris, M. A. Pessot, and G. A. Mourou, Time-resolved observation of electron-phonon relaxation in copper, [Physical Review Letters](#) **58**, 1212–1215 (1987).
- [210] R. W. Schoenlein, W. Z. Lin, J. G. Fujimoto, and G. L. Eesley, Femtosecond studies of nonequilibrium electronic processes in metals, [Physical Review Letters](#) **58**, 1680–1683 (1987).
- [211] R. H. M. Groeneveld, R. Sprik, and A. Lagendijk, Femtosecond spectroscopy of electron-electron and electron-phonon energy relaxation in Ag and Au, [Physical Review B](#) **51**, 11433–11445 (1995).
- [212] C.-K. Sun, F. Vallée, L. H. Acioli, E. P. Ippen, and J. G. Fujimoto, Femtosecond-tunable measurement of electron thermalization in gold, [Physical Review B](#) **50**, 15337–15348 (1994).
- [213] W. S. Fann, R. Storz, H. W. K. Tom, and J. Bokor, Electron thermalization in gold, [Physical Review B](#) **46**, 13592–13595 (1992).
- [214] C.-K. Sun, F. Vallée, L. Acioli, E. P. Ippen, and J. G. Fujimoto, Femtosecond investigation of electron thermalization in gold, [Physical Review B](#) **48**, 12365–12368 (1993).

- [215] A. Schirato, M. Maiuri, A. Toma, S. Fugattini, R. Proietti Zaccaria, P. Laporta, P. Nordlander, G. Cerullo, A. Alabastri, and G. Della Valle, Transient optical symmetry breaking for ultrafast broadband dichroism in plasmonic metasurfaces, *Nature Photonics* **14**, 723–727 (2020).
- [216] A. Schirato, A. Mazzanti, R. Proietti Zaccaria, P. Nordlander, A. Alabastri, and G. Della Valle, All-Optically Reconfigurable Plasmonic Metagrating for Ultrafast Diffraction Management, *Nano Letters* **21**, 1345–1351 (2021).
- [217] A. Schirato, G. Crotti, R. Proietti Zaccaria, A. Alabastri, and G. Della Valle, Hot carrier spatio-temporal inhomogeneities in ultrafast nanophotonics, *New Journal of Physics* **24**, 045001 (2022).
- [218] M. Zavelani-Rossi, D. Polli, S. Kochtcheev, A.-L. Baudrion, J. Béal, V. Kumar, E. Molotokaite, M. Marangoni, S. Longhi, G. Cerullo, P.-M. Adam, and G. Della Valle, Transient Optical Response of a Single Gold Nanoantenna: The Role of Plasmon Detuning, *ACS Photonics* **2**, 521–529 (2015).
- [219] G. Della Valle, F. Scotognella, A. R. S. Kandada, M. Zavelani-Rossi, H. Li, M. Conforti, S. Longhi, L. Manna, G. Lanzani, and F. Tassone, Ultrafast Optical Mapping of Nonlinear Plasmon Dynamics in Cu_{2-x}Se Nanoparticles, *The Journal of Physical Chemistry Letters* **4**, 3337–3344 (2013).
- [220] P. B. Allen, Theory of thermal relaxation of electrons in metals, *Physical Review Letters* **59**, 1460–1463 (1987).
- [221] L. Jiang and H.-L. Tsai, Improved Two-Temperature Model and Its Application in Ultrashort Laser Heating of Metal Films, *Journal of Heat Transfer* **127**, 1167–1173 (2005).
- [222] J. M. Ziman, *Electrons and Phonons: The Theory of Transport Phenomena in Solids* (Oxford University Press, Oxford, 2001).
- [223] H. Haug, *Statistische Physik: Gleichgewichtstheorie und Kinetik* (Springer, Berlin Heidelberg, 2006).
- [224] D. W. Snoke, W. W. Rühle, Y.-C. Lu, and E. Bauser, Evolution of a nonthermal electron energy distribution in GaAs, *Physical Review B* **45**, 10979–10989 (1992).
- [225] F. Rossi, S. Haas, and T. Kuhn, Ultrafast relaxation of photoexcited carriers: The role of coherence in the generation process, *Physical Review Letters* **72**, 152–155 (1994).
- [226] A. Knorr, S. Hughes, T. Stroucken, and S. Koch, Theory of ultrafast spatio-temporal dynamics in semiconductor heterostructures, *Chemical Physics* **210**, 27–47 (1996).
- [227] S. Hughes, A. Knorr, S. Koch, R. Binder, R. Indik, and J. Moloney, The influence of electron-hole-scattering on the gain spectra of highly excited semiconductors, *Solid State Communications* **100**, 555–559 (1996).
- [228] W. W. Chow, S. W. Koch, and M. Sargent III, *Semiconductor-Laser Physics* (Springer, Berlin Heidelberg, 1997).

-
- [229] N. Del Fatti, C. Voisin, M. Achermann, S. Tzortzakis, D. Christofilos, and F. Vallée, Nonequilibrium electron dynamics in noble metals, *Physical Review B* **61**, 16956–16966 (2000).
- [230] J. R. M. Saavedra, A. Asenjo-Garcia, and F. J. García de Abajo, Hot-Electron Dynamics and Thermalization in Small Metallic Nanoparticles, *ACS Photonics* **3**, 1637–1646 (2016).
- [231] B. Rethfeld, A. Kaiser, M. Vicanek, and G. Simon, Ultrafast dynamics of nonequilibrium electrons in metals under femtosecond laser irradiation, *Physical Review B* **65**, 214303 (2002).
- [232] B. Rethfeld, D. S. Ivanov, M. E. Garcia, and S. I. Anisimov, Modelling ultrafast laser ablation, *Journal of Physics D: Applied Physics* **50**, 193001 (2017).
- [233] A. Kaiser, B. Rethfeld, M. Vicanek, and G. Simon, Microscopic processes in dielectrics under irradiation by subpicosecond laser pulses, *Physical Review B* **61**, 11437–11450 (2000).
- [234] D. W. Snoke and J. P. Wolfe, Population dynamics of a Bose gas near saturation, *Physical Review B* **39**, 4030–4037 (1989).
- [235] C. Voisin, N. D. Fatti, D. Christofilos, and F. Vallee, Ultrafast Electron Dynamics and Optical Nonlinearities in Metal Nanoparticles, *Journal of Physical Chemistry B* **105**, 2264–2280 (2001).
- [236] J. H. Collet, Screening and exchange in the theory of the femtosecond kinetics of the electron-hole plasma, *Physical Review B* **47**, 10279–10291 (1993).
- [237] B. K. Ridley, *Quantum Processes in Semiconductors* (Oxford University Press, Oxford, 1999).
- [238] T. Winzer, *Ultrafast Carrier Relaxation Dynamics in Graphene*, *Ph.D. thesis*, Technische Universität Berlin, Berlin (2013).
- [239] T. Winzer, A. Knorr, and E. Malic, Carrier Multiplication in Graphene, *Nano Letters* **10**, 4839–4843 (2010).
- [240] M. Breusing, S. Kuehn, T. Winzer, E. Malić, F. Milde, N. Severin, J. P. Rabe, C. Ropers, A. Knorr, and T. Elsaesser, Ultrafast nonequilibrium carrier dynamics in a single graphene layer, *Physical Review B* **83**, 153410 (2011).
- [241] M. Hirschschulz, E. Malic, F. Milde, and A. Knorr, Excitation-induced dephasing and ultrafast intrasubband relaxation in carbon nanotubes, *Physical Review B* **80**, 085405 (2009).
- [242] V. Meden, C. Wöhler, J. Fricke, and K. Schönhammer, Hot-electron relaxation: An exactly solvable model and improved quantum kinetic equations, *Physical Review B* **52**, 5624–5636 (1995).
- [243] M. Selig, F. Katsch, R. Schmidt, S. Michaelis de Vasconcellos, R. Bratschitsch, E. Malic, and A. Knorr, Ultrafast dynamics in monolayer transition metal dichalcogenides: Interplay of dark excitons, phonons, and intervalley exchange, *Physical Review Research* **1**, 022007 (2019).

- [244] E. Malic, T. Winzer, and A. Knorr, Efficient orientational carrier relaxation in optically excited graphene, *Applied Physics Letters* **101**, 213110 (2012).
- [245] E. Malic, T. Winzer, E. Bobkin, and A. Knorr, Microscopic theory of absorption and ultrafast many-particle kinetics in graphene, *Physical Review B* **84**, 205406 (2011).
- [246] F. Bloch, Bremsvermögen von Atomen mit mehreren Elektronen, *Zeitschrift für Physik* **81**, 363–376 (1933).
- [247] H. Jensen, Eigenschwingungen eines Fermi-Gases und Anwendung auf die Blochsche Bremsformel für schnelle Teilchen, *Zeitschrift für Physik* **106**, 620–632 (1937).
- [248] S. C. Ying, Hydrodynamic response of inhomogeneous metallic systems, *Il Nuovo Cimento B Series (1971-1996)* **23**, 270–281 (1974).
- [249] A. Eguiluz and J. J. Quinn, Hydrodynamic model for surface plasmons in metals and degenerate semiconductors, *Physical Review B* **14**, 1347–1361 (1976).
- [250] A. D. Boardman, *Electromagnetic Surface Modes* (Wiley, New York, 1982).
- [251] S. Raza, S. I. Bozhevolnyi, M. Wubs, and N. A. Mortensen, Nonlocal optical response in metallic nanostructures, *Journal of Physics: Condensed Matter* **27**, 183204 (2015).
- [252] N. A. Mortensen, Mesoscopic electrodynamics at metal surfaces: From quantum-corrected hydrodynamics to microscopic surface-response formalism, *Nanophotonics* **10**, 2563–2616 (2021).
- [253] C. Ciraci, J. B. Pendry, and D. R. Smith, Hydrodynamic Model for Plasmonics: A Macroscopic Approach to a Microscopic Problem, *ChemPhysChem* **14**, 1109–1116 (2013).
- [254] Z. Cai, Y. Fan, R. Li, T. Lu, and Y. Wang, Quantum hydrodynamic model by moment closure of Wigner equation, *Journal of Mathematical Physics* **53**, 103503 (2012).
- [255] A. J. Bennett and C. B. Duke, Self-Consistent-Field Model of Bimetallic Interfaces. I. Dipole Effects, *Physical Review* **160**, 541–553 (1967).
- [256] J. R. Smith, Self-Consistent Many-Electron Theory of Electron Work Functions and Surface Potential Characteristics for Selected Metals, *Physical Review* **181**, 522–529 (1969).
- [257] S. Raza, G. Toscano, A.-P. Jauho, M. Wubs, and N. A. Mortensen, Unusual resonances in nanoplasmonic structures due to nonlocal response, *Physical Review B* **84**, 121412 (2011).
- [258] A. Sommerfeld, Zur Elektronentheorie der Metalle auf Grund der Fermischen Statistik, *Zeitschrift für Physik* **47**, 1–32 (1928).

