Density-functional theory and beyond for organic electronic materials

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Abstract

Organic electronics is a vibrant research field in both industry and academia as it promises easy-to-process, low-cost and flexible (opto)electronic devices. However, from a theoretical point of view the relevant materials open the Pandora’s box of ‘standard’ density-functional theory (DFT) with semi-local or hybrid approximations to the exchange correlation (XC) functional. These functionals lack the long-range tail of van der Waals (vdW) interactions and suffer from severe self-interaction errors. Both aspects need to be corrected when molecules weakly interact with each other. Otherwise, electron transfer and binding-curve artefacts may occur, which is demonstrated in this thesis for the tetrathiafulvalene (TTF) – tetracyanoquinodimethane (TCNQ) complex.

To overcome this limitation, I construct an XC functional that obtains the exchange energy by exploiting a formally exact condition of DFT and the single-particle Green’s function. With this procedure, the fraction of exact exchange is obtained in a non-empirical, material-specific way. The functional reduces the self-interaction error and exhibits significantly improved spectral properties compared to standard DFT functionals. It is able to satisfactorily describe the ground-state electron density of the TTF-TCNQ complex. Furthermore, it is compatible with the vdW correction scheme of Tkatchenko and Scheffler, which adds the long-range $1/R^6$ vdW tail to a given DFT functional with density-dependent $C_6$ coefficients.

Alternatively, vdW interactions can be described by methods based on the random-phase approximation to the correlation energy, most notably second-order renormalized perturbation theory (rPT2). As rPT2 resides in the framework of many-body perturbation theory, this thesis assesses its starting point dependence, i.e., the dependence on the unperturbed Hamiltonian. Extensive benchmark calculations show that rPT2 is sensitive to the starting point with a clear trend of performance loss upon increasing the fraction of exact exchange in the underlying DFT Hamiltonian.

Both, TTF and TCNQ form molecular crystals. Based on the implementation of the stress tensor and unit cell relaxation in the FHI-aims code, their basic geometric, energetic and electronic properties are investigated. It is shown that the inclusion of vdW interactions is crucial, in particular for the description of lattice parameters. The thermal crystalline expansion is estimated and shown to be anisotropic along the individual lattice vectors. Furthermore, the low-index surfaces of both crystals exhibit a strong orientation dependence in the ionization potential.
Kurzfassung


Um diese Beschränkungen zu überwinden, entwickle ich ein XC-Funktional, das die Austauschenergie aus einer formal exakten Bedingung der DFT und der Einteilchen-Greenfunktion gewinnt. Somit wird der Anteil am exakten Austausch rein theoretisch sowie materialspezifisch bestimmt. Im Vergleich zu Standardfunktionalen weist dieses Funktional einen verminderten Selbstwechselwirkungsfehler und deutlich verbesserte Spektraleigenschaften auf. So wird es ermöglicht die Grundzustandsdichte des TTF-TCNQ-Komplexes zu beschreiben und zudem ist es mit der vdW-Korrektur nach Tkatchenko und Scheffler verträglich, die den langreichweitigen $1/R^6$-Beitrag mit dichteabhängigen $C_6$-Koeffizienten zu einem gegebenen DFT-Funktional hinzufügt.

Alternativ können vdW-Wechselwirkungen mit Methoden erfasst werden, die auf der Random-phase Approximation beruhen –, insbesondere mittels der Renormalized Second-order Perturbation Theory (rPT2). Der theoretische Zugang von rPT2 liegt in der Vielteilchenstörungstheorie und ist deshalb abhängig vom Startpunkt, also abhängig vom ungestörten Hamiltonoperator. Diese Arbeit zeigt durch umfangreiche Benchmark-Rechnungen, dass die Genauigkeit von rPT2 stark vom gewählten Startpunkt abhängt, und ein erhöhter Anteil am exakten Austausch im zugrundeliegenden DFT-Funktional zu einem Genauigkeitsverlust führt.

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Symbols, Abbreviations and Notation

Symbols

\( H_v \) Hamilton operator with external potential \( v \)
\( N_a \) Number of atoms
\( r \) Electron position
\( v \) External potential
\( v_{\text{KS}} \) Kohn-Sham potential
\( v_H \) Hartree potential
\( E_H \) Hartree energy
\( \Phi \) Slater determinant
\( V_{\text{ee}} \) Electron-electron interaction
\( E_{\text{xc}} \) Exchange-correlation energy
\( v_{\text{xc}} \) Exchange-correlation potential
\( \epsilon_{\text{xc}} \) Exchange-correlation energy per electron
\( E_x \) Exchange energy
\( \epsilon_x \) Exchange energy per electron
\( E_c \) Correlation energy
\( \epsilon_c \) Correlation energy per electron
\( \Psi_0 \) Ground state
\( w \) Coulomb interaction
\( W \) Screened Coulomb interaction
\( F_{\text{HK}} \) Hohenberg-Kohn functional
\( F_{\text{LL}} \) Levy-Lieb functional
\( \psi \) Normalized \( N \)-electron wavefunction; field operator
\( F_{\text{HF}}^{\alpha} \) Hellman-Feynman force on nucleus \( \alpha \)
\( F_{\text{Pulay}}^{\alpha} \) Pulay force on nucleus \( \alpha \)
\( H^0 \) Unperturbed Hamilton operator
\( H_n \) (Approximate) Hessian matrix at optimization step \( n \)
Symbols, Abbreviations and Notation

\(f_n\) Force at optimization step \(n\)
\(x_n\) Geometry at optimization step \(n\)
\(s_n^*\) Optimization step \(n\)
\(\rho_n\) Quality ratio at optimization step \(n\) (trust-region method)
\(\Delta_n\) Trust region radius at optimization step \(n\)
\(\Delta_{\text{max}}\) Upper bound for trust region radius
\(M_n\) Harmonic model potential at optimization step \(n\)
\(p_n\) Line search direction at optimization step \(n\)
\(\alpha_n\) Line search step length at optimization step \(n\)
\(\Delta v\) Perturbing potential
\(\Sigma G_0 W_0\) \(G_0 W_0\) self energy
\(s_R\) Range parameter for the vdW damping function
\(H\) Hilbert space
\(\rho\) Electron density
\(E\) Total energy
\(\varphi_i\) Single particle/Kohn-Sham orbital
\(\epsilon_i\) Single particle eigenvalue
\(E_{\text{coh}}\) Cohesive energy
\(E_t\) Transfer energy
\(E_g\) Transport gap
\(\Theta\) Step function
\(\bar{\rho}\) Averaged electron density
\(\epsilon\) Strain tensor
\(\sigma\) Stress tensor
\(\bar{v}\) Averaged electrostatic potential
\(A\) Surface unit cell area
\(\Omega\) Unit cell volume
\(\mu\) Dipole moment
\(Z_i\) Charge of nucleus \(i\)
\(\{e_i, i = 1, 2, 3\}\) Standard cartesian basis of \(\mathbb{R}^3\)
\(I_{\mu\nu}\) Moment of inertia tensor (with component \(\mu, \nu\))
\(m_i\) Mass of nucleus \(i\)
\(R_i\) Position vector of nucleus \(i\)
\(R_i^\gamma\) Component \(\gamma\) of nuclear vector \(R_i\)
\(a_i\) Lattice vector \(i\)
\(b^i\) Dual (reciprocal) lattice vector
\(T\) Temperature
\(\gamma\) Cleavage energy
\(\|x\|_2 = (\sum_i |x_i|^2)^{1/2}\) 2-norm
\(\|x\|_\infty = \max_i |x_i|\) Infinity-norm
<table>
<thead>
<tr>
<th>Symbol</th>
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<tr>
<td>$G$</td>
<td>Single particle Green’s function</td>
</tr>
<tr>
<td>$G_0$</td>
<td>Unperturbed single particle Green’s function</td>
</tr>
<tr>
<td>$\chi$</td>
<td>Response function</td>
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<tr>
<td>$\chi_0$</td>
<td>Unperturbed response function</td>
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</table>
Abbreviations

BFGS  Broyden-Fletcher-Goldfarb-Shanno
BLYP  Becke-Lee-Yang-Parr
B3LYP  Becke-three-Lee-Yang-Parr
BZ  Brillouin zone
CBM  Conduction band minimum
CC  Coupled cluster
DE  Double excitations
DFT  Density-functional theory
DOS  Density of states
EA  Electron affinity
EX  Exact exchange
GGA  Generalized gradient approximation
GKS  Generalized Kohn-Sham
GS  Ground state
HEG  Homogeneous electron gas
HF  Hartree-Fock
HK  Hohenberg-Kohn
HOMO  Highest occupied molecular orbital
HSE  Heyd-Scuseria-Ernzerhof
IP  Ionization potential
IPES  Inverse photoemission spectroscopy
KS  Kohn-Sham
LDA  Local-density approximation
LUMO  Lowest unoccupied molecular orbital
LSM  Line search method
MP2  Second order Möller-Plesset perturbation theory
PBC  Periodic boundary conditions
PBE  Perdew-Burke-Ernzerhof
PBEh  PBE hybrid
PES  Potential energy surface, Photoemission spectroscopy
PW  Perdew-Wang
revPBE  Revised PBE
RPA  Random phase approximation
rPT2  Renormalized second order perturbation theory
rSE  Renormalized single excitations
RSPT  Rayleigh-Schrödinger perturbation theory
scGW  Self consistent GW
SE  Single excitations
Symbols, Abbreviations and Notation

SI  Self-interaction
SIE  Self-interaction error
SOSEX  Second order screened exact exchange
TS  Tkatchenko-Scheffler
TTF  Tetrathiafulvalene
TCNQ  Tetracyanoquinodimethane
TRM  Trust-region method
UPS  Ultraviolet photoemission spectroscopy
vdW  Van der Waals
VBM  Valence band maximum
VWN  Vosko-Wilk-Nusair
XC  Exchange-correlation
XPS  X-ray photoemission spectroscopy
XRD  X-ray diffraction

Formulas

Denote by \( \{a_i\} \) the set of \( n \) actual values and by \( \{f_i\} \) the corresponding \( n \) forecast values. The individual errors with respect to the actual values are given by:

\[
\begin{align*}
ME &= \frac{1}{n} \sum_{i=1}^{n} (a_i - f_i) & \text{Mean error} \\
MAE &= \frac{1}{n} \sum_{i=1}^{n} |a_i - f_i| & \text{Mean absolute error} \\
MAPE &= \frac{100}{n} \sum_{i=1}^{n} \left| \frac{a_i - f_i}{a_i} \right| & \text{Mean absolute percentage error}
\end{align*}
\]
The ultimate goal of organic electronics is to realize flexible, easy-to-process, high efficiency, and low-cost (opto)electronic devices, such as organic light-emitting diodes, organic photovoltaic cells, or organic field-effect transistors. The rich chemistry of organic molecules promises that materials can be synthesized that satisfy application-specific demands. Here, theory could help to screen the known chemical compound space, or even design new materials. For electronic ground-state properties, density-functional theory (DFT) offers a promising quantum mechanical description. It is based on the electron density, an object that is more compact than the full many-body wavefunction that is the solution of the many-body Hamiltonian in quantum mechanics. In its main philosophy, DFT obtains the exact ground-state density by an effective single particle Hamiltonian with an effective local potential that encodes all the exchange and correlation effects beyond a single-particle picture by the so called exchange-correlation (XC) density functional. However, the precise analytical form of the XC functional is unknown and has to be approximated.

Unfortunately, describing the electronic and geometric properties of materials that are relevant for organic electronics is challenging for state-of-the-art approximations to the XC functional. The main reason is the presence of weak intermolecular interactions in organic materials, which lead to strong electron localization on the individual molecules. Standard DFT functionals (in their local-density, gradient-corrected or hybrid flavor for the XC functional) are problematic for such a scenario for two main reasons: i) they all lack the long-range tail of the van der Waals (vdW) forces, and ii), they all suffer from the self-interaction error, which is pronounced when it comes to localized states. Problem ii) may lead to significant errors for the predicted charge transfer and interaction energies, in particular for donor-acceptor complexes. In this thesis this will be illustrated and analyzed for the example of the prototypical tetrathiafulvalene (TTF) – tetracyanoquinodimethane (TCNQ) donor-acceptor complex.

Donor-acceptor complexes are of interest from both a technological and a scien-
Outline

Tific perspective. In applications, donor-acceptor complexes are used to facilitate charge injection from an electrode into a charge-transport material,\(^1,^2\) while from a fundamental point of view unknown physical phenomena may occur. One notable example is the interface between the large band-gap semiconductors TTF and TCNQ, at which metallic conduction has been observed.\(^3\)

A key result of this work is a new XC functional, PBEh(\(\alpha^*\)), which incorporates a system-dependent fraction of exact exchange \(\alpha^*\). This is achieved by combining DFT with Green’s function methods within the framework of many-body perturbation theory. The PBEh(\(\alpha^*\)) functional is able to satisfactorily describe the relative alignment of the charge transfer levels of TTF and TCNQ. It is free from asymptotic artefacts that would arise from the self-interaction error in standard functionals, and its general applicability is demonstrated for the G2 test set.

For weakly interacting molecules, the inclusion of van der Waals interactions is crucial. This may be achieved in two ways: i) adding the long range 1/\(R^6\) tail to a given DFT functional (e.g., with the Tkatchenko Scheffler (TS) scheme) or, ii) by employing more sophisticated approximation to the XC energy, which are based on the random-phase approximation (RPA) to the response function. One of the most recent developments in the latter approach is the so called renormalized second-order perturbation theory (rPT2). rPT2 adds renormalized single excitations corrections and second-order screened exact exchange to exact exchange plus the correlation energy in the RPA. Both schemes are assessed by means of extensive benchmark calculations, with focus on their starting point dependence i.e., their dependence on the underlying DFT input orbitals. It turns out that for rPT2 the standard PBE starting point gives the most balanced performance over different chemical and electronic environments, with a clear trend of performance loss upon including a fraction of exact exchange in the underlying DFT functional. Nevertheless, the PBE starting point gives qualitatively wrong results if rPT2 is applied to the pathological TTF-TCNQ donor-acceptor complex. The TS vdW correction scheme exhibits the opposite trend as it gains accuracy in describing weak intermolecular interaction energies upon including exact exchange in the DFT functional. In particular, the TS scheme clearly benefits from a coupling to the developed PBEh(\(\alpha^*\)) functional as compared to the standard PBE or PBE0 functionals.

Both TTF and TCNQ form molecular crystals with monoclinic unit cells. In order to calculate the equilibrium configuration for such low-symmetry crystal shapes, I implemented the numerical stress tensor and unit cell relaxation in the FHI-aims code. Based on that, I investigated the geometric, energetic, and electronic properties of the TTF and TCNQ single crystals with focus on the performance of different XC functionals. In particular for the unit cell shape, the inclusion of the long-range tail of vdW interactions turns out to be crucial. For
the low-index crystalline surfaces, surface energies and surface ionization potentials are reported. The latter is shown to exhibit strong surface anisotropies.

This work establishes theoretical and computational methods for an improved description of organic materials. The main contributions of this thesis are threefold. First, the PBEh($\alpha^*$) functional allows one to describe donor-acceptor systems, which are widely used in organic electronics. Second, the implementation of the numerical stress tensor and unit cell relaxation allows one to compute equilibrium unit cell shapes. And third, the TTF and TCNQ molecular crystals, as well as their low-index surfaces, are theoretically characterized.

This thesis is organized as follows: Chapter 1 reviews the theoretical methods that were used. Chapter 2 contains methodological contributions. First, the PBEh($\alpha^*$) XC functional is introduced and applied to the TTF-TCNQ dimer. Then benchmark results are presented and rPT2 and the TS scheme are assessed. Chapter 2 is complemented with a detailed analysis of the performance and errors of various functionals for the TTF/TCNQ complex. Chapter 3 introduces the ingredients and concepts for finding local minima on the Born-Oppenheimer surface. Using these methods, the implementation of unit cell relaxation is illustrated. Chapter 4 presents results for geometric, energetic, and electronic properties of TTF and TCNQ single crystals. Chapter 5 summarizes cleavage energies and ionization potentials for the low-index surfaces of TTF and TCNQ. Finally, a summary and an outlook for potential future steps is given in Chapter 6.
This chapter summarizes the basic theoretical underpinnings and approximations, which were applied in this thesis. All presented theoretical buildings are understood as being constructed on the Born-Oppenheimer approximation and nuclei treated in their classical limit. Although many concepts also apply beyond these approximations, their subsequent applications to organic molecules and solids will use them. In order to keep the formulas as simple as possible, no explicit spin indices will be introduced and atomic units will be used throughout this chapter, except where noted.

Consider a many-electron Hamiltonian, acting on the $N$-electron Hilbert space $\mathcal{H}^\otimes N = \mathcal{H} \otimes \cdots \otimes \mathcal{H}$, which shall be of the form

$$H_v : \mathcal{H}^\otimes N \rightarrow \mathcal{H}^\otimes N$$

$$H_v = -\frac{1}{2} \sum_{i=1}^{N} \nabla_{r_i}^2 + \frac{1}{2} \sum_{i \neq j}^{N} \frac{1}{|r_i - r_j|} + \sum_{i=1}^{N} v(r_i), \quad r_i, r_j \in \mathbb{R}^3,$$

(2.1)

$$= T + V_{ee} + V_{ext},$$

(2.2)

where $r_i$ denotes the position of electron $i$. The Hamilton operator in expression (2.1) consists of the kinetic energy operator $T$, the electron-electron Coulomb potential $V_{ee}$, and an external potential $v(r)$. The external potential couples the electrons to an external source. An important class of such potentials is given by the electron-nuclear interaction within the Born-Oppenheimer approximation. The electron-nuclear interaction between $N_a$ nuclei and $N$ electrons is given by

$$V_{ext} = V_{e-nuc} = \sum_{i=1}^{N_a} \sum_{j=1}^{N_a} \frac{Z_j}{|r_i - R_j|} =: \sum_{i=1}^{N} v(r_i), \quad r_i, R_j \in \mathbb{R}^3.$$  

(2.3)

\footnote{The $N$-body Hilbert space is obtained by a completed $N$-fold tensor product of a single particle Hilbert space $\mathcal{H} = L^2(\mathbb{R}^3)$.}
2 Approaches to the many–electron problem

Consider the expectation value of the Hamiltonian with respect to a normalized state \( \Psi \) with \( \| \Psi \| = 1 \),

\[
\langle \Psi, H v \Psi \rangle = \langle \Psi, (T + V_{ee}) \Psi \rangle + \int \rho(r)v(r)d^3r,
\]

(2.4)

\[
\rho(r) = N \int |\Psi(r, r_2, \ldots, r_N)|^2 dr_2 \ldots dr_N
\]

(2.5)

where the contribution from the external potential was rewritten in terms of the electron density \( \rho \), using \( \sum_{i=1}^{N} v(r_i) = \sum_{i=1}^{N} \int v(r)\delta(r - r_i) d^3r. \)

For a given external potential \( v \), the ground state energy \( E \) is defined as the greatest lower bound (infimum) of Equation (2.4) over normalized trial functions \( \Psi \),

\[
E = \inf_{\Psi} \langle \Psi, H v \Psi \rangle, \quad \| \Psi \| = 1,
\]

(2.6)

If a minimizing \( \Psi \) exists, then it is called ground state \( \Psi_0 \). For a fixed \( V_{ee} \), the existence of a minimizer depends on the external potential. Denote the set of external potentials that have a minimizer by

\[
\mathcal{V}_N := \{ v \mid H_v \text{ has a } N \text{ particle groundstate} \}.
\]

(2.7)

For \( v \in \mathcal{V}_N \), \( \Psi_0 \) may then be obtained variationally by demanding that the ground state energy remains stationary upon a variation of the ground state under the side condition of wavefunction normalization:

\[
\langle \delta \Psi_0, (H_v - E) \Psi_0 \rangle = 0 \Rightarrow \langle \delta \Psi_0, (H_v - E) \Psi_0 \rangle = 0. \]

Hence, the ground state must obey the equations of motion (EOM), which is the time-independent Schrödinger Equation,

\[
H_v \Psi_0[v] = E[v] \Psi_0[v],
\]

(2.8)

where the functional dependence on the external potential is written in the square bracket.

2.1 Density-functional theory: A variational approach

Instead of solving the many electron Schrödinger equation, density-functional theory (DFT) allows to obtain the ground state energy and the ground state electron density by means of a variational principle that depends on the density, \( \rho \), only. In principle, this reduces the complexity significantly, because \( \rho \) depends only on three spatial coordinates, whereas the \( N \)-electron wavefunction depends on \( 3^N \) spatial coordinates. The cornerstone of DFT is the Hohenberg-Kohn (HK) theorem.\(^6\)
First define the set
\[ A_N := \{ \rho \mid \rho \text{ comes from a } N \text{ particle groundstate } \Psi_0[v], v \in \mathcal{V}_N \}, \] (2.9)
which allows to state the HK theorem\(^5\)–\(^7\),

**Theorem 1** (Hohenberg-Kohn). For an \( N \)-electron Hamiltonian with a given electron-electron interaction \( V_{ee} \), the following holds true

i) The external potential is determined up to a constant by the ground state density \( \rho \), i.e., the map \( \mathcal{V}_N \ni v + \text{const.} \mapsto \rho \in A_N \) is injective\(^b\), with \( \rho(r) = N \int |\Psi_0[v](r,r_2,\ldots,r_N)|^2 \, dr_2 \ldots dr_N \).

ii) Define the Functional \( F_{HK} : A_N \ni \rho \mapsto \langle \Psi_0[\rho], (T + V_{ee})\Psi_0[\rho] \rangle \). Then the ground state energy of the system for some fixed \( v \in \mathcal{V}_N \), is given by
\[ E[v] = \min_{\rho \in A_N} \left\{ F_{HK}[\rho] + \int \rho v \right\} \] (2.10)
where the minimizer is the ground stated density \( \rho \) with respect to the given \( v \).

\( F_{HK} \) is called Hohenberg-Kohn functional; it is a universal functional in the sense that it does not dependent of the external potential (although it depends on \( V_{ee} \)). Equation (2.10) is also called the HK variational principle. Since in Equation (2.10) the ground state energy is expressed as a minimum, it may be written as a variational equation and the ground state density may be obtained by solving the EOM,
\[ \frac{\delta F_{HK}}{\delta \rho} + v = \mu, \] (2.11)
where \( \mu \) is the Lagrange multiplier that assures the electron number to be fixed to \( N \).

\(^b\)For non degenerate ground states this map is bijective. In this case even a stronger statement holds: each map in the composition \( \mathcal{V}_N \ni v \mapsto \Psi[v] \mapsto \rho \) is injective\(^8\) (in the following sense: injective up to a phase factor for \( \Psi \) and up to a constant for \( v \), both physically irrelevant). Hence for a \( v \) with a non degenerate ground state the whole ground state \( \Psi_0[v] \) is determined by the ground state density \( \rho \) alone. For the degenerate case the map has to be understood ‘representative wise’. To this end, split the set \( A_N \) into a disjoint union of equivalence classes \( A_N = \bigcup [\rho] \), with the equivalence relation \( [\rho] = \{ \rho' \in A_N \mid \rho' \sim \rho \Rightarrow \rho \text{ and } \rho' \text{ come from ground states of a given } v \in \mathcal{V}_N \} \). Then the map in i) is a map on equivalence classes \( \mathcal{V}_N \ni v \mapsto [\rho] \) and it is a bijection for chosen representatives, i.e. the external potential is determined (up to a constant) by any representative of the equivalence class\(^9\). And by ii), the ground state energy is determined by any representative of the equivalence class of ground state densities.
2 Approaches to the many–electron problem

Adiabatic connection and Kohn-Sham formalism

While the HK theorem establishes the fundamental role of $\rho$ for the ground state, the Kohn-Sham (KS) scheme provides a recipe how to actually calculate $\rho$. The basic idea is to introduce a fictitious system of independent, non-interacting electrons in a common one-body, local potential (the Kohn-Sham potential $v_{KS}$) that has the same groundstate density as the real, fully-interacting system.

First, a slightly more general concept is considered by introducing the coupling constant Hamiltonian $H_v^\lambda = T + \lambda V_{ee} + V_{ext}^\lambda$, $\lambda \in [0, 1]$ (2.12)

The coupling constant $\lambda$ switches on the electron-electron coupling which is given by the coulomb potential $V_{ee}$. The domains of definition readily adapt to $H_v^\lambda$,

\[ V_N^\lambda := \{ v_\lambda \mid H_v^\lambda \text{ has a } N \text{ particle groundstate } \Psi_0^\lambda[v_\lambda] \}, \]

\[ A_N^\lambda := \{ \rho_\lambda \mid \rho_\lambda \text{ comes from a } N \text{ particle groundstate } \Psi_0^\lambda[v_\lambda], v \in V_N^\lambda \}, \]

where the $\lambda$-dependence will be omitted for the fully interacting Hamiltonian ($\lambda = 1$) in order to be consistent with the previous notation. The HK Theorem I applies for a given $V_{ee}$. Therefore it holds for every $\lambda$ individually, with a $\lambda$-dependent HK functional,

\[ A_N^\lambda \ni \rho_\lambda \mapsto F_{HK,\lambda}[\rho_\lambda] = \langle \Psi_0^\lambda[\rho_\lambda], (T + \lambda V_{ee}) \Psi_0^\lambda[\rho_\lambda] \rangle, \]

(2.15)

Now, for the fully interacting Hamiltonian with given external potential $v$ (and associated ground state density $\rho$), the aim is to construct an external potential for the $\lambda$-interacting Hamiltonian, $v_\lambda$, such that both Hamiltonians have the same ground state density. Hence, one would like to construct a map $f_\lambda : v \mapsto v_\lambda$ such that the following diagram is commutative,

\[ \begin{array}{ccc}
V_N \ni v & \longrightarrow & \rho \in A_N \\
\downarrow f_\lambda & & \downarrow id \\
V_N^\lambda \ni v_\lambda & \longrightarrow & \rho_\lambda \in A_N^\lambda 
\end{array} \]

(2.16)

For a given $\lambda$, the ground state density $\rho_\lambda$ must satisfy the EOM,

\[ \frac{\delta F_{HK,\lambda}}{\delta \rho_\lambda} + v_\lambda = \mu_\lambda. \]

(2.17)
2.1 Density-functional theory: A variational approach

Writing $\mu_\lambda = \mu + \text{const}$, absorbing\(^c\) the constant in $v_\lambda$, using Equation (2.11), and the requirement of Diagram (2.16), gives the desired map\(^d\):

$$f_\lambda : v_\lambda = v + \frac{\delta}{\delta \rho} [F_{HK} - F_{HK,\lambda}].$$  
(2.18)

This gives the external potential at the electronic ground state density of the $\lambda$-interaction Hamiltonian, which has the same ground state density as the fully interacting one.

In the special case of $\lambda = 0$, the Schrödinger Equation for the ground state reads,

$$\sum_{i=1}^{N} \left( -\frac{1}{2} \nabla^2_i + v_0(r_i) \right) \Phi_0 = E_0 \Phi_0,$$  
(2.19)

where the notation $\Psi_0^{\lambda=0} \equiv \Phi_0$ was used and the functional derivative in Equation (2.18) is taken at the ground state density associated with $\Phi_0$. Equation (2.19) is an effective single particle equation, and is known as the Kohn-Sham (KS) equations (in condensed form). In order to write down the KS equations in a more familiar form, define the exchange correlation (XC) functional,

$$E_{\text{xc}} = E_{H} + E_{\text{xc}}[\rho],$$  
(2.20)

where $E_H$ is the Hartree energy functional,

$$E_{H} := \frac{1}{2} \iint \frac{\rho(r) \rho(r')}{|r - r'|} d^3r d^3r'.$$  
(2.21)

Taking into account the fermionic nature of electrons, the effective single particle Equation (2.19) can be solved by an antisymmetrized product ansatz for $\Phi_0$ in terms of $N$ single particle orbitals $\{\varphi_i\}$.

$$\Phi_0 = \frac{1}{\sqrt{N!}} \sum_{\sigma \in S_N} \text{sign}(\sigma) \varphi_{\sigma(1)} \otimes \cdots \otimes \varphi_{\sigma(N)} =: \varphi_1 \wedge \cdots \wedge \varphi_N,$$  
(2.22)

where $S_N$ is the permutation group of $\{1, 2, \ldots N\}$ and $\text{sign}(\sigma)$ is the signature of permutation $\sigma \in S_N$. The expression (2.22) is also called single Slater determinant.

\(^c\)This is possible because one needs to obtain $v_0$ only up to a constant.

\(^d\) The potential obtained in this way is a function over $\mathbb{R}^3$ since only the (or any, in the case of degeneracy) groundstate density $\rho$ obeys the equation of motion. In a less condensed notation, Equation (2.18) reads $\mathbb{R}^3 \ni r \mapsto v_\lambda(r) = v(r) + \frac{\delta}{\delta \rho} [F_{HK}[\rho] - F_{HK,\lambda}[\rho]] |_{\rho(r)}$, i.e., the functional derivative is evaluated at the ground state density $\rho$. 

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2 Approaches to the many–electron problem

(for which the symbol $\Phi$ will be reserved) and gives with Equation (2.20) the KS equations in their standard form

$$\left( -\frac{1}{2} \nabla^2 + v_{KS}(r) \right) \varphi_i(r) = \epsilon_i \varphi_i(r),$$

(2.23)

$$\rho(r) = \sum_i f_i |\varphi_i|^2,$$

(2.24)

$$v_{KS}(r) \equiv v_0(r) = v(r) + \frac{\delta E_H}{\delta \rho(r)} + \frac{\delta E_{xc}}{\delta \rho(r)},$$

(2.25)

where the last line defines the Hartree potential $v_H$ and the XC potential $v_{xc}$. For an $N$ electron system the total charge density is built up by the $N$ lowest (the ‘occupied’) orbitals. This is taken into account in Equation (2.24) by the occupation numbers $f_i$, which are one for $i \leq N$ and zero otherwise. The KS potential $v_{KS}$ depends itself on the KS orbitals $\{\varphi_i\}$ via Equation (2.24). Therefore, Equation (2.23) needs to be solved in a self-consistent fashion. By the construction in Diagram (2.16), the KS Equations (2.23)–(2.25) a priori give only the exact ground state density. Neither the exact KS orbitals nor the KS eigenvalues $\{\epsilon_i\}$ have any physical meaning, except i) their relation to the ground state density by Equation (2.24), and ii) that the highest occupied $\epsilon_i$ corresponds to the ionization potential $^{12,13}$.

In particular, the second property will be exploited in Section 3.1 of this thesis.

Once $\rho$ is determined by the KS equations, the ground state total energy may be obtained by Equation (2.20) and the HK theorem,

$$E_v = F_{HK,0} + E_H + E_{xc} + \int \rho v$$

(2.26)

$$= \sum_i f_i \left( \epsilon_i, \frac{1}{2} \nabla^2 \varphi_i \right) + E_H + E_{xc} + \int \rho v$$

(2.27)

$$= \sum_i f_i \epsilon_i - E_H + E_{xc} - \int \rho v_{xc}$$

(2.28)

The approach presented so far is in principle (see remarks below) exact. However, the functional form of the employed $F_{HK}$ respectively $E_{xc}$ is unknown and needs to be approximated. In practice, it is rather the exchange correlation functional ($E_{xc}$) defined in Equation (2.20) than $F_{HK}$ that is approximated. This is, because two major contributions, the non-interacting kinetic energy $F_{HK,0}$ and $E_H$

$^a$For $\rho \in A_N$, $F_{HK,0}[\rho] = \langle \Phi_0[\rho], T\Phi_0[\rho] \rangle$ is the expectation value of the kinetic energy for
are already accounted for. One property of $E_{xc}$ follows immediately from Equations (2.20) and (2.15).

For a given ground state density, $\rho \in A_\lambda^N$, $\lambda \in [0, 1]$,

$$E_{xc} = F_{HK} - F_{HK,0} - E_H = \int_0^1 \left[ \frac{\partial}{\partial \lambda} F_{HK,\lambda} - E_H \right] d\lambda$$

(2.29)

$$= \int_0^1 \left[ \langle \Psi_0^\lambda, V_{ee} \Psi_0^\lambda \rangle - E_H \right] d\lambda =: \int_0^1 U_{xc}^\lambda[\rho] d\lambda,$$

(2.30)

where in the first line the difference between of $F_{HK}$ at the $\lambda$-boundaries was expressed as a coupling constant integral, and the $E_H$ was brought under the integral by virtue of Diagram 2.16 (i.e., $\rho$ is independent of $\lambda$). In the second line the derivative with respect to $\lambda$ was evaluated from Equation (2.15) with the aid of the Hellmann-Feynman theorem and the coupling constant integrand $U_{xc}^\lambda$ was defined. Hence, $E_{xc}$ may be obtained by a coupling constant integration over all adiabatic connection ground states between the KS system ($\lambda = 0$) and the physical one ($\lambda = 1$). For $\lambda = 0$, the coupling constant integrand has the form

$$U_{xc}^0[\rho] = \langle \Phi_0[\rho], V_{ee} \Phi_0[\rho] \rangle - E_H[\rho]$$

(2.31)

$$= -\frac{1}{2} \sum_{i,j=1}^N \int \int \frac{\varphi_i^*(r) \varphi_j^*(r') \varphi_j(r) \varphi_i(r')}{|r - r'|} d^3r d^3r' =: E_{EX}^x$$

(2.32)

where again the convention $\Psi_0^{\lambda=0} \equiv \Phi_0$ was used for the single Slater determinant of occupied KS orbitals and $E_H$ was expressed in terms of $\Phi_0$. $E_{EX}^x$ is called exact exchange energy; it is the expectation value of the Fock operator evaluated for the KS orbitals. It will be used for the construction of hybrid functionals in the next section.

Having set the basics of DFT, it is important to note that the HK theorem only holds on the domain of $v$-representable densities, that is $\rho \in A_N$. In other words, the trial densities in the HK variational procedure must come from the set $A_N$. If the KS scheme is applied then these must be in addition non-interacting $v$-representable, that is $\rho \in A_N^0$. From a theoretical point of view, this restriction is a severe one because there is no criterion known, whether a density is $v$-representable (except the hard one by solving the Schrödinger equation). Hence, one cannot easily select $v$-representable densities in a variational calculation. There exist several extensions of the HK functional, $F_{HK}$, which have a larger domain of definition. The most important one is the constraint search formalism by Levy andLieb. The densities that arise from a groundstate of a non-interacting Hamiltonian. Then $\Phi_0$ may be written as a single Slater determinant as given in Equation (2.22) and thus $F_{HK,0}$ is the sum of single particle kinetic energy terms. In the literature $F_{HK,0}$ is typically denoted as $T_s$. 

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where \( F_{HK} \) is replaced by \( F_{LL} \),

\[
\mathcal{J}_N := \left\{ \rho \mid \rho \geq 0, \sqrt{\rho} \in H^1(\mathbb{R}^3), \int \rho(r) d^3r = N \right\}
\]

\[
\mathcal{W}_N := \{ \psi \mid \|\psi\| = 1, T(\psi) < \infty \}
\]

\[
\mathcal{J}_N \ni \rho \mapsto F_{LL}[\rho] := \min_{\psi \mapsto \rho} \{ \langle \psi, (T + V_{ee}) \psi \rangle \mid \psi \in \mathcal{W}_N \}.
\]

\( F_{LL} \) searches over all normalized \( \psi \) with finite kinetic energy that yield the input density \( \rho \in \mathcal{J}_N \), and selects that one which gives the lowest expectation value. With this functional, the variational space is extended to densities with come from an \( N \)-electron wavefunction, \( \psi \in \mathcal{W}_N \), and not necessary any longer from a ground state (these density is then called \( N \)-representable). \( F_{LL} \) may be indeed regarded as an extension of \( F_{HK} \), because \( F_{HK} = F_{LL} \) for \( \rho \in \mathcal{A}_N \) and \( \mathcal{A}_N \subset \mathcal{J}_N \). Furthermore, if \( F_{HK} \) is replaced by \( F_{LL} \) in the variational principle of Equation (2.10), now defined over the densities \( \rho \in \mathcal{J}_N \), then it has its minimzer at the exact ground state density. Unfortunately, also the \( F_{LL} \) functional brings its own problems; more details on the mathematical formulation of DFT, its pitfalls, and extensions may be found in Refs. 4,5,8,16–45

Apart from the problem of the domain of valid trial densities that may enter the variational principle the main problem is that \( E_{xc} \) is is not known explicitly. This quantity needs to be approximated, which will be subject to the subsequent section.