-
- [259] M. Moeferd, T. Kiel, T. Sproll, F. Intravaia, and K. Busch, Plasmonic modes in nanowire dimers: A study based on the hydrodynamic Drude model including nonlocal and nonlinear effects, *Physical Review B* **97**, 075431 (2018).
- [260] M. Wubs and N. A. Mortensen, Nonlocal Response in Plasmonic Nanostructures, in *Quantum Plasmonics*, edited by S. I. Bozhevolnyi, L. Martin-Moreno, and F. J. García-Vidal (Springer, Cham, 2017).
- [261] N. A. Mortensen, Nonlocal formalism for nanoplasmonics: Phenomenological and semi-classical considerations, *Photonics and Nanostructures - Fundamentals and Applications* **11**, 303–309 (2013).
- [262] Á. Rodríguez Echarri, P. A. D. Gonçalves, C. Tserkezis, F. J. García de Abajo, N. A. Mortensen, and J. D. Cox, Optical response of noble metal nanostructures: Quantum surface effects in crystallographic facets, *Optica* **8**, 710–721 (2021).
- [263] Á. Rodríguez Echarri, J. D. Cox, F. Iyikanat, and F. J. García de Abajo, Nonlinear plasmonic response in atomically thin metal films, *Nanophotonics* **10**, 4149–4159 (2021).
- [264] S. Raza, W. Yan, N. Stenger, M. Wubs, and N. A. Mortensen, Blueshift of the surface plasmon resonance in silver nanoparticles: Substrate effects, *Optics Express* **21**, 27344–27355 (2013).
- [265] F. De Luca, M. Ortolani, and C. Ciraci, Free electron harmonic generation in heavily doped semiconductors: The role of the materials properties, *EPJ Applied Metamaterials* **9**, 13 (2022).
- [266] T. Christensen, W. Yan, A.-P. Jauho, M. Soljačić, and N. A. Mortensen, Quantum Corrections in Nanoplasmonics: Shape, Scale, and Material, *Physical Review Letters* **118**, 157402 (2017).
- [267] W. Zhu, R. Esteban, A. G. Borisov, J. J. Baumberg, P. Nordlander, H. J. Lezec, J. Aizpurua, and K. B. Crozier, Quantum mechanical effects in plasmonic structures with subnanometre gaps, *Nature Communications* **7**, 11495 (2016).
- [268] A. Babaze, E. Ogando, P. E. Stamatopoulou, C. Tserkezis, N. A. Mortensen, J. Aizpurua, A. G. Borisov, and R. Esteban, Quantum surface effects in the electromagnetic coupling between a quantum emitter and a plasmonic nanoantenna: Time-dependent density functional theory vs. semiclassical Feibelman approach, *Optics Express* **30**, 21159–21183 (2022).
- [269] P. A. D. Gonçalves, T. Christensen, N. M. R. Peres, A.-P. Jauho, I. Epstein, F. H. L. Koppens, M. Soljačić, and N. A. Mortensen, Quantum surface-response of metals revealed by acoustic graphene plasmons, *Nature Communications* **12**, 3271 (2021).
- [270] C. F. Bohren and D. R. Huffman, *Absorption and Scattering of Light by Small Particles* (Wiley, New York, 1983).
- [271] H. Wang, F. Tam, N. K. Grady, and N. J. Halas, Cu Nanoshells: Effects of Interband Transitions on the Nanoparticle Plasmon Resonance, *The Journal of Physical Chemistry B* **109**, 18218–18222 (2005).

- [272] P. B. Johnson and R. W. Christy, Optical Constants of the Noble Metals, [Physical Review B](#) **6**, 4370–4379 (1972).
- [273] E. D. Palik, *Handbook of Optical Constants of Solids* (Academic Press, Boston, 1991).
- [274] A. Vial, A.-S. Grimault, D. Macías, D. Barchiesi, and M. L. de la Chapelle, Improved analytical fit of gold dispersion: Application to the modeling of extinction spectra with a finite-difference time-domain method, [Physical Review B](#) **71**, 085416 (2005).
- [275] A. D. Rakić, A. B. Djurišić, J. M. Elazar, and M. L. Majewski, Optical properties of metallic films for vertical-cavity optoelectronic devices, [Applied Optics](#) **37**, 5271–5283 (1998).
- [276] J. Leng, J. Opsal, H. Chu, M. Senko, and D. E. Aspnes, Analytic representations of the dielectric functions of materials for device and structural modeling, [Thin Solid Films](#) **313–314**, 132–136 (1998).
- [277] P. G. Etchegoin, E. C. Le Ru, and M. Meyer, An analytic model for the optical properties of gold, [The Journal of Chemical Physics](#) **125**, 164705 (2006).
- [278] V. Myroshnychenko, J. Rodríguez-Fernández, I. Pastoriza-Santos, A. M. Funston, C. Novo, P. Mulvaney, L. M. Liz-Marzán, and F. J. García de Abajo, Modelling the optical response of gold nanoparticles, [Chemical Society Reviews](#) **37**, 1792–1805 (2008).
- [279] U. Kreibig and M. Vollmer, *Optical Properties of Metal Clusters* (Springer, Berlin Heidelberg, 2013).
- [280] R. Rosei, F. Antonangeli, and U. M. Grassano, D bands position and width in gold from very low temperature thermomodulation measurements, [Surface Science](#) **37**, 689–699 (1973).
- [281] E. C. Le Ru and P. G. Etchegoin, *Principles of Surface-Enhanced Raman Spectroscopy: And Related Plasmonic Effects* (Elsevier, Amsterdam, 2009).
- [282] F. J. García de Abajo, Multiple scattering of radiation in clusters of dielectrics, [Physical Review B](#) **60**, 6086–6102 (1999).
- [283] D. J. de Aberasturi, A. B. Serrano-Montes, and L. M. Liz-Marzán, Modern Applications of Plasmonic Nanoparticles: From Energy to Health, [Advanced Optical Materials](#) **3**, 602–617 (2015).
- [284] S. A. Maier, M. L. Brongersma, P. G. Kik, S. Meltzer, A. a. G. Requicha, and H. A. Atwater, Plasmonics - A Route to Nanoscale Optical Devices, [Advanced Materials](#) **13**, 1501–1505 (2001).
- [285] S. Linic, P. Christopher, and D. B. Ingram, Plasmonic-metal nanostructures for efficient conversion of solar to chemical energy, [Nature Materials](#) **10**, 911–921 (2011).

- [286] U. Aslam, V. G. Rao, S. Chavez, and S. Linic, Catalytic conversion of solar to chemical energy on plasmonic metal nanostructures, *Nature Catalysis* **1**, 656–665 (2018).
- [287] L. Yuan, A. Kuriakose, J. Zhou, H. Robatjazi, P. Nordlander, and N. J. Halas, Plasmonically enhanced hydrogen evolution with an Al–TiO₂-Based photoelectrode, *The Journal of Physical Chemistry C* **126**, 13714–13719 (2022).
- [288] C. Loo, A. Lowery, N. Halas, J. West, and R. Drezek, Immunotargeted nanoshells for integrated cancer imaging and therapy, *Nano Letters* **5**, 709–711 (2005).
- [289] X. Huang, P. K. Jain, I. H. El-Sayed, and M. A. El-Sayed, Gold nanoparticles: Interesting optical properties and recent applications in cancer diagnostics and therapy, *Nanomedicine* **2**, 681–693 (2007).
- [290] P. K. Jain, I. H. El-Sayed, and M. A. El-Sayed, Au nanoparticles target cancer, *Nano Today* **2**, 18–29 (2007).
- [291] J. A. Stratton, *Electromagnetic Theory*, IEEE Press Series on Electromagnetic Wave Theory (John Wiley & Sons, Hoboken, 2007).
- [292] M. Born and E. Wolf, *Principles of Optics: Electromagnetic Theory of Propagation, Interference and Diffraction of Light* (Cambridge University Press, Cambridge, 1999).
- [293] S. Baur, S. Sanders, and A. Manjavacas, Hybridization of Lattice Resonances, *ACS Nano* **12**, 1618–1629 (2018).
- [294] K. Ohtaka and M. Inoue, Light scattering from macroscopic spherical bodies. I. Integrated density of states of transverse electromagnetic fields, *Physical Review B* **25**, 677–688 (1982).
- [295] R. Gans, Über die Form ultramikroskopischer Goldteilchen, *Annalen der Physik* **342**, 881–900 (1912).
- [296] D. J. Griffiths, *Introduction to Electrodynamics* (Prentice Hall, Upper Saddle River, 1999).
- [297] J. Chen, M. Badioli, P. Alonso-González, S. Thongrattanasiri, F. Huth, J. Osmond, M. Spasenović, A. Centeno, A. Pesquera, P. Godignon, A. Zurutuza Elorza, N. Camara, F. J. García de Abajo, R. Hillenbrand, and F. H. L. Koppens, Optical nano-imaging of gate-tunable graphene plasmons, *Nature* **487**, 77–81 (2012).
- [298] T. Bucher, A. Vaskin, R. Mupparapu, F. J. F. Löchner, A. George, K. E. Chong, S. Fasold, C. Neumann, D.-Y. Choi, F. Eilenberger, F. Setzpfandt, Y. S. Kivshar, T. Pertsch, A. Turchanin, and I. Staude, Tailoring Photoluminescence from MoS₂ Monolayers by Mie-Resonant Metasurfaces, *ACS Photonics* **6**, 1002–1009 (2019).
- [299] Y. Yang, W. Liu, Z. Lin, R. Pan, C. Gu, and J. Li, Plasmonic hybrids of two-dimensional transition metal dichalcogenides and nanoscale metals: Architectures, enhanced optical properties and devices, *Materials Today Physics* **17**, 100343 (2021).

- [300] H.-L. Liu, B. D. Annawati, N. T. Hung, D. P. Gulo, P. Solís-Fernández, K. Kawahara, H. Ago, and R. Saito, Interference of excitons and surface plasmons in the optical absorption spectra of monolayer and bilayer graphene, *Physical Review B* **107**, 165421 (2023).
- [301] S. De Liberato, Light-Matter Decoupling in the Deep Strong Coupling Regime: The Breakdown of the Purcell Effect, *Physical Review Letters* **112**, 016401 (2014).
- [302] N. S. Mueller, Y. Okamura, B. G. M. Vieira, S. Juergensen, H. Lange, E. B. Barros, F. Schulz, and S. Reich, Deep strong light-matter coupling in plasmonic nanoparticle crystals, *Nature* **583**, 780–784 (2020).
- [303] A. Frisk Kockum, A. Miranowicz, S. De Liberato, S. Savasta, and F. Nori, Ultrastrong coupling between light and matter, *Nature Reviews Physics* **1**, 19–40 (2019).
- [304] A. Bayer, M. Pozimski, S. Schambeck, D. Schuh, R. Huber, D. Bougeard, and C. Lange, Terahertz Light-Matter Interaction beyond Unity Coupling Strength, *Nano Letters* **17**, 6340–6344 (2017).
- [305] P. A. Thomas, K. S. Menghrajani, and W. L. Barnes, Cavity-Free Ultrastrong Light-Matter Coupling, *The Journal of Physical Chemistry Letters* **12**, 6914–6918 (2021).
- [306] R. Pandya, R. Y. S. Chen, Q. Gu, J. Sung, C. Schnedermann, O. S. Ojambati, R. Chikkaraddy, J. Gorman, G. Jacucci, O. D. Onelli, T. Willhammar, D. N. Johnstone, S. M. Collins, P. A. Midgley, F. Auras, T. Baikie, R. Jayaprakash, F. Mathevet, R. Soucek, M. Du, A. M. Alvertis, A. Ashoka, S. Vignolini, D. G. Lidzey, J. J. Baumberg, R. H. Friend, T. Barisien, L. Legrand, A. W. Chin, J. Yuen-Zhou, S. K. Saikin, P. Kukura, A. J. Musser, and A. Rao, Microcavity-like exciton-polaritons can be the primary photoexcitation in bare organic semiconductors, *Nature Communications* **12**, 6519 (2021).
- [307] M. Kuisma, B. Rousseaux, K. M. Czajkowski, T. P. Rossi, T. Shegai, P. Erhart, and T. J. Antosiewicz, Ultrastrong Coupling of a Single Molecule to a Plasmonic Nanocavity: A First-Principles Study, *ACS Photonics* **9**, 1065–1077 (2022).
- [308] L. Jin, A. D. Sample, D. Sun, Y. Gao, S. Deng, R. Li, L. Dou, T. W. Odom, and L. Huang, Enhanced Two-Dimensional Exciton Propagation via Strong Light-Matter Coupling with Surface Lattice Plasmons, *ACS Photonics* **10**, 1983–1991 (2023).
- [309] Y. Sang, C.-Y. Wang, S. S. Raja, C.-W. Cheng, C.-T. Huang, C.-A. Chen, X.-Q. Zhang, H. Ahn, C.-K. Shih, Y.-H. Lee, J. Shi, and S. Gwo, Tuning of Two-Dimensional Plasmon-Exciton Coupling in Full Parameter Space: A Polaritonic Non-Hermitian System, *Nano Letters* **21**, 2596–2602 (2021).
- [310] S. N. Gupta, O. Bitton, T. Neuman, R. Esteban, L. Chuntonov, J. Aizpurua, and G. Haran, Complex plasmon-exciton dynamics revealed through quantum dot light emission in a nanocavity, *Nature Communications* **12**, 1310 (2021).

-
- [311] Y. Kim, A. Barulin, S. Kim, L. P. Lee, and I. Kim, Recent advances in quantum nanophotonics: Plexcitonic and vibro-polaritonic strong coupling and its biomedical and chemical applications, *Nanophotonics* **12**, 413–439 (2023).
- [312] H. Deng, G. Weihs, C. Santori, J. Bloch, and Y. Yamamoto, Condensation of Semiconductor Microcavity Exciton Polaritons, *Science* **298**, 199–202 (2002).
- [313] H. Deng, H. Haug, and Y. Yamamoto, Exciton-polariton Bose-Einstein condensation, *Reviews of Modern Physics* **82**, 1489–1537 (2010).
- [314] M.-E. Kleemann, R. Chikkaraddy, E. M. Alexeev, D. Kos, C. Carnegie, W. Deacon, A. C. de Pury, C. Große, B. de Nijs, J. Mertens, A. I. Tartakovskii, and J. J. Baumberg, Strong-coupling of WSe₂ in ultra-compact plasmonic nanocavities at room temperature, *Nature Communications* **8**, 1296 (2017).
- [315] N. S. Mueller, R. Arul, G. Kang, A. P. Saunders, A. C. Johnson, A. Sánchez-Iglesias, S. Hu, L. A. Jakob, J. Bar-David, B. De Nijs, L. M. Liz-Marzán, F. Liu, and J. J. Baumberg, Photoluminescence upconversion in monolayer WSe₂ activated by plasmonic cavities through resonant excitation of dark excitons, *Nature Communications* **14**, 5726 (2023).
- [316] M. S. Rider, R. Arul, J. J. Baumberg, and W. L. Barnes, Theory of strong coupling between molecules and surface plasmons on a grating, *Nanophotonics* **11**, 3695–3708 (2022).
- [317] X. Han, K. Wang, X. Xing, M. Wang, and P. Lu, Rabi Splitting in a Plasmonic Nanocavity Coupled to a WS₂ Monolayer at Room Temperature, *ACS Photonics* **5**, 3970–3976 (2018).
- [318] M. Geisler, X. Cui, J. Wang, T. Rindzevicius, L. Gammelgaard, B. S. Jessen, P. A. D. Gonçalves, F. Todisco, P. Bøggild, A. Boisen, M. Wubs, N. A. Mortensen, S. Xiao, and N. Stenger, Single-Crystalline Gold Nanodisks on WS₂ Mono- and Multilayers for Strong Coupling at Room Temperature, *ACS Photonics* **6**, 994–1001 (2019).
- [319] M. Stührenberg, B. Munkhbat, D. G. Baranov, J. Cuadra, A. B. Yankovich, T. J. Antosiewicz, E. Olsson, and T. Shegai, Strong Light-Matter Coupling between Plasmons in Individual Gold Bi-pyramids and Excitons in Mono- and Multilayer WSe₂, *Nano Letters* **18**, 5938–5945 (2018).
- [320] J. Wen, H. Wang, W. Wang, Z. Deng, C. Zhuang, Y. Zhang, F. Liu, J. She, J. Chen, H. Chen, S. Deng, and N. Xu, Room-Temperature Strong Light-Matter Interaction with Active Control in Single Plasmonic Nanorod Coupled with Two-Dimensional Atomic Crystals, *Nano Letters* **17**, 4689–4697 (2017).
- [321] J. Qin, Y.-H. Chen, Z. Zhang, Y. Zhang, R. J. Blaikie, B. Ding, and M. Qiu, Revealing Strong Plasmon-Exciton Coupling between Nanogap Resonators and Two-Dimensional Semiconductors at Ambient Conditions, *Physical Review Letters* **124**, 063902 (2020).

- [322] I. Abid, W. Chen, J. Yuan, A. Bohloul, S. Najmaei, C. Avendano, R. Péchou, A. Mlayah, and J. Lou, Temperature-dependent plasmon–exciton interactions in hybrid Au/MoSe₂ nanostructures, *ACS Photonics* **4**, 1653–1660 (2017).
- [323] X. Wu, S. K. Gray, and M. Pelton, Quantum-dot-induced transparency in a nanoscale plasmonic resonator, *Optics Express* **18**, 23633 (2010).
- [324] E. V. Denning, M. Wubs, N. Stenger, J. Mørk, and P. T. Kristensen, Quantum theory of two-dimensional materials coupled to electromagnetic resonators, *Physical Review B* **105**, 085306 (2022).
- [325] Y. Zhu, J. Yang, J. Abad-Arredondo, A. I. Fernández-Domínguez, F. J. Garcia-Vidal, and D. Natelson, Electroluminescence as a Probe of Strong Exciton–Plasmon Coupling in Few-Layer WSe₂, *Nano Letters* **24**, 525–532 (2024).
- [326] L. Ren, C. Robert, H. Dery, M. He, P. Li, D. Van Tuan, P. Renucci, D. Lagarde, T. Taniguchi, K. Watanabe, X. Xu, and X. Marie, Measurement of the conduction band spin-orbit splitting in WSe₂ and WS₂ monolayers, *Physical Review B* **107**, 245407 (2023).
- [327] G. Berghäuser and E. Malic, Analytical approach to excitonic properties of MoS₂, *Physical Review B* **89**, 125309 (2014).
- [328] T. Li and G. Galli, Electronic Properties of MoS₂ Nanoparticles, *The Journal of Physical Chemistry C* **111**, 16192–16196 (2007).
- [329] S. Lebegue and O. Eriksson, Electronic structure of two-dimensional crystals from *ab initio* theory, *Physical Review B* **79**, 115409 (2009).
- [330] K. F. Mak, K. He, J. Shan, and T. F. Heinz, Control of valley polarization in monolayer MoS₂ by optical helicity, *Nature Nanotechnology* **7**, 494–498 (2012).
- [331] H. Zeng, J. Dai, W. Yao, D. Xiao, and X. Cui, Valley polarization in MoS₂ monolayers by optical pumping, *Nature Nanotechnology* **7**, 490–493 (2012).
- [332] L. Novotny and B. Hecht, *Principles of Nano-Optics* (Cambridge University Press, Cambridge, 2012).
- [333] C. Cohen-Tannoudji, J. Dupont-Roc, and G. Grynberg, *Photons and Atoms: Introduction to Quantum Electrodynamics* (Wiley, Weinheim, 2004).
- [334] M. T. Mihnev, F. Kadi, C. J. Divin, T. Winzer, S. Lee, C.-H. Liu, Z. Zhong, C. Berger, W. A. de Heer, E. Malic, A. Knorr, and T. B. Norris, Microscopic origins of the terahertz carrier relaxation and cooling dynamics in graphene, *Nature Communications* **7**, 11617 (2016).
- [335] R. Schmidt, G. Berghäuser, R. Schneider, M. Selig, P. Tonndorf, E. Malić, A. Knorr, S. Michaelis de Vasconcellos, and R. Bratschitsch, Ultrafast Coulomb-Induced Intervalley Coupling in Atomically Thin WS₂, *Nano Letters* **16**, 2945–2950 (2016).