2.2 Approximations to the exchange-correlation energy

The KS equations are in principle exact, in the sense that they deliver the exact many-body ground state density and energy. However, the exchange-correlation energy functional \( E_{xc}[\rho] \) is unknown and has to be approximated. While there exists only one exact \( E_{xc}[\rho] \), (too) many approximations to it exist. These approximations are themselves called XC functionals and should be distinguished from the exact one. The exact XC functional is universal\(^{46} \), i.e., independent of the external potential. Approximate XC functionals may be universal in their functional form; however their performance is highly system dependent, and for a given system, it depends on the ground state quantity of interest. In particular, standard approximations may give qualitatively wrong results, which will be a subject of Chapter 3. The following review briefly summarizes a selection of approximate

\textsuperscript{4}H^1(\mathbb{R}^3) is the (Sobolev) space \( H^1(\mathbb{R}^3) = \{ f \mid f \in L^2(\mathbb{R}^3), \nabla f \in L^2(\mathbb{R}^3) \} \). The definition of \( F_{LL} \) is a ‘good’ one, because it can be proven that \( \forall \rho \in \mathcal{J}_N, \exists \psi \in \mathcal{W}_N \) such that the minimum in Equation (2.35) exists.\(^{4,5} \)
2.2 Approximations to the exchange-correlation energy

XC functionals, which were used in this thesis (see also Refs.\textsuperscript{9,14,47–50}).

$E_{xc}$ can be split into an exchange ($E_x$) and a correlation part ($E_c$)\textsuperscript{9}, $E_{xc}[\rho] = E_c[\rho] + E_x[\rho]$, which have by the aid of Equation (2.20) and (2.15) the specific form\textsuperscript{8}

\begin{align*}
E_x[\rho] &:= \langle \Phi_0[\rho], V_{xc} \Phi_0[\rho] \rangle - E_H[\rho] \\
E_c[\rho] &:= F_{HK}[\rho] - \{ F_{HK,0}[\rho] + E_H[\rho] + E_x[\rho] \} \\
&= \langle \Psi_0[\rho], (T + V_{xc}) \Psi_0[\rho] \rangle - \langle \Phi_0[\rho], (T + V_{xc}) \Phi_0[\rho] \rangle
\end{align*}  

(2.36)

(2.37)

(2.38)

where $\Phi_0 \equiv \Psi_0^0$ was used to stress that it is the (single Slater determinant) non-interacting KS groundstate that gives $\rho$. Hence, $E_x$ is the expectation value of the Fock operator taken at the KS orbitals. $E_c$ is all the rest what is missing. According to Equation (2.38), it is the difference between the expectation value of the operator $T + V_{xc}$ evaluated at the KS groundstate and the physical groundstate (both give the same density $\rho$, and therefore also $E_c[\rho] < 0$).

The local-density approximation (LDA)

The LDA is based on the homogeneous electron gas (HEG), for which the electron density is constant in space

$$\rho(r) = \rho^{\text{HEG}} = \text{constant in space} \quad (2.39)$$

Splitting the XC energy per electron of the HEG, $\epsilon^{\text{HEG}}_{xc}$, into an exchange ($\epsilon^{\text{HEG}}_x$) and a correlation part ($\epsilon^{\text{HEG}}_c$), allows to analytically determine the exchange part as a function of $\rho^{\text{HEG}}$\textsuperscript{51}

$$\epsilon^{\text{HEG}}_{xc} = \epsilon^{\text{HEG}}_x + \epsilon^{\text{HEG}}_c, \quad \epsilon^{\text{HEG}}_x(\rho^{\text{HEG}}) = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \rho^{\text{HEG}1/3}. \quad (2.40)$$

For the correlation part of the HEG, $\epsilon^{\text{HEG}}_c$, no closed analytic form is known except for the high\textsuperscript{52} and low\textsuperscript{53} density limits. At intermediate densities Quantum Monte-Carlo calculations\textsuperscript{54} exist, which were used to parametrize interpolations of $\epsilon^{\text{HEG}}_c$. Several such parametrizations have been proposed. This thesis uses the one by Perdew and Wang\textsuperscript{55}. The basic idea of the LDA is to approximate $E_{xc}[\rho]$ of a non-uniform electron gas by a spatial average, where at every point in space the XC energy density shall have the form of the HEG:

$$\rho^{\text{HEG}} \rightarrow \rho(r), \quad E_{xc}[\rho] \approx E^{\text{LDA}}_{xc}[\rho] = \int \rho(r) \epsilon^{\text{HEG}}_{xc}(\rho(r)) \, d^3 r. \quad (2.41)$$

\textsuperscript{8}For consistency with the previous section these definitions are given for the HK functional, however they extend also to $F_{LL}$.  

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2 Approaches to the many–electron problem

The LDA energy per electron as given in Eq. (2.41) only depends on the electron density and is local in space. It is per construction exact for the HEG, and may be a good approximations for systems where the electron density varies only moderately in space. Interestingly, the LDA also obtained acceptance for systems with strongly varying densities, which is often attributed to a fortunate cancellation of errors.

Generalized gradient approximations (GGAs)

In the mid 1980s, a new generation of XC functionals appeared that also included the gradient of the electron density. Via the historic meander of gradient-expansion approximations (GEA), this was achieved by generalized gradient approximations. GGAs are of the form

\[ E_{\text{GGA}}^{\text{xc}} = \int f(\rho, \nabla \rho) \] and are also called semilocal functionals due to their dependence on the density gradient \(\nabla \rho\). The choice of \(f(\rho, \nabla \rho)\) is in general not unique. Therefore, many flavours of GGAs exist in literature. Probably the most famous GGA is the PBE functional by Perdew, Burke and Ernzerhof\(^56\). It is based on the LDA and reads for the spin unpolarized case

\[ E_{\text{PBE}}^c = \int \rho \left\{ \epsilon_{\text{HEG}}^c(\rho) + H(\rho, \nabla \rho) \right\}, \]
\[ E_{\text{PBE}}^x = \int \rho \epsilon_{\text{HEG}}^x(\rho) F_x(\rho, \nabla \rho). \] (2.42)

The additional term \(H\) in the correlation part and the exchange enhancement factor, \(F_x\), carry the information about the density gradient. They are obtained as parametrized functions such that certain physical constraints are fulfilled (for details see Ref.\(^56\)), and are given by

\[ F_x(\rho, \nabla \rho) \rightarrow F_x(s) = 1 + \kappa - \frac{\kappa}{1 + \mu s^2/\kappa}, \]
\[ s = \frac{|\nabla \rho|}{2\rho^{4/3}(2\pi^{2})^{1/3}}, \quad \kappa, \mu = \text{const.,} \]
\[ H(\rho, \nabla \rho) \rightarrow H(r, t) = \frac{m_e}{\hbar^2} \gamma \ln \left\{ 1 + \frac{3\mu}{\pi^2 t^2} \left[ \frac{1 + At^2}{1 + At^2 + A^2 t^4} \right] \right\}, \]
\[ A = \frac{3\mu}{\pi^2 \gamma} e^{-a_0 \epsilon_{\text{HEG}}^c(\rho)/\gamma e^2} - 1, \]
\[ t = \frac{|\nabla \rho| \left( a_0 \pi \right)^{1/2}}{4\rho^{7/6}(2\pi^{2})^{1/6}}, \quad a_0 = \hbar^2/m_e e^2, \quad \gamma = \text{const.,} \] (2.44)

where the dimensionless density gradients \(s\) and \(t\) were introduced. Several revisions the Equations (2.45-2.44) were suggested in the literature. They either modify the form of \(F_x\) (RPBE\(^57\)), or use a different value for \(\kappa\) (revPBE\(^58\)).
The PBE functional is \textit{ab initio} in the sense that the functions \( H \) and \( F_x \) are ‘constraint-driven’ and therefore do not rely on experimental data. However, among the GGAs there exist also ‘desire-driven’ functionals that additionally employ empirical parameters and therefore cannot be regarded as being \textit{ab initio}; a prominent example is the BLYP functional\(^{59}\).

Hybrid functionals

The construction principle presented so far for approximate XC functionals \( (E_{xc}^{app}) \) is based on the HEG (LDA) and a semilocal refinement (GGA). Hybrid functionals introduce an additional construction principle which is closely related in the adiabatic connection formula. They admixture a fraction of exact exchange energy, \( E_{x}^{EX} \), to the semilocal exchange expression\(^{48,60}\).

\[
E_{x}^{hyb} = \alpha E_{x}^{EX} + (1 - \alpha) E_{x}^{GGA},
\]

where the exact exchange energy \( (EX) \) is defined in terms of a Fock integral over the \( N \) lowest occupied KS orbitals, and \( N \) is the number of electrons. Due to the explicit dependence of Equation (2.47) on the KS orbitals rather than the density, hybrid functionals are also considered as orbital functionals. \( E_{x}^{EX} \) is evaluated for KS orbitals and in general different from the Hartree-Fock (HF) exchange energy because KS and HF orbitals are not identical. For \( \alpha = 1 \) Equation (2.47) implies that the inter-orbital exchange contribution \( i \neq j \) is treated exactly while the term \( i = j \) cancels the Hartree self-energy that would arise in Equation (2.21) for the KS-orbital based density. Usually hybrid functionals employ an \( \alpha \neq 1 \). Therefore they reduce the Hartree self-interaction rather than canceling it exactly.

Similar to GGAs, many hybrid functionals exist; the first one was proposed by Becke\(^{60}\) and constructed by a linear interpolation of the adiabatic connection formula (2.30),

\[
E_{xc} = \int_0^1 U_{xc}^\lambda d\lambda \approx E_{xc}^{\lambda=0} + \int_0^1 \lambda(E_{xc}^{\lambda=1} - E_{xc}^{\lambda=0})d\lambda
\]

where Equation (2.32) and (2.38) was used (for a \( \lambda = 0 = V_{oc} \) system, the correlation energy is zero). With the additional approximation \( E_{xc}^{\lambda=1} \approx E_{xc}^{LDA} \), Becke’s original hybrid functional is obtained, which uses 50% of exact exchange. More
2 Approaches to the many–electron problem

generally, $U_{xc}^\lambda$ could be approximated in a non-linear fashion\textsuperscript{61}

$$U_{xc}^\lambda \approx U_{xc}^{\text{app},\lambda} + (E_{x}^{\text{EX}} - E_{x}^{\text{app}})(1 - \lambda)^{n-1},$$  \hspace{1cm} (2.49)

$$E_{xc}^{\text{app}} = \int_{0}^{1} U_{xc}^{\text{app},\lambda} d\lambda,$$  \hspace{1cm} (2.50)

where in Equation (2.50) a given approximate functional $E_{xc}^{\text{app}}$ (e.g. LDA or GGA) has been written in terms of a coupling constant decomposition. Also note, that within the ansatz of Equation (2.49) only the exchange part undergoes a polynomial coupling constant interpolation. The appropriate power $n$ in Equation (2.49) should be system dependent. However, the overall best single choice has been suggested to be $n = 4$\textsuperscript{61}. Coupling constant integrating of Equation (2.49) for the PBE approximation gives the PBE0 functional\textsuperscript{62}

$$E_{xc}^{\text{PBE0}} = \alpha E_{x}^{\text{EX}} + (1 - \alpha)E_{x}^{\text{PBE}} + E_{c}^{\text{PBE}}, \quad \alpha = 1/4,$$  \hspace{1cm} (2.51)

with 25\% of exact exchange. As an outlook, obtaining a system dependent $\alpha$ (and hence $n$) will be a subject of Chapter 3.

In an alternative approach to the adiabatic connection formula, the amount of exact exchange could be also fitted to experimental data. The most prominent example is the B3LYP functional\textsuperscript{63,64} which is of the form

$$E_{xc}^{\text{B3LYP}} = (\alpha E_{x}^{\text{EX}} + 1 - \alpha)E_{x}^{\text{LDA}} + \alpha' \Delta E_{x}^{\text{B88}} + \alpha'' E_{c}^{\text{LYP}} + (1 - \alpha'')E_{c}^{\text{VWN}},$$  \hspace{1cm} (2.52)

$\Delta E_{x}^{\text{B88}}$ is Becke’s gradient correction to the exchange functional\textsuperscript{65}. $E_{c}^{\text{LYP}}$ and $E_{c}^{\text{VWN}}$ are the LYP-GGA\textsuperscript{59} (after Lee, Yang and Parr) and the VWN LDA parametrization\textsuperscript{64,66} (after Vosko, Wilk and Nusair) of the correlation functional, respectively. The coefficients $\{\alpha, \alpha', \alpha''\}$ were fixed by a fit to thermochemical data sets – in particular the fraction of exact exchange amounts to 20\%. Even though relying on empirical data, the B3LYP functional is highly appreciated in the chemistry community and may be well regarded as its main DFT working horse. Indeed, developing new functionals that uniformly perform better than B3LYP (at comparable computational cost) may be regarded as one main challenge for DFT\textsuperscript{47}.

Screened hybrid functionals

Hybrid functionals of the above form were successfully applied to a wide range of molecular properties\textsuperscript{14,67}. However, for solids – especially for metals – calculating the exact exchange integral may become computationally very demanding\textsuperscript{68} due to the non-local and long-range nature of Eq. (2.47). Range separated, or screened
2.2 Approximations to the exchange-correlation energy

Hybrid functionals may resolve this difficulty. They are based on a spatial decomposition of the Coulomb interaction into a short range (SR) and a long range (LR) part,

\[
\frac{1}{|r - r'|} = \frac{\text{erf}(\omega |r - r'|)}{|r - r'|} + \frac{\text{erfc}(\omega |r - r'|)}{|r - r'|}, \quad \omega \in \mathbb{R}_{\geq 0}, \quad (2.53)
\]

\[
\text{erf}(x) := \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt, \quad \text{erfc}(x) := 1 - \text{erf}(x), \quad (2.54)
\]

where the range separation is introduced via the error function and controlled by the inverse screening length \(\omega\). Insertion of Equation (2.53) into the exchange part of PBE0 in Equation (2.51) gives the identity

\[
E_{\text{PBE0}}^x = \alpha (E_{\text{EX,SR}}^x(\omega) + E_{\text{EX,LR}}^x(\omega)) + (1 - \alpha) (E_{\text{PBE,SR}}^x(\omega) + E_{\text{PBE,LR}}^x(\omega)).
\]

While the impact of Equation (2.53) is clear for the exact exchange part from Equation (2.47), it is important to note that it also enters the PBE exchange energy via the so called exchange correlation hole\(^4^8,^6^8\). One now wishes to neglect the problematic long range exact exchange part \(E_{\text{EX,LR}}^x\). Because numerical tests indicate that the long range exact and PBE exchange contributions tend to cancel each other\(^h\), the introduced error may be partially compensated by also neglecting the \(\alpha\) weighted \(E_{\text{PBE,LR}}^x\) term. This yields the HSE06 functional:

\[
E_{\text{HSE06}}^x = \alpha E_{\text{EX,SR}}^x(\omega) + (1 - \alpha) E_{\text{PBE,SR}}^x(\omega) + E_{\text{PBE,LR}}^x(\omega), \quad (2.55)
\]

\[
E_c^{\text{HSE06}} = E_c^{\text{PBE0}} = E_c^{\text{PBE}}, \quad (2.56)
\]

\(\alpha = 1/4, \quad \omega = 0.11 \text{ bohr}^{-1} \).

HSE06 has the same expression for the correlation energy as PBE or PBE0. The only difference is in the exchange energy: It treats the short range part as in PBE0, whereas the long range part is treated exclusively by PBE. The value of the range separation parameter \(\omega\) was determined by a fit to molecular atomization energies\(^6^8,^6^9\). Comprehensive studies comparing HSE06, standard hybrid and semilocal functionals can be found in Refs.\(^6^7,^6^8,^7^0–^7^3\).

Similar to \(\alpha\), it has been argued that \(\omega\) should be in general system dependent by its relation to the dielectric function\(^7^4–^7^6\); or by the correlation between valence band width and formation energies\(^7^-^7\) in non-metals. Finally, the choice for the error function as range separation function in Equation (2.53) is not stringent, but

\(^h\)This is the argument given in the original HSE paper by Heyd et al.\(^6^8\). On the other hand, the results which will be presented in Chapter 3 indicate that the long range exact and PBE exchange contributions do not cancel each other (because otherwise the PBE0 and HSE06 results would be very similar, see also the references on the HSE06 performance given above).
is rather motivated technically because its simplicity in calculating the integrals in a Gaussian basis set.

Functional families

At this point, after having introduced a lot of functionals, it is relieving to categorize as many as possible into a unifying picture. To this end, denote the HSE-XC-family, which consists of the set of all functionals that can be parametrized by Eq. (2.55-2.56) by

$$\text{HSE}(\alpha, \omega), \quad (\alpha, \omega) \in [0, 1] \times \mathbb{R}_{\geq 0},$$

$$\text{PBEh}(\alpha) := \text{HSE}(\alpha, 0), \quad \text{PBEh}(\alpha) \subset \text{HSE}(\alpha, \omega).$$

It contains the PBEh-XC-family which is of the PBE0 form in Eq. (2.51). Using Eq. (2.51), (2.54) and (2.55-2.56) the following standard functionals can be identified as special elements of the HSE family, (with $\omega$ in units of bohr$^{-1}$)

$$\text{HSE06} = \text{HSE}(1/4, 0.11)$$

$$\text{PBE0} = \text{HSE}(1/4, 0) = \text{PBEh}(1/4)$$

$$\text{PBE} = \text{PBEh}(0) = \text{HSE}(0, \omega) = \lim_{\omega \to \infty} \text{HSE}(\alpha, \omega)$$

Fig. 2.1 illustrates the HSE family of XC functionals. It contains the widely used PBE, PBE0 and HSE06 functional for a fixed choice of $(\alpha, \omega)$. However, in principle $(\alpha, \omega)$ should be system dependent. While they are sometimes used as fitting parameters in order to adapt to experiment, Chapter 3 will be concerned to obtain them using a theoretically consistent approach.

2.3 Generalized Kohn-Sham density-functional theory

In the previous section several approximations to the XC energy, $E_{xc}^{\text{app}}$, were presented. In order to make use of them within the framework of Kohn-Sham DFT their local potential has to be evaluated according to Equation (2.25), by taking the functional derivative $\delta E_{xc}^{\text{app}} = \delta E_{xc}^{\text{app}}/\delta n$. For the LDA and GGAs this can be done straightforwardly. For the more general case of GGAs, which are of the form $E_{xc}^{\text{GGA}} = \int f(\varrho, \nabla \varrho)$, this can be shown by considering the density variation:

$$\delta E_{xc}^{\text{GGA}} = \int \frac{\partial f(\varrho, \nabla \varrho)}{\partial \varrho} \delta \varrho + \frac{\partial f(\varrho, \nabla \varrho)}{\partial \nabla \varrho} \delta \nabla \varrho = \int \left( \frac{\partial f(\varrho, \nabla \varrho)}{\partial \varrho} - \nabla \frac{\partial f(\varrho, \nabla \varrho)}{\partial \nabla \varrho} \right) \delta \varrho,$$

where in the last step $\delta \nabla \varrho = \nabla \delta \varrho$ was used together with integration by parts and the condition of vanishing density variation at the boundary. This gives an XC potential of
2.3 Generalized Kohn-Sham density-functional theory

\[ \alpha = 1/4 \]

\[ \omega = 0; \ PBEh \ family \]

\[ \omega = 0.11 \text{ bohr}^{-1} \]

\[ \alpha \in [0, 1] \]

\[ \omega = 0; \ PBEh \ family \]

Figure 2.1: Illustration of the HSE family of XC functionals. The subset HSE(\(\omega = 0, \alpha\)) corresponds to the PBEh family of XC functionals, which contains PBE and PBE0.

the form

\[ v_{xc} = \frac{\delta E_{xc}}{\delta \rho} = \frac{\partial f(\rho, \nabla \rho)}{\partial \rho} - \nabla \frac{\partial f(\rho, \nabla \rho)}{\partial \nabla \rho}. \]  \hspace{1cm} (2.62)

For the LDA \(f\) only depends on \(\rho\) and thus the second term in Equation (2.62) vanishes.

For hybrid functionals the exact exchange expression as given by Equation (2.47) complicates this variation significantly. A brute force way to obtain the functional derivative of an orbital dependent XC energy expression is to consider the KS orbitals as implicit functions of the density, \(\varphi_i = \varphi_i(\rho)\) and apply the chain rule,

\[ v_{xc}(r) = \frac{\delta E_{xc}}{\delta \rho(r)} = \sum_{i=1}^{N} \int d^3 r' d^3 r'' \frac{\delta E_{xc}}{\delta \varphi_i(r')} \frac{\delta \varphi_i(r')}{\delta v_{KS}(r'')} \frac{\delta v_{KS}(r'')}{\delta \rho(r)} + c.c., \]  \hspace{1cm} (2.63)

where c.c. denotes the complex conjugate arising from contributions of \(\varphi_i^*\) in Equation (2.47). An intermediate variation with respect to the KS potential \(v_{KS}\) was introduced because one cannot directly evaluate \(\delta \varphi_i/\delta \rho\). The right hand side of Equation (2.63) depends on the KS potential, that contains apart from the exter-

\[ ^1 \text{More sophisticated energy expressions, like the random-phase approximation (RPA, cf. section 2.7), may also depend on single particle eigenvalues } \epsilon_i. \text{ In this case an additional term appears in Equation (2.63), which is of the form } \sum_{i=1}^{N} \int d^3 r' \frac{\partial E_{xc}}{\partial \epsilon_i} \frac{\partial \epsilon_i}{\partial v_{KS}(r')} \frac{\delta v_{KS}(r')}{\delta \rho(r)} d^3 r'. \]
nal and Hartree potential also the XC potential: \( v_{\text{KS}} = v + v_H + v_{\text{xc}} \). Hence, within the KS framework, orbital dependent expressions for the XC energy lead to complicated non-linear integral equations for the XC potential. Equation (2.63) could be further processed by evaluating the second and third term under the integral by first order perturbation theory. This eventually leads to the optimized effective potential (OEP) equation for \( v_{\text{xc}} \).

Instead of squeezing the orbital dependent exact exchange energy of Equation (2.47) into the framework of KS-DFT by evaluating its local potential, one could rather extend the KS method itself. This leads to the generalized Kohn-Sham scheme which allows for a non-local treatment of the exchange energy.

Recall, that for the KS scheme a free reference system (\( \lambda = 0 \) in the coupling constant Hamiltonian of Equation (2.12)) is introduced, where according to Diagram (2.16), the external potential is chosen such that it has the same ground state density as the physical Hamiltonian (\( \lambda = 1 \)). The constraint search formalism of Equation (2.35) for the non-interacting KS system reduces to a search over single Slater determinants, \( F_{\text{LL},0}[\rho] = \min_{\Phi \rightarrow \rho} \langle \Phi, T \Phi \rangle \). The basic idea of generalized KS (GKS) DFT is to extend the search over single Slater determinants also for a \( \lambda \neq 0 \) by defining the functional \( S_{\lambda}[\rho] = \min_{\Phi \rightarrow \rho} \langle \Phi, (T + \lambda V_{\text{xc}}) \Phi \rangle \). Following the recipe of Section 2.1 an effective external potential \( v_{\text{GKS},\lambda} \) may be constructed, such that minimization of the problem

\[
\min_{\rho} \left\{ S_{\lambda}[\rho] + \int \rho v_{\text{GKS},\lambda} \right\}
\]

under the side condition of particle-number conservation yields the physical ground state density. Again, the functional derivative for the potential in Equation (2.65) has to be understood as evaluated on the ground state density. Further splitting the term \( F_{\text{LL},0}[\rho] - S_{\lambda}[\rho] \) defines the exchange-correlation energy,

\[
F_{\text{LL},0}[\rho] - S_{\lambda}[\rho] =: (1 - \lambda)(E_H + E_{x,\lambda}) + E_{c,\lambda},
\]

where \( E_H \) is the Hartree energy functional and the XC functional was split into an exchange and correlation part, according to the definitions in Equations (2.36) and (2.37), respectively. The prefactor \( 1 - \lambda \) takes into account the contributions which are already present in \( S_{\lambda} \). The minimization requirement (2.64) leads to a
non-local Hartree-Fock type equation, which is known as GKS equation,

\[
\left(-\frac{1}{2}\nabla^2 + v_H + v_{\text{GKS},\lambda}(r)\right)\varphi_i(r) - \lambda \int d^3r'v_{\text{NL}}^x(r, r')\varphi_i(r') = \epsilon_i \varphi_i(r), \tag{2.67}
\]

\[
v_{\text{GKS},\lambda} = v + (1 - \lambda)(v_H + v_{x,\lambda}) + v_{c,\lambda} \tag{2.68}
\]

\[
v_{\text{NL}}^x(r, r') = -\sum_{k=1}^N \frac{\varphi_k(r)\varphi_k^*(r')}{|r - r'|}, \tag{2.69}
\]

where \(v, v_H, v_{x,\lambda}\) and \(v_{c,\lambda}\) are the external, Hartree, exchange, and correlation potentials. \(v_{\text{NL}}^x(r, r')\) has the form of the non-local exact exchange potential which is built from the GKS orbitals \(\{\varphi_i\}\). Like the KS or Hartree-Fock (HF) equations the effective single particle equations have to be solved iteratively. The GKS effective external potential \(v_{\text{GKS},\lambda}\) is as in the KS scheme local. The non-locality in the GKS equations enter via the exact treatment of the electron-electron \(\lambda V_{ee}\) interaction on the single electron level (in the KS scheme only the single electron kinetic energy is treated exactly). Similar to the KS scheme, the highest occupied GKS eigenvalue \(\epsilon_i\) corresponds to the negative of the ionization potential\(^{80}\) (and for a discussion of the lowest unoccupied orbital, see Ref.\(^{81}\)).

For \(\lambda = 0\), the GKS scheme reduces the the KS scheme. The GKS scheme is formally exact, in so far that it gives the exact ground state density; in particular for \(\lambda = 1\) it does not reduce to the HF equations, because GKS employs an effective external potential \(v_{\text{GKS},\lambda}\) (that assures to have the physical ground state density), whereas HF employs the physical external potential, \(v\). Thus, also the GKS orbitals \(\{\varphi_i\}\) are in general different than the HF orbitals and therefore also the numerical value of the exact exchange energy.

The exchange and correlation energies defined in Equation (2.66) are \(\lambda\)-dependent and generally do not coincide with those obtained by the KS scheme (for which \(\lambda = 0\)). In practice, however, this dependence is ignored an the approximations for exchange and correlation energy functionals are taken from the KS scheme. In particular, the hybrid approximations from the previous section are incorporated by setting \(\lambda = \alpha\). The fraction of exact exchange that occurs in Equation (2.46) is treated within the \(S_\alpha\) functional, while the remaining exchange and correlation contributions are approximated on the GGA (or LDA) level of accuracy, \(E_{c,\alpha} \approx E_c^{\text{GGA}}\) and \((1 - \alpha)E_{x,\alpha} \approx (1 - \alpha)E_x^{\text{GGA}}\).

The technical advantage of the GKS approach is that it allows for an orbital-specific evaluation of the exact exchange potential via formula (2.69). A comparison between the KS and the GKS approach can be found in Ref.\(^{14}\) and for a discussion of the G(KS) eigenvalues see Ref.\(^{81}\).
2 Approaches to the many–electron problem

2.4 Dispersion corrections

All the functionals that have been introduced in Section 2.2 do not include the long range tail of van der Waals (vdW) interactions. The definition of vdW forces differs among different scientific communities; in this thesis it is referred to as induced multipole - induced multipole interaction, and the wording ‘vdW energy’ is equivalently used as ‘dispersion energy’. Three avenues of including this interactions are currently trailed in DFT-related research: i) development of semi-empirical methods that include the $1/R^6$ tail to existing approximate XC functionals, ii) construction of non-local vdW density functionals, and iii) development of methods based on the random-phase approximation (RPA).

The first approach needs to separate the vdW energy from energy contributions that are already present in a functional by a damping function, whereas the later two include vdW interactions in a seamless fashion. In this thesis, a species of the first class, which was proposed by Tkatchenko and Scheffler (TS), and the RPA are employed. This section introduces the TS scheme, whereas the RPA will be introduced in Section 2.7. Reviews on dispersion interactions can be found in Refs. 95–97.

Motivated by some earlier work by Grimme and by Grimme the TS-scheme adds to a DFT energy obtained by an approximate XC functional, a vdW correction energy $E_{vdW}$. In its first form it adds the pairwise interatomic $C_6 R^{-6}$ interactions between atoms $a$ and $b$. Therefore, it only takes into account the induced dipole - induced dipole interactions and reads,

$$ E_{vdW} = - \sum_{a,b\neq a} f_{damp}(R_a, R_b) \frac{C_{6ab}[\rho]}{|R_a - R_b|^6}, \quad (2.70) $$

$$ C_{6ab}[\rho] = \frac{2C_{6aa}[\rho]C_{6bb}[\rho]}{\alpha^a_0 C_{6aa}[\rho] + \alpha^b_0 C_{6bb}[\rho]}, \quad (2.71) $$

$$ C_{6aa}[\rho] \approx \left( \frac{\int |r|^3 w_a \rho}{\int |r|^3 f^\text{free}_a} \right)^2 C^\text{free}_{6aa}, \quad w_a(r) = \frac{\rho^\text{free}_a}{\sum_i \rho^\text{free}_i}, \quad (2.72) $$

$$ f_{damp}(R_a, R_b) = \left\{ 1 + \exp \left[ -d \left( \frac{|R_a - R_b|}{s_R(R_a[\rho] + R_b[\rho])} - 1 \right) \right] \right\}^{-1}, \quad (2.73) $$

with $R_a$ being the position of atom $a$, the damping function $f_{damp}(R_a, R_b)$ and the isotropic $C_{6ab}$ term that describes the vdW interactions between atom $a$ and $b$ within a molecule.

Equation $2.71^3$ expresses the hetero-nuclear $C_{6ab}$ coefficient in terms of the

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3 This follows from the Casimir-Polder integral for the leading isotropic $C_6$ term. $C_{6ab} =$
2.4 Dispersion corrections

homo-nuclear \( C_{6aa} \) parameters, and the static polarizability \( \alpha_a^0 \). The homo-nuclear \( C_{6aa}[\rho] \) are a functional of the density \( \rho \), which takes into account the influence of the chemical environment when an atom is placed into a molecule or a solid. In order to obtain an expression for the \( \rho \)-dependence, denote the \( C_6 \) coefficient of an isolated free atom \( a \) by \( C_{6aa}^{\text{free}} \), and its electron density by \( \rho_a^{\text{free}} \). From footnote j, a relationship between the free atom \( C_{6aa}^{\text{free}} \) and the \( C_{6aa} \) of an atom in a molecule may be obtained by

\[
\frac{C_{6aa}}{C_{6aa}^{\text{free}}} = \frac{\eta_a}{\eta_a^{\text{free}}} \left( \frac{\alpha^0_a}{\alpha_a^{\text{free}}} \right)^2 = \frac{\eta_a}{\eta_a^{\text{free}}} \left( \frac{\kappa_a^{\text{free}}}{\kappa_a} \right)^2 \left( \frac{V_a}{V_a^{\text{free}}} \right)^2, \quad (2.74)
\]

where in the last step a relation between polarizability \( \alpha_a^0 \) and the effective ‘volume’ \( V_a \) with proportionality constants \( \kappa_a \) (and similar for the free atom) was exploited\(^{100} \). Following Becke and Johnson\(^{101} \), the volume of a free atom \( a \) is defined as the density weighted integration \( V_a^{\text{free}} := \int |r|^3 \rho_a^{\text{free}} d^3r \). In order to apply this definition also for the effective volume of atom \( a \) within the molecule, its contribution to the total molecular charge density needs to be obtained. To this end, a chemical concept – the Hirshfeld partitioning scheme\(^{102} \) – is used, which obtains the atomic density of atom \( a \) within a molecule by \( \rho_a = \rho_{a,\text{free}} \) with the Hirshfeld weight \( w_a = \rho_{a,\text{free}} / \sum_i \rho_{i,\text{free}} \) determined by free atom densities. With this electron density partitioning scheme, the effective volume of atom \( a \) within a molecule is given by \( V_a = \int |r|^3 w_a \rho d^3r \). TS use these effective volumes in Equation (2.74) together with the estimate that the terms consisting of the effective frequencies and proportionality factors are unity and obtain the effective homo-nuclear \( C_{6aa} \) coefficients as given in Equation (2.72). The residual free atom \( C_{6aa}^{\text{free}} \) and static polarizability \( \alpha_a^0 \) are taken from tabulated reference data\(^{103} \).

The remaining ingredient to the vdW energy of Equation (2.70) is the damping function \( f_{\text{damp}} \). It lifts the divergence of the \( 1/R^6 \) vdW interaction and links to a given XC functional. Its ad-hoc functional form as given in Equation (2.73) depends on the atomic positions \( R_a \), vdW radii \( R_a^0 \) (which are again \( \rho \)-dependent via \( R_a^0 = R_a^{\rho}[\rho] = (V_a/V_a^{\text{free}})^{1/3} R_a^{\text{free}} \)), and two free parameters \( d \) and \( s \). Parameter \( d \) determines the steepness of the damping function and is numerically fixed. The

\[
3/\pi \int_0^\infty \alpha_a(i\omega) \alpha_b(i\omega) d\omega, \quad \text{where} \quad \alpha_a(i\omega) \quad \text{is the frequency dependent polarizability. Approximating} \quad \alpha_a(i\omega) \quad \text{by the leading term in the Padé series}^{99} \quad \alpha_a(i\omega) \approx \alpha_a^0/(1 - \omega^2/\eta_a^2) \quad \text{(with the static polarizability} \quad \alpha_a^0 \quad \text{and the effective frequency} \quad \eta_a) \quad \text{gives for the Casimir-Polder integral} \quad C_{6ab} \approx 3/2 \alpha_a^0 \alpha_b^0 \omega \eta_a \eta_b / (\eta_a + \eta_b) \quad \text{by means of partial fraction decomposition and the substitution} \quad \omega = \eta \tan(y) \quad \text{for integrals of the type} \quad \int 1/(\omega^2 + \eta^2) d\omega. \quad \text{Setting} \quad a = b, \quad \text{allows to rewrite} \quad \eta_a = \frac{1}{3} C_{6aa}(\alpha_a^0)^2 \quad \text{which leads to expression (2.71).}
\]

\(^{99} \rho \) is the total electron density of a molecule or solid; it should be distinguished from the electron density of the isolated, free atom \( a, \rho_a^{\text{free}} \).
remaining scaling coefficient $s_R$ determines the onset of the $1/R^6$ correction and is obtained in a functional-dependent way by a fit to the S22 database\textsuperscript{104}.

In summary, the TS vdW correction scheme has been reviewed. It is a pairwise, additive $C_6/R^6$ correction, that introduces a density-dependent flexibility in the $C_6$ and vdW radii via the ratio of atom-in-molecule and free atomic volumes. While this approach gives accurate results for a variety of systems (see Section 3.3 and Chapter 5) and is computationally appealing, it has its limitations. It breaks down when the atoms-in-molecule concept (or, at least the Hirshfeld scheme) cannot not be applied, or a pairwise summation of $C_6/R^6$ interactions is not adequate (e.g., metals\textsuperscript{105}). Also, the damping function could significantly affect the quality of this approach.\textsuperscript{106–108} Furthermore, the TS scheme is linked to a self-consistent electron density that comes from an approximate XC functional. In cases where the underlying functional gives a qualitative wrong charge density and/or DFT energy, this correction scheme is also doomed to fail. Section 3.3.5 will provide such an example. The set of Equations (2.70 – 2.73) introduces a density-dependence to the dispersion energy. In principle, $E_{vdW}$ should contribute to the KS potential via its functional derivative with respect to the density. However, the effect of the TS scheme on the self-consistent charge density is neglected in this thesis. Rather, the vdW correction is calculated in a post-processing fashion, based on a given self-consistent density coming from an underlying XC functional.