-
- [336] L. Greten, R. Salzwedel, M. Katzer, H. Mittenzwey, D. Christiansen, A. Knorr, and M. Selig, Dipolar Coupling at Interfaces of Ultrathin Semiconductors, Semimetals, Plasmonic Nanoparticles, and Molecules, [physica status solidi \(a\)](#) **221**, 2300102 (2023).
 - [337] R. Salzwedel, *Theory of Near-Field Phenomena in Transition Metal Dichalcogenides*, Master's thesis, Technische Universität Berlin, Berlin (2020).
 - [338] W. Schäfer and M. Wegener, *Semiconductor Optics and Transport Phenomena*, Advanced Texts in Physics (Springer, Berlin Heidelberg, 2002).
 - [339] M. Selig, *Exciton-Phonon Coupling in Monolayers of Transition Metal Dichalcogenides*, Ph.D. thesis, Technische Universität Berlin, Berlin (2018).
 - [340] T. C. Berkelbach, M. S. Hybertsen, and D. R. Reichman, Theory of neutral and charged excitons in monolayer transition metal dichalcogenides, [Physical Review B](#) **88**, 045318 (2013).
 - [341] P. Cudazzo, I. V. Tokatly, and A. Rubio, Dielectric screening in two-dimensional insulators: Implications for excitonic and impurity states in graphane, [Physical Review B](#) **84**, 085406 (2011).
 - [342] M. Kira, F. Jahnke, W. Hoyer, and S. W. Koch, Quantum theory of spontaneous emission and coherent elects in semiconductor microstructures, [Progress in Quantum Electronics](#) **23**, 189–279 (1999).
 - [343] E. Malic, M. Selig, M. Feierabend, S. Brem, D. Christiansen, F. Wendler, A. Knorr, and G. Berghäuser, Dark excitons in transition metal dichalcogenides, [Physical Review Materials](#) **2**, 014002 (2018).
 - [344] T. Stroucken, A. Knorr, P. Thomas, and S. W. Koch, Coherent dynamics of radiatively coupled quantum-well excitons, [Physical Review B](#) **53**, 2026–2033 (1996).
 - [345] M. L. Trolle, T. G. Pedersen, and V. Véniard, Model dielectric function for 2D semiconductors including substrate screening, [Scientific Reports](#) **7**, 39844 (2017).
 - [346] S. Latini, T. Olsen, and K. S. Thygesen, Excitons in van der Waals heterostructures: The important role of dielectric screening, [Physical Review B](#) **92**, 245123 (2015).
 - [347] P. Marauhn and M. Rohlfing, Image charge effect in layered materials: Implications for the interlayer coupling in MoS₂, [Physical Review B](#) **107**, 155407 (2023).
 - [348] M. Kira and S. Koch, Many-body correlations and excitonic effects in semiconductor spectroscopy, [Progress in Quantum Electronics](#) **30**, 155–296 (2006).
 - [349] D. Y. Qiu, T. Cao, and S. G. Louie, Nonanalyticity, Valley Quantum Phases, and Lightlike Exciton Dispersion in Monolayer Transition Metal Dichalcogenides: Theory and First-Principles Calculations, [Physical Review Letters](#) **115**, 176801 (2015).
 - [350] M. M. Glazov, T. Amand, X. Marie, D. Lagarde, L. Bouet, and B. Urbaszek, Exciton fine structure and spin decoherence in monolayers of transition metal dichalcogenides, [Physical Review B](#) **89**, 201302 (2014).

- [351] F. J. García de Abajo, Optical excitations in electron microscopy, [Reviews of Modern Physics](#) **82**, 209–275 (2010).
- [352] N. Moiseyev, *Non-Hermitian Quantum Mechanics* (Cambridge University Press, Cambridge, 2011).
- [353] I. Gilary, A. Fleischer, and N. Moiseyev, Calculations of time-dependent observables in non-Hermitian quantum mechanics: The problem and a possible solution, [Physical Review A](#) **72**, 012117 (2005).
- [354] H. Barkay and N. Moiseyev, Complex density probability in non-Hermitian quantum mechanics: Interpretation and a formula for resonant tunneling probability amplitude, [Physical Review A](#) **64**, 044702 (2001).
- [355] A. Knorr, B. Hanewinkel, H. Giessen, and S. W. Koch, Theory for semiconductor near-field optics: Selection rules and coherent spatio-temporal dynamics, in *Advances in Solid State Physics*, edited by B. Kramer (Springer, Berlin Heidelberg, 1999).
- [356] L. Greten, R. Salzwedel, T. Göde, D. Greten, S. Reich, S. Hughes, M. Selig, and A. Knorr, Strong Coupling of Two-Dimensional Excitons and Plasmonic Photonic Crystals: Microscopic Theory Reveals Triplet Spectra (2023), [arxiv:2309.09673](#) .
- [357] J. B. Khurgin, Two-dimensional exciton–polariton–light guiding by transition metal dichalcogenide monolayers, [Optica](#) **2**, 740–742 (2015).
- [358] Z. Fei, M. E. Scott, D. J. Gosztola, J. J. Foley, J. Yan, D. G. Mandrus, H. Wen, P. Zhou, D. W. Zhang, Y. Sun, J. R. Guest, S. K. Gray, W. Bao, G. P. Wiederrecht, and X. Xu, Nano-optical imaging of WSe₂ waveguide modes revealing light-exciton interactions, [Physical Review B](#) **94**, 081402 (2016).
- [359] F. Hu, Y. Luan, M. E. Scott, J. Yan, D. G. Mandrus, X. Xu, and Z. Fei, Imaging exciton–polariton transport in MoSe₂ waveguides, [Nature Photonics](#) **11**, 356–360 (2017).
- [360] F. Hu, Y. Luan, J. Speltz, D. Zhong, C. H. Liu, J. Yan, D. G. Mandrus, X. Xu, and Z. Fei, Imaging propagative exciton polaritons in atomically thin WSe₂ waveguides, [Physical Review B](#) **100**, 121301 (2019).
- [361] D. W. Pohl, W. Denk, and M. Lanz, Optical stethoscopy: Image recording with resolution $\lambda/20$, [Applied Physics Letters](#) **44**, 651–653 (1984).
- [362] E. Betzig, A. Lewis, A. Harootunian, M. Isaacson, and E. Kratschmer, Near Field Scanning Optical Microscopy (NSOM): Development and Biophysical Applications, [Biophysical Journal](#) **49**, 269–279 (1986).
- [363] A. L. Ivanov and H. Haug, Self-consistent theory of the biexciton optical nonlinearity, [Physical Review B](#) **48**, 1490–1504 (1993).
- [364] R. Perea-Causín, S. Brem, R. Rosati, R. Jago, M. Kulig, J. D. Ziegler, J. Zipfel, A. Chernikov, and E. Malic, Exciton Propagation and Halo Formation in Two-Dimensional Materials, [Nano Letters](#) **19**, 7317–7323 (2019).

-
- [365] R. Rosati, R. Schmidt, S. Brem, R. Perea-Causín, I. Niehues, J. Kern, J. A. Preuß, R. Schneider, S. Michaelis de Vasconcellos, R. Bratschitsch, and E. Malic, Dark exciton anti-funneling in atomically thin semiconductors, *Nature Communications* **12**, 7221 (2021).
- [366] R. Rosati, R. Perea-Causín, S. Brem, and E. Malic, Negative effective excitonic diffusion in monolayer transition metal dichalcogenides, *Nanoscale* **12**, 356–363 (2020).
- [367] D. Erkensten, S. Brem, R. Perea-Causín, and E. Malic, Microscopic origin of anomalous interlayer exciton transport in van der Waals heterostructures, *Physical Review Materials* **6**, 094006 (2022).
- [368] F. Lengers, R. Rosati, T. Kuhn, and D. E. Reiter, Spatiotemporal dynamics of Coulomb-correlated carriers in semiconductors, *Physical Review B* **99**, 155306 (2019).
- [369] J. Hohlfeld, S.-S. Wellershoff, J. Güdde, U. Conrad, V. Jähnke, and E. Matthias, Electron and lattice dynamics following optical excitation of metals, *Chemical Physics* **251**, 237–258 (2000).
- [370] Z. Lin, L. V. Zhigilei, and V. Celli, Electron-phonon coupling and electron heat capacity of metals under conditions of strong electron-phonon nonequilibrium, *Physical Review B* **77**, 075133 (2008).
- [371] R. E. Prange and L. P. Kadanoff, Transport Theory for Electron-Phonon Interactions in Metals, *Physical Review* **134**, A566–A580 (1964).
- [372] L. D. Pietanza, G. Colonna, S. Longo, and M. Capitelli, Non-equilibrium electron and phonon dynamics in metals under femtosecond laser pulses, *The European Physical Journal D* **45**, 369–389 (2007).
- [373] A. M. Brown, R. Sundararaman, P. Narang, W. A. Goddard, and H. A. Atwater, *Ab Initio* phonon coupling and optical response of hot electrons in plasmonic metals, *Physical Review B* **94**, 075120 (2016).
- [374] A. M. Brown, R. Sundararaman, P. Narang, A. M. Schwartzberg, W. A. Goddard, and H. A. Atwater, Experimental and *Ab Initio* Ultrafast Carrier Dynamics in Plasmonic Nanoparticles, *Physical Review Letters* **118**, 087401 (2017).
- [375] A. Rudenko and J. V. Moloney, Coupled kinetic Boltzmann electromagnetic approach for intense ultrashort laser excitation of plasmonic nanostructures, *Physical Review B* **104**, 035418 (2021).
- [376] O. Hess and T. Kuhn, Maxwell-Bloch equations for spatially inhomogeneous semiconductor lasers. I. Theoretical formulation, *Physical Review A* **54**, 3347–3359 (1996).
- [377] F. Steininger, A. Knorr, T. Stroucken, P. Thomas, and S. W. Koch, Dynamic Evolution of Spatiotemporally Localized Electronic Wave Packets in Semiconductor Quantum Wells, *Physical Review Letters* **77**, 550–553 (1996).