### 2.5 Perturbative approaches

An alternative approach to the many-electron problem offers perturbation theory. Two methods are common. Stationary perturbation theories, like Rayleigh-Schrödinger perturbation theory (RSPT) and Green’s function methods. This section describes first and second order RSPT, which eventually leads to second order corrections from single excitations.

Consider a standard form of the $N$-electron Hamiltonian, acting on the $N$-body Hilbert space $\mathcal{H}^{\otimes N} = \mathcal{H} \otimes \cdots \otimes \mathcal{H}$,

$$H : \mathcal{H}^{\otimes N} \rightarrow \mathcal{H}^{\otimes N}$$

$$H = \sum_{j=1}^{N} \left( -\frac{1}{2} \nabla_j^2 + v(r_j) \pm v^{MF}(r_j) \right) + \sum_{j<k}^{N} \frac{1}{|r_j - r_k|}, \quad r_j, r_k \in \mathbb{R}^3,$$

(2.75)

which consists of the external potential $v$ and the Coulomb potential. The last term in the bracket formally introduces a mean field (MF) single particle potential,
v\textsuperscript{MF}. Re-ordering of the Hamiltonian (2.75) gives

\[ H = H^0 + \Delta v, \quad (2.76) \]

\[ H^0 := \sum_{j=1}^{N} h^0_j, \quad (2.77) \]

\[ h^0_j := -\frac{1}{2}\nabla_j^2 + v(r_j) + v\textsuperscript{MF}(r_j), \quad (2.78) \]

\[ \Delta v := \sum_{j<k}^{N} \frac{1}{|r_j - r_k|} - \sum_{j}^{N} v\textsuperscript{MF}(r_j), \quad (2.79) \]

\[ (2.80) \]

Let there be given the eigenvalue solution of the single particle Hamiltonian

\[ h^0 : \mathcal{H} \rightarrow \mathcal{H} \]

\[ h^0 \phi_k = \epsilon_k \phi_k, \quad k \in \mathbb{N}, \quad (2.81) \]

with the eigenfunctions \{\phi_k\} and eigenvalues \{\epsilon_k\}. If v\textsuperscript{MF} is of the form such that \( h^0 \) is self-adjoint, then the set \{\phi_k\} forms an orthonormal basis over \( \mathcal{H} \) with real eigenvalues \{\epsilon_k\}. Assume that an order relation with respect to the single particle eigenvalues \( \epsilon_1 < \epsilon_2 < \ldots \) exists. The fermionic eigenfunctions \{\Phi_k\} with eigenvalues \{E_k\} of the non-interaction \( N \)-electron Hamiltonian that satisfy

\[ H^0 : \mathcal{H}^{\otimes N} \rightarrow \mathcal{H}^{\otimes N} \]

\[ H^0 \Phi_k = E_k \Phi_k, \quad k \in \mathbb{N}, \quad (2.82) \]

are then given by the antisymmetrized, normalized tensor product (or, Slater determinant) of \( N \) single particle wavefunctions. The eigenvalue \( E_k \) is given by the corresponding sum of single-particle eigenvalues. For the \( N \) lowest single particle wavefunctions this reads for example,

\[ \Phi_0 = \frac{1}{\sqrt{N!}} \sum_{\sigma \in S_N} \text{sign}(\sigma) \phi_{\sigma(1)} \otimes \cdots \otimes \phi_{\sigma(N)} =: \varphi_1 \wedge \cdots \wedge \varphi_N, \quad E_0 = \sum_{i=1}^{N} \epsilon_i, \quad (2.83) \]

where \( S_N \) is the permutation group of \{1, 2, \ldots N\} and \text{sign}(\sigma) is the signature of permutation \( \sigma \in S_N \). The ordering of the \{\epsilon_k\} induces an ordering of the \{E_k\}. In particular, the the Slater determinant built by the \( N \) lowest \{\varphi_i, i = 1 \ldots N\} has the lowest eigenvalue in (2.82), and is therefore the ground state of \( H^0 \). This is also the reason for the zero-index in Equation (2.83). In quantum chemistry the
ordering of the \( \{ \epsilon_i \} \) is further exploited in order to classify the solutions of (2.82). To this end, define the set \( O = \{1, 2, \ldots, N\} \). A single electron state \( \varphi_i \) is called occupied if \( i \in O \), otherwise it is called unoccupied, or excited. This allows to label the solutions of Equation (2.82) with respect to their ‘excitations’,

\[ \begin{align*}
\text{GS: } & \Phi_0 = \bigwedge_{k \in O} \varphi_k, & E_0 = \sum_{k \in O} \epsilon_k, \\
\text{SE: } & \Phi_i = \bigwedge_{k \in O \setminus \{a\}} \varphi_k \wedge \varphi_a, & E_{i,a} = \sum_{k \in O \setminus \{a\}} \epsilon_k + \epsilon_a, \quad a \in \mathbb{N} \setminus O, \\
\text{DE: } & \Phi_{ij} = \bigwedge_{k \in O \setminus \{a,b\}} \varphi_k \wedge \varphi_a \wedge \varphi_b, & E_{ij,ab} = \sum_{k \in O \setminus \{a,b\}} \epsilon_k + \epsilon_a + \epsilon_b, \quad a, b \in \mathbb{N} \setminus O
\end{align*} \]

where \( \epsilon_n \) denotes the \( n \)-th order perturbation to the ground state energy \( E_0 \).

The groundstate (GS) is formed only by occupied single-electron states, a single excited (SE) state by \( N - 1 \) occupied and one unoccupied states, a double excited state by \( N - 2 \) occupied an 2 excited states and so forth.

### First and second order contributions

Having categorized the spectrum of the non-interacting many electron Hamiltonian \( H_0 \), allows to proceed to the fully interacting many-body Hamiltonian \( H \) as given in Eq. (2.76). Let \( H^0 \) be the Hamiltonian of the unperturbed system and \( \Delta v \) the perturbing potential. RSPT\textsuperscript{109} with respect to the ground state of \( H^0 \) for the first two orders gives:

\[ \begin{align*}
\text{0th order: } & E_0^{(0)} = E_0 = \sum_{k \in O} \epsilon_k, \\
\text{1st order: } & E_0^{(1)} = \langle \Phi_0, \Delta v \Phi_0 \rangle, \\
\text{2nd order: } & E_0^{(2)} = \sum_{n \neq 0} \frac{\langle \Phi_0, \Delta v \Phi_n \rangle}{E_0 - E_n},
\end{align*} \]

where \( E_0^{(n)} \) denotes the \( n \)-th order perturbation to the ground state energy \( E_0 \). If the unperturbed single particle Hamiltonian corresponds to the single particle Hartree-Fock (HF) operator, \( h^0 = \hat{f} \), then the sum \( E_0^{(0)} + E_0^{(1)} \) is the HF ground state (in essence because there occurs a factor of two upon orbital optimization in the HF theory). For a different unperturbed Hamiltonian then the first order contributions add a HF-type exchange and Hartree energy (evaluated at \( h^0 \)-orbitals \( \{ \varphi_i \} \)) and remove the density-integrated mean field potential. Therefore, \( E_{\text{EX}} := \)
$E_0^{(0)} + E_0^{(1)}$ is also called ‘exchange-only’ total energy, and in the case of HF it corresponds to the HF ground state energy.

Because the Coulomb interaction is a two point interaction, the second order correction may only contain single and double excitations – otherwise the matrix elements would vanish. Taking into account the classification from above, the second order corrections from single excitations (SE) may be written in terms of single particle orbitals and eigenvalues\(^{110}\),

$$E_{0}^{\text{SE}} = \sum_{i \in O} \sum_{a \notin \{O \}} \frac{\langle \varphi_i, \hat{f}\varphi_a \rangle}{\epsilon_i - \epsilon_a}, \tag{2.90}$$

where $\hat{f}$ is again the single particle HF Hamiltonian. If the $\{\varphi_i\}$ are the HF solutions, then this contribution vanishes, otherwise it is in general non-zero. $E_{0}^{\text{SE}}$ will be abbreviated as ‘SE@functional’, where the ‘@’ symbol stresses the dependence on the underlying unperturbed Hamiltonian (and similar for $E_{0}^{\text{EX}}$). For example, SE-correction evaluated with PBE orbitals.

Equation (2.90) indicates that SE correction diverge if the band gap goes to zero. This is avoided by the so called renormalized single excitation (rSE) correction scheme, which is detailed in the supplementary material of Ref.110,111.

### 2.6 Green’s function methods

For the remaining theoretical methods that shall be reviewed it is necessary to extent the mental framework into the realm of quantum field theory (QFT). In this section i) the Green’s function within QFT is introduced, ii) it’s physical content is reviewed, and iii), it’s EOMs and the $GW$ approximation are summarized.

Correlation, or Green’s function play an important role in QFT, since they are closely related to scattering amplitudes via the Lehmann-Symanzik-Zimmermann (LSZ) reduction formula.\(^{112-114}\) This Section is restricted to the single particle Green’s function (which is also known as two-point Green’s function, two-point correlation function, or propagator).

The Hamiltonian of the many-electron system in second quantization is of the form

$$H = \int d^3 r \psi^\dagger(r) \left[ -\frac{1}{2} \nabla^2 + v(r) \right] \psi(r) + \frac{1}{2} \int d^3 r d^3 r' \psi^\dagger(r) \psi^\dagger(r') w(r - r') \psi(r') \psi(r), \tag{2.91}$$

where $w(r - r') = 1/|r - r'|$ is the two body Coulomb interaction and $v(r)$ is the
external potential. Only one type field $\psi$ occurs because only one type of fermions (the electrons) is considered. The field operators $\psi$ and $\psi^\dagger$ are called annihilation and creation operators respectively and they obey the canonical anti-commutator relations

$$
[\psi(r), \psi^\dagger(r')]_+ = \delta(r - r'), \quad [\psi(r), \psi(r')]_+ = [\psi^\dagger(r), \psi^\dagger(r')]_+ = 0.
$$

(2.92)

**Definition 2** (Single particle Green’s function). Let $\psi$ and $\psi^\dagger$ be field operators in the Heisenberg picture acting on the antisymmetrized Fock space $\bigoplus_n \mathcal{H}^{\otimes n}$ and denote by $\Psi_0$ the ground state of a $N$-electron system. The single particle Green’s function is defined as

$$
i G(rt, r't') := \langle \Psi_0 | T [\psi(r, t) \psi^\dagger(r', t')] | \Psi_0 \rangle,
$$

(2.93)

where $T$ is the timer ordering operator,

$$
T [\psi(r, t) \psi^\dagger(r', t')] := \left\{ \begin{array}{ll}
\psi(r, t) & \text{if } t > t' \\
-\psi^\dagger(r', t') & \text{if } t < t'
\end{array} \right.
$$

(2.94)

As a notational convention, the Heisenberg picture is indicated by writing the time dependence explicitly (note that $\psi(r, 0) = \psi(r)$).

### 2.6.1 Physical content of $G$

The single particle Green’s function of a system contains the following physical properties\textsuperscript{115–117}: 1.) the charged excitation spectrum, 2.) the expectation value of any single-particle operator with respect to the ground state, and 3.) the ground state energy.

The first property follows from the spectral representation. Insertion of a complete set of (Fock space) eigenstates of the Hamiltonian between the field operators in the definition of $G(rt, r't')$, Equation (2.93), and noting that only the $N \pm 1$ Hilbert space slices survive gives,

$$
\begin{align*}
i G(xt, r't') &= \Theta(t - t') \sum_n \langle \Psi_0 | \psi(r, t) | \Psi_n^{N+1} \rangle \langle \Psi_n^{N+1} | \psi^\dagger(r', t') | \Psi_0 \rangle \\
&\quad - \Theta(t' - t) \sum_n \langle \Psi_0 | \psi^\dagger(r', t') | \Psi_n^{N-1} \rangle \langle \Psi_n^{N-1} | \psi(r, t) | \Psi_0 \rangle,
\end{align*}
$$

(2.95)

where the time ordering has been incorporated by the step function. Taking into
account the time evolution of the field operators in the Heisenberg picture,

\[ \psi(r, t) = e^{iHt} \psi(r, 0) e^{-iHt}, \quad \psi^\dagger(r', t') = e^{iH't'} \psi^\dagger(r', 0) e^{-iH't'}, \quad (2.96) \]

and using \( H \Psi^M_n = E^M_n \Psi^M_n \) (with the notation for the \( N \)-electron groundstate, \( \Psi_0 \equiv \Psi^N_0 \) with energy \( E_0 \)), gives together with the realization of the \( \Theta \)-function,

\[ \Theta(\pm \tau) = \mp \frac{1}{2\pi i} \lim_{\delta \to 0^+} \int_{-\infty}^{+\infty} e^{-\omega \tau} \frac{d\omega}{\omega \pm i\delta}, \quad (2.97) \]

the Fourier-transformed Green’s function,

\[ G(r, r'; \omega) = \lim_{\delta \to 0^+} \sum_n \frac{\langle \Psi_0 | \psi(r, 0) | \Psi^{N+1}_n \rangle \langle \Psi^{N+1}_n | \psi^\dagger(r', 0) | \Psi_0 \rangle}{\omega - E^{N+1}_n + E_0 + i\delta} + \lim_{\delta \to 0^+} \sum_n \frac{\langle \Psi_0 | \psi^\dagger(r', 0) | \Psi^{N-1}_n \rangle \langle \Psi^{N-1}_n | \psi(r, 0) | \Psi_0 \rangle}{\omega + E^{N-1}_n - E_0 - i\delta}. \quad (2.98) \]

Equation (2.98) is also called Lehmann representation and clarifies the analytic behavior of \( G(\omega) \). For each eigenstate \( \Psi^{N+1}_n \) of the \( N + 1 \) electron system there is a pole at \( E^{N+1}_n - E_0 \) in the lower half complex plane. Similarly, for each eigenstate \( \Psi^{N-1}_n \) of the \( N - 1 \) electron system there is a pole at \( E_0 - E^{N-1}_n \) in the upper half complex plane. The poles in the lower half plane start at the chemical potential of the \( N + 1 \) electron system, \( \mu^{N+1} := E^{N+1}_0 - E_0 \) and extend until \( +\infty \). The poles in the upper half plane go from \( -\infty \) up to the chemical potential of the \( N \) electron system, \( \mu^N := E_0 - E^{N-1}_0 \). In short, the poles of the Green’s function are located at the energy difference of the \( N \)-electron ground state and some \( N + 1 \) or \( N - 1 \) electronic state. Therefore, they correspond the the single-particle excitation energies upon addition or removal of an electron to or from the \( N \) electron ground state.

### 2.6.2 The GW approximation

Instead of obtaining the EOMs for \( G \) via the Heisenberg EOM of the field operators, they can be also obtained via the Schwinger variational principle.\(^{118-122}\) This (also) leads to the Dyson equation,

\[ \left[ \frac{i}{\partial t} - h_0(r) \right] G(rt, r't') - \iiint d^3r'' dt'' \Sigma(rt, r''t'') G(r''t', r't') = \delta(r - r')\delta(t - t'), \quad (2.99) \]
where $\Sigma$ is the self energy and $h_0 = -1/2\nabla^2 + v_H + v$ is the unperturbed Hamiltonian that contains the Hartree and the external potential. The Dyson equation can be recast in a more familiar form by aid of the unperturbed Green’s function $\tilde{G}_0$, which satisfies the equation

$$ \left[ i\frac{\partial}{\partial t} - h_0(r) \right] \tilde{G}_0(rt, r't') = \delta(r - r')\delta(t - t'). $$

(2.100)

Then Equation (2.99) may be written as

$$ G(1, 2) = \tilde{G}_0(1, 2) + \int d(34) \tilde{G}_0(1, 3) \Sigma(3, 4) G(4, 2), $$

(2.101)

where the notation $(1) = (x_1, t_1)$ was used and the integration is performed over time and space. The equations that determine $\Sigma$ are called Hedin equations. They may be obtained by Schwinger’s variational principle and read

$$ \Sigma(1, 2) = i \int d(34) W(1^+, 3) G(1, 4) \Gamma(4, 2, 3), $$

(2.102)

$$ W(1, 2) = w(1, 2) + \int d(34) W(1, 3) P(3, 4) w(4, 2), $$

(2.103)

$$ P(1, 2) = -i \int d(34) G(2, 3) G(4, 2) \Gamma(3, 4, 1), $$

(2.104)

$$ \Gamma(1, 2; 3) = \delta(1 - 2)\delta(2 - 3), $$

$$ + \int d(4567) \frac{\delta \Sigma(1, 2)}{\delta G(4, 5)} G(4, 6) G(7, 5) \Gamma(6, 7, 3), $$

(2.105)

where $w(1, 2) = 1/|r_1 - r_2|\delta(t_1 - t_2)$ is the (instantaneous in time) bare Coulomb potential, $W$ the screened Coulomb potential, $P$ the polarization function, and $\Gamma$ the vertex function. The Hedin equations are a set of coupled integral equations, which also couple to the Green’s function. If all occurring quantities were known, then the Dyson Equation (2.101) and the Hedin Equation (2.102–2.105) are identities. Conversely, if $\Sigma$ is not known, solving for these equations gives an iterative method for a systematic approximation. If one starts with $\Sigma = 0$, the first iteration of Equations (2.105–2.102) from bottom to top gives the famous...
2.6 Green’s function methods

*GW* approximation,

\[
\Sigma(1,2) = iG(1,2)W(1^+,2), \tag{2.106}
\]

\[
W(1,2) = w(1,2) + \int d(34)W(1,3)P(3,4)w(4,2), \tag{2.107}
\]

\[
P(1,2) = -iG(1,2)G(2,1^+). \tag{2.108}
\]

The name *GW* approximations lends itself from Equation (2.106). In this approximation the vertex function is given by a product of \(\delta\) distributions, \(\Gamma(1,2,3) = \delta(1-2)\delta(2-3)\), and does not occur explicitly in the *GW* equations. However, one could further climb the tower of approximation by re-iterating the Hedin equations with the *GW* equations as an input. This would lead to non-trivial vertex contributions. However, in the *GW* approach this is not pursued and the Equations (2.106–2.108) together with the Dyson Equation (2.101) is considered as a closed set of equation.

These coupled set of equations needs to be solved self consistently. One starts with with a guess \(G_0\) and computes the polarization function \(P_0\) from Equation (2.108). This yields with Equation (2.107) the screened Coulomb potential, \(W_0\) and from Equation (2.106) the self energy \(\Sigma_0\). Using \(\Sigma_0\), and solving the Dyson Equation (2.101) gives an updated Green’s function \(G_1\). Iterating this procedure gives the self-consistent Green’s function within the *GW* approximation.\(^{126}\)

In common practice, however, the Dyson equation is rarely iterated. Instead, one relies on Equations (2.106–2.108) and calculates the self energy based on a single shot \(G_0\) (and the associated \(W_0\) that comes from a DFT or HF Hamiltonian. This approach is also called *GW* \(W_0\). In order to be specific, consider an effective single particle Hamiltonian of the form \(h^0 = -1/2\nabla^2 + v + v_H + v_{xc}\), with eigenvalues \(\{\epsilon_i\}\) and eigenfunctions \(\{\phi_i\}\) that solve \(h^0\phi_i = \epsilon_i\phi_i\). The exchange-correlation potential \(v_{xc}\) shall be any of the approximations, which were introduced in Section 2.2. On the frequency axis, the associated Green’s function that solves \([\omega - h^0(r)]G(r,r';\omega) = \delta(r-r')\) assumes the form\(^{127}\)

\[
G_0(r,r';\omega) = \lim_{\eta \to 0^+} \sum_n \frac{\phi_n(r)\phi_n^*(r')}{\omega - \epsilon_n - i\eta \text{sgn}(\epsilon_F - \epsilon_n)}, \tag{2.109}
\]

where \(\epsilon_F\) is the Fermi energy. This expression may be obtained from the Lehmann representation for the unperturbed Green’s function in the basis of \(h^0\) and the approximation \(\mu^{N+1} \approx \mu^N\).

The \(G_0W_0\) does not make use of the Dyson equation, rather the single particle orbital energies are obtained by first order perturbation theory,

\[
\epsilon_n^{G_0W_0} = \epsilon_n + \langle \phi_n, (\Sigma^{G_0W_0} - v_{xc}) \phi_n \rangle. \tag{2.110}
\]
2 Approaches to the many-electron problem

By Equation (2.109) \( G_0 \) and by virtue of Equations (2.107 – 2.108) also \( W_0 \) depend on the ‘input’ orbitals and eigenvalues that emerge from the DFT or HF Hamiltonian \( h^0 \). In order to stress this dependence on the underlying Hamiltonian, the notation ‘method@functional’ is introduced. For example \( G_0W_0@PBE \) corresponds to a \( G_0W_0 \) calculation with PBE reference states. In Chapter 3, a scheme will be proposed that obtains a starting point, which is consistent with DFT.

2.7 Exchange-correlation energy in the random-phase approximation

In principle, the ground state total energy may be obtained by the single particle Green’s function, because all ground state expectation values that appear in the Hamiltonian of Equation (2.91) can be expressed in terms of \( G \).\(^{115,116}\) However, in this approach, diagrammatic perturbation theory becomes difficult, because the interplay between the kinetic energy and the Coulomb interaction hinders to express the ground state energy in terms of the Green’s function and the self energy only. In order to avoid the evaluation of the kinetic energy expectation value, the adiabatic connection approach as introduced in Section 2.1 is used.

Within the adiabatic connection approach, the exchange correlation functional is given by Equation (2.30), where the coupling constant integrand translates into second quantization, according to

\[
\langle \Psi^\lambda_0, V_{ex} \Psi^\lambda_0 \rangle = \frac{1}{2} \int \int d^3rd^3r' \langle \Psi^\lambda_0 | \psi^\dagger(r) \psi^\dagger(r') w(r-r') \psi(r') \psi(r) | \Psi^\lambda_0 \rangle \\
= \frac{1}{2} \int \int d^3rd^3r' w(r-r') \langle \Psi^\lambda_0 | \hat{\rho}(r) [\hat{\rho}(r') - \delta(r-r')] | \Psi^\lambda_0 \rangle
\]

where in the last line the expression was rewritten in terms of the density operator \( \psi^\dagger(r) \psi(r) =: \hat{\rho}(r) \) by aid of the anti-commutator relations of Equation (2.92). This expression may be reformulated in terms of the linear density-density response function \( \chi^\lambda(r, r'; i\omega) \) (on the imaginary frequency axis) via the so called fluctuation-dissipation theorem.\(^{94,116,128,129}\) The XC energy then takes the form

\[
E_{xc} = \frac{1}{2\pi} \int_0^1 d\lambda \int \int drdr' w(r-r') \left[ -\frac{1}{\pi} \int_0^\infty d\omega \chi^\lambda(r, r'; i\omega) - \delta(r-r') \rho(r) \right].
\] (2.111)

Since the adiabatic connection path is taken as in Section 2.1 at constant density, \( \rho \) does not depend on \( \lambda \). Therefore, the only \( \lambda \)-dependence enters via the response
function. The response function is given by the retarded polarization propagator and is thus closely related to the two particle Green’s function. Defining the density fluctuation operator (in the Heisenberg picture)

\[
\delta \hat{\rho}(r, t) := \hat{\rho}(r, t) - \rho(r),
\]

the frequency dependent response function is given by

\[
\chi^\lambda(r, r'; \omega) = -i \Theta(t - t') \langle \Psi_0^\lambda | [\hat{\rho}(r, t), \hat{\rho}(r', t')] | \Psi_0^\lambda \rangle.
\] (2.112)

In analogy to the single particle Green’s function the Lehmann representation in frequency space may be obtained:

\[
\chi(r, r'; \omega) = \lim_{\delta \to 0^+} \sum_n \frac{\langle \Psi_0^\lambda | \hat{\rho}(r, 0) | \Psi_n^\lambda \rangle \langle \Psi_n^\lambda | \hat{\rho}(r', 0) | \Psi_0^\lambda \rangle}{\omega - E_n + i\delta},
\] (2.113)

implying that the poles of the response function are now located at neutral, or optical excitations. In the non-interacting case (\(\lambda = 0\)) \(\chi^0\) may be obtained explicitly by the Lehmann representation in terms of KS orbitals \(\{\varphi_i\}\), eigenvalues \(\{\epsilon_i\}\), and occupation numbers \(\{f_i\}\):

\[
\chi^0(r, r'; \omega) = \lim_{\delta \to 0^+} \sum_{ij} (f_i - f_j) \frac{\varphi_i^*(r) \varphi_j(r) \varphi_j^*(r') \varphi_i(r')}{\omega - \epsilon_j + \epsilon_i + i\delta}.
\] (2.114)

Otherwise it may be obtained by solving the Dyson equation for the response function

\[
\chi^\lambda(r, r'; \omega) = \chi^0(r, r'; \omega) + \int dr_1 dr_2 \chi^0(r, r_1; \omega) f^\lambda_{Hxc}(r_1, r_2; \omega) \chi^\lambda(r_2, r'; \omega),
\] (2.115)

where \(f^\lambda_{Hxc}(r_1, r_2; \omega)\) is the \(\lambda\) and frequency dependent Hartree, exchange and correlation kernel. In the random-phase approximation it is approximated by the bare coulomb interaction \(f^\lambda_{Hxc}(r_1, r_2; \omega) \approx \lambda/(r_1 - r_2)\), yielding with equation (2.115) the EOM

\[
\chi^\lambda_{RPA}(r, r'; \omega) = \chi^0(r, r'; \omega) + \lambda \int dr_1 dr_2 \chi^0(r, r_1; \omega) w(r_1 - r_2) \chi^\lambda_{RPA}(r_2, r'; \omega),
\] (2.116)

which allows to solve for \(\chi^\lambda_{RPA}\) and to perform the \(\lambda\) integration. Insertion of

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Equation (2.116) into Equation (2.111) gives the XC energy in the RPA,

\[ E_{xc}^{RPA} = E_x^{EX} + E_c^{RPA} \]  
(2.117)

where the shorthand notation \( \text{Tr}[AB] = \int d\mathbf{r}d\mathbf{r}' A(r, \mathbf{r}')B(\mathbf{r}', \mathbf{r}) \) was used. Hence, the exchange energy is treated exactly in the RPA while the correlation energy depends on the independent particle response function (i.e., for \( \lambda = 0 \)).

The RPA total energy is given by Equations (2.114) and (2.26)

\[ E_v = F_{HK,0} + E_H + \int \rho v + E_x^{EX} + E_c^{RPA}, \]  
(2.119)

where \( F_{HK,0} \equiv T_s \) is the non-interacting kinetic energy, \( v \) the external potential, \( E_H \) the Hartree energy, and \( E_x^{EX} \) the exact exchange energy.

Equation (2.119) may be alternatively written as

\[ E_c^{RPA} = \frac{1}{2\pi} \int_0^\infty d\omega \sum_{ia,jb} |i|w|ab\rangle \langle ij|\tilde{W}(\omega)|ab\rangle F_{ia}(i\omega)F_{jb}(i\omega) \]  
(2.120)

with

\[ \tilde{W}(i\omega) = \int_0^1 d\lambda W_\lambda(i\omega), \quad W_\lambda(i\omega) = \frac{\lambda w}{1 - \lambda\chi^0(i\omega)w}, \quad F_{ia}(i\omega) = \frac{2\epsilon_i - \epsilon_a}{(\epsilon_i - \epsilon_a)^2 + \omega^2}, \]

and the sum over \( \{i, j\} \) and \( \{a, b\} \) being over occupied and unoccupied states, respectively. The second order screened exact exchange (SOSEX) correction is obtained by antisymmetrizing the matrix element with the bare Coulomb interaction in Eq. (2.120): \( \langle ij|w|ab\rangle \rightarrow -\langle ij|w|ba\rangle \).

Combining the various total energy expressions leads to the so-called renormalized second order perturbation theory (rPT2), \( \text{rPT2} = \text{RPA} + \text{SOSEX} + \text{rSE} \), consisting of the RPA total energy, the SOSEX correction and renormalized single excitations. The diagramatic representation of rPT2 can be found in references 111 and 94. Similar to the \( G_0W_0 \) method, in common practice the rPT2 energy is not evaluated self-consistently. In order to stress this an analogue notation as for the \( G_0W_0 \) method is introduced, by declaring \( '(\text{rPT2}@functional)' \) to be the total rPT2 energy evaluated at input orbitals coming from a given functional.

The implementation of non-local expressions (hybrid functionals, \( G_0W_0 \), RPA, SOSEX, rSE) in the FHI-aims code is documented in Reference 127. It relies on the resolution of identity (RI) technique. The basic idea is to rewrite the pair product of atomic basis functions \( \{\phi_i\} \) (for the definition see Appendix A.1 or Ref-
2.7 Exchange-correlation energy in the random-phase approximation

In terms of auxiliary basis functions (ABF) \{P_\mu\}, \phi_i(r)\phi_j(r) \approx C_{ij}^\mu P_\mu. For a given set of ABF, the expansion coefficients are obtained by minimizing the error in the pair product or in the four center integrals (the former scheme is called RI-SVS and the latter RI-V). The ABF are constructed from the radial part of the atomic basis functions (equation A.2) by taking their product and orthogonalizing the ensuing product basis. The RI method has the advantage that it allows to rewrite four center integrals in terms of 3 and 2 center integrals and thus significantly reduces the computational cost, whereas at the same time it exhibits high accuracy (for more details and exhaustive convergence tests see Reference 127).

In this Chapter, standard DFT and QFT methods were summarized. Original and new research work will be presented in the subsequent Chapters.
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3.1 Hybrid density-functional theory meets quasiparticle calculations: a consistent electronic structure approach

In this Chapter, we propose a new scheme to obtain a system dependent fraction of exact exchange (α) within the framework of hybrid density-functional theory, that is consistent with the G₀W₀ approach, where G₀ is the non-interacting Green’s function of the system and W₀ the screened Coulomb interaction. At the same time, this scheme corresponds to an ‘effective self consistency’ of the GW approach. We exploit the formally exact condition of exact DFT that the energy of the highest occupied molecular orbital (HOMO) corresponds to the ionization potential (IP) of a finite system. We identify the optimum α-value for which this statement is obeyed as closely as possible and thereby remove the starting point dependence from the G₀W₀ method. As we will also show, this combined approach is essential for describing electron transfer (as exemplified by the TTF/TCNQ complex) and yields the vertical ionization potentials of the G2 data set with a mean absolute percentage error of only ≈3%.

3.1.1 Determining the fraction of exact exchange

Predicting charge transfer from first principles is currently regarded as a great challenge. Kohn-Sham (KS) density-functional theory (DFT) calculations with approximate functionals are plagued by the self-interaction error and the absence of the derivative discontinuity. As a consequence, artificial charge transfer between two molecules can result when the highest occupied molecular orbital (HOMO) level of one molecule erroneously moves above the lowest unoccupied molecular orbital (LUMO) level of the other. The solution would be to resort to

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\(^{a}\)The ‘we’ in the present section does not refer to the ‘royal we’, but rather stands for ‘the co-authors and me’, since these results are accepted for publication in Phys. Rev. B.
3 Methodology

a method that gives both correct (or at least improved) orbital energies and total energies.

One common way is to employ hybrid functionals that contain a fraction $\alpha$ of exact exchange within the generalized KS (GKS) approach. The problem translates into finding an appropriate $\alpha$ value. Theoretical considerations have led to global values of $1/4$\textsuperscript{61,62} or $0.5$\textsuperscript{135}, neglecting the system dependency of $\alpha$ due to its relation to the inverse of the dielectric function\textsuperscript{75}. In a pragmatic approach $\alpha$ was rendered material dependent by fitting to experimental band gaps\textsuperscript{136} or to cohesive properties\textsuperscript{77}. However, fitting is theoretically unsatisfying as it introduces an empirical parameter and it relies on the accuracy and existence of experimental data. For finite systems, an \textit{ab initio} way of accessing $\alpha$ has recently been proposed\textsuperscript{137,138} by employing the difference in self-consistent field calculations ($\Delta$ SCF) approach.

An alternative solution to the level-alignment problem is found in many-body perturbation theory in e.g. the \textit{GW} approach\textsuperscript{123}. In order to obtain a well defined total energy, \textit{GW} would have to be carried out fully self-consistency by solving the Dyson equation. This is computationally expensive and subject of active research\textsuperscript{126}. Instead, the majority of all \textit{GW} calculations is carried out perturbatively, i.e. as a single shot calculation taking wave function $\psi_{n\sigma}$ and orbital energy $\epsilon_{n\sigma}$ input from DFT (the so called $G_0W_0$ approach),

$$\epsilon_{G_0W_0}^{n\sigma} = \epsilon_{n\sigma} + \langle \psi_{n\sigma}, \left( \Sigma^{G_0W_0} - v^{xc} \right) \psi_{n\sigma} \rangle. \tag{3.1}$$

The indices $n$ and $\sigma$ label the main quantum numbers and spin states respectively, $v^{xc}$ is the DFT exchange correlation potential and $\Sigma$ is the self-energy within the $G_0W_0$ approximation which itself depends on $\psi_{n\sigma}$ and $\epsilon_{n\sigma}$. However, in $G_0W_0$ one looses access to the ground state properties and introduces a starting point dependence. For charge transfer between two molecules this would imply that even if one would apply $G_0W_0$ for a given DFT functional one could not be sure that it gives sensible results. Let us assume that we start with the PBE functional and find (erroneous) charge transfer. The subsequent $G_0W_0$ calculation is now based on an incorrect density. Moreover, even if $G_0W_0$ would produce a level alignment that does not give rise to charge transfer, we could not utilize this result, because $G_0W_0$ does not give us a new density, a new total energy or new wave functions. In other words, there is no way back from the $G_0W_0$ spectrum to the ground state properties of the system.

In the following, we propose a scheme that solves this problem, by making the DFT starting point internally consistent with $G_0W_0$, and thereby lifting the ambiguity in the choice of $\alpha$. We consider the PBE hybrid functional (PBEh) with
3.1 The PBEh(α*) functional

The exchange energy $E_X$ being regarded as a function of $\alpha$,

$$E_X = \alpha E_{EX} + (1 - \alpha) E_{PBE}^X, \quad \alpha \in [0, 1],$$

(3.2)

where $E_{PBE}^X$ and $E_{EX}^X$ denote PBE exchange and exact exchange energies, respectively. In order to stress the $\alpha$ dependence in the exchange part we introduce the notation PBEh(\alpha) for the corresponding functional. For example $\alpha = 0$ corresponds to the PBE and $\alpha = 0.25$ to the PBE0 functional. It should be noted that for $\alpha = 1$, that is for full exact exchange, the GKS equation does not reduce to the Hartree-Fock equation as there is still a PBE contribution to the correlation energy. Instead of fixing $\alpha$ globally we consider it as a system dependent parameter (that in principle depends on the electron density by the Hohenberg-Kohn theorem). For a given system we then chose $\alpha$ by minimizing the QP correction to the HOMO-level according to Equation (3.1)

$$\alpha^* = \arg \min_{\alpha} \left| \left\langle \psi_H(\alpha), \left( \Sigma G_0W_0(\alpha) - v_{xc}(\alpha) \right) \psi_H(\alpha) \right\rangle \right|,$$

(3.3)

where the index H denotes the HOMO level and the dependence of the XC potential, the KS-orbitals and the self-energy on $\alpha$ has been taken into account explicitly. In exact DFT the HOMO level of a finite system can be rigorously assigned to the IP, and therefore the self-energy correction to the HOMO is strictly zero. For any other level no such statement holds. However, in standard approximations to the XC functional the HOMO is typically not given accurately, because of the self-interaction error (SIE). Equation (3.3) therefore implies that the self-energy correction to the HOMO level is as small as possible. This is equivalent to demanding that the correspondence between HOMO and IP in exact DFT is obeyed as closely as possible. Hence, from a DFT perspective Equation (3.3) also reduces the SIE.