- [378] D. M. Nenno, B. Rethfeld, and H. C. Schneider, Particle-in-cell simulation of ultrafast hot-carrier transport in Fe/Au heterostructures, *Physical Review B* **98**, 224416 (2018).
- [379] F. Langer, M. Hohenleutner, C. P. Schmid, C. Poellmann, P. Nagler, T. Korn, C. Schüller, M. S. Sherwin, U. Huttner, J. T. Steiner, S. W. Koch, M. Kira, and R. Huber, Lightwave-driven quasiparticle collisions on a subcycle timescale, *Nature* **533**, 225–229 (2016).
- [380] F. Rossi and T. Kuhn, Theory of ultrafast phenomena in photoexcited semiconductors, *Reviews of Modern Physics* **74**, 895–950 (2002).
- [381] N. E. Christensen and B. O. Seraphin, Relativistic Band Calculation and the Optical Properties of Gold, *Physical Review B* **4**, 3321–3344 (1971).
- [382] F. Ladstädter, U. Hohenester, P. Puschnig, and C. Ambrosch-Draxl, First-principles calculation of hot-electron scattering in metals, *Physical Review B* **70**, 235125 (2004).
- [383] T. Rangel, D. Kecik, P. E. Trevisanutto, G.-M. Rignanese, H. Van Swygenhoven, and V. Olevano, Band structure of gold from many-body perturbation theory, *Physical Review B* **86**, 125125 (2012).
- [384] J. W. Lynn, H. G. Smith, and R. M. Nicklow, Lattice Dynamics of Gold, *Physical Review B* **8**, 3493–3499 (1973).
- [385] X. Tang and B. Fultz, First-principles study of phonon linewidths in noble metals, *Physical Review B* **84**, 054303 (2011).
- [386] N. Singh and S. Prakash, Phonon frequencies of gold, *Physical Review B* **10**, 2652–2653 (1974).
- [387] G. D. Mahan, *Many-Particle Physics*, Physics of Solids and Liquids (Kluwer Academic/Plenum Publishers, New York, 2013).
- [388] G. Czycholl, *Theoretische Festkörperphysik. Band 2: Anwendungen: Nichtgleichgewicht, Verhalten in äußeren Feldern, kollektive Phänomene* (Springer, Berlin Heidelberg, 2017).
- [389] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Harcourt College Publishers, Fort Worth, 1976).
- [390] C. Cohen-Tannoudji, J. Dupont-Roc, and G. Grynberg, *Atom-Photon Interactions: Basic Processes and Applications* (Wiley, New York, 1992).
- [391] W.-R. Hannes and T. Meier, Higher-order contributions and nonperturbative effects in the nondegenerate nonlinear optical absorption of semiconductors using a two-band model, *Physical Review B* **99**, 125301 (2019).
- [392] E. Wigner, On the Quantum Correction For Thermodynamic Equilibrium, *Physical Review* **40**, 749–759 (1932).

-
- [393] V. I. Tatarskii, The Wigner representation of quantum mechanics, *Soviet Physics. Uspekhi* **26**, 312–327 (1983).
- [394] Y. Kluger, E. Mottola, and J. M. Eisenberg, Quantum Vlasov equation and its Markov limit, *Physical Review D* **58**, 125015 (1998).
- [395] O. Von Roos, Boltzmann-Vlasov Equation for a Quantum Plasma, *Physical Review* **119**, 1174–1179 (1960).
- [396] R. Binder, D. Scott, A. E. Paul, M. Lindberg, K. Henneberger, and S. W. Koch, Carrier-carrier scattering and optical dephasing in highly excited semiconductors, *Physical Review B* **45**, 1107–1115 (1992).
- [397] L. P. Kadanoff and G. A. Baym, *Quantum Statistical Mechanics: Green's Function Methods in Equilibrium and Nonequilibrium Problems* (Perseus Books, Cambridge, MA, 2000).
- [398] T. Venanzi, M. Selig, S. Winnerl, A. Pashkin, A. Knorr, M. Helm, and H. Schneider, Terahertz-Induced Energy Transfer from Hot Carriers to Trions in a MoSe₂ Monolayer, *ACS Photonics* **8**, 2931–2939 (2021).
- [399] S. Link, C. Burda, Z. L. Wang, and M. A. El-Sayed, Electron dynamics in gold and gold–silver alloy nanoparticles: The influence of a nonequilibrium electron distribution and the size dependence of the electron–phonon relaxation, *The Journal of Chemical Physics* **111**, 1255–1264 (1999).
- [400] S. Link and M. A. El-Sayed, Spectral Properties and Relaxation Dynamics of Surface Plasmon Electronic Oscillations in Gold and Silver Nanodots and Nanorods, *The Journal of Physical Chemistry B* **103**, 8410–8426 (1999).
- [401] R. Jago, R. Perea-Causin, S. Brem, and E. Malic, Spatio-temporal dynamics in graphene, *Nanoscale* **11**, 10017–10022 (2019).
- [402] P. Grua, J. P. Morreeuw, H. Bercegol, G. Jonusauskas, and F. Vallée, Electron kinetics and emission for metal nanoparticles exposed to intense laser pulses, *Physical Review B* **68**, 035424 (2003).
- [403] H. Grad, On the kinetic theory of rarefied gases, *Communications on Pure and Applied Mathematics* **2**, 331–407 (1949).
- [404] C. L. Gardner, The Quantum Hydrodynamic Model for Semiconductor Devices, *SIAM Journal on Applied Mathematics* **54**, 409–427 (1994).
- [405] R. Salzwedel, A. Knorr, D. Hoeing, H. Lange, and M. Selig, Theory of radial oscillations in metal nanoparticles driven by optically induced electron density gradients, *The Journal of Chemical Physics* **158**, 064107 (2023).
- [406] A. Eguiluz, S. C. Ying, and J. J. Quinn, Influence of the electron density profile on surface plasmons in a hydrodynamic model, *Physical Review B* **11**, 2118–2121 (1975).
- [407] L. H. Thomas, The calculation of atomic fields, *Mathematical Proceedings of the Cambridge Philosophical Society* **23**, 542–548 (1927).

- [408] E. Fermi, Zur Quantelung des idealen einatomigen Gases, *Zeitschrift für Physik* **36**, 902–912 (1926).
- [409] A. J. Bennett, Influence of the Electron Charge Distribution on Surface-Plasmon Dispersion, *Physical Review B* **1**, 203–207 (1970).
- [410] M. Moeferd, *Nonlocal and Nonlinear Properties of Plasmonic Nanostructures Within the Hydrodynamic Drude Model*, Ph.D. thesis, Humboldt Universität Berlin, Berlin (2017).
- [411] J. Grumm, *Microscopic Theory of Spatiotemporal Electron Dynamics in Metal Nanoparticles*, Master’s thesis, Technische Universität Berlin, Berlin (2023).
- [412] M. G. Ramchandani, Energy band structure of gold, *Journal of Physics C: Solid State Physics IOP Publishing*, **3**, S1–S9 (1970).
- [413] M. Pfeifer, D.-N. Huynh, G. Wegner, F. Intravaia, U. Peschel, and K. Busch, Time-domain modeling of interband transitions in plasmonic systems, *Applied Physics B* **130**, 7 (2024).
- [414] S. Reich, J. Maultzsch, C. Thomsen, and P. Ordejón, Tight-binding description of graphene, *Physical Review B* **66**, 035412 (2002).
- [415] A. Baba, K. Tada, R. Janmanee, S. Sriwichai, K. Shinbo, K. Kato, F. Kaneko, and S. Phanichphant, Controlling Surface Plasmon Optical Transmission with an Electrochemical Switch Using Conducting Polymer Thin Films, *Advanced Functional Materials* **22**, 4383–4388 (2012).
- [416] Y. Cui, J. Zhou, V. A. Tamma, and W. Park, Dynamic Tuning and Symmetry Lowering of Fano Resonance in Plasmonic Nanostructure, *ACS Nano* **6**, 2385–2393 (2012).
- [417] P. A. Kossyrev, A. Yin, S. G. Cloutier, D. A. Cardimona, D. Huang, P. M. Alsing, and J. M. Xu, Electric Field Tuning of Plasmonic Response of Nanodot Array in Liquid Crystal Matrix, *Nano Letters* **5**, 1978–1981 (2005).
- [418] H. Lange, B. H. Juárez, A. Carl, M. Richter, N. G. Bastús, H. Weller, C. Thomsen, R. von Klitzing, and A. Knorr, Tunable Plasmon Coupling in Distance-Controlled Gold Nanoparticles, *Langmuir* **28**, 8862–8866 (2012).
- [419] C. Ruppert, F. Förster, A. Zrenner, J. B. Kinzel, A. Wixforth, H. J. Krenner, and M. Betz, Radio Frequency Electromechanical Control over a Surface Plasmon Polariton Coupler, *ACS Photonics* **1**, 91–95 (2014).
- [420] C. Novo, A. M. Funston, A. K. Gooding, and P. Mulvaney, Electrochemical Charging of Single Gold Nanorods, *Journal of the American Chemical Society* **131**, 14664–14666 (2009).
- [421] F. Zeuner, M. Muldarisnur, A. Hildebrandt, J. Förstner, and T. Zentgraf, Coupling Mediated Coherent Control of Localized Surface Plasmon Polaritons, *Nano Letters* **15**, 4189–4193 (2015).