In practice Equation (3.3) can be solved by just a few single shot $G_0W_0$ calculations, which makes it computationally much more efficient than fully self-consistent $GW$ calculations. $\alpha^*$ can be obtained by interpolating to that $\alpha$-value, for which the difference between the KS and QP HOMO level is minimized.

Our scheme - choosing $\alpha$ by minimizing the $G_0W_0$ perturbation to the generalized KS Hamiltonian - is conceptually similar to the QP self-consistent $GW$ (QSGW) theory as proposed by Schilfgaarde et al. However, in our scheme the choice of the optimum potential is restricted to a subset that emerges from hybrid KS DFT. As a consequence, the corresponding ground state energy is still variational with respect to the density, unlike in QSGW. To avoid potential misconceptions, we reiterate at this stage that our requirement of internal consistency between DFT and $G_0W_0$ in Equation (3.3) does not imply any fitting. At no point in our procedure is $\alpha$ adjusted to reproduce an experimental value.
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Figure 3.1: QP (filled circles) and KS (open circles) HOMO level as a function of $\alpha$ for the TTF (a) and TCNQ (b) molecule. To the right the individual molecules are shown, whereas white denotes hydrogen, gray carbon, blue nitrogen and yellow sulfur.

3.1.2 Application 1: TTF, TCNQ and their complex

We apply the scheme to the TTF/TCNQ dimer, a prototypical donor/acceptor system in the field of organic electronics\textsuperscript{3,141,142}. It was shown that standard semilocal and hybrid XC functionals can fail\textsuperscript{134} in describing their electronic structures. First we consider the individual molecules. We adopt the notation ‘method@functional’, for example $G_0W_0@PBE$ corresponds to a $G_0W_0$ calculation with PBE reference states. Figure 3.1(a,b) shows the KS and QP HOMO levels as a function of $\alpha$. The calculations were performed using the all-electron FHI-aims code\textsuperscript{127,132} based on numeric atom-centered orbitals, with a tier 3 basis set for the $G_0W_0$ calculations (Appendix A.1 gives a summary of the employed basis set). The geometry of the individual molecules was optimized in PBE and a tier 2 basis set using a quasi-newton method with a convergence criterion of $10^{-3}$ eV/$\text{Å}$ for the residual maximum force component. We obtain $\alpha^* = 0.8$ for both TTF and TCNQ. Similar values for $\alpha$ were reported\textsuperscript{143} for benzene ($\alpha = 0.7$), bithiophene ($\alpha = 0.6$) and benzoquinone ($\alpha = 0.5$) by minimizing the many-electron self-interaction error\textsuperscript{144}. These are all much higher than $\alpha = 0.25$ used in the PBE0 functional.

Experimentally, the ionization potential (IP) of TTF obtained by photoelectron spectroscopy is 6.70 eV\textsuperscript{145}. For different $G_0W_0$ starting points the TTF IPs are (these values are compared with the experimental value): (6.14 eV, $-9.1\%$) for $G_0W_0@PBE$, (6.40 eV, $-4.7\%$) for $G_0W_0@PBE0$, and (6.66 eV, $-0.6\%$) for
3.1 The PBEh($\alpha^*$) functional

Figure 3.2: Contour plots of the TTF (a) and TCNQ (d) HOMO levels as a function of $\alpha$ and $\omega$ for the HSE functional family. The green filled circles indicate solutions according to Equation (3.3) in the $(\alpha,\omega)$ space, whereas the green crosses mark solutions where Equation (3.3) is applied to the LUMO level.

$G_0W_0@PBEh(\alpha^*)$. TCNQ has an experimental IP of 9.61 eV\textsuperscript{146}. In comparison, the calculated IPs read: (8.88 eV, $-8.2\%$) for $G_0W_0@PBE$, (9.21 eV, $-4.3\%$) for $G_0W_0@PBE0$, and (9.70 eV, $+1.0\%$) for $G_0W_0@PBEh(\alpha^*)$. In both cases, the IP obtained by $G_0W_0@PBEh(\alpha^*)$ is in excellent agreement with the experimental value. Coupled cluster calculations including single, double and perturbative triple excitations (CCSD(T)) predict an electron affinity (EA) of 3.22 eV\textsuperscript{147} for TCNQ. We find TCNQ EAs of (4.06 eV, 26.1\%) for $G_0W_0@PBE$, (3.95 eV, 22.7\%) for $G_0W_0@PBE0$, and (3.73 eV, 15.8\%) for $G_0W_0@PBEh(\alpha^*)$. All $G_0W_0$ results give too high EAs as compared to CCSD(T). However, the lowest error is obtained for $G_0W_0@PBEh(\alpha^*)$, even though the LUMO level is not explicitly taken into account in Equation (3.3).

At this point we note that Fig. 3.1 (a) and (b) imply that for a given system there is only one $\alpha$ that satisfies Equation (3.3). This raises the question whether a unique solution can also be found for the HSE\textsuperscript{69} family of XC functionals, which additionally depends on the inverse screening length $\omega$. Figure 3.2 (a) and (b) shows the optimum $(\alpha,\omega)$ values if Equation (3.3) is generalized to the HSE family of XC functionals. For both, TTF and TCNQ, we find that several choices of $(\alpha,\omega)$ satisfy the optimization requirement and hence the solution is in general not unique. For solids this could be exploited to reduce the computational cost by working at higher screening parameters $\omega$ and therefore more short-ranged exact
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![Graph showing the absolute value of the dipole moment (a) and charge transfer by means of Hirshfeld charge partitioning analysis (c) for the TTF/TCNQ complex as function of dimer distance. A positive sign for the charge transfer indicates electron transfer to TCNQ. (b) illustrates the geometry of the complex.](image)

Figure 3.3: Absolute value of the dipole moment (a) and charge transfer by means of Hirshfeld charge partitioning analysis (c) for the TTF/TCNQ complex as function of dimer distance. A positive sign for the charge transfer indicates electron transfer to TCNQ. (b) illustrates the geometry of the complex.

exchange. However, $\omega = 0$ (that is the PBEh family of XC functionals) gives the best compromise in describing the location of both, the HOMO and the LUMO level.

Next, we evaluate the impact of $\alpha$ in describing dipole moments and the charge transfer for the TTF/TCNQ dimer. We chose our geometry (Fig. 3.3 (b)) by cutting out a dimer of an interface of TTF and TCNQ crystals along the [001] surface of TCNQ. Figure 3.3 (a) shows the absolute value of the dipole moment as a function of the distance. At the interface equilibrium distance ($d_0$) the dipole moment differs significantly between PBE, PBE0 and PBEh($\alpha^*$). In particular the dipole moment for PBE and PBE0 does not vanish for long distances, as it should since in the long range limit the total dipole moment should be given by the individual molecules which have both zero net dipole moments. Only the PBEh($\alpha^*$) functional reproduces the correct asymptotic limit. The unphysical behavior of PBE and PBE0 in the long range limit can be traced back to their description of charge transfer, as also shown in Fig. 3.3 (c); both PBE and PBE0

---

bThe choice of this geometry is motivated by a recent experiment in which it was shown that the TTF/TCNQ interface exhibits metallic conduction although the individual crystals are large band-gap semiconductors. The mutual crystal interface distance was optimized on the PBE level of theory including van der Waals corrections. We define the distance between the TTF and TCNQ crystals $d_0$ as the distance between the planes spanned by the hydrogen atoms of TTF and the Nitrogen atoms of TCNQ (Fig. 3.3 (b)) for which we obtain $d_0 = 2.1 \text{ Å}$.  

---

60
3.1 The PBEh($\alpha^*$) functional

Figure 3.4: Difference ($\Delta$) of the generalized KS LUMO of TCNQ and HOMO of TTF as a function of $\alpha$ (open circles). Also shown are the corresponding $G_0W_0$ values (filled circles). The vertical dotted line denotes $\alpha = 0.25$ which corresponds to PBE0. For $\alpha < 0.3$, $\Delta$ is negative indicating artificial charge transfer in the non-interacting limit. The right hand side shows an illustration of $\Delta$ which is defined as the difference TCNQ HOMO and TTF LUMO.

predict non vanishing charge transfer in the long range limit.

In order to proceed we consider the limit of infinite molecular separation. In this limit electron transfer between the molecules is determined by the ratio of the EA of TCNQ and the IP of TTF. However, the CCSD(T) and $G_0W_0$ EA of TCNQ is smaller than the IP of TTF, and thus does not allow for interaction free electron transfer. This indicates that both, PBE and PBE0 fail to describe the ground state density for this system. Within the framework of KS DFT the total electron density is built up by occupying orbitals with respect to their energetic ordering. It is thus the relative alignment of the TCNQ-LUMO and the TTF-HOMO that determines electron transfer between the two molecules in this limit. Fig. 3.4 illustrates the difference of the GKS LUMO of TCNQ and the HOMO of TTF, $\Delta$, as a function of $\alpha$. For $\alpha < 0.3$ the TCNQ-LUMO level is located below the TTF-HOMO level. Thus, TCNQ will receive a certain amount of charge just by occupying orbitals with respect to the energetic ordering. In line with Ref.134, for $\alpha > 0.3$ the level alignment of the TTF-TCNQ frontier orbitals qualitatively agrees with experiment (CCSD(T)) for which $\Delta$ is positive. In particular both, PBE ($\alpha = 0$) and PBE0 ($\alpha = 0.25$) are below the critical $\alpha$ value of 0.3 and therefore have an artificial contribution to charge transfer. On the other hand PBEh($\alpha^*$) has a level alignment that is consistent with experiment (CCSD(T)) and a vanishing QP correction to $\Delta$. As a consequence the PBEh($\alpha^*$) functional is free from spurious asymptotic charge transfer.
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Figure 3.5: Mean absolute percentage error (MAPE) of theoretical IPs obtained from the $G_0W_0$ method (a), the (generalized) KS HOMO level (b), the $\Delta$-SCF method (c), and the Slater-Janak model (SJM, (d)). The errors are with respect to experimental vertical IPs for 50 molecules of the G2 test set.

3.1.3 Application 2: the G2 test set

We also examined the performance of the proposed scheme for a subset of the G2 test set for ionization energies, consisting of 50 atoms and molecules for which experimental geometries and vertical IP are available. All calculations were carried out for experimental geometries using the tier 4 FHI-aims basis augmented with diffuse functions from aug-cc-pV5Z. Following Equation (3.3) we obtain $\alpha^*$ values $\geq 0.7$. A compilation of the detailed results is given in table A.2 of appendix A.4. Figure 3.5 (a) and (b) summarizes the results in comparison to experimental reference data for the $G_0W_0$ and GKS IPs which were obtained by taking the negative of the respective HOMO level.

For the given test set the dependence of $G_0W_0$ on the fraction of exact exchange was found to be relatively weak (FIG. 3.5 (a)). $G_0W_0$ based on PBE reference states
performs very well even though it tends to underestimate the IP and has a mean absolute percentage error (MAPE) of 5%. \( G_0W_0@PBE0 \) and \( G_0W_0@PBEh(\alpha^*) \) perform similarly with a MAPE of 2% and 3% respectively, and thus further reduce the error as compared to \( G_0W_0@PBE \). In contrast to \( G_0W_0 \) the KS HOMO depends quite sensitively on \( \alpha \) which is shown Fig. 3.5 (b). In particular PBE underestimates the IP by as much as 39%. An \( \alpha \) value of 1/4 as used in PBE0 improves the IPs over PBE, however the error is still as large as 27%. A realistic description can only be achieved by PBEh(\( \alpha^* \)), which brings down the MAPE to 2.9%.

Alternatively the IP may be calculated by the \( \Delta \)-SCF approach or the Slater-Janak model (SJM). The \( \Delta \)-SCF method obtains the IP by taking ground-state energy difference between the neutral and charged molecule, whereas the SJM obtains the IP by the HOMO level with half of an electron removed. Figure 3.5 (c) and (d) shows the G2 results for the \( \Delta \)-SCF method and the SJM, respectively. For all three functionals the SJM gives essentially the same IP as the \( \Delta \)-SCF scheme with very small MAPEs that are in between 2% (PBE0) and 3% (PBEh(\( \alpha^* \))). This implies in particular that both, the \( \Delta \)-SCF method and the SJM are compatible with the PBEh(\( \alpha^* \)) functional.

### 3.1.4 Summary

In summary we have presented a quasi self-consistent scheme that obtains a system dependent fraction of EX (\( \alpha \)) by combining hybrid DFT and the \( G_0W_0 \) method. In particular our scheme lifts the ambiguity in the choice of \( \alpha \). By this we obtained a hybrid functional that is both consistent in the choice of the fraction of EX and as a \( G_0W_0 \) starting point. The former implies an improvement of the GKS spectrum and thus an improved charge density. This is of particular importance for weakly interacting donor-acceptor systems in the field of organic electronics where standard XC functional may give qualitatively wrong electron transfer and multipole moments.

This section shall end with a comparison to two recent publications by Körzdörfer et al.\(^{152}\) and Sini et al.\(^{134}\) that are related to our results. Independent of us Körzdörfer et al. suggest an alternative \( G_0W_0 \) starting point within the PBEh-family of XC functionals. Splitting the \( G_0W_0 \) of Equation (3.1) of state \( n \) into its exchange and correlation part gives

\[
\epsilon_n^{G_0W_0} = \epsilon_n + \langle \psi_n, (\sum \epsilon_{G_0W_0} - v^{xc}) \psi_n \rangle \\
= \epsilon_n + \langle \psi_n, (\sum \epsilon_{G_0W_0} - v^c) \psi_n \rangle + (1 - \alpha) \langle \psi_n, (v^{EX} - v^{PBE}) \psi_n \rangle \\
=: \epsilon_n + \Delta v_{c,n} + (1 - \alpha) \Delta v_{x,n}, \tag{3.4}
\]
Table 3.1: IP and EA [eV] for the TTF and TCNQ molecules obtained by taking the negative of the $G_0W_0$ HOMO and LUMO level. In brackets the corresponding GKS values are tabulated. The bottom summarizes the experimental IPs and the TCNQ EA obtained by CCSD(T).

<table>
<thead>
<tr>
<th></th>
<th>TTF</th>
<th>TCNQ</th>
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<tr>
<td></td>
<td>IP</td>
<td>EA</td>
</tr>
<tr>
<td>$G_0W_0$@PBEh($\alpha^*$)</td>
<td>6.66 (6.66)</td>
<td>-0.67 (-0.68)</td>
</tr>
<tr>
<td>$G_0W_0$@PBEh($\bar{\alpha}$)</td>
<td>6.27 (4.29)</td>
<td>-0.17 (1.61)</td>
</tr>
<tr>
<td>Exp</td>
<td>6.71$^{145}$</td>
<td>–</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>–</td>
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where $v_x^{\text{EX}}$ is the exact exchange potential and the specific form of $v_x$ within the PBEh family was inserted. The basic idea is to require the relative $G_0W_0$ shift of the occupied eigenvalues $\{\epsilon_n, n \in O\}$ to be zero,

$$
\Delta v_{c,n} + (1 - \alpha)\Delta v_{x,n} = \text{const}, \quad n \in O,
$$

(3.5)

The constant allows that the occupied GKS and the $G_0W_0$ spectra may still differ by a rigid shift. From requirement (3.5) the optimum $\alpha$ value, $\bar{\alpha}$ can be obtained. For a given guess of $\alpha$ the self consistent (G)KS eigenvalues and orbitals are calculated. These eigenvalues are used to calculate $\Delta v_{c,n}$ and $\Delta v_{x,n}$ according to Equation (3.4). If the plot $\Delta v_{c,n}$ vs. $\Delta v_{x,n}$ is close to a straight line, then the slope is determined by linear regression. Adapting $\alpha$ and iteration of this procedure until the slope determined by the linear regression is equal to the slope in Equation (3.5) determines $\bar{\alpha}$.

For TTF and TCNQ this procedure obtains $\bar{\alpha} = 0.1$ and $\bar{\alpha} = 0.24$, respectively. These values are much lower than those obtained for PBEh($\alpha^*$) for which $\alpha^* = 0.8$, for both molecules (see Figure 3.1). By design, PBEh($\bar{\alpha}$) represents an optimum $G_0W_0$ starting point for the occupied spectrum. In order to assess its performance for the ground state properties, the TTF, TCNQ molecules are considered individually. Table 3.1 compares the EA and the IP of PBEh($\bar{\alpha}$) with PBEh($\alpha^*$). On the $G_0W_0$ side the IP of PBEh($\bar{\alpha}$) tends to be underestimated with respect to both, experiment and PBEh($\alpha^*$). On the other hand the EA tends to be further overestimated as compared to PBEh($\alpha^*$), and CCSD(T). On the GKS level of theory PBEh($\bar{\alpha}$) moves the IP of TTF erroneously above the EA of TCNQ and hence predicts the wrong charge transfer behavior.

That a relatively high $\alpha$-value is necessary in order to obtain a reliable DFT description of the TTF-TCNQ complex has been also discussed by Sini et al.$^{134}$
In this work the performance of several XC functionals has been evaluated for a co-facial configuration of the TTF-TCNQ complex. The authors concluded that functionals with $\alpha > 0.6$ are necessary in order to describe this system, which is in agreement with the presented PBEh($\alpha^*$) functional. From a methodological point of view, Sini et al. draw their conclusion empirically based on extensive benchmark tests. In contrast, the findings in the present work are implications of imposing the HOMO-IP condition in Equation (3.1) only.

3.2 Self-interaction error

In the previous section, an approach for optimizing the XC functional was proposed and escorted by the example of the prototypical donor-acceptor complex TTF/TCNQ. The basic quantity of DFT is the electron density. This section is devoted to establish a density-based point of view on the performance and errors of XC functionals. The illustrative example remains the TTF/TCNQ complex. This will lead to a well known deficiency in standard approximations to the XC functional, which is known as the self-interaction error.

First, the definition of many-electron self-interaction (SI) freeness is introduced. The entrance gate of this definition is a result for the exact XC functional in the grand canonical ensemble: The ground state total energy $E_v(N)$ is continuous and a piecewise linear function between integer charges. For a system with fractional number of electrons $N \in \mathbb{R} \geq 0$ this reads

$$N = N_0 + \omega, \quad N_0 \in \mathbb{N}_0, \quad \omega \in [0,1] \subset \mathbb{R},$$

$$E_v(N_0 + \omega) = (1 - \omega)E_v(N_0) + \omega E_v(N_0 + 1).$$

For an approximate XC functional this gives raise to the following definition:

**Definition 3** (Many electron self-interaction free). A density functional is many-electron SI free, if it obeys for any external potential $v$ the condition 3.6.

If a density functional is not SI free according to this definition, then the corresponding error is called many-electron self-interaction error (SIE).

Transfer energy

In order to analyze the performance of approximate XC functionals for charge transfer, consider two non-interacting molecules. This will be later identified with the TTF-TCNQ complex at infinite intermolecular separation. The total Hamiltonian can be then written as a sum of two without a mutual interaction term. Let $v_1$ be the external potential of subsystem 1 with electron number $N_1 \in \mathbb{N}_0$, and
3 Methodology

similar for subsystem 2. Without loss of generality, assume \( N_2 \geq N_1 \) and define the transfer energy \( E_t \),

\[
[-N_1, N_2] \to \mathbb{R} \\
\delta q \mapsto E_t(\delta q) \\
E_t(\delta q) := E_{v1}(N_1 + \delta q) + E_{v2}(N_2 - \delta q) - E_{v1}(N_1) - E_{v2}(N_2).
\]

The map (3.7) establishes an energetic measure for electron transfer between two molecules in the limiting case of vanishing intermolecular interaction, under the constraint of overall electron conservation. If \( E_t \) becomes negative for some \( \delta q \), then the system gains energy upon electron transfer from one molecule to the other, even though they do not interact. This electron transfer could be fractional, or integer, however some properties of \( E_t \) follow immediately:

i) If a density functional is many-electron SI free, then \( E_t \) is piecewise linear between integer charges.

ii) Consider a density functional that is many-electron SI free and the derivative \( \partial E_t / \partial \delta q \neq 0 \), at points \( \delta q \notin \mathbb{Z} \). If \( E_t \) is bound from below, then only integer charge transfer between non-interacting molecules occurs.

iii) The minimum of \( E_t \) determines the asymptotic limit of the intermolecular interaction energy between subsystem 1 and 2. Furthermore, if the minimum of \( E_t \) sits at \( \delta q = 0 \), then the interaction energy between non-interacting molecules is zero.

Having the above tools at hand, one can go back to the charge transfer problem of the previous Section 3.1. Figure 3.6 (a) illustrates the charge transfer as a function of the TTF-TCNQ distance obtained by various XC functionals. The charge transfer was obtained by means of Hirshfeld partitioning analysis\(^\text{102}\), and the intermolecular distance is given with respect to the (vdW corrected PBE) equilibrium distance \( d_0 \), which the dimer would have in the TTF-TCNQ interface. The three semilocal functionals (gray curves) behave similar. In particular they exhibit non-vanishing electron transfer in the long range limit. In comparison, the electron transfer curves obtained by the PBE0 or HSE06 hybrid functionals (black curves) are essentially shifted towards smaller charge transfer. Albeit these hybrid functionals improve the erroneous charge transfer of semilocal functionals, they are not able to fix the unsatisfactory interaction-free charge transfer. However, the PBEh(\(\alpha^+\)) functional (depicted in red), is able to bring the long-range charge transfer to zero.

A density-based rational for the long-range charge transfer can be obtained by considering the transfer energy \( E_t \), which is plotted in Figure 3.6 (b). \( E_t \) is an energetic measure for non-interacting charge transfer, and its minimum determines
3.2 Self-interaction error

Figure 3.6: (a) Hirshfeld charge transfer for various semilocal (grey) and hybrid (black) XC functionals for the TTF-TCNQ complex (a positive sign indicates electron transfer on TCNQ). The red curve shows the PBEh(α*) result. (b) shows the corresponding transfer energies \( E_t \); its minimum determines the asymptotic limit for charge transfer (illustrated by the red and gray arrows for PBEh(α*) and semilocal XC functionals, respectively).

The charge transfer in the asymptotic limit (illustrated by the red and gray arrows for PBEh(α*) and semilocal XC functionals, respectively). For the standard functionals the minimum is caused by the convexity of \( E_t \) as a function of transferred charge. For semilocal functionals this minimum is located at about \( \approx 0.2 \) transferred electrons. It is shifted towards smaller electron transfer for HSE06, B3LYP or PBE0. But still these hybrid functionals exhibit non vanishing asymptotic charge transfer. In contrast, PBEh(α*) does not have a convexity-caused minimum at fractional charge transfer. Rather, its minimum is located at zero
charge transfer and hence PBEh(α*) does not suffer from spurious charge transfer in the asymptotic limit.

The cause for the convexity of $E_t$ follows from the SIE of the underlying XC functional. If a density functional is many electron SI free then $E_t$ is piecewise linear between integer charges. Conversely, if $E_t$ is not piecewise linear then the density functional is not SI free. Thus, asymptotic fractional charge transfer is caused by the SIE.

Link to Kohn-Sham eigenvalues

In Section 3.1.2, the ability of an XC functional in describing charge transfer, was argued via the relative alignment of the TCNQ-LUMO and the TTF-HOMO. This poses the simple question: how is this level alignment argument related to the argument based on the transfer energy?

It is illustrative to revisit Figure 3.6 (b). There, the convexity-caused minimum of $E_t$ for semi-local functional emerges because the first derivative, $\partial E_t/\partial \delta q$, changes sign on the interval $\delta q \in (0, 1)$. In particular the first derivative is negative in the region where $\delta q < 0.2$.

The following consideration focuses on the semi-local functionals (however, the obtained conclusions are still valid for the presented hybrid functionals within the GKS framework). The basic idea is to link the first derivative of $E_t$ to the Kohn-Sham eigenvalues. This can be achieved by exploiting Janak’s theorem \cite{155,156}

\[
\frac{\partial E_v}{\partial f_i} = \epsilon_i, \quad (3.8)
\]

where $f_i$ is the occupation number of KS state $i$ with eigenvalue $\epsilon_i$. Now, one may calculate the derivative $\partial E_t/\partial \delta q$ on the open interval $\delta q \in (0, 1)$. Since $\delta q > 0$, the derivative corresponds to the derivative of the TCNQ (TTF) total energy with respect to the fractionally occupied LUMO (HOMO) level with occupation $f_L = \delta q \quad (f_H = 1 - \delta q)$. Together with Equation (3.7) it follows,

\[
\frac{\partial E_t}{\partial \delta q}(\delta q) = \frac{\partial}{\partial \delta q} E_{TCNQ}(N_{TCNQ} + \delta q) + \frac{\partial}{\partial \delta q} E_{TTF}(N_{TTF} - \delta q) = \frac{\partial}{\partial f_L} E_{TCNQ} - \frac{\partial}{\partial f_H} E_{TTF} = \epsilon^\text{TCNQ}_L(f_L) - \epsilon^\text{TTF}_H(f_H), \quad (3.9)
\]

where the minus sign follows from the chain rule, and the residual dependence on the Kohn-Sham eigenvalues on the occupation numbers was indicated for clarity. Equation (3.10) tells, that the slope of the transfer energy is given by the difference between the TCNQ-LUMO level and the TTF-HOMO level at a given $\delta q$.

The argument via the relative alignment of the TCNQ-LUMO and the TTF-
3.2 Self-interaction error

HOMO in Section 3.1.2 has been given for the neutral molecules (i.e., the electronic and nuclear charge compensates each other). Hence, taking the limit from the right

$$\left. \frac{\partial E_t}{\partial \delta q} \right|_{\lim \delta q \to 0^+} = \epsilon_{TCNQ}^{L} - \epsilon_{TTF}^{H},$$

(3.10)

gives the desired result. Thus, the relative alignment of the TCNQ-LUMO and the TTF-HOMO determines the first derivative of $E_t$ in the limit of vanishing charge transfer. In particular, it has been shown in Section 3.1.2 that for standard semi-local functionals $\epsilon_{TCNQ}^{L} - \epsilon_{TTF}^{H} < 0$. This implies that that the transfer energy may become negative with a minimum that is located at fractional charge transfer (compare Figure 3.6 (b)).

Finally, it should be noted, that for a SIE free XC functional Janak’s theorem implies that the Kohn-Sham eigenvalues must be constant between integer charges. This could be exploited to obtain the fraction of exact exchange $\alpha$ in a different way as proposed in Section 3.1. One could choose $\alpha$ such that the KS eigenvalues (in particular the frontier levels) remain constant between integer charges upon fractionally charging the system. This approach has been recently pursued using the range seperated BNL hybrid functional$^{138,157,158}$, as proposed by Baer, Neuhauser, and Livshits. Alternatively, the condition of constant KS eigenvalues between integer charges has been directly imposed on the construction or correction of XC functionals.$^{159-161}$

**Charge density difference**

Returning to the TTF-TCNQ complex at the interface equilibrium distance $d_0$, Figure 3.6 (a) implies, that the amount of partially transferred predicted by semilocal functionals is one order of magnitude larger than what would predict PBEh($\alpha^*$). The other investigated PBE0 and HSE06 hybrid functionals predict charge transfer that is in between PBE and PBEh($\alpha^*$). Albeit depending on the charge partitioning scheme in use, PBEh($\alpha^*$) predicts essentially zero charge transfer. Instead of relying on a charge partitioning scheme, one could directly consider the charge density difference

$$\Delta \rho := \rho - \rho_{TTF} - \rho_{TCNQ},$$

(3.11)

where $\rho$ is the total electron density of the TTF-TCNQ complex, and $\rho_{TTF}$ ($\rho_{TCNQ}$) is the electron density of the free TTF (TCNQ) molecule. $\Delta \rho$ as obtained from PBE, PBEh($\alpha^*$) and a fully self consistent GW$^{126}$ (scGW, with a tier 1 basis set) calculation is shown in Figure 3.7. PBEh($\alpha^*$) and scGW give electron density differences that are very similar (the red and blue color code denotes electron
Figure 3.7: Charge density difference between the TTF-TCNQ complex and its individual molecules on the PBE, PBEh(\(\alpha^*\)) and self-consistent GW (scGW) level of theory. Red and blue colors indicate electron accumulation and depletion respectively (with an isosurface of 0.005 e/Å\(^3\)). To the left the TTF-HOMO and TCNQ-LUMO orbital (PBE) is shown, where the yellow/pink colors encode the +/- sign of the KS orbital.

density accumulation and depletion respectively). In particular both methods rather show electron density re-arrangement than electron density transfer.

In contrast, PBE predicts significant electron density transfer from TTF to TCNQ. Closer inspection of Figure 3.7 shows that the PBE \(\Delta \rho\) essentially consists of two contributions, a re-arrangement part in a region where the molecules are close and a delocalized part which spreads over the individual molecules. The re-arrangement part resembles the PBEh(\(\alpha^*\)) or scGW result, whereas the delocalized part has a similar character as the LUMO-derived (HOMO-derived) electron density of TCNQ (TTF). The later is indicated by the dashed arrows from the PBE LUMO and HOMO orbital of TCNQ and TTF, respectively. This can be easily rationalized in the light of Section 3.1. There, it was argued that the SIE in PBE erroneously moves the TTF-HOMO above the TCNQ-LUMO. As a result the TCNQ-LUMO receives a certain amount of electrons from the TTF-HOMO, which is reflected in the the PBE charge density difference in Figure 3.7.

In summary, a density based point of view on the performance of standard approximations to the XC functional was given. With the help of the transfer energy \(E_t\) it was shown that a density functional that gives fractional interaction-free charge transfer, suffers from the SIE. While for the TTF/TCNQ complex
standard semilocal and hybrid functional exhibit this feature, PBEh(α∗) is free from spurious asymptotic charge transfer.

### 3.3 Assessment of correlation energies

So far, the main focus was put on spectral properties: The PBEh(α∗) functional was constructed and it was shown that it significantly reduces the many electron self-interaction error. This has turned out to be essential for the description of the ground state electron density of the TTF/TCNQ donor/acceptor complex.

In this section, a comprehensive study is presented to assess the PBEh(α∗) functional, and more importantly the starting point dependence of the renormalized second-order perturbation theory (rPT2).

The rPT2 theory was put forward recently; it obtains the electron correlation energy by

\[
rPT2 := EX + cRPA + SOSEX + rSE,
\]

consisting of the exact exchange total energy (EX), the RPA correlation energy, second-order screened exact exchange (SOSEX), and renormalized single excitations.

This approach resides in the framework of many-body perturbation theory and thus depends on the spectrum of the unperturbed reference Hamiltonian — in the present study these are the PBE, PBE0 and PBEh(α∗) (G)KS Hamiltonians. In order to stress this dependence on the input orbitals the notation ‘method@functional’ will be used. In the literature, rPT2 has only been evaluated on PBE reference orbitals (i.e., rPT2@PBE), whereas in the following results for rPT2@PBE0 and rPT2@PBEh(α) will be given for the first time.

Principal results will be presented in form of statistical summaries over test sets across different chemical and electronic environments. These are i) weak intermolecular interaction energies (S66 testset), ii) atomization energies (G2-1 testset), and iii) barrier heights for chemical reactions (HTBH38 and NHTBH38 testsets).

Probably the main reason why RPA based methods such as expression (3.12) are of interest is because it generically contains dispersion interactions. Alternatively on could describe these interactions by adding the long range van der Waals tail to a given functional as proposed among others by Tkatchenko and Scheffler (TS). Since for weakly interacting materials dispersion interactions are crucial, also the TS van der Waals correction scheme will be studied for the S66 test set.

Table 3.2 gives an overview of the studied methods and test sets. The right column clarifies which of these methods have not been reported in the literature before. Apart from rPT2@PBE0, rPT2@PBEh(α∗), and PBEh(α∗) itself together with
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<table>
<thead>
<tr>
<th>Testset</th>
<th>Method</th>
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<tr>
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<td>Other</td>
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<td></td>
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</table>

Table 3.2: Overview of testsets (left) and applied total energy methods (right). The right column reviews which of these methods have been applied for the first time in this thesis and gives an exemplary reference otherwise.

its vdW corrected version, an additional total energy ansatz shall be proposed: EX@PBEh(α*)+cRPA@PBE. This ‘hybrid method’ evaluates the RPA correlation energy at PBE orbitals while the exact exchange total energy at PBEh(α*) orbitals. This ansatz shall be motivated in the following before discussing the actual benchmark results.

3.3.1 EX@PBEh(α*)+cRPA@PBE

First, the argument of Ren et al.\textsuperscript{110} is repeated that lead to (renormalized) single excitations in order to overcome the systematic underbinding behavior of EX+cRPA.\textsuperscript{164,173–176} It is based on the following observation for binding energy contributions:

\[
E_b^{\text{EX}}@\text{HF} - E_b^{\text{EX}}@\text{PBE} < 0 \quad (3.13)
\]

\[
E_b^{\text{cRPA}}@\text{HF} - E_b^{\text{cRPA}}@\text{PBE} > 0. \quad (3.14)
\]

Here \(E_b^{\text{EX}}\) and \(E_b^{\text{cRPA}}\) denotes the binding energy contribution from EX and the RPA correlation energy, respectively (\(E_b^{\text{EX}}\) contains additionally the kinetic energy, the external potential, and the Hartree energy). Inequalities (3.13-3.14) indicate, that the PBE EX contribution to the binding energy is more repulsive than that of HF and conversely —but to a less extent— for cRPA. In order to account for the too repulsive behavior of \(E_b^{\text{EX}}@\text{PBE}\), Ren et al. make the ansatz for the total
3.3 Assessment of correlation energies

\[ E_b^{\text{EX}} @ PBEh(\alpha^*) < E_b^{\text{EX}} @ HF < E_b^{\text{EX}} @ PBE. \]  (3.16)

SE contributions vanishes for HF reference states by Brillouin’s theorem \(^{109}\), while they are slightly attractive for PBE and repulsive for PBEh(\(\alpha^*\)) reference state,

\[ E_b^{\text{SE}} @ HF = 0, \quad E_b^{\text{SE}} @ PBE < 0, \quad E_b^{\text{SE}} @ PBEh(\alpha^*) > 0. \]  (3.17)

In other words: single excitations correct towards the HF binding energy. In
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the particular case of the unperturbed PBEh(α⁺) Hamiltonian, this correction is repulsive because the corresponding binding energy on the EX level of theory is lower in energy than the HF binding energy (remember that the HF total energy is given by EX@HF).

In order to improve over the systematic underbinding behavior of EX+cRPA, SE do not appear to be beneficial for PBEh(α⁺) reference states, since they give a repulsive contribution to the binding energy. Rather, inequalities (3.16) together with the argument by Ren et al. suggests to make the following ansatz for the total energy:

\[ \text{EX@PBEh}(α⁺) + c\text{RPA@PBE}. \]  

Adding equation (3.18) to the methods-to-benchmark catalog, we now proceed to the results.

3.3.2 Weak interactions: The S66 testset

Random-phase approximation & co

Probably the main reason why the RPA gained increasingly attention in material science in the last decade is its \(1/R^6\) asymptotic decay of interaction energies between closed shell subsystems. Hence, the RPA generically contains the long range van der Waals tail. RPA-based methods were extensively studied for vdW-bond systems; here the S66 testset by Hobza and co workers will be considered. It consists of 66 molecular complexes, for which accurate CCSD(T) reference interaction energies are calculated. S66 is a testset for weak interactions because it includes the most common types of non-covalent interactions, i.e., hydrogen bonds, dispersion bonds, and bonds of mixed character.

The error statistics is presented in Fig. 3.9; the detailed numerical results are given in tables A.3–A.5 of appendix A.4. In practice, results based on the RPA are very sensitive to the quality of the basis set. Following Ren et al., this work employed a tier 4 basis set augmented with diffuse functions from aug-cc-pV5Z (except for the TS van der Waals correction: tier 3) and a counterpoise correction was performed. For this basis, Ren et al. obtained a mean absolute error of EX+cRPA@PBE for the S22 dataset that differs by 0.1 kcal/mol (4 meV) by results extrapolated to the complete basis set limit as reported by Es-huis and Furche. Hence, the subsequently presented results are estimated to be accurate within 4 meV.

It is already established in the literature that standard EX+cRPA@PBE underestimates the S66 binding energies, which may be alleviated by rPT2@PBE,
3.3 Assessment of correlation energies

![Figure 3.9: Mean absolute percentage error (MAPE) of the S66 testset for RPA based methods and the TS-vdW scheme at various starting points. The errors are relative to CCSD(T) results at the complete basis set limit taken from Ref. 167.](image)

and thus, by adding the rSE and SOSEX terms. Here, the question is addressed how dependent are these conclusions on the underlying XC functional, more precisely on its employed fraction of exact exchange. First, note from Fig 3.9 that
EX+cRPA tends to underestimate binding energies irrespective of the DFT starting point. However, Figure 3.9 also reveals, that rPT2 depends sensitively on the starting point with the tendency of increased errors upon increasing the fraction of exact exchange $\alpha$ in the underlying PBE hybrid functional. rPT2@PBE ($\alpha = 0$) has an overall MAPE of 7% with a slight tendency to overestimate binding energies, whereas rPT2@PBE0 ($\alpha = 1/4$) and rPT2@PBEh($\alpha^*$) ($\alpha^* \sim 0.7 - 0.8$, see table A.4) exhibit a clear trend to underestimate them with a MAPE of 12% and 24%, respectively. This loss in performance may be clearly attributed to a vast underbinding of dispersion-dominated and mixed bonds.

For dispersion-dominated bonds, SOSEX acts in average attractive irrespective of the functional. However, the magnitude of the SOSEX correction decreases with increasing $\alpha$. In particular, for PBEh($\alpha^*$) reference states SOSEX decreases the MAPE only by 0.8% as compared to EX+cRPA and is thus essentially ineffective. Similar to SOSEX, also the rSE correction acts less attractive upon increasing $\alpha$ in the DFT starting point. Hence, rSE@PBE appears to be most attractive, which is reduced if evaluated at PBE0 reference states. For PBEh($\alpha^*$) reference states the rSE correction even changes sign since it acts repulsive.

The very same features as for dispersion dominated systems hold true for mixed bonds. A significant improvement over EX+cRPA is observed only for PBE reference states. rPT2@PBE0 benefits from SOSEX and rSE correction to a less extent because these correction terms are less attractive. In fact, for PBEh($\alpha^*$) reference states rPT2 deteriorates the performance, since the SOSEX correction is very small and the rSE correction acts repulsive.

While the overall performance for the S66 test set follows the trend of dispersion and mixed bonds, hydrogen bonds are exceptional. In line with Ren et al.\textsuperscript{111} Fig. 3.9 implies that rPT2@PBE predicts hydrogen bonds to be too attractive (7.1% MAPE). This behavior is reduced for rPT2@PBE0 and rPT2@PBEh($\alpha^*$), which have a MAPE of 4.0% and 4.8%, respectively. Both, the rSE and SOSEX correction follow the same trend with respect to $\alpha$ as described above for dispersion-dominated or mixed bonds: They act less attractive upon increasing $\alpha$. Thus, adding SOSEX+rSE on PBE reference states overshoots hydrogen bonds, whereas the more moderate correction obtained by hybrid functionals appears to be more accurate. The peculiar behavior of rPT2@PBE for hydrogen bonds is also the reason why EX+cRPA+rSE@PBE is the overall most accurate rPT2 subdiagram evaluated in this study, with an MAPE of 6.1% for the whole S66. Adding SOSEX to EX+cRPA+rSE@PBE is more accurate for dispersion-dominated and mixed bonds, while it adulterates the otherwise excellent performance for hydrogen bonds.

EX@PBEh($\alpha^*$)+cRPA@PBE as proposed in Section 3.3.1, has a MAPE of 4.3%. It is the most accurate method considered in this the study, indicating that ex-
pression (3.18) is indeed a possible avenue in order to overcome the notorious underbinding behavior of EX+cRPA. While EX@PBEh(α*)+cRPA@PBE predicts too strong hydrogen bonds as compared to EX+cRPA+rSE@PBE, it performs most accurately for dispersion-dominated and mixed bonds among all RPA-based methods. This leads to an overall well-adjusted performance across all bonding types present in the S66 test set.

In order to analyze EX@PBEh(α*)+cRPA@PBE and the starting point dependence of rPT2 in more detail, the example of the benzene dimer — item number 24 of the S66 data set— will be discussed. The benzene dimer was labeled by Ren et al.\textsuperscript{94,111} as a challenging system for RPA based methods, and thus, represents a stern case. Figure 3.10 shows the computed binding curves, whereas the reference CCSD(T) curve was taken from the S66×8 dataset\textsuperscript{167}. The S66×8 data set contains for each element of the S66 set of 8 different intermolecular separations. These are set by scaling the equilibrium distance by a factor of 0.9, 0.95, 1.0, 1.05, 1.1, 1.15, 1.2, near the equilibrium distance rPT2@PBE (Fig. 3.10 (a)) underestimates the binding energy by about 30%. An increase of α in the DFT functional amplifies the underbinding behavior of rPT2. Figure 3.10(c) displays the corresponding SOSEX and rSE corrections. While all starting points give the same repulsive SOSEX contribution, rSE@PBE acts slightly attractive, whereas repulsive for the hybrid starting points. For PBE reference states, SOSEX and rSE tend to cancel each other, while add up in a repulsive fashion otherwise. As a consequence, rPT2 does not improve over EX+cRPA for PBE input orbitals and performs worse for hybrid orbitals.

Still, at the EX+cRPA level of theory inclusion of exact exchange in the underlying functional does not appear to be beneficial (Fig. 3.10(b)), since it dictates a similar, but less pronounced trend as rPT2. The α-dependence of the exchange-only (EX) contribution and the RPA correlation energy (cRPA) to the binding energy is shown in Fig. 3.10(c). Plotted are the differences of the respective quantities with respect to the PBE starting point. For example, ΔEX@PBE0 = EX@PBE0 − EX@PBE. Increasing α, renders cRPA less attractive, while at the same time the EX contribution gets less repulsive. These α induced deviations from EX@PBE and cRPA@PBE cancel each other only partly; in particular the cRPA trend towards weaker binding energies dominates the opposite trend of EX. Thus, EX+cRPA decreases the intermolecular interaction strength as α increases.

EX@PBEh(α*)+cRPA@PBE combines those starting points, which are most attractive on either, the EX and cRPA side. Comparing Figs. 3.10(c) and (d) shows that EX@PBEh(α*) acts significantly more attractive than EX+rSE@PBE. Therefore, EX@PBEh(α*)+cRPA@PBE is more attractive than EX+cRPA+rSE@PBE and, thus, than rPT2@PBE (because SOSEX@PBE acts repulsive). Indeed, in Fig. 3.10(a) the EX@PBEh(α*)+cRPA@PBE binding curve closely follows the
CCSD(T) reference curve within 10 meV, and is therefore able to describe the benzene dimer accurately.

At this point, it must be stressed, that EX@PBEh(α*)+cRPA@PBE is an ansatz for the total energy. In the light of its accurate performance for the S66 and the ability of getting the benzene dimer in very close agreement with CCSD(T), motivates future research in order to extend rPT2 within the framework of many-body perturbation theory.
3.3 Assessment of correlation energies

Tkatchenko-Scheffler van der Waals correction

Leaving the realm of RPA-based methods, the results for the S66 shall end with an assessment of the van der Waals correction method by Tkatchenko-Scheffler (TS).\(^{67}\) Recall that the TS method adds the long range \(C_6/R^6\) vdW tail to a given XC functional, with density dependent \(C_6\) coefficients. Looking back to Fig. 3.9 shows an overall error decrease upon increasing the fraction of exact exchange with a MAPE of 12.1% 8.9% and 6.5% in the sequence PBE+TS, PBE0+TS and PBEh(\(\alpha^*\))+TS. Figure 3.9 assigns this increase of accuracy to dispersion-dominated systems: While hydrogen and mixed bonds are scarcely affected by an increase of \(\alpha\), dispersion-dominated bonds are. PBE+TS overshoots dispersion bonds with a MAPE of 21.9%, which is reduced, but still notable for PBE0 (14.5% MAPE), and strongly reduced by PBEh(\(\alpha^*\))+TS (6.0% MAPE, see table A.3 for a detailed error statistics)

That PBE+TS and PBE0+TS overbind dispersion-dominated systems was observed in the literature before.\(^{172}\) This was attributed\(^{172,185,186}\) to many-body and screening effects of the static polarizability, which are not present in TS model. Tkatchenko et al.\(^{185}\) have included these effects that go beyond a pairwise \(C_6/R^6\) summation by extending the TS scheme to a many-body dispersion (MBD) method. PBE+MBD (PBE0+MBD) was shown to reduce the overbinding behavior of PBE+TS (PBE0+MBD)\(^{185}\) and to be substantially more accurate for molecular solids\(^ {172}\). The authors of Refs.172,185–187 further argue that MBD interactions are already significant for small molecules, as given in the S66 test set, for which they report a MAPE of 6.1% for PBE0+MBD.

However, the results above offer an additional perspective: Alternatively to MBD, also a suitable choice of the DFT functional improves the TS method—at least for small molecules, for which the S66 set is representative. Indeed, PBE0+MBD has a very similar performance for the S66 than PBEh(\(\alpha^*\))+TS with MAPEs of 6.1% and 6.5%, respectively.

Focusing on the TS starting point dependence, I will argue subsequently that the improved performance of PBEh(\(\alpha^*\))+TS results from the damping function present in the TS method. To this end, the binding curve of the Pentane dimer (item number 34 in the S66 test set) is plotted in Fig. 3.11. Geometries and CCSD(T) reference data were taken from the S66×8 set.\(^ {167}\) The pentane dimer is that element of the S66 test set, for which PBE+TS exhibits the largest deviation with respect to the CCSD(T). Figure 3.11 (a) shows that the PBE+TS overbinds by about 60 meV near the equilibrium distance (\(d \sim 1\)). While all TS corrected functionals predict slightly too large equilibrium distances, the binding curves are shifted towards the CCSD(T) reference curve upon increasing the fraction of exact exchange. As a consequence, the PBEh(\(\alpha^*\))+TS binding curve is close the reference curve.
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Figure 3.11: Binding curves for the pentane dimer (illustrated in the inset) obtained by the TS method (a), and its contributions from the (generalized) Kohn-Sham (G)KS functionals (b), the TS-vdW tail (c), and the TS-vdW tail where the $s_R$ parameter is set to one (d). The binding distance is given by the scaling parameter $d$ with respect to the equilibrium distance. The CCSD(T) reference curve was taken from Ref. 167.

Tracing the reason for this observation, Fig. 3.11 (b) and (c) show the binding contribution from the (G)KS functionals and their TS corrections, respectively. Without the TS contribution —Fig. 3.11 (b)— all functionals predict a basically unbound pentane dimer due to the lack of the long range vdW part in the PBE hybrid family of XC functionals. Near the equilibrium geometry, all three functionals give binding curves that differ among each other to a minor extent, and hence, are not the main reason for the trend observed in Fig. 3.11 (a). As a consequence, the difference in the binding curves of Fig. 3.11 (a) must arise predominantly from the TS correction.
Table 3.3: Range seperation parameter $s_R$ and MAPEs for the S22 test set\textsuperscript{104} for the PBE, PBE0 and PBEh($\alpha^*$) functional. The errors are relative to CCSD(T) extrapolated to the complete basis set limit taken from reference\textsuperscript{188}.

<table>
<thead>
<tr>
<th></th>
<th>$s_R$</th>
<th>H-bonds</th>
<th>Dispersion</th>
<th>Mixed</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE</td>
<td>0.94</td>
<td>8.1%</td>
<td>106.7%</td>
<td>51.8%</td>
<td>57.8%</td>
</tr>
<tr>
<td>PBE0</td>
<td>0.96</td>
<td>7.3%</td>
<td>104.6%</td>
<td>46.8%</td>
<td>55.2%</td>
</tr>
<tr>
<td>PBEh($\alpha^*$)</td>
<td>1.02</td>
<td>6.4%</td>
<td>96.6%</td>
<td>32.2%</td>
<td>47.8%</td>
</tr>
</tbody>
</table>

Indeed, Fig. 3.11 (b) shows that the TS correction differs significantly between the individual functionals, in particular in a regime near the equilibrium distance. In principle, the reason could be twofold: By the density dependence of the $C_6[\rho]$ coefficients (equation 2.72), which could be different for different $\alpha$ values, or, by the range separation parameter $s_R$ of the damping function (equation 2.73). Figure 3.11 (d) shows the TS correction for all three functionals where the $s_R$ parameter is set to unity. All three curves are essentially on top of each other, implying that the $C_6$ coefficients do not change with $\alpha$. \textit{Tertium non datur}, it is the $s_R$ parameter in the damping function that causes the difference in the curves of Fig. 3.11 (c), and hence, of Fig. 3.11 (a).

The $s_R$ parameter is the empirical part of the TS method. Thus, from a theoretical point of view, the strong dependence on the $s_R$ parameter is an unpleasant feature of the TS approach, and has been observed before by means of a sensitivity analysis.\textsuperscript{106} The TS scheme obtains\textsuperscript{87} the $s_R$ parameter by a fit to CCSD(T) reference data extrapolated to the complete basis set limit\textsuperscript{188} of the S22 data set.\textsuperscript{104} The S22 test set is the forerunner of the S66 test set containing 22 gas phase dimers of hydrogen, dispersion, and mixed bond types. The $s_R$ fit needs to be done for each functional; the ensuing $s_R$ values are collected in table 3.3. As a function of $\alpha$ the $s_R$ parameter increases from 0.94 (PBE) to 1.02 (PBEh($\alpha^*$)).\textsuperscript{d} The $s_R$ parameter in the damping function as given by Eq. (2.73) determines the onset of the vdW tail, whereas larger $s_R$ values result in a reduction of the vdW correction. Therefore, PBEh($\alpha^*$)+TS is less attractive and alleviates the overbinding behavior of PBE+TS or PBE0+TS.

The reason for an increase of $s_R$ upon increasing $\alpha$ is also given in table 3.3. In spite of the large error for the PBE hybrid family of XC functionals when dispersion contributions are important, there is a clear trend: The error reduces for all bonding types present in the S22 upon increasing $\alpha$. Now, the TS scheme obtains $s_R$ by fitting to the S22 test set. If the underlying functional is already in

\textsuperscript{d}I thank Alexandre Tkatchenko for providing this value.
better agreement with the CCSD(T) reference data, the vdW contribution reduces; within the TS formalism this can only be achieved by ‘pushing’ the vdW tail further out via increasing the $s_R$ parameter in the damping function. Hence, PBEh($\alpha$) is assigned the largest $s_R$ parameter among all considered functionals.

In summary, various theoretical approaches were benchmarked against the S66 dataset. It was shown, that rPT2 –the most recent RPA-based method– strongly depends on the starting point. Only rPT2@PBE significantly improves the underbinding behavior of EX+RPA. For other starting points than PBE, the addition of the rSE and SOSEX correction is less effective (PBE0) or even a drawback (PBEh($\alpha^*$)). Instead of trying to improve the underbinding behavior of EX+cRPA via rPT2, an alternative total energy ansatz, EX@PBEh($\alpha^*$)+cRPA@PBE was suggested. It was demonstrated that this ansatz performs better than rPT2@PBE for the S66 test set, and gives a remarkable accuracy for the benzene dimer, for which other RPA-based method significantly underestimate the binding energy. In contrast to rPT2, PBEh($\alpha^*$) was proven to significantly improve the performance of the Tkatchenko-Scheffler scheme that adds the long range $1/R^6$ van der Waals tail to a given functional. This has been attributed to a larger value of the range separation parameter contained in the damping function, which results from an overall error reduction of the plain PBEh($\alpha^*$) functional as compared to PBE or PBE0 for the S22 test set.

### 3.3.3 Atomization energies: The G2-1 testset

The atomization energy of a molecule determines the ability of a molecule for bond braking and bond making. It is defined as the ground state energy difference of the molecule $E_{mol}$ and the sum of it of the individual atoms $E_{\text{atom}} := - (E_{mol} - \sum_i E_{\text{atom}}^i)$. The minus sign takes into account that it takes energy in order to break a molecule into its atoms. The G2-1 test set contains 55 small molecules with experimental reference values that are corrected for zero-point effects.

Figure 3.12 shows the MAPEs, whereas the detailed numerical results are given in tables A.6 and A.7 of appendix A.4. Following Ren et al., a Gaussian cc-pV6Z basis set was used and a counterpoise correction performed. EX+cRPA@PBE and r2PT@PBE results for the G2-1 have been published by Paier et al. and Ren et al.

rPT2 strongly depends on the underlying XC functional. Among the three considered starting points, rPT2@PBE shows the best performance with a MAPE of 2.8%. Increasing the fraction of exact exchange $\alpha$ in the DFT functional results in the tendency of rPT2 to underestimate atomization energies. The pronounced rPT2 starting point dependence emerges from both the rSE and SOSEX correction to EX+cRPA. EX+cRPA itself depends relatively weakly on the starting point,
3.3 Assessment of correlation energies

whereas it has the overall tendency to underestimate atomization energies. That EX+cRPA@PBE underestimates atomization energies has been first observed by Furche\textsuperscript{184} and repeatedly reported in the literature for the G2-1 set.\textsuperscript{94,111,164,166} However, Fig. 3.12 and table A.6 additionally indicate that this behavior is independent of the starting point, at least within the PBE hybrid family of XC functionals. The inclusion of the rSE correction increases atomization energies and thus appears to be beneficial, irrespective of the underlying functional. However, the magnitude of the rSE correction depends sensitively on the functional and reduces upon increasing $\alpha$. In particular, for the PBEh($\alpha^*$) functional the rSE correction is very small, leading to a very small improvement in error of 0.2\% compared to EX+cRPA@PBEh($\alpha^*$).

The SOSEX correction is even more dependent on the starting point. SOSEX@PBE0 or SOSEX@PBEh($\alpha^*$) tends to decrease atomization energies. As a consequence, adding SOSEX to EX+cRPA degrades the description of atomization energies for these two starting points. While this effect is negligible for SOSEX@PBE0 (the MAPE increases by 0.2\%) this downgrade in accuracy amounts to a 2.3\% higher MAPE for the PBEh($\alpha^*$) starting point. On the other hand, SOSEX@PBE increases atomization energies, with a reduction in error that is similar than rSE@PBE. As a consequence adding up both, which eventually leads to rPT2@PBE abates the notorious underestimation of atomization energies present in EX+cRPA@PBE. This improvement is reduced for rPT2@PBE0 which still ben-
efits to some extent from the rSE correction, while the SOSEX correction makes rPT2 perform worse than EX+cRPA for the PBEh(α*) starting point.

The proposed total energy ansatz EX@PBEh(α*)+cRPA@PBE has a MAPE of 4.5% and performs thus similar to EX+cRPA+rSE@PBE or EX+cRPA+SOSEX@PBE. Therefore, it partially alleviates the underbinding of EX+cRPA, though it still tends to underestimate atomization energies. In contrast to weak interactions, rPT2@PBE appears to be more accurate than EX@PBEh(α*)+cRPA@PBE in the prediction of atomization energies. Thus, among all RPA based methods considered in this study, rPT2@PBE is the most accurate one for predicting atomization energies. At the same time PBE0 gives the overall most accurate atomization energies. PBE0 has a MAPE of 2.7%, which is slightly lower than the 2.8% MAPE of rPT2@PBE. Figure 3.12 shows that the error for the PBE hybrid family of XC functionals itself strongly depends on the fraction of exact exchange α. PBE tends to overestimate atomization energies, whereas an increase of α decreases atomization energies. This lets PBEh(α*) underestimate atomization energies and, as a consequence, the best performing α value should lie in between zero and α*, which is met by PBE0 (α = 1/4) for the set of considered functionals.

3.3.4 Hydrogen-transfer and non-hydrogen transfer barrier heights: The HTBH38 and NHTBH38 testsets

Chemical reaction barrier heights —defined as the energy difference between the reactants and the transition state— play a decisive role in the description of chemical reactions. This work considers the HTBH38\textsuperscript{169} and NHTBH38\textsuperscript{170} testset by Truhlar and co-workers. Each of which contains forward and backward barrier heights of 19 hydrogen transfer reactions (HTBH38) and non-hydrogen transfer reactions (NHTBH38). The latter contains heavy-atom transfer, nucleophilic substitution, unimolecular und association reactions.

Figure 3.13 shows the MAPEs, whereas the detailed numerical results are given in tables A.8–A.11 of appendix A.4. The reference data were obtained either using the Weizmann-1 theory\textsuperscript{190} or by other “best theoretical estimates”, as detailed in Refs. 169,170. EX+cRPA@PBE has been benchmarked before by Eshuis et al.\textsuperscript{129}, Paier et al.\textsuperscript{166}, and Ren et al.,\textsuperscript{94,111} whereas the latter authors also present rPT2@PBE results. Following Ren et al.,\textsuperscript{94,111} this work obtained the results with the Gaussian cc-pV6Z basis set.

In general, the scale of Fig. 3.13 implies that all considered methods perform much worse for barrier heights as compared to atomization energies or weak interactions. In particular non-hydrogen transfer barrier heights appear problematic. While rPT2@PBE exhibits a slightly better performance as rPT2@PBE0 for HTBH38, the PBE0 starting point appears much more accurate than PBE for
3.3 Assessment of correlation energies

<table>
<thead>
<tr>
<th>Method</th>
<th>HTBH MAPE</th>
<th>NHTBH MAPE</th>
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<td>GKS</td>
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<td>rPT2</td>
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<td>EX@PBEh(α*)+cRPA@PBE</td>
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Figure 3.13: Mean absolute percentage error (MAPE) of the HTBH38 and NHTBH38 testsets for barrier heights obtained with different total energy methods (using the Gaussian cc-pV6Z basis set). The errors are relative to reference data of Refs. 169 and 170 for HTBH38 and NHTBH38, respectively.

NHBH38. Therefore—in contrast to the previous testsets— rPT2@PBE0 shows the best rPT2 performance for barrier heights. However, for all three starting points adding SOSEX and rSE corrections adulterate the results as compared to EX+cRPA. In average, adding the rSE correction to EX+cRPA underestimates barrier heights while the SOSEX correction exhibits the opposite behavior. These errors cancel each other partly upon combining these schemes to rPT2. On the EX+cRPA level the starting point dependence is most pronounced for non-hydrogen transfer reactions, for which EX+cRPA@PBE tends to underestimate barrier heights. Increasing \(\alpha\) in the PBE hybrid functional results in increased EX+cRPA barrier heights, whereas the choice \(\alpha = 1/4\), i.e., the PBE0 functional yields the best agreement with the reference barrier heights. Further increasing \(\alpha\) to PBEh(\(\alpha^*\)) overshoots non-hydrogen transfer barrier heights quite significantly.
3 Methodology

The trend of increased barrier heights upon increasing $\alpha$ is already present for the PBE hybrid family itself. PBE tends to underestimate barrier heights, whereas PBEh($\alpha^*$) overestimates them. As a consequence, a functional with an intermediate value of $\alpha$ should give the best compromise. For the considered set of functionals this is achieved by PBE0, which exhibits the lowest MAPE while still having the tendency to underestimate barrier heights.

EX@PBEh($\alpha^*$)+cRPA@PBE performs disappointingly for barrier heights. While it competes with rPT2@PBE for weak interactions (S66 test set) and atomization energies (G2-1 test set) it fails in predicting barrier heights. From table A.11 and A.9 it follows that EX@PBEh($\alpha^*$)+cRPA@PBE clearly underestimates barrier heights.

As already remarked by Ren et al.\textsuperscript{111} EX+cRPA has the best performance in predicting barrier heights. As an additional insight of the present study it was shown that EX+cRPA@PBE0 gives the overall best performance for both hydrogen transfer and non-hydrogen transfer barrier heights.

3.3.5 A pathological case: TTF-TCNQ

While the above benchmark calculations lend itself to the conclusion that rPT2@PBE gives an overall satisfying performance, the next section will demonstrate that the PBE starting point may lead to unphysical results. In Section 3.2 it has been argued that PBEh($\alpha^*$) significantly reduces the self-interaction error (SIE) within the PBE hybrid family. While the above test sets do not include cases where the SIE strikes qualitatively the performance of PBE, the subsequent example of TTF-TCNQ does. This will highlight the importance of improving the rPT2 theory such that it will get compatible with DFT functionals, which reduce the self-interaction error. Furthermore, the impact of the self-interaction error on the Tkatchenko-Scheffler\textsuperscript{87} scheme will be discussed. In order to disentangle the vdW contributions, the performance of various DFT functionals will be discussed as well.

(Generalized) Kohn-Sham schemes

First, the binding curves for various semilocal (PBE, revPBE, and LDA), standard hybrid (PBE0 and HSE06), and the PBEh($\alpha$) XC functionals are investigated. Figure 3.14 (a) shows the intermolecular binding energy $E_b$ as a function of the TTF-TCNQ distance. The dimer geometry is the same as in Sections 3.1 and 3.2 (i.e. a dimer was cut out of an interface of TTF and TCNQ crystals along the [001] surface of TCNQ, with $d_0$ being the equilibrium interface distance on the PBE+vdW level of theory). An illustration of this geometry is given in Figure 3.3 (b).
3.3 Assessment of correlation energies

Figure 3.14: (a) Binding curves for various semilocal (gray) and hybrid (black) XC functionals for the TTF-TCNQ complex. The red curve shows the PBEh(α*) result, and the dotted ones are TS-vdW corrected results. (b) shows the corresponding transfer energies $E_t$; its minimum determines the asymptotic limit of the binding energy.

The binding curves among different functionals differ in the location of the minimum of $E_b$. The minimum of $E_b$ determines the equilibrium intermolecular binding distance ($d_b$) and the associated binding energy $E_b(d_b)$. Table 3.4 summarizes the fitted binding distance —with respect to the interface equilibrium distance—, and binding energies for a set of XC functionals. All functionals predict a dimer binding distance $d_b$, that is shifted towards larger distances as compared to the PBE+vdW interface distance $d_0$. The LDA gives the shortest binding distance and the highest binding energy. Compared to the LDA, the semilocal PBE and revPBE functional predict larger $d_b$ at a reduced binding energy. The binding energy is further reduced for hybrid functionals. Among the hybrids, HSE06 gives
Table 3.4: Equilibrium intermolecular TTF/TCNQ binding distance $d_b$ (with respect to the TTF-TCNQ interface distance $d_0$), equilibrium binding energy $E_b(d_b)$ and the asymptotic binding energy $E_b(\infty)$. The equilibrium distance and binding energy was obtained by a fit to the minimum of the binding curve, whereas $E_b(\infty)$ was obtained by a fit to the minimum of the transfer energy.

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>PBE</th>
<th>revPBE</th>
<th>HSE06</th>
<th>B3LYP</th>
<th>PBE0</th>
<th>PBEh($\alpha^*$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_b - d_0$ [Å]</td>
<td>0.111</td>
<td>0.340</td>
<td>0.538</td>
<td>0.379</td>
<td>0.519</td>
<td>0.451</td>
<td>0.505</td>
</tr>
<tr>
<td>$E_b(d_b)$ [eV]</td>
<td>0.404</td>
<td>0.305</td>
<td>0.266</td>
<td>0.160</td>
<td>0.106</td>
<td>0.148</td>
<td>0.052</td>
</tr>
<tr>
<td>$E_b(\infty)$ [eV]</td>
<td>0.180</td>
<td>0.160</td>
<td>0.154</td>
<td>0.066</td>
<td>0.024</td>
<td>0.008</td>
<td>0.0</td>
</tr>
</tbody>
</table>

the largest and PBEh($\alpha^*$) the lowest binding energy, which amounts to 0.16 and 0.05 eV respectively. The intermolecular binding distances predicted by hybrid functionals lie in between the lowest HSE06 and the highest B3LYP result (not shown in Figure 3.14 (a)).

None of the considered functionals contains the long range $1/R^6$ vdW tail. The addition of vdW interactions\(^{87}\) according to Tkatchenko and Scheffler leads to an enhancement of the binding well, which results in larger binding energies at lower binding distances. For the case of the PBE hybrid family this is shown by the dotted curves in Figure 3.14 (a). The binding distance upon addition of vdW corrections to the standard (PBE, B3LYP, PBE0) functionals reads (0.283, 0.345, 0.365) Å, with a binding energy of (0.341, 0.145, 0.180) eV, whereas the PBEh($\alpha^*$) functional predicts an equilibrium distance of 0.389 Å with a binding energy of 0.084 eV. Hence, the Tkatchenko-Scheffler scheme\(^{87}\) reduces the binding distance by about 0.1-0.2 Å and increases the equilibrium binding energy by about 30-40 meV, depending on the functional.

All vdW corrected functionals differ significantly in their predicted binding energy —in particular PBE+vdW and PBEh($\alpha^*$)+vdW differ by a factor of four. The reason becomes obvious from the long range behavior of the binding curves in Figure 3.14 (a). The long range behavior is dictated by the underlying functional since the vdW contribution decays to zero. None of the standard functionals exhibits a binding energy that decays to zero in the long range. Such a behavior is counter intuitive, since in the large separation limit the intermolecular interaction should vanish. While $E_b$ goes to zero only for PBEh($\alpha^*$), the remaining state-of-the-art functionals have binding curves that appear to be shifted downwards in energy. The asymptotic behavior of the binding curves may be analyzed in terms of the transfer energy $E_t$. The minimum of the transfer energy determines both, the asymptotic limit of charge transfer and the binding energy $E_b(\infty)$. $E_t$
3.3 Assessment of correlation energies

is plotted in Figure 3.14 (b). The determination of $E_b(\infty)$ is sketched by gray and red arrows for semilocal and the PBEh($\alpha^*$) functional respectively. Numerically, $E_b(\infty)$ as determined by the transfer energy coincides with that obtained by the binding curve for distances $d - d_0 > 10$ Å.

Table 3.4 compiles the fitted values for $E_b(\infty)$. Semilocal functionals exhibit an asymptotic binding energy of 0.5-0.8 eV, which is significantly reduced for hybrid functionals, and zero for PBEh($\alpha^*$). $E_t$ as defined in Equation (3.7) is an energetic measure for charge transfer if the two molecules do not interact. For semilocal functionals, the systems gains energy upon fractional charge transfer (gray lines in Figure 3.14 (b)), which is responsible for the non-zero binding energy in the asymptotic limit. This behavior is reduced for hybrid functionals, albeit still present for HSE06, PBE0 or B3LYP (not shown in the Figure).

From Figure 3.14 (b), it follows that the minimum for standard semilocal and hybrid functionals is caused by the convexity of $E_t$. On the other hand side, if a density functional is many electron SI free, then $E_t$ is piecewise linear between integer charges. Conversely, a convex $E_t$ curve between integer charges implies that a density functional suffers from the many electron SIE. As a consequence the SIE present in standard semilocal and hybrid functionals implies a non-vanishing binding energy between the non-interacting TTF and TCNQ molecule. In contrast, PBEh($\alpha^*$) shows a piecewise linear $E_t$ curve, with the minimum located at zero charge transfer and zero $E_t$. This renders PBEh($\alpha^*$) to have the correct asymptotic behavior for both, charge transfer and binding energy.

Adding the vdW term gives an attractive contribution to the binding energy. As shown in Fig. 3.14 (a), this results in an enhanced overbinding behavior for functionals that predict a wrong charge density caused by the SIE. In particular, this rules out PBE+vdW and PBE0+vdW to give sensitive results for the TTF/TCNQ dimer. In contrast, PBEh($\alpha^*$) is not exposed to these complications. From this, together with the benchmark performance for the S66 (Section 3.3.2), it follows that PBEh($\alpha^*$)+vdW gives the most accurate vdW-corrected description of the TTF/TCNQ dimer with a binding energy of about 80 meV. This is in very good agreement with the estimate of $80 \pm 10$ meV based on more sophisticated quantum-chemical methods given below.

It should be noted that the presence of the SIE is a sufficient but not necessary condition for asymptotic charge transfer or non-zero binding energy, for two reasons: First, even if the SIE exists for a given density functional, the $E_t$ curve could be still linear. This can happen if the SIE manifests itself in a delocalization error (i.e. the total energy is convex as a function of fractional charge) for one subsystem and a localization error (i.e. the total energy is concave as a function of fractional charge) for the other subsystem. In principle both errors could cancel and thereby yield a linear $E_t$. Second, even if $E_t$ is a convex function
between integer charges, its minimum could be still located at zero asymptotic charge transfer/binding energy. In other words, the convexity does not cause $E_t$ to cross the zero-line in Figure 3.14 (b)) at fractional charge. As a consequence, the SIE would not introduce qualitative errors.

In summary, the performance of vdW corrected DFT functionals in describing the binding energy of the TTF-TCNQ complex was investigated. It was found that all standard semilocal and hybrid functionals give a spurious attractive binding contribution in the long-range limit, which is caused by the many electron SIE. As a consequence the addition of an attractive vdW correction is not beneficial. In particular, for the TTF-TCNQ complex, this rules out PBE+vdW and PBE0+vdW, and only PBEh($\alpha^*$)+vdW was shown to give sensitive results.

RPA based methods

Turning to RPA-based methods, Fig. 3.15 (b) shows that rPT2@PBE qualitatively fails in describing the TTF-TCNQ complex. In the long range limit (about 4 Å away from the equilibrium) rPT2@PBE predicts an intermolecular repulsion energy of about 0.7 eV. This is unphysical, since in the long range the TTF-TCNQ binding energy should approach zero. This unphysical behavior is already present for EX+cRPA@PBE, for which the addition of (renormalized) SE and SOSEX is not able to cure the incorrect binding behavior at large intermolecular separation. EX+cRPA@PBE0 also predicts an erroneous binding curve although less pronounced as for the PBE starting point. Among the considered starting points, only PBEh($\alpha^*$) shows a physically meaningful behavior since EX+cRPA@PBEh($\alpha^*$) decays to zero at large intermolecular separation.

The binding curves near the equilibrium distance for various subdiagrams of rPT2@PBEh($\alpha^*$) is shown in Fig. 3.15 (a). For comparison, also the binding curve obtained by second order Møller-Plesset perturbation theory (MP2) is shown. The fitted equilibrium binding distances and energies are summarized in Table 3.5. rPT2@PBEh($\alpha^*$) results in an enhanced binding well as compared to PBEh($\alpha^*$) and slightly reduces the intermolecular binding distance. However, in line with Section 3.3.2 the addition of rSE+SOSEX gives only a small contribution to EX+cRPA for PBEh($\alpha^*$) reference states. Therefore, the rPT2 and EX+cRPA binding cures agree closely. MP2 on the other hand predicts a deeper binding well at shorter binding distances as the RPA-based methods. The S66 benchmark calculations in Section 3.3.2 have revealed that EX+cRPA@PBEh($\alpha^*$) has the tendency to underestimate binding energies. At the same time, MP2 has the tendency to overestimate dispersion interaction energies. Therefore, the binding energy for the given TTF-TCNQ complex can be estimated to 80 ± 10 meV. A brief comparison to Table 3.4 underlines the previous conclusions for DFT functionals, based on the SIE: the binding energy obtained by standard functionals overshoots this
3.3 Assessment of correlation energies

Figure 3.15: (a) EX+cRPA binding curves near their minimum for PBEh(α*) (red) and HF (black) unperturbed reference states for the TTF-TCNQ complex (see Figure 3.3 (b) for the geometry). Also shown are rPT2@PBEh(α*) and MP2 result as well as the addition of renormalized single excitations, rSE, to EX+cRPA@PBEh(α*) (they vanish for HF reference states). (b) compares the long range binding behaviour for PBE, PBE0 (black) and PBEh(α*) (red) reference states.