-
- [422] A. Kuhlicke, S. Schietinger, C. Matyssek, K. Busch, and O. Benson, In Situ Observation of Plasmon Tuning in a Single Gold Nanoparticle during Controlled Melting, *Nano Letters* **13**, 2041–2046 (2013).
 - [423] V. J. Sorger, N. D. Lanzillotti-Kimura, R.-M. Ma, and X. Zhang, Ultra-compact silicon nanophotonic modulator with broadband response, *Nanophotonics* **1**, 17–22 (2012).
 - [424] S. Zhu, G. Q. Lo, and D. L. Kwong, Phase modulation in horizontal metal-insulator-silicon-insulator-metal plasmonic waveguides, *Optics Express* **21**, 8320–8330 (2013).
 - [425] J. T. Kim, CMOS-compatible hybrid plasmonic modulator based on vanadium dioxide insulator-metal phase transition, *Optics Letters* **39**, 3997–4000 (2014).
 - [426] B. S. Dennis, M. I. Haftel, D. A. Czaplewski, D. Lopez, G. Blumberg, and V. A. Aksyuk, Compact nanomechanical plasmonic phase modulators, *Nature Photonics* **9**, 267–273 (2015).
 - [427] E. Hendry, F. J. García-Vidal, L. Martin-Moreno, J. G. Rivas, M. Bonn, A. P. Hibbins, and M. J. Lockyear, Optical Control over Surface-Plasmon-Polariton-Assisted THz Transmission through a Slit Aperture, *Physical Review Letters* **100**, 123901 (2008).
 - [428] P. Dombi, Z. Pápa, J. Vogelsang, S. V. Yalunin, M. Sivilis, G. Herink, S. Schäfer, P. Groß, C. Ropers, and C. Lienau, Strong-field nano-optics, *Reviews of Modern Physics* **92**, 025003 (2020).
 - [429] J. E. Houle and D. M. Sullivan, *Electromagnetic Simulation Using the FDTD Method with Python* (Wiley, Hoboken, 2019).
 - [430] R. Salzwedel and J. Grumm, Coupled kinetic Maxwell-Boltzmann engine, git.tu-berlin.de/r.salzwedel.2911/fdtd_boltzmann (2023).
 - [431] J. Baxter, A. C. Lesina, and L. Ramunno, Parallel FDTD modelling of nonlocality in plasmonics, *IEEE Transactions on Antennas and Propagation* **69**, 3982–3994 (2021), [arxiv:2005.06997](https://arxiv.org/abs/2005.06997).
 - [432] K. R. Hiremath, L. Zschiedrich, and F. Schmidt, Numerical solution of nonlocal hydrodynamic Drude model for arbitrary shaped nano-plasmonic structures using Nédélec finite elements, *Journal of Computational Physics* **231**, 5890–5896 (2012).
 - [433] N. Schmitt, C. Scheid, J. Viquerat, and S. Lanteri, Simulation of three-dimensional nanoscale light interaction with spatially dispersive metals using a high order curvilinear DGTD method, *Journal of Computational Physics* **373**, 210–229 (2018).
 - [434] X. Zheng, M. Kupresak, R. Mittra, and G. A. E. Vandenbosch, A Boundary Integral Equation Scheme for Simulating the Nonlocal Hydrodynamic Response of Metallic Antennas at Deep-Nanometer Scales, *IEEE Transactions on Antennas and Propagation* **66**, 4759–4771 (2018).

- [435] K. Yee, Numerical solution of initial boundary value problems involving maxwell's equations in isotropic media, [IEEE Transactions on Antennas and Propagation](#) **14**, 302–307 (1966).
- [436] A. Taflov, *Advances in Computational Electrodynamics: The Finite-Difference Time-Domain Method* (Artech House, Boston, 1998).
- [437] J.-P. Berenger, A perfectly matched layer for the absorption of electromagnetic waves, [Journal of Computational Physics](#) **114**, 185–200 (1994).
- [438] Z. Sacks, D. Kingsland, R. Lee, and J.-F. Lee, A perfectly matched anisotropic absorber for use as an absorbing boundary condition, [IEEE Transactions on Antennas and Propagation](#) **43**, 1460–1463 (1995).
- [439] D. Sullivan, An unsplit step 3-D PML for use with the FDTD method, [IEEE Microwave and Guided Wave Letters](#) **7**, 184–186 (1997).
- [440] C. Carlson, *Theory and Simulation Techniques of Broadband Light-Matter Interactions in Nanophotonics*, Ph.D. thesis, Queen's University, Kingston, Ontario, Canada (2021).
- [441] C. Van Vlack and S. Hughes, Finite-difference time-domain technique as an efficient tool for calculating the regularized Green function: Applications to the local-field problem in quantum optics for inhomogeneous lossy materials, [Optics Letters](#) **37**, 2880–2882 (2012).
- [442] W. K. Cartar, *Theory and Modelling of Light-Matter Interactions in Photonic Crystal Cavity Systems Coupled to Quantum Dot Ensembles*, Ph.D. thesis, Queen's University, Kingston, Ontario, Canada (2017).
- [443] S. Prahl, [Miepython: Pure python implementation of Mie scattering](#), Zenodo (2023).
- [444] J. Grumm, Microscopic Boltzmann Equation, [git.tu-berlin.de/jonasgrumm/microscopic_boltzmann_equation](#) (2023).
- [445] M. A. Ordal, R. J. Bell, R. W. Alexander, L. L. Long, and M. R. Querry, Optical properties of Au, Ni, and Pb at submillimeter wavelengths, [Applied Optics](#) **26**, 744–752 (1987).
- [446] W. Yan, M. Wubs, and N. A. Mortensen, Hyperbolic metamaterials: Nonlocal response regularizes broadband supersingularity, [Physical Review B](#) **86**, 205429 (2012).
- [447] H. Lamb, On the Vibrations of an Elastic Sphere, [Proceedings of the London Mathematical Society](#) **1**, 189–212 (1881).
- [448] G. V. Hartland, Coherent vibrational motion in metal particles: Determination of the vibrational amplitude and excitation mechanism, [The Journal of Chemical Physics](#) **116**, 8048–8055 (2002).

-
- [449] J. H. Hodak, A. Henglein, and G. V. Hartland, Size dependent properties of Au particles: Coherent excitation and dephasing of acoustic vibrational modes, *The Journal of Chemical Physics* **111**, 8613–8621 (1999).
- [450] M.-Y. Ng and Y.-C. Chang, Laser-induced breathing modes in metallic nanoparticles: A symmetric molecular dynamics study, *The Journal of Chemical Physics* **134**, 094116 (2011).
- [451] A. Crut, P. Maioli, N. Del Fatti, and F. Vallée, Acoustic vibrations of metal nano-objects: Time-domain investigations, *Physics Reports* **549**, 1–43 (2015).
- [452] M. A. van Dijk, M. Lippitz, and M. Orrit, Detection of Acoustic Oscillations of Single Gold Nanospheres by Time-Resolved Interferometry, *Physical Review Letters* **95**, 267406 (2005).
- [453] K. Ishioka and O. Misochko, Coherent Lattice Oscillations in Solids and Their Optical Control: Part II. New Detection Techniques and Optical Control., in *Progress in Ultrafast Intense Laser Science V*, edited by K. Yamanouchi, A. Giulietti, and K. Ledingham (Springer, Berlin Heidelberg, 2010).
- [454] S. V. Boriskina, T. A. Cooper, L. Zeng, G. Ni, J. K. Tong, Y. Tsurimaki, Y. Huang, L. Meroueh, G. Mahan, and G. Chen, Losses in plasmonics: From mitigating energy dissipation to embracing loss-enabled functionalities, *Advances in Optics and Photonics* **9**, 775–827 (2017).
- [455] L. V. Besteiro, P. Yu, Z. Wang, A. W. Holleitner, G. V. Hartland, G. P. Wiederrecht, and A. O. Govorov, The fast and the furious: Ultrafast hot electrons in plasmonic metastructures. Size and structure matter, *Nano Today* **27**, 120–145 (2019).
- [456] G. V. Hartland, Optical Studies of Dynamics in Noble Metal Nanostructures, *Chemical Reviews* **111**, 3858–3887 (2011).
- [457] S. Linic, S. Chavez, and R. Elias, Flow and extraction of energy and charge carriers in hybrid plasmonic nanostructures, *Nature Materials* **20**, 916–924 (2021).
- [458] Y.-J. Kim, H. Jung, S. W. Han, and O.-H. Kwon, Ultrafast Electron Microscopy Visualizes Acoustic Vibrations of Plasmonic Nanorods at the Interfaces, *Matter* **1**, 481–495 (2019).
- [459] J. N. Clark, L. Beitra, G. Xiong, A. Higginbotham, D. M. Fritz, H. T. Lemke, D. Zhu, M. Chollet, G. J. Williams, M. Messerschmidt, B. Abbey, R. J. Harder, A. M. Korsunsky, J. S. Wark, and I. K. Robinson, Ultrafast Three-Dimensional Imaging of Lattice Dynamics in Individual Gold Nanocrystals, *Science* **341**, 56–59 (2013).
- [460] J. N. Clark, L. Beitra, G. Xiong, D. M. Fritz, H. T. Lemke, D. Zhu, M. Chollet, G. J. Williams, M. M. Messerschmidt, B. Abbey, R. J. Harder, A. M. Korsunsky, J. S. Wark, D. A. Reis, and I. K. Robinson, Imaging transient melting of a nanocrystal using an X-ray laser, *Proceedings of the National Academy of Sciences* **112**, 7444–7448 (2015).