The addition of pairwise vdW interactions increases the binding energy further, such that all vdW corrected standard functionals give binding energies that are at least a factor of two higher than the estimated 80 meV obtained by the limiting EX+cRPA@PBEh(α*) and MP2 methods.

Returning to the erroneous binding curve of rPT2@PBE, it is interesting to observe that the inclusion of exact exchange and SOSEX still predicts physically wrong results. One might expect that exact exchange cancels the Hartree self-interaction error and SOSEX alleviates the self-correlation error present in the estimated value.
Table 3.5: Equilibrium intermolecular TTF/TCNQ binding distance \( d_b \) (with respect to the TTF-TCNQ interface distance \( d_0 \)), and the equilibrium binding energy \( E_b(d_b) \). The results were obtained by a fit to the minimum of the binding curve in Figure 3.15 (a).

<table>
<thead>
<tr>
<th></th>
<th>( d - d_0 ) [Å]</th>
<th>( E_b(d_b) ) [meV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBEh(( \alpha^* ))</td>
<td>0.505</td>
<td>52</td>
</tr>
<tr>
<td>rPT2@PBEh(( \alpha^* ))</td>
<td>0.477</td>
<td>76</td>
</tr>
<tr>
<td>EX+cRPA@PBEh(( \alpha^* ))</td>
<td>0.459</td>
<td>74</td>
</tr>
<tr>
<td>MP2</td>
<td>0.375</td>
<td>95</td>
</tr>
</tbody>
</table>

RPA correlation energy.\(^{192}\) However, in rPT2 the exact exchange and SOSEX subdiagrams are evaluated in a non-self consistent fashion. Therefore, these terms remove the Hartree self-interaction and the RPA self-correlation only from the energy but not from the orbitals. On the other hand in Section 3.1 it was shown that PBE gives a qualitatively wrong charge density, indicating that the additional effect from the orbitals may be significant.

In order to proceed, the special case of EX+cRPA is considered focusing at large intermolecular TTF-TCNQ separation distances. Figure 3.16 (a) shows the EX+cRPA@PBEh(\( \alpha \)) binding energy as a function of \( \alpha \) at an intermolecular distance of \( d - d_0 = 8 \) Å. For EX+cRPA@PBEh(\( \alpha \)), \( E_b \) decreases strictly monotonically to zero in the interval \([0, 0.3]\), whereas the underlying PBEh(\( \alpha \)) functional increases strictly monotonically to zero in the same interval. For \( \alpha > 0.3 \) both EX+cRPA@PBEh(\( \alpha \)) and PBEh(\( \alpha \)) have zero binding energy. A critical \( \alpha \)-value of 0.3 is in line with Section 3.1, where it was argued that \( \alpha > 0.3 \) gives a qualitative correct level alignment between the TTF-HOMO and the TCNQ-LUMO level (cf. Figure 3.4).

On the DFT side, a PBEh(\( \alpha \)) functional with \( \alpha < 0.3 \), allows the TTF-TCNQ complex to gain energy via some partial electron transfer from TTF to TCNQ, which is caused by the SIE. This allows for a wrongly, non-zero attractive binding energy in the large separation limit. The asymptotic limit for the binding energy may be obtained by the minimum of the transfer energy \( E_t \), which is illustrated for PBE=PBEh(\( \alpha = 0 \)) by the black dashed curve in Figure 3.16 (c). The lower red circle indicates the PBE-minimum of \( E_t \). Since the PBE calculation is performed in a self-consistent fashion, the charge density will follow this minimum and the system will exhibit an attractive binding energy in the asymptotic limit.

On the other hand, EX+cRPA@PBE is not carried out self-consistently, and is therefore based on the PBE charge density (red solid arrow in Figure 3.16 (c)). On top of the PBE electron density, the transfer energy for EX+cRPA@PBE is
3.3 Assessment of correlation energies

Figure 3.16: (a) long range \((d - d_0 = 8 \text{Å})\) binding energy for the TTF-TCNQ dimer as a function of exact exchange \(\alpha\). (b) PBE (black dashed) and EX+cRPA@PBE (black solid) binding energy as a function of the TTF-TCNQ distance (see Figure 3.3 (b) for the geometry). (c) PBE and EX+cRPA@PBE transfer energy \((E_t)\) as a function of transferred charge (a positive sign indicates partial electron transfer on the TCNQ molecule). The lower red circle indicates the PBE-minimum of \(E_t\), whereas the upper one shows the corresponding EX+cRPA@PBE result at that minimum.

strongly repulsive (upper red circle), and so is the asymptotic limit of the binding energy, which is plotted in Figure 3.16 (b). It is worth stressing, that the convexity-caused minimum of the PBE transfer energy is a consequence of the spurious SIE. A different XC functional —such as PBEh(\(\alpha^*\))— that does not qualitatively suffer from the SIE, will have its minimum at zero charge transfer and \(E_t\). As a result, the subsequent EX+cRPA calculation will have the correct asymptotic limit. From this perspective, one may conclude, that a non-self consistent EX+cRPA calculation ‘inherits’ the SIE of the underlying DFT functional.

Summary and discussion

In summary, this section investigated the starting point dependence of rPT2 and its subdiagrams. It extended the previously published rPT2@PBE results to two alternative starting points: The commonly used PBE0 and the PBEh(\(\alpha^*\)) XC functional, whereas the latter greatly reduces the self-interaction error present in standard XC functionals. As a main result, rPT2 depends quite sensitively on
the starting point with a clear trend of performance loss upon increasing the fraction of exact exchange $\alpha$ in the DFT functional. As a consequence, this confirms the conclusion already drawn by Ren et al, that rPT2@PBE gives the most “balanced” description over different chemical and electronic environments. The word “balanced” needs to be taken in its full semantic elasticity since for none of the individual test sets rPT2@PBE outperforms all other methods.

The superior PBE starting point for the rPT2 method poses the question whether it is the specific parametrization of PBE itself that makes its spectrum suited for rPT2, or —more fundamentally— whether the rPT2 method constrained to reference orbitals that come from a Kohn-Sham (KS) system (recall that PBE0 and PBEh($\alpha^*$) are considered within the generalized Kohn-Sham (GKS) framework that allows for a non-local treatment of exact-exchange). The authors of Ref. 111 claim that rPT2 shall be used with KS reference orbitals, but unfortunately do not give any reason why this constraint is necessary. In addition, rPT2@PBE0 performs significantly better for non-hydrogen barrier heights or hydrogen bonds than rPT2@PBE, indicating the GKS orbitals may be indeed compatible. Whether or not rPT2 is restricted to Kohn-Sham orbitals would be important to know, in particular in the light of the poor performance of the PBEh($\alpha^*$) starting point.

Furthermore it was shown that rPT2@PBE gives qualitatively wrong results for the TTF-TCNQ dimer, which was traced back to a wrong PBE charge density. Hence, the presented results motivate future research on the compatibility of rPT2 with GKS starting points in general, and, in particular, how to extent rPT2 such that the starting point dependence gets reduced.
4 Local minima on the Born-Oppenheimer surface

In Chapter 2 the DFT formulation for the ground state energy in an external potential $v$ was presented. Within the Born-Oppenheimer approximation $v$ is generated by the nuclei according to Eq. (2.3). The Born-Oppenheimer potential energy is given by the sum of the electronic energy and the nuclear-nuclear repulsion term

$$E = E_v[\rho] + \frac{1}{2} \sum_{\alpha \neq \beta}^{N_a} \frac{Z_\alpha Z_\beta}{|R_\alpha - R_\beta|}, \quad R_\alpha \in \mathbb{R}^3. \quad (4.1)$$

The sum runs over all $N_a$ atoms of the system with $R_\alpha$ and $Z_\alpha$ being the position and nuclear charge of atom $\alpha$. The map $\{R_\alpha\} \mapsto E$ according to Eq. (4.1) defines the potential energy surface (PES). If the nuclei are regarded as classical objects, then at low temperature their motion may be neglected as a first approximation. The stable and metastable nuclear geometries will be located at the minima of the PES.

This Chapter is concerned with finding the local minima: first, gradients on the PES will be introduced within the framework of DFT. Second, two standard numerical techniques for finding local minima will be presented. Finally, the implementation of the unit cell relaxation will be illustrated.

4.1 Energy derivatives

This section introduces two types of energy derivatives. The derivative with respect to atomic positions yields atomic forces, while the derivative with respect to the strain tensor gives the stress tensor.
4 Local minima on the Born-Oppenheimer surface

4.1.1 Atomic forces

The atomic forces are defined by \(-dE/dR\). From Equation (4.1) the energy derivative with respect to atom \(\gamma\) reads,

\[
dE_{\gamma} = \frac{\partial}{\partial R_{\gamma}} \left[ E_v[\rho] + \frac{1}{2} \sum_{\alpha,\beta}^{N_a} \frac{Z_{\alpha}Z_{\beta}}{|R_{\alpha} - R_{\beta}|} \right] + \int \frac{\delta E_v[\rho]}{\delta \rho(r)} \frac{\partial \rho(r)}{\partial R_{\gamma}} d^3r, \quad (4.2)
\]

where the second term takes into account an implicit \(R_{\gamma}\)-dependence of the electron density. The electronic ground state energy is of the form \(E[\rho] = F[\rho] + \int \rho v\). Since \(F[\rho]\) is universal it does not depend explicitly on \(R_{\gamma}\). Hence, the only term that explicitly depends on \(R_{\gamma}\) is the external potential. Specifying it to the nuclear-electron interaction as given in Eq. (2.3) gives the term in the square bracket

\[
\frac{\partial}{\partial R_{\gamma}} \ldots = \int \rho(r) \frac{Z_{\gamma}(R_{\gamma} - r)}{|R_{\gamma} - r|^3} d^3r - \sum_{\alpha,\alpha \neq \gamma}^{N_a} Z_{\alpha} \frac{R_{\gamma} - R_{\alpha}}{|R_{\gamma} - R_{\alpha}|^3} =: -F_{HF}^{\gamma}, \quad (4.3)
\]

Taking the negative of this expression yields the so called Hellmann-Feynman force\(^{193,194}\), \(F_{HF}^{\gamma}\).

For an atom centered basis set like employed in FHI-aims, the charge density depends on the atomic positions, which leads to additional force contributions from the last term in Equation (4.2). In order to obtain these additional contributions, the variational term in Equation (4.2) is translated into the KS language by using Equation (2.27) and twice the chain rule,

\[
\int \frac{\delta E_v[\rho]}{\delta \rho(r)} \frac{\partial \rho(r)}{\partial R_{\gamma}} d^3r = \int \frac{\delta E_v[\rho]}{\delta \varphi_{\gamma}^*(r)} \frac{\delta \varphi_{\gamma}^*(r)}{\delta v_{KS}(r')} \frac{\delta v_{KS}(r')}{\delta \rho(r'')} \frac{\partial \rho(r'')}{\partial R_{\gamma}} d^3r d^3r' d^3r'' + c.c
\]

\[
= \int \frac{\delta E_v[\rho]}{\delta \varphi_{\gamma}^*(r)} \frac{\partial \varphi_{\gamma}^*(r)}{\partial R_{\gamma}} d^3r + c.c \quad (4.4)
\]

\[
= \sum_{i} f_i \int \left[ \left( -\frac{1}{2} \nabla^2 + v_{KS} - \epsilon_i \right) \varphi_i(r) \right] \frac{\partial \varphi_{\gamma}^*(r)}{\partial R_{\gamma}} d^3r + c.c \quad (4.5)
\]

\[
= 2 \text{Re} \sum_{i} f_i \left\langle \frac{\partial \varphi_i}{\partial R_{\gamma}}, \left( -\frac{1}{2} \nabla^2 + v_{KS} - \epsilon_i \right) \varphi_i \right\rangle =: -F_{\text{Pulay}}^{\gamma}, \quad (4.6)
\]

where \(f_i\) are the occupation numbers and c.c denotes the complex conjugate.

In Equation (4.5) the functional derivative with respect to the KS orbitals under the side condition of orbital normalization (using Lagrangian multipliers \(\epsilon_i\)) was evaluated. Expression (4.6) is also called Pulay term\(^{195}\). Expanding the KS orbitals \(\varphi_i\) in \(N_b\) atom centered basis functions \(\{\phi_{j(a)}(r - R_a)\}\) gives \(\varphi_i = \ldots\)
4.1 Energy derivatives

$\sum_{j(\alpha)}^N c_{ij(\alpha)} \phi_j(\alpha)(r - R_\alpha)$. Hence the partial derivative in Equation (4.6) in general does not vanish for this basis type (in contrast to plane waves for which the Pulay contributions vanish). The ‘ket’ part in Equation (4.6) are just the KS equations. This implies, that the Pulay contribution may be reduced with increasing accuracy of the solution of the KS equations\textsuperscript{196}.

The force on atom $\gamma$ is given by the negative of the sum of expression (4.3) and (4.6),

$$F_\gamma = F_\gamma^{\text{Pulay}} + F_\gamma^{\text{HF}} \in \mathbb{R}^3. \quad (4.7)$$

However, there are additional terms for GGA-type functionals and implementation specific contributions such as the multipole correction to the Hartree potential or grid effects (cf. Refs.\textsuperscript{132,197–200}).

4.1.2 Stress tensor

The formulation of stress in a quantum mechanical systems is based on the action principle by considering a class of wavefunction variations that emerge from scaling transformations of space. This approach has been pioneered by Fock\textsuperscript{201}, who considered the linear transformation $x \mapsto \lambda x, \lambda \in \mathbb{R}_{>0}$ acting on an arbitrary real space vector $x \in \mathbb{R}^3$. The scaling transformation that leads to the stress tensor is a generalization of the form

$$x \mapsto (1 + \varepsilon)x, \quad x \in \mathbb{R}^3, \quad 1, \varepsilon \in \mathbb{R}^{3 \times 3}, \quad \varepsilon = \varepsilon^T. \quad (4.8)$$

The $3 \times 3$ matrix $\varepsilon$ is also called strain tensor\textsuperscript{202} – it shall be symmetric, because an asymmetric part would act as a pure rotation\textsuperscript{203}. Equation (4.8) acts on all points $x$ in space. In particular for a solid with periodic boundary conditions, lattice vectors and atomic positions are deformed. A change in the geometric configuration changes the interatomic interaction energy but also also the electronic ground state energy, because the external potential is changed. The stress tensor $\sigma \in \mathbb{R}^{3 \times 3}$ is defined as the first order change of the total energy under a strain transformation\textsuperscript{204,205},

$$\sigma^{\mu\nu} := \frac{1}{\Omega} \left. \frac{\partial E}{\partial \varepsilon_{\mu\nu}} \right|_{\varepsilon_{\mu\nu}=0}, \quad (4.9)$$

where $\Omega$ is the unit cell volume and the derivative is taken component-wise. For a periodic system the total energy $E$ is understood as the periodic refinement of Equation (4.1), which takes into account lattice periodicity and treats the formally divergent nuclear-nuclear interaction by the Ewald method (for details see Ref.\textsuperscript{132}).

The concept of the stress tensor was introduced in the DFT framework by
Local minima on the Born-Oppenheimer surface

Nielsen and Martin\textsuperscript{204,205}, the remainder of this Section explains my implementation of the stress tensor and derives from the stress tensor a formula for forces on lattice vectors. The latter is necessary for the unit cell relaxation.

Equation (4.9) is implemented numerically by (i) applying two distortions per component, $\varepsilon_{\mu\nu} = h$, $\varepsilon_{\mu\nu} = -h$, (ii) calculating for each distortion the total energy and taking the difference $\Delta E$, and (iii) obtaining the derivative numerically

$$\sigma_{\mu\nu} \approx \frac{1}{\Omega} \frac{\Delta E}{2h}. \quad (4.10)$$

The step width $h$ should be chosen sufficiently small. At the same time $h$ must not be too small, which may lead to numerical noise caused by the discrete integration grid used by FHI-aims\textsuperscript{132,197}. Numerical tests for FCC-Al, cubic-Polyethylene, and diamond-Si crystals show that $h = 10^{-4}$ is a sensible choice (see Appendix A.2 for detailed convergence tests). Evaluation of the numerical stress tensor takes 18 total energy calculations. Taking into account the symmetry\textsuperscript{206} of $\varepsilon$ and thus of $\sigma$ this number reduces to 12. The computational burden could be further reduced if one calculates instead of the numerical stress tensor its analytic version (implemented into FHI-aims by Franz Knuth).

Once $\sigma$ is calculated, the forces on the lattice vectors can be determined. First, denote the component $\mu$ of the nuclear position $R_j$ by $R_{j\mu}$. The matrix $R = (R_1 \ldots R_{N_a})^T \in \mathbb{R}^{N_a \times 3}$ with components $R_{j\mu}$ contains in row $j$ the position vector $R_j$. Similar for the lattice vectors, where $a_{j\mu}$ shall be component $\mu$ of lattice vector $a_j$, and $a \in \mathbb{R}^{3 \times 3}$ being the corresponding matrix that contains the lattice vector components as entries. Since the external potential and the nuclear-nuclear interaction is determined by the lattice vectors and the atomic positions within the unit cell, the stress tensor may be written as

$$\Omega \sigma_{\mu\nu} = \frac{\partial E}{\partial R'_{j\gamma}} \frac{\partial R'_{j\gamma}}{\partial \varepsilon_{\mu\nu}} + \frac{\partial E}{\partial a'_{j\gamma}} \frac{\partial a'_{j\gamma}}{\partial \varepsilon_{\mu\nu}} \bigg|_{\varepsilon_{\mu\nu}=0}, \quad (4.11)$$

$$\frac{\partial}{\partial \varepsilon_{\mu\nu}} a_{j\gamma}' = \frac{\partial}{\partial \varepsilon_{\mu\nu}} a_{j\beta}(\delta_{\gamma}^{\beta} + \delta_{\lambda}^{\beta} \varepsilon_{\lambda\gamma}) = a_{j\mu} \delta_{\gamma}^{\nu} \quad (4.12)$$

where the sum convention over co- and contravariant indices was used and the prime indicates strained quantities. Equation (4.12) evaluates the derivative of the lattice vector components, using definition (4.8). Insertion of Eq. (4.12) and its
analogue for $\partial R'/\partial \epsilon_{\mu\nu}$ into Equation (4.11) gives

$$\Omega^{\mu\nu} = R_{j}^{\mu} \frac{\partial E}{\partial R_{j\nu}} + a_{j}^{\mu} \frac{\partial E}{\partial a_{j\nu}} = \left( R^{T} \frac{\partial E}{\partial R} \right)^{\mu\nu} + \left( a^{T} \frac{\partial E}{\partial a} \right)^{\mu\nu} \quad (4.13)$$

$$\Rightarrow -F_{\text{latt}} := \frac{\partial E}{\partial a} = \Omega a^{-1T} \sigma + (Ra^{-1})^{T} F, \quad (4.14)$$

where Equation (4.14) is understood as a matrix equation of $3 \times 3$ matrices and $F$ as the matrix of atomic forces. The force component $\alpha$ on lattice vector $a_i$ is given by the matrix component $F_{\text{latt}}^{i\alpha}$. The matrix product $Ra^{-1}$ translates the atomic positions from the standard basis $\{e_i\}$, $i = 1, 2, 3$, to that spanned by the lattice vectors $\{e_a\}$. Hence its entries are just the ‘fractional’ atomic coordinates. The forces on lattice vectors according to Equation (4.14) consist then of a contribution from the stress tensor and a contribution from ‘fractionally scaled’ atomic forces.

4.2 Local structure optimization

This Section reviews the basic concepts of local structure optimization and introduces the trust region and line search method, following the textbook by Nocedal and Wright.\textsuperscript{207}

Once the total energy $E$ and its derivatives are known for a given point on the PES this information can be used to find a local minimum. In order to treat atoms and lattice vectors on equal footing first define the object $x = \{a_{1x}, a_{1y}, \ldots, a_{3z}, R_{1x}, R_{1y}, \ldots, R_{Na}z\} \in \mathbb{R}^{3Na+9}$ which contains lattice vectors and atoms. The corresponding generalized force reads $f = -\partial_x E \in \mathbb{R}^{3Na+9}$. Its entries are given by the lattice vector forces, given by Equation (4.14) and the atomic forces which are given in Equation (4.7). If the PES is smooth, then a necessary condition for a point $x^*$ to be a local minimum is that the force vanishes

$$f(x^*) = 0, \quad (4.15)$$

and the Hessian matrix $\partial^2_x E|_{x^*}$ being positive semidefinite.

In the following two standard optimization schemes\textsuperscript{207} are presented, the line search method (LSM) and the trust region method (TRM). Both schemes iteratively search for structures that minimize the energy of a given system until the force condition (4.15) is satisfied. In order to stress the iterative nature the index $n$ is introduced to label the $n$th optimization step. The corresponding geometry and force at optimization step $n$ then reads $x_n$ and $f_n := f(x_n)$ respectively. The
4 Local minima on the Born-Oppenheimer surface

The basic idea is to approximate the PES by an harmonic model with respect to \( x_n \):

\[
M_n(x_n + s_n) := x_n - f_n^T s_n + \frac{1}{2} s_n^T H_n s_n,
\]

with \( H_n \in \mathbb{R}^{3N_a+9 \times 3N_a+9} \). Based on this a series of structures \( \{x_k\} \) is created which eventually converges to a local minimum \( \|x_k - x^*\|_2 \to 0 \).

If \( H_n \) is the Hessian matrix \( \partial^2 x_n E \) then \( M_n \) is the second order Taylor expansion of the PES. However, this need not be necessarily the case. In fact the power of the presented optimization techniques is that they do not rely on an exact Hessian and therefore are applicable to methods for which the calculation of the Hessian is prohibitively expensive (just like DFT). Instead of the exact Hessian, \( H_n \) is then an approximation to the Hessian which is updated during the optimization process starting from an initial guess \( H_0 \). The most common scheme for the update of the approximate Hessian in \textit{ab initio} structure optimization is the Broyden-Fletcher-Goldfarb-Shanno (BFGS)\textsuperscript{208,209} formula,

\[
H_{n+1} = H_n - \frac{H_n \Delta x_n \Delta x_n^T H_n}{\Delta x_n^T H_n \Delta x_n} - \frac{\Delta f_n \Delta f_n^T}{\Delta f_n^T \Delta x_n},
\]

with \( \Delta x_n = x_{n+1} - x_n \), \( \Delta f_n = f_{n+1} - f_n \). The approximate Hessian at optimization step \( n+1 \) is thus obtained by the one at step \( n \) plus additional information obtained from structural and force changes along the search direction. Obviously the BFGS update preserves symmetry if the initial guess is chosen to be symmetric. If \( H_0 \) is positive definite and \( \Delta f_n^T \Delta x_n < 0 \), then it can be shown\textsuperscript{207} that the BFGS update generates positive definite Hessian-approximations - this feature makes it particularly appealing for the line search method. In practice the initial guess \( H_0 \) is often taken as a multiple of the identity \( H_0 = \beta \cdot 1 \), \( \beta \in \mathbb{R}_{>0} \).

4.2.1 Line search method

The LSM\textsuperscript{207} uses the quadratic model PES (4.16) in order to obtain a search direction \( p_n \in \mathbb{R}^{3N_a+9} \) for each iteration. The optimization step \( s_n^* \) is obtained along \( p_n \) with a certain step length \( \alpha_n \in \mathbb{R}_{>0} \), \( s_n^* = \alpha_n p_n \). From the step the updated structure is then obtained by \( x_{n+1} = x_n + s_n^* \). The search direction \( p_n \) is typically chosen to be a descent direction, that is a direction for which the energy decreases: \( f_n^T p_n > 0 \) (forces are defined as the negative energy gradient). The harmonic model suggests to take that search direction which minimizes (4.16),

\[
p_n = H_n^{-1} f_n.
\]

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4.2 Local structure optimization

$p_n$ is also called Newton step for the exact Hessian and quasi Newton step for an approximate Hessian. However a (quasi) Newton step is only then a descent direction if the Hessian is positive definite, which is in general not the case. Therefore either the Hessian has to be modified in such a way that it gets positive definite, or the BFGS update is employed which assures a positive definite Hessian during the optimization process. This is the reason why in practice the line search method is tightly linked to the BFGS update of the Hessian.

Once a search direction $p_n$ is identified by a (quasi) Newton step, the step length $\alpha_n$ has to be determined. In principle the best choice would be an $\alpha_n$ that minimizes the energy along the direction $p_n$. This is in general too expensive to evaluate. In practice an inexact line search is therefore performed to estimate $\alpha_n$ at modest computational cost. This is done by imposing conditions on $\alpha_n$. One possible choice are the Wolfe conditions,

\begin{align}
E(x_n + \alpha_n p_n) &\leq E(x_n) - c_1 \alpha_n f_n^T p_n, \quad c_1 \in (0, 1) \tag{4.19} \\
f(x_n + \alpha_n p_n)^T p_n &\leq c_2 f_n^T p_n, \quad c_2 \in (c_1, 1) \tag{4.20}
\end{align}

Inequality (4.19) is also called Armijo condition and assures a sufficient decrease in energy along the search direction. Condition (4.20) is called curvature condition. It requires the force component in the search direction to decrease and therefore avoids too short steps for points on the PES far away from the minimum with steep energy gradients. It can be shown that for a smooth PES which is bounded from below always an $\alpha_n$ can be found that satisfies both, condition (4.19) and (4.20) and thus the Wolfe conditions.

For a search direction $p_n$ and an $\alpha_n$ that satisfies the Wolfe conditions the updated structure is obtained by $x_{n+1} = x_n + s^*_n$, with $s^*_n = \alpha_n p_n$. This procedure is iterated until a convergence criterion for the force $\|f_n\|_\infty < \epsilon \in \mathbb{R}_{>0}$ is met. The line search method with a BFGS update for the approximate Hessian is summarized in Algorithm 4.

\begin{algorithm}
\textbf{Algorithm 4 (BFGS line search).}
\begin{algorithmic}
\Require $x_0, H_0, \epsilon > 0$
\State $n \leftarrow 0$
\While {$\|f_n\|_\infty > \epsilon$}
\State Get $p_n \Leftarrow \text{eq. (4.18)}$
\State Get $\alpha_n \Leftarrow \text{Wolfe conditions}$
\State $x_{n+1} = x_n + s^*_n$, $s^*_n = \alpha_n p_n$
\EndWhile
\end{algorithmic}
\end{algorithm}

The requirements for the BFGS update of the Hessian being positive definite are met if the initial guess $H_0$ is chosen to be positive definite and $\Delta f_n^T \Delta x_n = \Delta f_n^T s_n < 0$. The later requirement holds if $p_n$ is a descent direction and the curvature condition (4.20) is satisfied: $\Delta f_n^T s_n = \alpha_n \Delta f_n^T p_n \leq \alpha_n (c_2 - 1) f_n^T p_n < 0$. 

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Update approximate Hessian $\Leftarrow$ eq. (4.17)

$n \leftarrow n + 1$

end while

An example for the LSM with a BFGS update for the approximate Hessian is shown in the left column of Figure 4.1 for the Rosenbrock function as a test PES. Plotted are the first three optimization steps from top to bottom. The function is shown as a contour plot (gray isolines), whereas darker colors indicate lower function values. The global minimum is shown by the white cross. In green are the contour lines of the quadratic model PES for the approximate BFGS Hessian, whereas in white dashed those which correspond to an exact Hessian. The green dots and arrows indicate the individual optimization steps. For the first step – Figure 4.1 (a) – the model Hessian is isotropic, which can be seen by the equidistant green isolines. The second step – Figure 4.1 (b) – is a full quasi Newton step (i.e. $\alpha_2 = 1$), because the updated geometry corresponds to the minimum of the BFGS model potential. The third step – Figure 4.1 (c) – is again a rather small quasi Newton step. A comparison of the model PES for the exact Hessian (white dashed lines) and the BFGS approximation to the Hessian (green lines) gives an impression about the quality of the BFGS update. From the top left Figure it can be seen that the initial guess for the Hessian is totally different in character as the exact Hessian. However, the first Hessian update already gives a significant improvement. The third step gives only little change in the geometry, whereas the Hessian update gives a pronounced improvement of the approximate Hessian.

It should be noted that the criteria which determine the step length (Wolfe conditions) are not unique - therefore different flavors of the line search method come from different conditions for obtaining the step length.

4.2.2 Trust region method

The TRM ‘trusts’ that the harmonic model PES (4.16) behaves like the total energy within a certain region around $x_n$. This region is characterized by the so called trust-region radius $\Delta_n$. Define the trust region by the ball $T_n := \{s_n : \|s_n\|_2 \leq \Delta_n\} \subset \mathbb{R}^{3N_a+9}$. The TRM obtains the next trial step $s_n^*$ by minimizing the quadratic model function (4.16) over the compact set $T_n$:

$$s_n^* = \arg \min_{s_n \in T_n} M_n(x_n + s_n)$$ (4.21)
Figure 4.1: **Top-down**: first three optimization steps for the LSM (a)–(c) and the TRM (d)–(f) with an initial guess $x_0$ at $(1.3, 0.8)$. As model PES the Rosenbrock function was taken which is shown as a contour plot (gray isolines), whereas darker colors indicate lower function values, with a global minimum at $(1, 1)$ (marked by the white cross). The individual optimization steps are marked by green dots and arrows. Also shown are the contour lines of the quadratic model for the exact Hessian in white dashed lines. (a)–(e) Line search with BFGS update for the approximate Hessian ($H_0 = 50 \cdot 1$). Green contour lines denote the model PES with for the approximate BFGS Hessian. (d)–(f) TRM with the trust-region radius ($\Delta_0 = 0.2$) depicted by the green circles. Both algorithms converge within $\sim 20$ optimization steps.
4 Local minima on the Born-Oppenheimer surface

The ratio between the actual reduction of the total energy $E$ upon taking the step $s^*_n$ and the reduction predicted by the model function $M_n$

$$\rho_n := \frac{E(x_n) - E(x_n + s^*_n)}{M_n(x_n) - M_n(x_n + s^*_n)},$$

is a measure for the quality of the harmonic model. Because of (4.21) the predicted reduction is always nonnegative. Hence, a negative trust radius $\rho_n$ implies an increase in the total energy. Thus for negative or small positive values of $\rho_n$ the step must be rejected ($x_{n+1} = x_n$) and the trust-region radius reduced. On the other hand if $\rho_n$ is close to one, the agreement between the model $M_n$ and the PES around $X_n$ is good. Then the step is accepted, $x_{n+1} = x_n + s^*_n$ and the trust radius can be enlarged. Therefore $\rho_n$ may serve as a criterion to choose the trust region radius for the next iteration,

$$\Delta_{n+1} = \begin{cases} \frac{1}{4}\Delta_n & \text{if } \rho_n < \frac{1}{4}, \\ \min\{2\Delta_n, \Delta_{\text{max}}\} & \text{if } \rho_n > \frac{3}{4} \land \|s^*_n\|_2 = \Delta_n, \\ \Delta_n & \text{else}, \end{cases}$$

with some upper bound $\Delta_{\text{max}}$ for the trust-region radius. For the updated trust-region radius $\Delta_{n+1}$ and geometry $x_{n+1}$ this procedure is iterated until a convergence criterion for the force $\|f_n\|_\infty < \epsilon$ is met. The TRM is summarized in Algorithm 5.

**Algorithm 5** (Trust region method).

**Require:** $x_0$, $\Delta_0 \in (0, \Delta_{\text{max}})$, $\eta \in [0, \frac{1}{4}]$, $\epsilon > 0$

$n \leftarrow 0$

while $\|f_n\|_\infty > \epsilon$ do

Get $s^*_n \leftarrow$ eq. (4.21)

Get $\rho_n \leftarrow$ eq. (4.22)

Update trust-region radius $\leftarrow$ eq. (4.23)

Update approximate Hessian $\leftarrow$ eq. (4.17)

if $\rho_n > \eta$ then

$x_{n+1} = x_n + s^*_n$

else

$x_{n+1} = x_n$

end if

$n \leftarrow n + 1$

end while

In practice the minimization problem (4.21) can be solved approximately or (nearly) exactly, depending on the system size. It can be shown that the exact solution can be characterized by
4.2 Local structure optimization

**Theorem 6** (TRM subproblem). \( s_n^* \) is a global solution of the trust region problem (4.21) iff \( s_n^* \in T_n \) and \( \exists \lambda \in \mathbb{R}_{\geq 0} \) such that the following conditions are satisfied:

\[
\begin{align*}
(H_n + \lambda I)s_n^* &= f_n \quad (4.24) \\
\lambda(\Delta_n - \|s_n^*\|) &= 0 \quad (4.25) \\
(H_n + \lambda I) &\text{ is positive semi-definite} \quad (4.26)
\end{align*}
\]

From (4.25) it follows that either \( \lambda = 0 \) (then \( H_n \) is positive semi definite and \( s_n^* = H_n^{-1} f_n \)), or \( s_n^* \) lies on the boundary of the trust region. (4.24) implies, that \( s_n^* \) is collinear to the model force \( -\nabla s_n M_n s_n^* \). By Theorem 6 the solution can by found by analyzing the Hessian\(^b\).

An example for the TRM is shown in the right column of Figure 4.1 for the Rosenbrock function\(^{210} \). Plotted are the first three optimization steps from top to bottom. The function is shown as a contour plot (gray isolines), whereas darker colors indicate lower function values. The global minimum is shown by the white cross. Also shown are the contour lines of the quadratic model PES for the exact Hessian in white dashed. The green dots and arrows indicate the individual optimization steps, whereas the green circle indicates the trust radius for a given optimization step. The first step – Figure 4.1 (a) – lies at the boundary of the trust region radius. As the improvements in energy are similar for both, the model and the real potential, the trust radius is enlarged for the second relaxation step. The subsequent step – Figure 4.1 (b) – is again at the trust-region boundary, however the trust radius is not altered by this step. The third step – Figure 4.1 (c) – is at the interior of the trust-region, and is therefore a full Newton step.

In summary two relatively simple and robust optimization schemes, the LSM and the TRM have been presented. Both can be classified as modified quasi Newton methods\(^{212} \), as they are based on a quadratic model PES without requiring the

\(^b\) For fixed \( n \), consider the map \( \lambda \mapsto \tilde{s}_n(\lambda) = (H_n + \lambda I)^{-1} f_n \). If the Hessian \( H_n \) is symmetric, then an eigenvalue decomposition \( H_n = Q \Lambda Q^T \) exists with \( \Lambda = \text{diag}(\lambda_1, \lambda_2, ...) \), \( \lambda_1 \leq \lambda_2 \ldots \) and eigenvectors \( q_i \) being the \( i \)-th column of \( Q \). Thus, for \( \lambda_i \neq \lambda \), \( \tilde{s}_n(\lambda) = \sum_{i \geq 1} q_i^T f_n (\lambda_i - \lambda) q_i \).

Per construction \( \tilde{s}_n(\lambda) \) satisfies (4.24). The task is to find \( \lambda \), such that (4.25) and (4.26) hold true as well.

**Case 1** \( H_n \) positive semidefinite (\( \lambda_i \geq 0 \)): if \( \tilde{s}_n \in T_n \), then \( \lambda = 0 \) is a solution. If \( \tilde{s}_n(0) \) lies outside the trust region, then \( \lambda \) must be in the open interval (0, \( \infty \)) for which (4.25) gives a one dimensional root finding problem in \( \lambda \), \( \|\tilde{s}(\lambda)\|_2 - \Delta_n = 0 \), which can be solved numerically (e.g. by the Newton method - in this sense the solution is nearly exact).