- [461] A. von Reppert, R. M. Sarhan, F. Stete, J. Pudell, N. Del Fatti, A. Crut, J. Koetz, F. Liebig, C. Prietzel, and M. Bargheer, Watching the Vibration and Cooling of Ultrathin Gold Nanotriangles by Ultrafast X-ray Diffraction, *The Journal of Physical Chemistry C* **120**, 28894–28899 (2016).
- [462] K. Ayyer, P. L. Xavier, J. Bielecki, Z. Shen, B. J. Daurer, A. K. Samanta, S. Awel, R. Bean, A. Barty, M. Bergemann, T. Ekeberg, A. D. Estillore, H. Fangohr, K. Giewekemeyer, M. S. Hunter, M. Karnevskiy, R. A. Kirian, H. Kirkwood, Y. Kim, J. Koliyadu, H. Lange, R. Letrun, J. Lübke, T. Michelat, A. J. Morgan, N. Roth, T. Sato, M. Sikorski, F. Schulz, J. C. H. Spence, P. Vagovic, T. Wollweber, L. Worbs, O. Yefanov, Y. Zhuang, F. R. N. C. Maia, D. A. Horke, J. Küpper, N. D. Loh, A. P. Mancuso, and H. N. Chapman, 3D diffractive imaging of nanoparticle ensembles using an x-ray laser, *Optica* **8**, 15–23 (2021).
- [463] J. Shin, C. Jung, Y. Ihm, S.-P. Heo, D. Nam, S. Kim, M. Kim, I. Eom, J. H. Shim, D. Y. Noh, and C. Song, Ultrafast Energy Transfer Process in Confined Gold Nanospheres Revealed by Femtosecond X-ray Imaging and Diffraction, *Nano Letters* **23**, 1481–1488 (2023).
- [464] A. V. Kuznetsov and C. J. Stanton, Theory of Coherent Phonon Oscillations in Semiconductors, *Physical Review Letters* **73**, 3243–3246 (1994).
- [465] R. Scholz, T. Pfeifer, and H. Kurz, Density-matrix theory of coherent phonon oscillations in germanium, *Physical Review B* **47**, 16229–16236 (1993).
- [466] H. J. Zeiger, J. Vidal, T. K. Cheng, E. P. Ippen, G. Dresselhaus, and M. S. Dresselhaus, Theory for displacive excitation of coherent phonons, *Physical Review B* **45**, 768–778 (1992).
- [467] D. Wigger, S. Lüker, D. E. Reiter, V. M. Axt, P. Machnikowski, and T. Kuhn, Energy transport and coherence properties of acoustic phonons generated by optical excitation of a quantum dot, *Journal of Physics: Condensed Matter* **26**, 355802 (2014), [arxiv:1312.3754](#).
- [468] J. Kabuss, A. Carmele, T. Brandes, and A. Knorr, Optically Driven Quantum Dots as Source of Coherent Cavity Phonons: A Proposal for a Phonon Laser Scheme, *Physical Review Letters* **109**, 054301 (2012).
- [469] P. Karwat, D. E. Reiter, T. Kuhn, and O. Hess, Coherent phonon lasing in a thermal quantum nanomachine, *Physical Review A* **98**, 053855 (2018).
- [470] T. D. Krauss and F. W. Wise, Coherent Acoustic Phonons in a Semiconductor Quantum Dot, *Physical Review Letters* **79**, 5102–5105 (1997).
- [471] T. Czerniuk, D. Wigger, A. V. Akimov, C. Schneider, M. Kamp, S. Höfling, D. R. Yakovlev, T. Kuhn, D. E. Reiter, and M. Bayer, Picosecond Control of Quantum Dot Laser Emission by Coherent Phonons, *Physical Review Letters* **118**, 133901 (2017).
- [472] J. H. Hodak, A. Henglein, and G. V. Hartland, Photophysics of Nanometer Sized Metal Particles: Electron-Phonon Coupling and Coherent Excitation of Breathing Vibrational Modes, *The Journal of Physical Chemistry B* **104**, 9954–9965 (2000).

-
- [473] M. Perner, S. Gresillon, J. März, G. von Plessen, J. Feldmann, J. Porstendorfer, K.-J. Berg, and G. Berg, Observation of Hot-Electron Pressure in the Vibration Dynamics of Metal Nanoparticles, *Physical Review Letters* **85**, 792–795 (2000).
- [474] C. Voisin, N. Del Fatti, D. Christofilos, and F. Vallée, Time-resolved investigation of the vibrational dynamics of metal nanoparticles, *Applied Surface Science* **164**, 131–139 (2000).
- [475] A. E. H. Love, *A Treatise on the Mathematical Theory of Elasticity* (University Press, Cambridge, 1892).
- [476] F. P. Bonafé, B. Aradi, M. Guan, O. A. Douglas-Gallardo, C. Lian, S. Meng, T. Frauenheim, and C. G. Sánchez, Plasmon-driven sub-picosecond breathing of metal nanoparticles, *Nanoscale* **9**, 12391–12397 (2017).
- [477] K. Sytwu, M. Vadai, F. Hayee, D. K. Angell, A. Dai, J. Dixon, and J. A. Dionne, Driving energetically unfavorable dehydrogenation dynamics with plasmonics, *Science* **371**, 280–283 (2021).
- [478] Y. Zhang, S. He, W. Guo, Y. Hu, J. Huang, J. R. Mulcahy, and W. D. Wei, Surface-Plasmon-Driven Hot Electron Photochemistry, *Chemical Reviews* **118**, 2927–2954 (2018).
- [479] S. Tan, A. Argondizzo, J. Ren, L. Liu, J. Zhao, and H. Petek, Plasmonic coupling at a metal/semiconductor interface, *Nature Photonics* **11**, 806–812 (2017).
- [480] L. Zhou, M. Lou, J. L. Bao, C. Zhang, J. G. Liu, J. M. P. Martinez, S. Tian, L. Yuan, D. F. Swearer, H. Robotjazi, E. A. Carter, P. Nordlander, and N. J. Halas, Hot carrier multiplication in plasmonic photocatalysis, *Proceedings of the National Academy of Sciences* **118**, e2022109118 (2021).
- [481] G. Baffou, F. Cichos, and R. Quidant, Applications and challenges of thermoplasmonics, *Nature Materials* **19**, 946–958 (2020).
- [482] A. Arbouet, N. Del Fatti, and F. Vallée, Optical control of the coherent acoustic vibration of metal nanoparticles, *The Journal of Chemical Physics* **124**, 144701 (2006).
- [483] A. Ahmed, M. Pelton, and J. R. Guest, Understanding How Acoustic Vibrations Modulate the Optical Response of Plasmonic Metal Nanoparticles, *ACS Nano* **11**, 9360–9369 (2017).
- [484] K. Yu, P. Zijlstra, J. E. Sader, Q.-H. Xu, and M. Orrit, Damping of Acoustic Vibrations of Immobilized Single Gold Nanorods in Different Environments, *Nano Letters* **13**, 2710–2716 (2013).
- [485] T. Gorkhover, S. Schorb, R. Coffee, M. Adolph, L. Foucar, D. Rupp, A. Aquila, J. D. Bozek, S. W. Epp, B. Erk, L. Gumprecht, L. Holmegaard, A. Hartmann, R. Hartmann, G. Hauser, P. Holl, A. Hömke, P. Johnsson, N. Kimmel, K.-U. Kühnel, M. Messerschmidt, C. Reich, A. Rouzée, B. Rudek, C. Schmidt, J. Schulz, H. Soltau, S. Stern, G. Weidenspointner, B. White, J. Küpper, L. Strüder, I. Schlichting, J. Ullrich, D. Rolles, A. Rudenko, T. Möller, and C. Bostedt,

- Femtosecond and nanometre visualization of structural dynamics in superheated nanoparticles, *Nature Photonics* **10**, 93–97 (2016).
- [486] S. Pandey, R. Bean, T. Sato, I. Poudyal, J. Bielecki, J. Cruz Villarreal, O. Yefanov, V. Mariani, T. A. White, C. Kupitz, M. Hunter, M. H. Abdellatif, S. Bajt, V. Bondar, A. Echelmeier, D. Doppler, M. Emons, M. Frank, R. Fromme, Y. Gevorkov, G. Giovanetti, M. Jiang, D. Kim, Y. Kim, H. Kirkwood, A. Klimovskaia, J. Knoska, F. H. M. Koua, R. Letrun, S. Lisova, L. Maia, V. Mazalova, D. Meza, T. Michelat, A. Ourmazd, G. Palmer, M. Ramilli, R. Schubert, P. Schwander, A. Silenzi, J. Sztuk-Dambietz, A. Tolstikova, H. N. Chapman, A. Ros, A. Barty, P. Fromme, A. P. Mancuso, and M. Schmidt, Time-resolved serial femtosecond crystallography at the European XFEL, *Nature Methods* **17**, 73–78 (2020).
 - [487] R. Neutze, R. Wouts, and J. Hajdu, Potential for biomolecular imaging with femtosecond X-ray pulses, *Nature* **406**, 752–757 (2000).
 - [488] N. Del Fatti, C. Voisin, F. Chevy, F. Vallée, and C. Flytzanis, Coherent acoustic mode oscillation and damping in silver nanoparticles, *The Journal of Chemical Physics* **110**, 11484–11487 (1999).
 - [489] N. Del Fatti, S. Tzortzakis, C. Voisin, C. Flytzanis, and F. Vallée, Time resolved investigation of coherent acoustic mode oscillations in silver nanoparticles, *Physica B: Condensed Matter* **263–264**, 54–56 (1999).
 - [490] A. I. Lobad and A. J. Taylor, Coherent phonon generation mechanism in solids, *Physical Review B* **64**, 180301(R) (2001).
 - [491] Y. U. Staechelin, D. Hoening, F. Schulz, and H. Lange, Size-Dependent Electron-Phonon Coupling in Monocrystalline Gold Nanoparticles, *ACS Photonics* **8**, 752–757 (2021).
 - [492] T. Pfeifer, W. Kütt, H. Kurz, and R. Scholz, Generation and detection of coherent optical phonons in germanium, *Physical Review Letters* **69**, 3248–3251 (1992).
 - [493] T. K. Cheng, J. Vidal, H. J. Zeiger, G. Dresselhaus, M. S. Dresselhaus, and E. P. Ippen, Mechanism for displacive excitation of coherent phonons in Sb, Bi, Te, and Ti_2O_3 , *Applied Physics Letters* **59**, 1923–1925 (1991).
 - [494] W. Albrecht, Th. Kruse, and H. Kurz, Time-resolved observation of coherent phonons in superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ thin films, *Physical Review Letters* **69**, 1451–1454 (1992).
 - [495] G. D. Sanders, A. R. T. Nugraha, K. Sato, J.-H. Kim, J. Kono, R. Saito, and C. J. Stanton, Theory of coherent phonons in carbon nanotubes and graphene nanoribbons, *Journal of Physics: Condensed Matter* **25**, 144201 (2013).
 - [496] D. Wigger, T. Czerniuk, D. E. Reiter, M. Bayer, and T. Kuhn, Systematic study of the influence of coherent phonon wave packets on the lasing properties of a quantum dot ensemble, *New Journal of Physics* **19**, 073001 (2017).
 - [497] E. Clementi, D. L. Raimondi, and W. P. Reinhardt, Atomic Screening Constants from SCF Functions. II. Atoms with 37 to 86 Electrons, *The Journal of Chemical Physics* **47**, 1300–1307 (1967).