**Case 2** \( H_n \) indefinite: (4.26) requires that \( \lambda \in [-\lambda_1, \infty) \). If \( q_i^T f_n \neq 0 \) then \( \|\tilde{s}(\lambda)\|_2 \) is a non-increasing function in the range (\( \infty, 0 \)). Therefore there exists a \( \lambda \) satisfying (4.25), which again can be found numerically by solving \( \|\tilde{s}(\lambda)\|_2 - \Delta_n = 0 \). If \( q_i^T f_n = 0 \), then set \( \lambda = -\lambda_1 \) (ensuring (4.26)), and parametrize the the step by \( \tilde{s}(\tau) = \sum_{i \geq 1} \frac{q_i^T f_n}{\lambda_i - \lambda_1} q_i + \tau q_i \). \( \tilde{s}(\tau) \) satisfies (4.24), and (4.25) can be used to calculate \( \tau \). Theorem 6 ensures that these optimization steps are indeed solutions to the trust region problem (4.21).
knowledge of the exact Hessian. They search for stationary points for which the
force vanishes and therefore rely on the assumption of a smooth PES. Although
this assumption seems reasonable for physical systems, it need not be always true.
For example if the electronic structure changes in a non-continuous fashion with
respect to structural changes, then there can be points on the PES for which the
first derivative does not even exist. In any case, it should be stressed that both
schemes are only capable of finding a local energy minimum - in general global
minima cannot be accessed.

The determination of the step length for the LSM is typically done iteratively
until the Wolfe conditions are satisfied. For \textit{ab initio} methods this can lead to an
unacceptable high number of energy and force evaluations. Therefore in practice
the Wolfe conditions are replaced by a heuristic line search, which potentially can
weaken the performance of the algorithm. The TRM on the other hand, does
not rely on additional energy evaluations in order to determine the trust radius,
and is therefore somewhat better suited for \textit{ab initio} structure optimization from
a theoretical point of view.

4.3 Unit cell relaxation

In this section the implementation of the unit cell relaxation in the FHI-aims
code\textsuperscript{132} is illustrated. As test case the Si-diamond is considered which has experi-
mental primitive lattice vectors of length $\|a_i\|_2 = 3.84\text{ Å} \forall i$, which span a mutual
angle of $60^\circ$. The basis consists of two Si-atoms that are located at $(0, 0, 0)$ and
$(1/4, 1/4, 1/4)$ fractional coordinates.

For the structure relaxation a non-uniformly, strongly distorted start geometry
was taken with lattice vectors: $\|a_1\|_2 = 4.0\text{ Å}$, $\|a_2\|_2 = 3.8\text{ Å}$, $\|a_3\|_2 = 3.2\text{ Å}$, and
angles $\alpha = 55.4^\circ$, $\beta = 57.6^\circ$, $\gamma = 57.1^\circ$. The structure was then optimized for lat-
tice vectors and atomic positions simultaneously, whereas no symmetry constraints
have been explicitly imposed.

As the presented optimizers search for structures that minimize the energy un-
til the force gets sufficiently small, both, the total energy and maximum force
component must decrease (not necessarily monotonically) during the optimization
process. Figure 4.2 shows the convergence behavior of total energy differences $\Delta E_n$
and the infinity norm of the force $\|f_n\|_\infty$ as a function of the optimization step $n$.
Compared are different starting points of an initial diagonal Hessian $H_0 = \beta \cdot 1$ for
the BFGS update, whereas Figure 4.2 (a) shows the results for the LSM and (b)
those for the TRM. Both algorithms decrease the total energy and force during the
optimization process. However the rate of convergence strongly depends on the
initial guess for the Hessian. In particular the LSM converges almost three times
faster for $\beta = 10$ than for $\beta = 100$. For this particular system the TRM converges
4.3 Unit cell relaxation

Figure 4.2: Convergence of the LSM (left) and the TRM (right) with respect to the optimization step \( n \) for the Si-diamond crystal. Shown are total energy differences \( \Delta E \) (top) and the infinity norm of the forces \( \|f\|_\infty \) (bottom) for the individual optimization steps on a logarithmic scale. For both algorithms a BFGS update for the approximate Hessian was employed. Compared are different starting points for the initial Hessian \( H_0 = \beta \cdot I \) (in units of eV/Å\(^2\)).

worse than the LSM - though this is in general system dependent. In Figure 4.2 the following rule of thumb can be observed: the energy converges approximately one order of magnitude faster than the force.

For simple structures, the crystal parameters can be obtained 'by hand' with feasible effort and therefore offers a way to further test the implementation. A common way is to calculate the PES along the direction of lattice vectors and then perform a fit to the Murnaghan equation of state\(^{214}\). For the Si-diamond the data points for the Murnaghan-fit are chosen by varying the experimental lattice parameter by \(-3\%, -2\%, \ldots, +2\%, +3\%\) with the atoms held fix at their fractional coordinates. The energetic minimum then determines the equilibrium lattice constants.

Table 4.1 compares primitive lattice vectors and total energy differences for Si-
Table 4.1: Primitive lattice vectors of Si-diamond obtained by a Murnaghan-fit (Murn.)\textsuperscript{214} and unit cell relaxations using the LSM and the TRM on the LDA\textsuperscript{55} level of theory. A convergence criterion of $10^{-3}$ eV/Å for the residual force was chosen. Also tabulated are the LDA total energy differences for the optimized structures with respect to the one obtained by the Murnaghan-fit.

<table>
<thead>
<tr>
<th>Method</th>
<th>$|a_i|_2$ , (Å)</th>
<th>$\alpha, \beta, \gamma$ , (°)</th>
<th>$\Delta E$ [meV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Murn.</td>
<td>(3.826, 3.826, 3.826)</td>
<td>(60.0, 60.0, 60.0)</td>
<td>0</td>
</tr>
<tr>
<td>TRM</td>
<td>(3.830, 3.830, 3.826)</td>
<td>(59.9, 59.9, 60.0)</td>
<td>-2</td>
</tr>
<tr>
<td>LSM</td>
<td>(3.829, 3.829, 3.826)</td>
<td>(59.9, 59.9, 59.9)</td>
<td>-2</td>
</tr>
<tr>
<td>Exp.\textsuperscript{213}</td>
<td>(3.840, 3.840, 3.840)</td>
<td>(60.0, 60.0, 60.0)</td>
<td>–</td>
</tr>
</tbody>
</table>

diamond obtained by a Murnaghan-fit, the LSM and the TRM on the LDA\textsuperscript{55} level of theory. It can be seen that the TRM and the LSM give virtually the same crystal structure and energy. The agreement with the Murnaghan fit is excellent. It should be noted that the LSM and the TRM give structures that are not perfectly symmetric anymore, whereas the structure obtained by the Murnaghan-fit strictly preserves the crystal symmetry by construction. On the other hand the total energy of the structures obtained by the optimizers are about 2 meV more stable. This can be attributed to the fact that no symmetry requirements were imposed, neither for the structure optimization and its starting point nor on the electronic structure level. However the deviations are on a meV energy scale and therefore negligible. All methods agree with experiment within $\sim 0.01$ Å for the length of the lattice vectors. Admittedly, all theoretical methods underestimate them, which can be attributed to the underlying LDA XC functional which is known to underestimate binding lengths.

In summary the implementation of the unit cell relaxation has been presented. It has been implemented for the LSM and the TRM, whereas lattice vectors and atoms are relaxed simultaneously. Importantly the optimization space is the DFT-PES. In particular this implies that no structural effects from electronic excitations and thermal nuclear effects can be taken into account.

It should be noted that an alternative to the above optimization techniques for the unit cell shape may be found within the framework of molecular dynamics (MD). In an early formulation of variable cell shape MD, Anderson\textsuperscript{215} included a fictitious kinetic energy for the cell volume in the MD Lagrangian, which was repeatedly refined over time by Parrinello and Rhaman\textsuperscript{216,217}, Cleveland\textsuperscript{218}, Wentzcovitch\textsuperscript{219}, and, Souza and Martins.\textsuperscript{220}
Organic semiconducting materials can be classified into (at least partly) disordered π-conjugated polymers and crystals that are built up by small molecules. Molecular crystals can be grown with very high purity and have been shown to have charge-carrier mobilities that can be orders of magnitudes higher than those of polymers. Thus, organic crystals offer a promising way to design high mobility organic materials. In this chapter, basic structural, energetic, and electronic properties of TTF and TCNQ single crystals are discussed. Both crystals, as well as crystals formed of TTF or TCNQ derivatives have been widely used as semiconducting materials in organic field-effect transistors. Hence, they can be regarded as prototypical semiconducting organic materials belonging to the class of crystals that are composed of small molecules. As a common feature, these crystals are to a large extent held together by the weak vdW and electrostatic (quadrupole-quadrupole) forces between the molecules. This implies weak intermolecular electronic orbital overlap and, hence, small electronic bandwidths and low carrier mobilities compared to inorganic semiconductors.

From a theoretical point of view, modeling organic molecular crystals is challenging, since an accurate description of both the strong intramolecular and weak intermolecular interactions is necessary. In this chapter, focus will be put on the performance and limitations of standard approximations of the XC functional.

5.1 Introduction

Historically, TTF and TCNQ crystals have received attention because they have been regarded as building blocks of the TTF-TCNQ crystal, which is one of the first organic conducting materials discovered. In this introduction, the existing experimental and theoretical studies are reviewed, followed by a summary of the computational setup that has been used in this chapter.
5 Molecular crystals of TTF and TCNQ

Experimental crystal structures

Experimentally, TTF crystals are known to exhibit polymorphism with three known phases, the $\alpha$\textsuperscript{245}, $\beta$\textsuperscript{246} and $\gamma$\textsuperscript{247}-phase. The crystal structure of the $\alpha$ and $\gamma$ phases are both monoclinic with $P2_1/c$ and $P2_1/n$ space group symmetry, respectively. The triclinic $\beta$-phase has space group $P\bar{1}$. At low temperatures of about 190 K, $\alpha$-TTF undergoes a second order phase transition\textsuperscript{247} into the $\gamma$-phase. At room temperature the most stable polymorph\textsuperscript{246} is $\alpha$-TTF, whereas at elevated temperatures it becomes the $\beta$-phase\textsuperscript{248}. Here, focus will be put on the most stable structure at ambient temperature, $\alpha$-TTF, which will be referred to as simply TTF from now on.

Figure 5.1 (a) illustrates the crystal structure of TTF as a view on the $a_2 - a_3$ plane with its herringbone motif that is typical for organic molecular crystals. The individual molecules form stacks along the $a_2$-axis and thereby weakly interact with each other. The dashed rectangle indicates the unit cell which is built up by two molecules. An alternative view of the monoclinic unit cell on the $a_1 - a_3$ plane is shown in Figure 5.1 (b); the experimental\textsuperscript{247} lattice parameters obtained by X-ray diffraction (XRD) measurements are summarized in Table 5.2.

In the case of TCNQ only one crystal phase is known and illustrated in Figure 5.1 (d). Again the molecules adapt a herringbone structure in the $a_2 - a_3$ plane with stacked molecules in the $a_2$ direction. The monoclinic unit cell is shown in Figure 5.1 (c) and the experimental lattice parameters\textsuperscript{249}, obtained by XRD measurements, are summarized in Table 5.3. TCNQ has $C_2/c$ space symmetry with four molecules in the unit cell - twice as much as in the TTF crystal.

Experimental measurements of IP and EA

Before summarizing specific results for TTF and TCNQ, some remarks regarding experimental techniques and uncertainties are given. The relative positions of occupied states with respect to the Fermi level of a conducting substrate can be probed by photoelectron spectroscopy\textsuperscript{250} (PES), using UV (UPS) or X-ray (XPS) excitations. PES is based on the photoelectric effect, where an electron is ejected from a sample after a scattering event with an incident photon of a given energy. Energy conservation then determines the electron binding energy as the difference between the photon energy and the kinetic energy of the photo-electron. Similarly, unoccupied states can be measured by the inverse process, which is referred to as inverse photoelectron spectroscopy (IPES)\textsuperscript{251}. In IPES an incident electron with a given kinetic energy is scattered at the sample. The electron undergoes a radiative transition into a lower-lying unoccupied state and thereby emits a photon. From the difference of the kinetic energy of the incident electron and the emitted photon energy, the unoccupied energy level is deduced. By combining PES and IPES the
5.1 Introduction

Figure 5.1: TTF (a) and TCNQ (d) crystal structures with the individual unit cells being indicated with dashed lines. The middle panel shows the TTF (b) and the TCNQ (c) monoclinic unit cell, which is characterized by the length of the lattice vectors $|a_i|, i \in \{1, 2, 3\}$ and the monoclinic cell angle $\beta = \angle(a_1, a_3)$. 
energy gap between the lowest unoccupied and the highest occupied state can be obtained. In the experimental literature this gap is often called the transport gap, $E^{t}_{g}$ and is commonly associated with the theoretically determined fundamental gap.\textsuperscript{252,253}

Typically, organic films are prepared by evaporation techniques on a substrate. The film morphologies may be very different from those of the crystalline phase and may depend on the preparation conditions. The PES measurements are sensitive to the conditions of the prepared samples. In particular, film thickness\textsuperscript{254–257}, film morphology\textsuperscript{258,259}, temperature\textsuperscript{252}, and additional experimental difficulties such as sample charging may be influential. Additionally, IPES is experimentally even more challenging due to the low efficiency of the inverse photo-electron process, low energy resolution, and potential irradiation damage of the organic sample\textsuperscript{258}.

In typical organic materials UPS/IPES spectra have broad peaks, with a full width at half maximum (FWHM) of the order of 0.5-1 eV\textsuperscript{257}. The origin of this peak broadening is still debated in the literature\textsuperscript{257}, which leads to different ways in defining the transport gap: Either by taking the peak maxima\textsuperscript{252,260,261} or the peak onsets\textsuperscript{258,262,263} as valence band maxima (UPS) and conduction band minima (IPES), respectively.

The difference between these two approaches can be significant. For example, the peak-to-peak energy gap is about 1.2 (1.3) eV higher than the onset-to-onset energy gap for pentacene\textsuperscript{252} (PTCDA\textsuperscript{257}). The different level definitions, depend on the interpretation of the peak broadening. In the peak-to-peak approach, the molecular levels are assumed to have zero dispersion, and the peak broadening originates from molecular static disorder in the sample. In contrast, the onset-to-onset approach assumes band dispersion. However, in practice additional effects\textsuperscript{264} such as electron-phonon coupling, band-dispersion, lifetime broadening, and instrumental resolution could also contribute.

The experimental UPS/IPES values for IP and EA of TTF and TCNQ films are summarized in Table 5.1. The IP of TTF is about 5 to 5.6 eV, depending whether the peak onset or the peak maximum is chosen as reference. For TTF, no measurements on the EA exist to the best of my knowledge. For TCNQ, both UPS and IPES measurements are reported in literature. The onset-to-onset band gap is about 3.5-3.7 eV, while the peak-to-peak gap can be expected to be more than 1 eV larger. The gap has been also determined by means of photconductivity experiments along the [001] TCNQ crystal direction, yielding a value of 1.7 eV\textsuperscript{268}, and is thus 2 eV smaller than the onset-to-onset gap obtained by UPS/IPES. In the face of the large discrepancy between the onset-to-onset, the peak-to-peak, and the photoconductivity gap I will consider none of these values as a reliable estimate for the crystalline TCNQ fundamental gap.
Table 5.1: Experimental IP, EA and energy gaps determined by various experimental techniques together with the type of substrate and the sample film thickness (if available).

<table>
<thead>
<tr>
<th>Method</th>
<th>TCNQ</th>
<th>TTF</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>IP UPS onset</td>
<td>7.7\textsuperscript{260}</td>
<td>5.0\textsuperscript{260}</td>
<td>Thin film (1 nm) on Au</td>
</tr>
<tr>
<td>IP UPS onset</td>
<td>7.9\textsuperscript{265}</td>
<td></td>
<td>Film on Au</td>
</tr>
<tr>
<td>IP UPS onset</td>
<td>7.9\textsuperscript{266}</td>
<td></td>
<td>Film on Au</td>
</tr>
<tr>
<td>IP UPS onset</td>
<td>8.5\textsuperscript{265}</td>
<td></td>
<td>Film on oxidized Al</td>
</tr>
<tr>
<td>IP UPS peak</td>
<td>8.3\textsuperscript{260}</td>
<td>5.6\textsuperscript{260}</td>
<td>Thin film (1 nm) on Au</td>
</tr>
<tr>
<td>EA IPES onset</td>
<td>4.2\textsuperscript{258}</td>
<td></td>
<td>Thin film (5 nm) on Au</td>
</tr>
<tr>
<td>$E_g$ Photoconductivity</td>
<td>1.7\textsuperscript{268}</td>
<td></td>
<td>Crystal</td>
</tr>
</tbody>
</table>

Theoretical approaches

Theoretically, the TTF and TCNQ single crystals have been mainly investigated with respect to their vibrational properties.\textsuperscript{269–272} To the best of my knowledge, there exists no \textit{ab initio} calculation on the electronic structure of the TTF crystal, whereas there exists one DFT-GGA calculation for crystalline TCNQ by Shokaryev et al.\textsuperscript{273} However, in that study the unit cell geometry was fixed to the experimental lattice parameters. In this chapter DFT calculations are performed for both crystals, where also the unit cell shape is determined from first principles.

In the following the performance of (semi-)local Kohn-Sham DFT in describing structural, energetic and electronic properties of TTF and TCNQ single crystals is studied. The investigated functionals are: LDA in the Perdew-Wang parametrization, PBE and van der Waals corrected\textsuperscript{87} PBE (PBE+vdW).

The line search method (LSM) and trust-region method (TRM) method as discussed in Section 4.2 have been employed for a full structure optimization including the unit cell shape. Experimental geometries taken from Refs.\textsuperscript{247,249} for TTF and TCNQ respectively have been used as an initial guess for both optimization schemes and a convergence criterion of $10^{-2}$ eV/Å for the residual force in the structure optimization was chosen. It has been found that TRM and LSM perform very similar in terms of efficiency (i.e., the number of optimization steps) and deliver the same ground state geometry with sub-meV differences in the ground state total energy. Only for PBE+vdW convergence for the TRM was harder to achieve than for the LSM. This is attributed to the non self-consistent treatment of vdW contributions which can lead to force-energy inconsistencies to which the TRM is more vulnerable (see Algorithm 5).
For the unit cell relaxation the most important quantity is the stress tensor $\sigma$ and sufficient numerical accuracy needs to be guaranteed. Figure 5.2 displays its convergence with respect to the most important technical settings. These are the step width for the numerical evaluation of the stress tensor according to equation (4.10), the basis set, and the $k$-mesh sampling of the Brillouin zone. The convergence is shown for the maximum norm of the stress tensor $\|\sigma\|_{\text{max}} := \max_{ij} |\sigma_{ij}|$ with respect to the lowest value of a given convergence test. The overall convergence behavior is similar to the convergence study of Appendix A.2 and a rather economic setup already gives an accurate description for the stress tensor. In particular the default value of $10^{-3}$ for the step width (Fig. 5.2 (a)) and a tier two basis set (Fig. 5.2 (b)) assures convergence $< 1 \text{ meV/Å}^3$. Therefore, these settings will be used for the unit cell relaxation. The convergence behavior for the $k$-grid sampling of the Brillouin zone is shown in Fig. 5.2 (c). For the production calculations a $4 \times 4 \times 2$ ($2 \times 2 \times 1$) $k$-grid was used for TTF (TCNQ), which is also converged $< 1 \text{ meV/Å}^3$.

The same computational settings provide sufficient accuracy for the electronic structure. Fig. 5.3 shows the convergence of the electronic density of states (DOS) with respect to the basis set size and the $k$-grid sampling. The energy zero was set to the valence band maximum. For both crystals, the DOS is unchanged upon increasing the basis set size beyond a tier 1 basis, which is shown in Fig. 5.3 (a).
5.1 Introduction

![Figure 5.3: Convergence of the PBE electronic density of states (DOS, arbitrary units) with respect to the basis set (a) and k-mesh sampling (b) for TTF (the corresponding TCNQ plots are shown in (c) and (d), respectively). The energy zero was set to the valence band maximum and the DOS was Gauss broadened by 0.05 eV.](image)

and (c) for TTF and TCNQ, respectively. The k-grid convergence of the DOS is shown in Fig. 5.3 (b) for TTF and in (d) for TCNQ. The DOS changes only to a minor extent upon changing the $4 \times 4 \times 2$ ($2 \times 2 \times 1$) TTF (TCNQ) k-grid to a denser sampling. In particular, the valence band widths and the Kohn-Sham band gap remains unchanged. As a compromise of accuracy and computational efficiency the very same computational setup as for the unit cell relaxation will be used for the calculation of the electronic properties (bandstructure and DOS) of TTF and TCNQ.

The unit cell optimization obtains lattice vectors and atomic positions from a local minimum of the DFT potential energy surface within the Born-Oppenheimer approximation. Therefore, pressure and temperature effects as well as nuclear zero point effects are not included. However, experimentally the crystal parameters are determined under real world conditions at room temperature and pressure. In order to estimate these effects the thermal expansion along the three lattice vectors is computed within the quasi-harmonic approximation (QHA) by means of phonon calculations.  

At a given temperature $T$ and pressure $p$ thermodynamic quantity of interest is
the Gibbs free energy \(G(T, p)\). It is obtained as the Legendre transformation with respect to the unit cell volume \(V\) of the Helmholtz free energy \(F(T, V)\),

\[
G(T, p) = \min_V \{ F(T, V) + pV \} .
\]  

From the minimization conditions, the volume at thermodynamic equilibrium is obtained, which becomes temperature and pressure dependent. For a solid within the adiabatic approximation, the free energy can be written as a sum of an electronic and a vibronic term

\[
F(T, V) = F^{\text{el}}(T, V) + F^{\text{vib}}(T, V).
\]  

Both, the TTF and TCNQ crystal are essentially insulators with a PBE Kohn-Sham band gap > 1 eV (a detailed discussion of the electronic structure will be given in Section 5.4). Therefore, electronic entropic effects are negligible (at least at room temperature) and the electronic free energy may be calculated by the DFT ground state total energy \(F^{\text{el}}(T, V) \approx E(V)\), which becomes independent of the temperature but still depends on the unit cell volume. The vibrational part is approximated by the phonon contribution within the QHA. It is based on a quadratic (‘harmonic’) expansion of the DFT Born Oppenheimer surface and obtains the phonon free energy by

\[
F^{\text{vib}}(T, V) \approx F^{\text{qh}}(V, T) = k_B T \sum_{q,i} \ln \left\{ 2 \sinh \left( \frac{\hbar \omega_{q,i}}{2k_B T} \right) \right\} + k_B T \int g(\omega) \ln \left\{ 1 - e^{-\frac{\hbar \omega}{k_B T}} \right\} d\omega.
\]

The sum is performed over all phonon branches \(i\) and over all wave vectors \(q \in \mathbb{R}^3 \approx \mathbb{R}^3\) in the first Brillouin zone (BZ); \(\omega_{q,i}\) is the phonon frequency at branch \(i\) with wavevector \(q\) and \(k_B\) is the Boltzmann constant. In the second line the expression was reformulated by aid of the phonon DOS (number of phonon modes per volume), \(g(\omega) = \frac{1}{(2\pi)^3} \sum_i \int \delta(\omega - \omega_{q,i}) d^3q\) where the integration is performed over the first Brillouin zone. The first term in Eq. (5.4) is temperature independent and accounts for the zero-point contribution while the second term arises from thermal excitations of the phonons. Note that in the QHA the volume does not occur explicitly in Eqs. (5.3) or (5.4). In fact, for a perfectly harmonic material no thermal expansion would occur because the inversion symmetry of a quadratic potential carries over to the nuclear wavefunction. In the QHA anharmonic effects are captured only partially and enter from the backdoor (‘quasi’) by the volume dependence of the phonon frequencies \(\omega_{q,i} = \omega_{q,i}(V)\). More details on the theoretical and technical machinery of phonons can be found in standard textbooks.\(^{213,275}\)
5.1 Introduction

Figure 5.4: Convergence of the phonon density of states (DOS, arbitrary units) with respect to the $q$-mesh sampling (a) and the supercell size (b) for TTF (the corresponding TCNQ plots are shown in (c) and (d), respectively). A Gauss broadening of 1 cm$^{-1}$ was used.

and in Refs. 276 and 274.

The phonon calculations were performed with the Phonopy code $^{277}$ using an interface to the FHI-aims code $^{132}$ provided by Jörg Meyer. Phonopy uses the Parlinsky-Li-Kawazoe method, $^{278}$ which is based on the supercell finite displacement method. In this approach the Hessian in the dynamical matrix is computed numerically via finite differences taking into account additional contributions from surrounding unit cells. The latter is controlled by the supercell size and needs to be converged together with the $q$-point sampling of reciprocal space. Figure 5.4 shows the convergence of the phonon DOS for the TTF and TCNQ single crystals (the dynamical matrix was obtained using the PBE+vdW functional at the PBE+vdW optimized unit cell and a tier 2 basis set). A $10 \times 10 \times 10$ $q$-mesh sampling is already converged for both, the TTF (Fig. 5.4 a) and TCNQ (Fig. 5.4 c) crystal. Convergence with respect to the TTF supercell size is shown in Fig. 5.4 (b). Compared to the $1 \times 1 \times 1$ supercell, a further increase in the supercell size results in a softening of the phonon modes at around 50 cm$^{-1}$ and an additional spectral weight at around 100 cm$^{-1}$. TTF has the shortest lattice parameter in the $a_2$ direction for which PBE+vdW predicts a length of about 4 Å. Hence, interatomic interactions between neighboring unit cells in this direction may be expected
to be responsible for the underconverged $1 \times 1 \times 1$ supercell (i.e., the central unit cell). Doubling the unit cell in the $a_2$ direction leads to the $1 \times 2 \times 1$ supercell and shows a phonon DOS in close agreement with the $2 \times 2 \times 2$ or $3 \times 3 \times 3$ supercell. As compromise between accuracy and computational cost, the $1 \times 2 \times 1$ supercell will be used for the TTF calculation. In contrast, to TTF, the TCNQ phonon DOS is already converged for a $1 \times 1 \times 1$ supercell as shown in Fig. 5.4 (d). This can be attributed to the C2/c symmetry of TCNQ, which introduces an additional layer of molecules along the $a_2$ direction (see Fig. 5.1 c) and increases the unit cell size in this direction by about 3 Å. This appears to be sufficient for a converged phonon DOS and therefore $1 \times 1 \times 1$ supercell will be used for the TCNQ phonon calculations.

5.2 Geometric properties: Theoretical description

In this section basic structural properties of TTF and TCNQ single crystals are investigated. Compared to the electronic structure, the performance of XC functionals in describing lattice parameters has been investigated to a less extent for organic molecular crystals. This can be attributed to two characteristics: first the lattice structure for such systems is relatively complicated, which makes an optimization by hand cumbersome. Second, and more importantly, a proper description of dispersion interactions is crucial, but has not been possible in DFT until recently. Therefore this section is first concerned with the performance of semilocal XC functionals on the lattice parameters followed by a discussion of intra–and intermolecular geometric properties. The performance of the individual XC functionals will be assessed by comparison to experimental XRD reference data. Since these experiments were performed at room temperature, first the effect of thermal expansion will be estimated.

5.2.1 Thermal lattice expansion

The thermal expansion of the individual crystals is estimated by computing the thermal expansion along the three lattice vectors within the quasi-harmonic approximation (QHA). Focus will be put on the thermal expansion of the theoretical crystal shapes which were obtained with PBE+vdW. In essence, one needs to minimize the Helmholtz free energy $F(T,V)$ along the individual lattice vectors, which can be achieved by the following procedure:

1. Starting with the PBE+vdW optimized crystal, deform the unit cells along
5.2 Geometric properties: Theoretical description

lattice vector $a_i$ by a distances $\delta \|a_i\|$ according to the strain transformation$^a$

$$\mathbb{R}^3 \rightarrow \mathbb{R}^3 : x \mapsto (1 + \epsilon)x = x + \delta \|a_i\| \frac{\langle a_i, x \rangle}{\|a_i\|^2} a_i,$$  \hspace{1cm} (5.5)$$

where $x$ denotes lattice vectors and atomic positions. The deformations along the lattice vectors are chosen to be $\delta \|a_i\| = -0.15, -0.1 \ldots 0.35, 0.4 \text{Å}.$

2. Relax the atomic position for each deformed unit cell keeping the lattice parameters fixed.

3. Compute the phonon free energy according to Eq. (5.4).

4. For a given $T$ and $p$ find the minimum of the total free energy according to Eq. (5.1) via a Murnaghan fit.$^{214}$

An illustration of this procedure is given in Figure 5.5 (a). Shown is the free energy as a function of the volume of the strained TTF unit cell along the $a_2$ lattice vector. The equilibrium unit cell volumes is then given by the minimum of the free energy at given volume and pressure as obtained by a Murnaghan fit$^{214}$, which is shown by the red circles. For a given temperature, there are actually two curves in the graph, which are on top of each other: one at zero pressure and one at atmospheric pressure ($\approx 0.1$ Mpa) under which the XRD experiments were performed.$^{247,249}$ While only shown for this specific example, this behavior holds true for all investigated free energy landscapes. Hence, the $pV$ term is negligible for both crystals under atmospheric pressure. However, the phononic part does contribute. At $T = 0$ K the free energy consists of the PBE+vdW total energy plus the phononic zero-point energy. Increasing the temperature to the experimental condition ($T = 290$ K$^{247}$), results in a decrease of the Helmholtz free energy (via the second term of Eq. 5.4 for the phonon free energy) and an shift of its minimum towards larger unit cell volume.

Determination of the minimum analogue Figure 5.5 (a) for a sequence of temperatures leads to Figure 5.5 (b). It shows the thermal expansion as a function of temperature along the three lattice vectors of TTF (black curves) and TCNQ (red curves). In the case of TTF it can be seen that the zero-point effect ($T = 0$ K) are rather similar along the different lattice vectors, which increases the unit cell volume by about 0.8%. However, at experimental conditions of 290 K the thermal

$^a$ For a given $a_i$ the strain matrix $\epsilon$ may be found by requiring $(1 + \epsilon) a_i = a_i + a_i \delta \|a_i\|/\|a_i\|_2$, i.e. that $\epsilon$ shall stretch $a_i$ by $\delta \|a_i\|$. Therefore, the strain matrix is a multiple of the unit matrix $\epsilon = \delta \|a_i\|/\|a_i\| \cdot 1$. Since the strain transformation acts on all atoms and lattice vectors it's components need to be projected on the $a_i$ direction. This can be achieved by defining the projection operator $P_i := a_i a_i^\top /\|a_i\|^2$. Applying $P_i$ on $\epsilon$ gives the desired strain transformation.
expansion appears to be anisotropic. While the expansion along the $a_1$ and $a_3$ direction are similar with a volume change of 1.5\% and 1.3\%, the volume change along $a_2$ amounts to 3.7\%. TCNQ shows a similar behavior: At $T = 300$ K\textsuperscript{b} the most pronounced thermal expansion of 3.4\% is along the $a_2$ direction and 0.8\% (1.7\%) in the remaining $a_1$ ($a_3$) direction.

The anisotropy in the thermal expansion can be explained by the strain dependence of the phonon frequencies. To this end those directions, which exhibit the strongest ($a_2$) and the weakest ($a_1$) thermal expansion of the TTF crystal are considered. Figure 5.6 shows the phonon DOS at the DFT (PBE+vdW) equilibrium volume and at deformed unit cell volumes along the $a_2$ (a) and $a_1$ (b) direction. The unit cell volumes were deformed by $\delta ||a|| = 0.1$ Å according to the strain transformation in (5.5) and the atomic positions were relaxed subsequently. For both deformations, the phonon spectrum shifts towards lower frequencies at elongated

\textsuperscript{b}The representative value of 300K for will be used for TCNQ because the experimental Reference 249 does not quantify the word ‘room temperature’.
5.2 Geometric properties: Theoretical description

unit cells. At a given temperature, the phonon free energy thus increases (Eq. 5.4) upon extending the unit cell, which eventually locates the minimum of the total free energy at larger lattice parameters. However, comparing Figure 5.6 (a) and (b), the softening of phonon modes is more pronounced along the $a_2$ direction than along the $a_1$ direction. As a consequence, the thermal expansion of the crystal will be enhanced along the $a_2$ direction. That both crystals expand predominantly along the $a_2$ direction is not very surprising, because the $a_2$ is direction is weakly bound by vdW forces (see discussion below). Therefore, one may expect, that the crystal mainly expands in this direction.

In summary, the thermal expansion of the theoretical PBE+vdW TTF and TCNQ crystals was estimated, by computing the thermal expansion along the individual lattice vectors within the QHA. It was found that both crystals expand in a non-uniform fashion. At ‘room temperature’ the change in volume amounts to 1% to 4%, depending on the lattice direction. Subsequently, the performance of semilocal DFT functionals (LDA, PBE, and PBE+vdW) in describing the unit cell volume will be assessed by comparing to experimental XRD measurements. From the above discussion, thermal and zero-point effects are estimated to additionally enlarge the theoretical unit cell volume by about 5-6%.

5.2.2 Unit cell

The TTF unit cell parameters are compiled in Table 5.2. Compared to experimental X-ray diffraction measurements, the LDA underestimates the unit cell volume by 16% whereas PBE overestimates it by as much as 29%. Therefore, the description of cell volumes is unsatisfactory at the LDA and PBE level of theory. Including vdW corrections on top of PBE yields an excellent agreement with
The drastic improvement upon the inclusion of dispersion forces to PBE shows that the TTF crystal is predominantly vdW bound. For all three functionals the monoclinic angle $\beta$ is well described and differs from experiment by at most $1^\circ$ for the LDA. In a monoclinic system the remaining cell angles are $90^\circ$. While $\gamma$ has been constrained to this value during the structure optimization process, $\alpha$ was allowed to vary freely. Again all three functionals give values for $\alpha$ very close to $90^\circ$. In particular LDA and PBE+vdW deviate by $0.1^\circ$ whereas the PBE value differs by about $2^\circ$.

Turning to the lattice constants $|a_i|$, $i \in \{1, 2, 3\}$ they are found to be underestimated within the LDA by 4-6% which results in a too small cell volume. In particular all three lattice constants show approximately the same error, in contrast to PBE. There, the $a_1$ and $a_3$ directions agree with experiment within 3% and 1% respectively whereas $a_2$ is vastly overestimated by 24%. This is cured upon adding long-range vdW interactions - in particular the error of $a_2$ is reduced to 2% which goes along with a further error reduction in the remaining directions. The PBE+vdW error in the $a_1$ ($a_3$) direction reads 0.3 (0.5)%, indicating that vdW interactions also contribute to the crystal binding in these directions. However, from the significant error reduction in the $a_2$ direction upon inclusion of dispersion interactions it can be concluded that the TTF crystal is largely vdW bound in this direction.

The TCNQ lattice parameters are compiled in Table 5.3. LDA and PBE perform poor in predicting the unit cell volume, as LDA underestimates it by 13%, whereas PBE overestimates by 17%. Similar to TTF, only PBE+vdW reproduces the experimental cell volume within 1%. This implies that vdW interactions contribute significantly also for TCNQ. In line what has been found for the TTF crystal the TCNQ lattice angles are reproduced within $2^\circ$ for all three functionals. Thus, the unit cell angles are relatively insensitive to the treatment of correlation. The length of lattice vectors on the other hand differ significantly for different functionals, which has been already illustrated for TTF. The same holds true for TCNQ.