-
- [498] Z.-Y. Shi, C. Gao, and H. Zhai, Ideal-Gas Approach to Hydrodynamics, *Physical Review X* **11**, 041031 (2021).
- [499] R. B. Wilson and S. Coh, Parametric dependence of hot electron relaxation timescales on electron-electron and electron-phonon interaction strengths, *Communications Physics* **3**, 179 (2020).
- [500] R. Sundararaman, P. Narang, A. S. Jermyn, W. A. Goddard III, and H. A. Atwater, Theoretical predictions for hot-carrier generation from surface plasmon decay, *Nature Communications* **5**, 5788 (2014).
- [501] A. Tamura, K. Higeta, and T. Ichinokawa, Lattice vibrations and specific heat of a small particle, *Journal of Physics C: Solid State Physics* **15**, 4975–4991 (1982).
- [502] A. Tamura, K. Higeta, and T. Ichinokawa, The size dependence of vibrational eigenfrequencies and the mean square vibrational displacement of a small particle, *Journal of Physics C: Solid State Physics* **16**, 1585–1592 (1983).
- [503] J. Meija, T. B. Coplen, M. Berglund, W. A. Brand, P. De Bièvre, M. Gröning, N. E. Holden, J. Irrgeher, R. D. Loss, T. Walczyk, and T. Prohaska, Atomic weights of the elements 2013 (IUPAC Technical Report), *Pure and Applied Chemistry* **88**, 265–291 (2016).
- [504] D. R. Lide, G. Baysinger, S. Chemistry, L. I. Berger, R. N. Goldberg, and H. V. Kehiaian, *CRC Handbook of Chemistry and Physics* (CRC Press, Boca Raton, 2004).
- [505] M. de Podesta, *Understanding the Properties of Matter* (CRC Press, London, 2020).
- [506] L. Greten, *Quantum Theory of Exciton-Plasmon Coupling in Two-Dimensional Semiconductors Functionalized with Metal Nanoparticles*, Master’s thesis, Technische Universität Berlin, Berlin (2021).
- [507] F. Katsch, *Theory of Exciton–Exciton Interactions in Monolayer Transition Metal Dichalcogenides*, Ph.D. thesis, Technische Universität Berlin, Berlin (2020).

Acknowledgments

Zunächst möchte ich mich bei Andreas Knorr herzlich bedanken. Besonders herausstellen möchte ich die vielen Möglichkeiten und Freiräume, die ich trotz den Herausforderungen der Pandemie genießen durfte, die zahllosen Türen, die du mir bereits innerhalb der Wissenschaft geöffnet hast, sowie die vielen, oft auch kritischen Diskussionen, die für mich am Ende immer sehr lehrreich waren.

I would also like to thank Asger Mortensen for his kind offer to act as examiner for my PhD. thesis which I gladly accepted. I highly appreciate that you carved out some of your precious time from your busy schedule to come all the way to Berlin for my PhD defense.

In diesem Sinne möchte ich mich auch bei Stefan Eisebitt dafür bedanken, dass er mir einen Teil seiner kostbaren Zeit zur Verfügung stellt und den Weg von Adlershof auf sich nimmt, um den Vorsitz meines Prüfungsausschusses zu übernehmen.

Mein Dank geht auch an Malte Selig, der mich vor Jahren für dieses Wissenschaftsgebiet begeistert hat, mich in die Geheimnisse der Festkörpertheorie eingeführt hat und mir in all den Jahren eine unvergleichliche Unterstützung war. Danke, dass deine Tür für mich immer offen war - und ich mit jeder Idee oder Frage willkommen war - du bist und bleibst mir ein großes Vorbild, sowohl privat als auch beruflich. Es war mir eine Ehre, deine erste Doktorandenstelle zu bekleiden.

Außerdem möchte ich mich ganz herzlich bei Jonas Grumm bedanken, mit dem ich seit seiner Bachelorarbeit zusammenarbeiten durfte. Wir sind gemeinsam viele spannende wissenschaftliche Wege gegangen, die einen großen Teil dieser Arbeit ausmachen. Es ist mir eine große Freude zu sehen, wie sich aus dem anfänglichen Betreuer-Student Verhältnis ein Verhältnis auf Augenhöhe entwickelt hat und ich bin gespannt, wie unser wissenschaftlicher Weg weitergehen wird. Lieben Dank für all die schönen und die lehrreichen Momente.

Ein riesengroßes Dankeschön auch an Manuel, der mich seit dem Bachelorstudium und jetzt bis zur Promotion begleitet hat, mit dem ich nicht nur Erfolge gefeiert, sondern auch Rückschläge erfahren habe, bei dem ich jederzeit meinen Frust abladen konnte und mit dem ich an Orten über Physik geredet habe, an denen ich es nie vorhatte. Toll, wie du immer für mich da warst, sei es mit einer Frage, wie das nochmal mit der Thermalisierung funktioniert, um die Erlebnisse des Wochenendes zu teilen oder einfach nur um wieder einen Witz auf deine Kosten zu machen :D. Danke - ich freue mich auf unser Dachgeschossbüro.

Weiterhin will ich hier Lara explizit erwähnen, die mir als Büromitbewohnerin sehr ans Herz gewachsen ist, der ich jederzeit sehr grundlegende Fragen stellen konnte und mit der ich die spannendsten Diskussionen während meiner Promotionszeit hatte.

Weiterhin gilt mein Dank der restlichen Arbeitsgruppe, ich denke dabei insbesondere an Joris, Henry, Aycke, Florian, Dominik, Sebastian und Kisa, die mir während meiner Zeit in der Arbeitsgruppe mit Rat und Tat zur Seite standen, bei denen ich mich wissenschaftlich immer hervorragend aufgehoben gefühlt habe, mit denen es (zumindest

menschlich) immer eine Freude war Mittagspausen zu verbringen, auf Konferenzreisen zu gehen, in den Biergarten zu fahren oder einfach nur gepflegt über Physik zu diskutieren.

Ein weiterer Dank geht an die Studierenden, die ich im Laufe der Jahre betreuen durfte, Lisanne, Jonas, Amanda, Stefan, Valdemar, Manuel, Robert, bei denen ich ausnahmslos das Gefühl hatte, dass ich mindestens genauso viel gelernt habe wie umgekehrt. Danke, dass ihr mich als Betreuer so angenommen habt, dass wir gemeinsam spannende Sachen ausprobiert haben und dass der Wissenstransfer immer in beide Richtungen funktioniert hat und ich mich auch als Betreuer ausprobieren durfte.

I would also like to thank Stephen Hughes for hosting me during my research stay in Kingston which was one of the most enjoyable times of my life. I appreciate the extraordinary amount of time you spent teaching me how to run efficient FDTD simulations, and how to run efficiently (progressively). (I am very impressed by your recent times.) Thank you for the scientific excursion you took me on, the opportunity to live in a city like Kingston, which has just the most beautiful combination of ups - I promise I did not want to leave. It was a pleasure, both scientifically and personally.

In that spirit, I want to thank the people in Steve's group, especially Sofia, for making my time in and out of the nanophotonics lab far more enjoyable than I anticipated. I would also like to thank all the other people from Queen's for an unforgettable time - Juanjuan, Ari and Becca. On that note, another big thank you to all the people in Kingston who took me in like a childhood friend and almost didn't let me go, first and foremost Rafa, for your incredible spirit and all the adventures we had together, but also Irene, Chris, Matt, Isaac, Frieder and Jen, it was an absolute pleasure.

Another big thank you goes out to all the students of BOS.QT who supported me with their trust and allowed me to be their "Mr. President". In particular, I would like to give a special thank you to Gaby, who in addition to being an amazing person, organized an entire conference with me without it feeling too overwhelming. Great team, looking forward to future joint endeavors.

Ein großes Dankeschön geht an meine langjährigen Kooperationspartner an der Universität Hamburg, insbesondere an Dominik, Yannic und Holger. Danke dafür, dass ihr es mir nicht habt langweilig werden lassen, dass ich auch mal dumme Fragen zum Experiment stellen durfte und für die guten Ideen, die inzwischen in mehreren Publikationen veröffentlicht wurden.

Nachdem nun die rein wissenschaftlichen Danksagungen abgeschlossen sind, geht der Dank als Erstes an Irena, danke für die Zusammenarbeit auf kurzen Wegen, die viel Arbeit auf einmal ganz klein werden ließ, dass manchmal Dinge schon erledigt waren, bevor ich selbst daran gedacht habe und natürlich die unzähligen Momente des Abschaltens und der guten Geschichten und vor allem danke dafür, dass sich der Rhabarber-Konsum auf die Zeit vor (und vielleicht auch nach) meiner Promotion beschränkt hat. An gleicher Stelle natürlich auch ein großes Dankeschön an Andrea, die als Universalgelehrte immer alle Hebel in Bewegung gesetzt hat, um ans Ziel zu kommen, für die fröhlichen Kommentare am Morgen - ich verspreche, nach der Promotion wird die Haarbürste eine größere Rolle in meinem Leben spielen. Vielen Dank auch an Aylin und unsere Olympiasiegerin Norma für die viele Hilfe, wenn sie gebraucht wurde und den Spaß, den wir hatten. In diesem Sinne auch vielen Dank an Marten und Peter dafür, dass die Dinge einfach funktionieren oder ich zumindest schnell fragen kann, ohne mich stundenlang damit beschäftigen zu müssen, auch wenn ich meist nur die Hälfte verstehe.

Danke an all die Menschen, die das Ökosystem, in dem ich arbeiten darf, aufrechter-

halten, hier denke ich in erster Linie an Viola, Magerita, Janet in der Mensa, deren Gespräche den Tag immer gleich viel schöner machen und bei denen ich mich immer rundum versorgt gefühlt habe und an Martin Pfannkuchen, bei dem ich mich jeden Tag ein bisschen ausheulen konnte und etwas unglaublich Leckeres zu essen bekommen habe.

Vielen Dank an meinen Lesezirkel, Benni, Paul, Zoi, Tobi, Konsti, Gaby, Isaac, Paul und Paula. Für all die Fehler, die ihr noch gefunden habt.

Danke an die tollen Menschen vom Experimental Stage Project, mit denen ich zum einen viel Physik außerhalb der Physik erleben durfte und vorrangig unglaublich viel Spaß hatte. Danke auch an die tollen Menschen von Changing Cities, auf die ich mich schon wieder freue - danke, dass ihr auch ohne mich weitergemacht habt.

Ohne wen diese Arbeit natürlich auch nicht schaffbar gewesen wäre, sind all die guten Freund*innen, die mich umgeben - Danke an Dilan, Anneke, Benni, Paul, Enya, Konsti, Olga, Paul, Hayri, Richard, Andi, Johanna, Joscha, Arne, Melissa, Bernadette, Nele, Franzi, Robin, Caro, Lara und Paula. Danke, dass ihr mir den Freiraum lässt diesen Kram hier zu machen - Ich hab jetzt wieder Zeit <3

Zu guter Letzt: Danke an meine Familie, Mama, Papa, Leon und Vincent, danke, dass ich mich immer auf euch verlassen kann und dass ihr mich auf diesem Weg jederzeit unterstützt, dass ihr mich hierher gebracht habt - ohne euch wäre ich jetzt nicht hier.

Vielen Dank!