### Table 5.2: Experimental (XRD at 290 K) and theoretical lattice parameters and unit cell volumes of the TTF crystal.

| XC       | $|a_i|$, $i = 1, 2, 3$ [Å] | $(\alpha, \beta, \gamma)^{\circ}$ | Vol [Å$^3$] |
|----------|---------------------------|-----------------------------------|-------------|
| Experiment$^{247}$ | (7.352, 4.018, 13.901) | (90.0, 101.4, 90.0) | 402.5       |
| LDA      | (7.093, 3.785, 13.132)   | (90.1, 100.4, 90.0) | 346.8       |
| PBE      | (7.589, 4.969, 14.072)   | (91.9, 101.2, 90.0) | 520.2       |
| PBE+vdW  | (7.371, 3.949, 13.972)   | (89.9, 101.9, 90.0) | 397.9       |
5.2 Geometric properties: Theoretical description

Table 5.3: Experimental (XRD at room temperature; no precise temperature given in Ref.249) and theoretical lattice parameters and unit cell volumes of the TCNQ crystal.

| XC         | \(|a_i|, i = 1, 2, 3\) [Å] | \((\alpha, \beta, \gamma)\) [°] | Vol[Å³] |
|------------|---------------------------|---------------------------------|---------|
| Experiment | (8.906, 7.060, 16.395)    | (90.0, 98.5, 90.0)               | 1019.4  |
| LDA        | (8.628, 6.502, 16.239)    | (90.5, 97.4, 90.0)               | 903.3   |
| PBE        | (9.126, 7.959, 16.604)    | (88.1, 98.3, 90.0)               | 1192.9  |
| PBE+vdW    | (8.874, 6.795, 16.858)    | (89.6, 97.9, 90.0)               | 1006.9  |

where the LDA underestimates \(|a_i|, \forall i\), whereas the largest error of 9% is found in the \(a_2\) direction. PBE gives the opposite behavior, as it predicts too long lattice vectors. While the PBE error in the \(a_1\) and \(a_3\) directions are small (2% and 1% respectively), the \(a_2\) direction is significantly overestimated by 13%. Again, PBE+vdW improves the description in the \(a_2\) direction and brings the error down to 4%. Similar to TTF this implies that the \(a_2\) direction is mainly vdW bound. However, the employed vdW correction tends to underestimate \(|a_2|\), which is accompanied by an overestimation of \(|a_3|\) by 3%.

In summary, the performance of LDA, PBE and PBE+vdW on the description of lattice parameters for the TTF and TCNQ crystals has been investigated. It was found that the three functionals give significantly different results for both crystals. In particular for a proper description of the weakly bound \(a_2\) direction the inclusion of dispersion interactions is crucial. This is reflected in the fact, that PBE+vdW gives the overall best agreement with the experimental lattice constants. If one would include thermal effects as in the last section, the overall picture of the functional performance does not change. For PBE, additional thermal and zero-point effects would additional expand the unit cell, which is already too large. For the PBE+vdW, the inclusion of thermal effects would lead to a overestimation of the unit cell volume by about 4-5%, which is still in very good agreement with experiment. The LDA, which gives too small unit cell volumes would benefit from the inclusion of thermal effects as the unit cell volume would increase. However, adding the above estimate of 5% volume expansion, would still predict significantly too small unit cell volumes\(^c\). Therefore, the inclusion of thermal effects does not alter the main conclusions in the assessment of the presented XC functionals.

\(^c\)One may argue, that the estimate was obtained using the PBE+vdW functional and a consistent estimate for thermal expansion using the LDA functional would bring the LDA results in better agreement with experiment. However, a definite answer would require LDA phonon calculations in the same fashion as in Section 5.2.1.
5 Molecular crystals of TTF and TCNQ

Figure 5.7: Illustration for the definition of the Euler angles. The rotational axis always points out of the plane of the paper and is indicated by a circle. The thin solid line in the right hand figure represents the principal axis before the rotation, whereas the rectangle in the first figure indicates the unit cell in the $a_1 - a_2$ plane. The dashed arrows indicate the principal axis of the molecule.

The next Sections will discuss the molecular and atomic arrangements within the crystals. There, thermal and zero-points effects will be neglected, which could modify details in the results, but are not expected to affect the main conclusions.

5.2.3 Intermolecular structure

Having discussed the overall shape of the unit cell, and thus the most important intermolecular distances, the next step is to evaluate the orientation of the molecules within the unit cell. In principle TTF (TCNQ) consists of 2 (4) molecules per unit cell. However as their geometric positions are related by the underlying space-group it is enough to consider the orientation of one molecule only. Here the molecule that has the center of mass at the origin of the unit cell is considered.

One obvious way to characterize its orientation in space is to calculate its principal axes. They are given by the eigenvectors of the symmetric, positive semi-definite moment of inertia tensor

$$I_{\mu\nu} := \sum_i m_i (R_{i\alpha} R_{i\delta \mu \nu} - R_{i\mu} R_{i\nu}),$$

where $R_{i\alpha}$ denotes (the covariant) component $\alpha$ of nucleus $i$ with mass $m_i$. Denote the normalized eigenvectors of $I$ by $\{ e_k^\lambda, k = 1, 2, 3 \}$. By the spectral theorem $I$ can be written in the form $I = Q\Lambda Q^{-1}$, where $\Lambda$ is a diagonal matrix and the matrix $Q$ contains in its $k$-th column the eigenvector $e_k^\lambda$. Since $I$ is symmetric and the eigenvectors are normalized it follows that $Q \in SO(3)$. Thus, $Q$ establishes
5.2 Geometric properties: Theoretical description

Table 5.4: Euler angles [°] and mean absolute error (MAE) [°] of the TTF and TCNQ molecule centered at the origin of the unit cell (see Figure 5.7 for the definition of the angles).

<table>
<thead>
<tr>
<th></th>
<th>TTF</th>
<th>TCNQ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exp.²⁴⁷</td>
<td>LDA</td>
</tr>
<tr>
<td>α</td>
<td>44.6</td>
<td>45.2</td>
</tr>
<tr>
<td>β</td>
<td>69.0</td>
<td>66.9</td>
</tr>
<tr>
<td>γ</td>
<td>74.9</td>
<td>76.3</td>
</tr>
<tr>
<td>MAE</td>
<td>—</td>
<td>1.4</td>
</tr>
</tbody>
</table>

a basis transformation (passive transformation) from the standard cartesian basis \{e_i\} to the basis spanned by the eigenvectors of \(I, Q : e_i \mapsto e'_i\). The corresponding rotation of the molecule (active transformation) is then generated by \(Q^{-1} = Q^T\). In order to analyze the rotation matrix \(Q^T\) it is convenient to parametrize it by Euler angles²⁷⁹,

\[ Q^T = R(\alpha, \beta, \gamma) = R_{e_3}(\gamma)R_{e_2}(\beta)R_{e_3}(\alpha), \tag{5.7} \]

where \(R_{e_i}(\omega)\) denotes a rotation around the cartesian \(e_i\)-axis by an angle \(\omega\). Thus solving Equation 5.7 for the Euler angles \((\alpha, \beta, \gamma)\) determines the orientation of the molecule.

The effect of equation (5.7) is illustrated in Figure 5.7 for the TTF molecule. The coordinate system was chosen such that it coincides with unit vectors of the lattice \(\{e_1, e_2, e_3\} = \{e_{a_1}, e_{a_2}, e_{a_3}^*\}\), where \(e_{a_3}^*\) guarantees an orthonormal basis despite the monoclinic lattice structure. First, the molecule is rotated by an angle \(\alpha\) around the \(a_3\)-axis, followed by a rotation around the \(a_2\)-axis of an angle \(\beta\). Finally the molecule is again rotated around the \(a_1\)-axis by \(\gamma\).

Table 5.4 summarizes the Euler angles obtained in this way for TTF and TCNQ. In general, the functional dependence is relatively weak, which amounts to MAEs below 2° with respect to experiment. For TTF the LDA and PBE perform similar for the intermolecular orientation, whereas PBE+vdW gives Euler angles that are very close to the experimental ones with a MAE of 0.5°. For the case of TCNQ, PBE+vdW describes the molecular orientation worse with a MAE of 1.8°, compared to PBE, which gives the smallest MAE of 0.5°. PBE+vdW tends to arrange the molecules in the \(a_2 - a_3\) plane (see Figure 5.1) in a more parallel way as compared to PBE or experiment. This enlarges the \(\pi\) overlap between adjacent molecules and decreases the molecular distance in the \(a_2\) direction. The flatter orientation also goes along with an increased spatial extend of the molecules in
5 Molecular crystals of TTF and TCNQ

Table 5.5: Symmetry inequivalent intermolecular bond distances [Å] and angles [°] for the TTF crystal. The bottom of the Table summarizes the mean absolute error for bond lengths (MAE (Å)) and angles (MAE (°)). The figure to the right illustrates the labeling of the atoms.

<table>
<thead>
<tr>
<th></th>
<th>Exp.</th>
<th>LDA</th>
<th>PBE</th>
<th>PBE+vdW</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1-C2</td>
<td>1.736</td>
<td>1.729</td>
<td>1.746</td>
<td>1.744</td>
</tr>
<tr>
<td>S1-C3</td>
<td>1.756</td>
<td>1.743</td>
<td>1.769</td>
<td>1.764</td>
</tr>
<tr>
<td>C1-C2</td>
<td>1.319</td>
<td>1.337</td>
<td>1.343</td>
<td>1.343</td>
</tr>
<tr>
<td>C3-C4</td>
<td>1.341</td>
<td>1.350</td>
<td>1.359</td>
<td>1.358</td>
</tr>
<tr>
<td>C1-C2-S1</td>
<td>118.0</td>
<td>118.0</td>
<td>117.9</td>
<td>117.8</td>
</tr>
<tr>
<td>C2-S1-C3</td>
<td>94.7</td>
<td>94.5</td>
<td>95.1</td>
<td>95.0</td>
</tr>
<tr>
<td>S1-C3-C4</td>
<td>122.6</td>
<td>122.4</td>
<td>123.0</td>
<td>122.8</td>
</tr>
<tr>
<td>S1-C3-S2</td>
<td>114.4</td>
<td>115.4</td>
<td>114.3</td>
<td>114.5</td>
</tr>
<tr>
<td>MAE (Å)</td>
<td>–</td>
<td>0.01</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>MAE (°)</td>
<td>–</td>
<td>0.35</td>
<td>0.25</td>
<td>0.20</td>
</tr>
</tbody>
</table>

the $a_3$ direction. As a consequence, the $a_3$ lattice constant is overestimated whereas the $a_2$ lattice constant is underestimated, which is consistent with the findings for the lattice parameters (see Table 5.3). The overestimation of the effective stacking area of the $\pi$ orbitals in the $a_2$ direction upon adding vdW correction, indicates that the employed dispersion correction scheme tends to overestimate vdW forces for the TCNQ crystal.

5.2.4 Intramolecular structure

Following the route from top to bottom in the description of the crystalline structural properties, the remaining quantities to be discussed are the intramolecular bond distances and angles. Table 5.5 and 5.6 summarize the experimental and theoretical values for TTF and TCNQ respectively. The experimental values have been obtained by X-ray diffraction (XRD) measurements, in which hydrogen atoms are almost invisible and thus their position cannot be determined reliably. Therefore, the hydrogen atoms will not be considered in the following comparison between experiment and theory.

For both crystals all investigated functionals are able to describe bond distances and angles accurately which results in a MAE $\leq 0.02$ Å for bond distances and $\leq 0.42^\circ$ for bond angles. The biggest deviation from the experimental bond angles is found for the LDA with a MAE of 0.35° and 0.42° for TTF and TCNQ respectively.
Table 5.6: Symmetry inequivalent intermolecular bond distances [Å] and angles [°] for the TCNQ crystal. The bottom of the Table summarizes the mean absolute error for bond lengths (MAE (Å)) and angles (MAE (°)). The figure to the right illustrates the labeling of the atoms.

<table>
<thead>
<tr>
<th></th>
<th>Exp.\textsuperscript{249}</th>
<th>LDA</th>
<th>PBE</th>
<th>PBE+vdW</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-C1</td>
<td>1.141</td>
<td>1.159</td>
<td>1.166</td>
<td>1.165</td>
</tr>
<tr>
<td>C1-C2</td>
<td>1.441</td>
<td>1.405</td>
<td>1.420</td>
<td>1.418</td>
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<tr>
<td>C2-C3</td>
<td>1.374</td>
<td>1.386</td>
<td>1.399</td>
<td>1.397</td>
</tr>
<tr>
<td>C3-C4</td>
<td>1.450</td>
<td>1.425</td>
<td>1.441</td>
<td>1.438</td>
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<tr>
<td>C4-C5</td>
<td>1.346</td>
<td>1.352</td>
<td>1.361</td>
<td>1.360</td>
</tr>
<tr>
<td>N-C1-C2</td>
<td>179.6</td>
<td>179.6</td>
<td>179.2</td>
<td>179.5</td>
</tr>
<tr>
<td>C1-C2-C3</td>
<td>121.8</td>
<td>121.5</td>
<td>122.3</td>
<td>122.1</td>
</tr>
<tr>
<td>C2-C3-C4</td>
<td>120.7</td>
<td>120.4</td>
<td>120.8</td>
<td>120.7</td>
</tr>
<tr>
<td>C3-C4-C5</td>
<td>120.7</td>
<td>120.3</td>
<td>120.7</td>
<td>120.7</td>
</tr>
<tr>
<td>C4-C3-C6</td>
<td>118.3</td>
<td>119.4</td>
<td>118.5</td>
<td>118.7</td>
</tr>
</tbody>
</table>

| MAE (Å)   | –                           | 0.02 | 0.02 | 0.02  |
| MAE (°)   | –                           | 0.42 | 0.24 | 0.16  |

Although this error is already small, it is reduced by taking gradient corrections to the XC potential into account. The PBE MAE for bond angles reads 0.25° for TTF and 0.24° for TCNQ. Upon adding vdW corrections on top of PBE the intramolecular geometry improves even further. In particular PBE+vdW gives the smallest deviation with respect to both experimental bond distances and angles for TTF and TCNQ. While in the gas phase the inclusion of vdW forces does not alter the geometry of a single molecules, it improves the molecular geometry within a crystal. Hence, this must be attributed to the better performance of PBE+vdW in describing the unit cell structure. This indicates that intramolecular geometries are slightly affected by intermolecular interactions. However, the change in geometry is very small and the intramolecular geometric structure can be regarded to a good approximation as being essentially independent of the applied approximations to the XC functional.

**Summary.** The performance of standard semilocal approximations to the XC functional in describing the TTF and TCNQ crystals has been investigated in this section. While intramolecular bond lengths and angles are well captured within all the investigated levels of theory the inter molecular structure delicately depends on the choice of the functional. This applies first and foremost to the length of
5 Molecular crystals of TTF and TCNQ

the lattice vectors, which correspond to inter molecular distances. But also, to a less extend, to the monoclinic unit cell angle and to the molecular orientation within the unit cell. It has been shown that the inclusion of dispersion forces is essential for both crystals. This has been most demonstrative for the weakly interacting $a_\perp$ direction. In particular for the TTF crystal the TS method has been shown to perform excellent in describing both, intra- and intermolecular structural properties. For TCNQ the TS scheme gives results that agree well with experiment, although it tends to overestimate vdW forces. While PBE fails severely in describing the overall lattice structure, the LDA has been found to reproduce experimental results to some extent. However, the LDA is clearly outperformed by PBE+vdW. Having assessed the performance of XC functionals in describing geometric properties, the next section is devoted to cohesive properties.

5.3 Cohesive energy

The molecular cohesive energy $E_{\text{coh}}$ is a measure for the energy gain when a crystal is formed from isolated molecules. It is defined by

$$E_{\text{coh}} = -(E_{\text{bulk}} - nE_{\text{mol}})/n$$

where $E_{\text{mol}}$ and $E_{\text{bulk}}$ are the total energies for the (relaxed) single molecule in the gas phase and the bulk with $n$ molecules in the unit cell. This definition implies positive cohesive energy for bound systems, which gain energy upon forming a solid.

First the impact of the unit cell shape predicted by different XC functionals on the cohesive energy is inspected. To this end the cohesive energy for different XC functionals is calculated for unit cells where (i) the lattice vectors are kept fixed at their experimental values, relaxing only the atomic positions and (ii) fully relaxed structures, including lattice vectors. If a given functional predicts exactly the experimental unit cell shape then the cohesive energy will not change whether or not the lattice vectors are optimized. Conversely, if the cohesive energies differ than the cell shape obtained by a given functional will differ from the experimental one. Thus the change in the cohesive energy upon optimizing the lattice parameters establishes an energetic criterion for the quality of a given functional in predicting the unit cell structure.

Figure 5.8 presents cohesive energies for TTF (left) and TCNQ (right) for fully relaxed structures (solid lines) and structures where the lattice vectors were constrained to their experimental values (dashed line). In both cases the atomic positions have been fully relaxed within a given functional. The experimental lattice constants were taken from Refs. 247, 249 for TTF and TCNQ respectively. In general,
5.3 Cohesive energy

Figure 5.8: Cohesive energy for TTF (left) and TCNQ (right) crystals obtained by different XC functionals. The dashed lines correspond to structures where the unit cells are kept fixed to their experimental values with fully relaxed atomic positions within the given functional, whereas the solid lines correspond to a full structure optimization including unit cell relaxation. The red line shows the experimental value which was corrected for temperature and vibrational effects according to Equation (5.9).

the cohesive energy increases upon unit cell optimization, because the bulk total energy is decreased. This feature can be seen in Figure 5.8 (the numerical results are summarized in Table 5.7) where LDA and PBE exhibit similar energy gain upon unit cell relaxation, in contrast to to PBE+vdW for which it is essentially zero. More specifically, for the TTF (TCNQ) crystal the cohesive energy increases by about 0.14 (0.13) eV for LDA and 0.13 (0.11) eV for PBE, whereas it is insignificant for PBE+vdW (3 (6) meV). This implies that the PBE+vdW predicted unit cell shape is consistent with experiment in terms of the cohesive energy. It should be noted that the change in $E_{coh}$ upon cell relaxation corresponds to the change in the total energy divided by the number of molecules per unit cell since the molecular contributions cancel for the energy difference.

Experimentally, the enthalpy of sublimation $\Delta H_s$ was measured to be 0.99 (1.31) eV at a temperature of 345 (432) K for TTF (TCNQ)\textsuperscript{281,282} by means of torsion and mass loss effusion techniques. For a comparison with the theoretical cohesive energy at 0 K the relation\textsuperscript{179,280,283}

$$E_{coh} \approx \Delta H_s + 2RT$$

(5.9)

is used in order to estimate temperature and vibrational effects, where $T$ denotes
5 Molecular crystals of TTF and TCNQ

<table>
<thead>
<tr>
<th>XC</th>
<th>TTF</th>
<th>TCNQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDA</td>
<td>0.922</td>
<td>1.373</td>
</tr>
<tr>
<td>PBE</td>
<td>0.050</td>
<td>0.458</td>
</tr>
<tr>
<td>PBE+vdW</td>
<td>1.167</td>
<td>1.447</td>
</tr>
<tr>
<td>Exp.</td>
<td>1.047</td>
<td>1.412</td>
</tr>
</tbody>
</table>

Table 5.7: Cohesive energy [eV] of the TTF and TCNQ crystal for different XC functionals. The energies are compared between relaxed unit cells (UC) and unit cells that are fixed to their experimental values (in both cases the molecules were relaxed). The experimental values have been corrected for temperature and vibrational effects according to Equation (5.9).

Remarkably, the LDA predicts cohesive energies that are close to experimental values. Despite the fact that LDA predicts compressed unit cell shapes for both crystals (cf. Section 5.2.2) its cohesive energy further improves if the unit cell is allowed to relax. Clearly, PBE fails to describe the cohesive energy as it lacks the long range tail of vdW interactions and thus yields a cohesive energy that is almost zero for the TTF crystal. Similar holds true for TCNQ. However its PBE cohesive energy of 0.46 eV indicates that TCNQ is not purely vdW bound. In contrast, PBE+vdW gives cohesive energies that are close to experiment, although the TTF (TCNQ) result is overestimated by 11 (5)%.

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It should be noted, that the approximation (5.9) assumes that the molecules can be treated as rigid. This approximation is limited for the rather flexible TTF and TCNQ molecules. Therefore, no quantitative judgment on the performance of the presented (dispersion-corrected) semilocal XC functionals can be made. However, the observed trend, that a pairwise vdW correction overestimates cohesive energies was confirmed recently for several molecular crystals by a more elaborate treatment of vibrational effects via phonon calculations. This was attributed to the
lack of many-body contributions in a pairwise, additive $1/R^6$ correction scheme such as the Tkatchenko-Scheffler method.

5.4 Electronic properties

In this section basic electronic properties of the TTF and TCNQ single crystals will be presented. First, the band structures will be discussed for the ‘best’ theoretical geometries obtained in this study, which are for both crystals the PBE+vdW structures (see Section 5.2.2). After that, the electronic structure for strained geometries will be considered. While the main results of this section will be obtained using the PBE approximation, also other approximations to the XC functional (hybrid functionals) will be eventually discussed Section 5.4.3.

5.4.1 PBE electronic structure

Figure 5.9 (a) and (b) shows the Kohn-Sham PBE band structures of TTF and TCNQ crystals, respectively. The energy zero was set to the valence band maximum (VBM). The bands are plotted along paths connecting high symmetry points in the Brillouin zone (BZ), which is sketched in the bottom of the figure.

Upon building a crystal from free molecules the electronic structure of the molecules will be modified by intermolecular interactions. As there are two (four) molecules in the TTF (TCNQ) unit cell, each molecular state will be split into two (four) states per unit cell. Therefore, there are twice as many bands for the TCNQ crystal as compared to the TTF crystal.

The insets show the wavefunction of the uppermost valence band (VB) and the lowermost conduction band (CB) at the Γ point. For comparison, the HOMO is plotted Figs. 5.9 (d) and (f) and the LUMO in Figs. 5.9 (c) and (e) for the TTF and TCNQ molecules, respectively. Since in both crystals intermolecular interactions are weak, Fig. 5.9 shows that the VB and CB are built by the corresponding molecular HOMO and LUMO orbitals.

An additional consequence of the weak intermolecular interactions are relatively small bandwidths. They are of the order of tenths of an eV and thus, about one order of magnitude smaller than bandwidths of inorganic semiconductors, which are typically covalently bound.\textsuperscript{285–290} As a consequence, both crystals will exhibit a relatively poor band-like transport behavior.

Furthermore, the band dispersions are strongly anisotropic. This is a consequence of the anisotropic geometric arrangement of the molecules within their crystals and the anisotropy of the molecular orbitals.\textsuperscript{291} The VB dispersion of TTF, which is shown in Figure 5.9 (a), is most pronounced in the ΓX, and parallel to it, in the ZA and YC direction. The bands along the two other main directions,
Figure 5.9: Kohn-Sham (PBE) electronic band structure of (a) the TTF and (b) the TCNQ crystal for their PBE+vdW geometries. The energy zero was set to the VBM. The high symmetry points read in the dual basis: $\Gamma = (0, 0, 0)$, $Y = (0, 0, 1/2)$, $C = (0, 1/2, 1/2)$, $X = (0, 1/2, 0)$, $Z = (1/2, 0, 0)$, $A = (1/2, 1/2, 0)$ and $E = (1/2, 1/2, 1/2)$. The inset show isosurface plots the VB/CB electron wavefunction at $\Gamma$. For comparison, isosurface plots for the LUMO/HOMO of TTF (c)/(d) and TCNQ (e)/(f) molecules are shown in the bottom panel together with a sketch of the monoclinic Brillouin zone. The projection plane for the isosurface plots was chosen to be 0.5 Å parallel to the plane spanned by the sulfur atoms (nitrogen atoms for TCNQ) of the TTF molecule. The black and white color code corresponds to the ± sign on the wavefunction respectively. An isovalue of 0.05 Å$^{-3}$ was chosen for all isosurface plots.
### 5.4 Electronic properties

Table 5.8: Bandwidth [eV] for TTF and TCNQ along the $\Gamma Y$, $\Gamma X$, and $\Gamma Z$ direction in reciprocal space.

<table>
<thead>
<tr>
<th></th>
<th>VB:$\Gamma Y$</th>
<th>VB:$\Gamma X$</th>
<th>VB:$\Gamma Z$</th>
<th>CB:$\Gamma Y$</th>
<th>CB:$\Gamma X$</th>
<th>CB:$\Gamma Z$</th>
</tr>
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<tbody>
<tr>
<td>TTF</td>
<td>0.094</td>
<td>0.628</td>
<td>0.105</td>
<td>0.130</td>
<td>0.145</td>
<td>0.368</td>
</tr>
<tr>
<td>TCNQ</td>
<td>0.027</td>
<td>0.003</td>
<td>0.022</td>
<td>0.061</td>
<td>0.152</td>
<td>0.127</td>
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</tbody>
</table>

$\Gamma Y$ and $\Gamma Z$ have a similar dispersion, which is much less than the $\Gamma X$ direction. The bandwidths along the main directions in reciprocal space are summarized in Table 5.8. The TTF valence bandwidth along $\Gamma X$ amounts to 0.6 eV, whereas along $\Gamma Y$ and $\Gamma Z$ the bandwidth is about five times smaller. This indicates that the preferred hole transport channel is parallel to the $b^2$ direction, while the hole mobility is expected to be reduced in the remaining directions. For the TTF CB the strongest dispersion can be observed along the $\Gamma Z$ direction with a band with of about 0.4 eV. In the other directions the band dispersion is much smaller with a bandwidth of about 0.1 eV. Therefore, the main transport channel for electron transport is expected to be parallel to the $b^1$ direction.

Turning to TCNQ, the band structure is shown Figure 5.9 (b). The VB dispersion is essentially zero irrespective of the Brillouin zone direction. Therefore TCNQ is expected to exhibit poor band-like hole transport properties. However, the CB shows dispersive character, where the bandwidths are similar along the $\Gamma X$ and $\Gamma Z$ directions of about 0.2 and 0.1 eV, respectively. As a consequence, the TCNQ crystal exhibits only electron band-like transport, with a relatively weak direction dependence.

The PBE Kohn-Sham band gap amounts to 1.28 eV and 1.23 eV for TTF and TCNQ, respectively. The latter is in excellent agreement with 1.20 eV obtained by Shokaryev et al.\textsuperscript{273} using the GGA-PW91 XC functional.\textsuperscript{273} At this point no assessment for the PBE Kohn-Sham band gap can be made due to the lack (TTF) or the large discrepancy of 3-4 eV (TCNQ, see Table 5.1) of experimental data. However, it must be anticipated that the calculated PBE Kohn-Sham band gap substantially underestimates the crystalline band gap. This is known as a typical feature of the PBE approximation and has been shown for several oligoacene-based molecular crystals.\textsuperscript{293} For a better description of band gaps one could resort to hybrid functionals, which employ a fraction of exact exchange; their impact on the band gap of the TTF and TCNQ crystals will be discussed in Section 5.4.3.

\textsuperscript{d} The result in Ref.\textsuperscript{273} was obtained with a plane wave DFT implementation\textsuperscript{292}. It should be noted that the experimental TCNQ lattice parameters were adapted in this study. In this case (i.e. relaxing the atomic degrees of freedom only, using PBE), the FHI-aims\textsuperscript{132} result for the band gap amounts to 1.19 eV.
5 Molecular crystals of TTF and TCNQ

<table>
<thead>
<tr>
<th></th>
<th>Gas phase HOMO-LUMO gap [eV]</th>
<th>Molecule HOMO-LUMO gap [eV]</th>
<th>Crystal band gap [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TTF</td>
<td>1.95</td>
<td>1.95</td>
<td>1.28</td>
</tr>
<tr>
<td>TCNQ</td>
<td>1.43</td>
<td>1.44</td>
<td>1.23</td>
</tr>
</tbody>
</table>

Table 5.9: PBE HOMO-LUMO gap [eV] of the individual TTF and TCNQ molecules in their gas phase and their in-crystal configuration. In comparison, the crystalline band gaps are also tabulated. For the actual experimental/CCSD(T) IP and EA values, see Section 3.1

Next, the qualitative change in the electronic structure upon forming a crystal from individual molecules is considered. To this end the crystalline band gap is compared to the HOMO-LUMO gap of the individual molecules. Upon forming a crystal from molecules the electronic structure may be influenced by, (i) a change of the intramolecular structure and by (ii), intermolecular interactions, which lead to band splitting and band dispersion.

Table 5.9 compares the HOMO-LUMO gaps of the individual molecules with the crystalline band gaps. For the free molecules two configurations are compared, one with the gas phase geometry, and one where the molecule adapts the geometry, which it has within the crystal. The impact of intramolecular relaxation on the band gap is \( \leq 10 \) meV, and is therefore of minor importance for the band gap of both crystals.

Once the individual molecules have adapted their in-crystal geometry they can be thought as put together to form a crystal and thereby undergo intermolecular interactions. Compared to the HOMO-LUMO gap of the in-crystal configuration the crystalline band gap is about 0.7 (0.2) eV smaller for TTF (TCNQ). The stronger band gap reduction for TTF is mainly due to the overall stronger band dispersion of the VB and CB as compared to TCNQ (see Figure 5.9).

For both systems, the difference between the HOMO-LUMO gap of the free molecules and the band gap is below 1 eV in PBE. This would indicate that the crystalline band gap can be approximated by the HOMO-LUMO gap of the molecule. On the other hand the dielectric constant should be different between a molecule and a solid, because in the solid additional screening effects from the surrounding molecules are present. This eventually leads to a further reduction of the crystalline band gap as compared to the molecule. This has been shown for Pentacene and PTCDA by means of \( G_0W_0\)@PBE calculations, for which the crystalline band gap is reduced by 2 eV. Hence, the crystalline gap should not be approximated by that of the molecules.
5.4 Electronic properties

5.4.2 TTF and TCNQ under strain

So far, the electronic structure for the equilibrium crystal geometries were discussed. In the following, the electronic structure for strained geometries will be presented. Starting with the PBE+vdW equilibrium structures with unit cell Volume $V_0$ (obtained in Section 5.2), the change in the band structure upon compressing and expanding the individual crystals will be considered. In Section 5.2 it was shown that the LDA predicts smaller, and PBE predicts larger unit cell volumes as PBE+vdW. Therefore, the LDA and PBE unit cell geometries will be considered as realizations of strain transformations acting on the PBE+vdW equilibrium geometry $V_0$. In particular, the LDA geometries will be taken as compressed geometries, which reduce the unit cell volume by $\delta V_{\text{LDA}} = -13\%$ (TTF) and $\delta V_{\text{LDA}} = -10\%$ (TCNQ). Similar, as expanded geometries serve the PBE geometries which enhance the unit cell volume by $\delta V_{\text{PBE}} = +30\%$ (TTF) and $\delta V_{\text{PBE}} = +18\%$ (TCNQ).

The band structures and density of states (DOS) plots for the expanded geometries are shown in Figs. 5.10 (c) and (d) for TTF and TCNQ, respectively. In comparison to the equilibrium geometries —Figs. 5.10 (e) and (f)— the Kohn-Sham band gap reduces by 0.32 eV for TTF and 0.05 eV for TCNQ. This is mainly caused by a reduction of the valence (TTF) and conduction (TCNQ) band dispersion, which shifts the valence band minimum and the conduction band maximum further apart. This can be attributed to a decrease in the intermolecular interaction strength upon expanding the crystal, which leads to electronic states that are more localized on the individual molecules. As a consequence, the bands become flatter and the DOS sharper peaked.

For compressed geometries —Figs. 5.10 (a) and (b)— the opposite behavior is observed. The Kohn-Sham band gap reduces by 0.25 eV (TTF) and 0.12 eV (TCNQ) with respect to the equilibrium geometries $V_0$. Again, the change in the Kohn-Sham band gap is mainly caused by a change in the conduction (TTF) and valence (TCNQ) band dispersion, which is enhanced for compressed geometries and brings the valence band minimum and the conduction band maximum closer to each other. Upon compressing the crystal structures the intermolecular orbital overlap is increased. As a consequence, the electronic wavefunctions is more delocalized, which results in an increased band dispersion and a broader DOS.

In summary, the qualitative change of the PBE electronic structure for strained geometries was discussed. For expanded geometries it was found that for both crystals the Kohn-Sham band gap increases which is associated with a decrease of the band dispersion. And conversely for compressed geometries, for which band gap decreases due to an increase of the band dispersion. In particular, this implies, that the the electron (TCNQ) and hole (TTF) mobilities will increase if the crystals are under pressure.
5 Molecular crystals of TTF and TCNQ

Figure 5.10: PBE band structure and DOS (gray shaded, arbitrary units) for compressed ($\delta V_{\text{LDA}} = -13\% \ (-10\%)$ for TTF (TCNQ)) and expanded ($\delta V_{\text{PBE}} = 30\% \ (18\%)$ for TTF (TCNQ)) geometries obtained by a unit cell relaxation using LDA and PBE as well as for the PBE+vdW equilibrium geometry ($V_0$, top to bottom). The energy zero was set to the VBM. The left column shows the TTF results whereas those for TCNQ are shown to the right. At the top the TTF (left) and TCNQ (right) unit cells are shown. A tier 2 basis set was used and the DOS has been Gauss broadened by 0.08 eV.
5.4 Electronic properties

5.4.3 Electronic structure from hybrid functionals

So far the PBE electronic structure was presented for the equilibrium geometry (obtained by a unit cell relaxation using PBE+vdW), as well as for strained geometries. Here, the influence of other approximations for the XC functions than PBE for the electronic structure of TTF and TCNQ will be inspected. Specifically the PBE electronic structure will be compared to that of the HSE06 and PBE0 functional. The underlying geometry will be kept fixed at the PBE+vdW equilibrium geometry.

The three functionals differ in the treatment of the exchange energy. PBE0 admixtures to PBE $1/4$ of the exact exchange, $E_{\text{PBE0}}^X = 3/4E_{\text{PBE}}^X + 1/4E_{\text{EX}}^X$. HSE06 treats the short range exchange energy on the PBE0 level of theory while it obtains the long range exchange in PBE. The transition from PBE0 to PBE exchange energy is controlled by the range separation parameter $\omega$, which has a standard value of $0.11 \text{ bohr}^{-1}$. Hence HSE06 can be expected to lie in between PBE and PBE0.

Figure 5.11 shows the DOS plots and band gaps obtained in the PBE, HSE06 and PBE0 approximation to the XC functional for TTF and TCNQ single crystals. The energy zero was set to the VBM in all plots. Most prominent, the various approximations to the exchange energy differ in the (generalized) Kohn-Sham gap between occupied and unoccupied states. For TTF (Figure 5.11 (a)), the band gap opens from 1.28 eV to 2.25 and 2.98 eV in the sequence PBE, HSE06 and PBE0. The TCNQ band gap (Figure 5.11 (b)) amounts to 1.23 eV, 1.79 eV, and 2.43 eV for the same progression of XC functionals. The HSE06 band gap of TCNQ is remarkably close to the photoconductivity gap of 1.7 eV. UPS/IPES measurements of TCNQ films have determined the onset-to-onset gap to be 3.5-3.7 eV (cf. Table 5.1). Comparing to (inverse) photoemission experiments implies that all introduced XC functionals underestimate the the band gap by > 1 eV. Given the significant deviation between experimental data, and controversy in interpreting photoemission experiments (see also section 5.1) a judgment on the ability of standard hybrid XC functionals in describing the band gap of TCNQ cannot be delivered. This also holds true for TTF since there are no experimental data on the band gap to the best of my knowledge.

Apart from the difference in the Kohn-Sham band gap, the overall shape of the DOS is similar among the different functionals. Compared to HSE06 or PBE0, the PBE states lower than -2 eV appear to be squeezed for TTF. A similar behavior is found for TCNQ, where lower lying states appear to be shifted towards the VBM. This might be also the reason for the change in the PBE DOS character of TCNQ for energies below $-2.5$ eV. PBE0 and HSE06 give DOS plots that have virtually the same shape, although for HSE06 the occupied states tend to be slightly shifted towards larger energies.
Instead of judging the XC functional with respect to the Kohn-Sham band gap, Ramprasad et al.\textsuperscript{77} have proposed to seek for correlations between electronic structure features and cohesive properties of a material. Specifically a linear relationship between the valence bandwidth and formation energies for point defects was observed over the ($\alpha, \omega$) parameter space of the HSE family. The valence band width amounts to (0.97, 1.02, 1.03) eV for TTF and (0.37, 0.39, 0.41) eV for TCNQ in the sequence PBE, HSE06 and PBE0. Therefore, it is essentially independent of $\alpha$ and $\omega$ for the TTF and TCNQ crystals. Thus, for vdW bonded organic materials the valence bandwidth does not appear to be a good descriptor for the quality of the XC functional. Infact, it should be noted that these crystals are bound to a large extent by vdW forces (cf. Section 5.2 and 5.3). This implies, that rather the correlation energy than the exchange energy (which is varied within the HSE
5.4 Electronic properties

family) is responsible for cohesive properties.

In conclusion, the band gap strongly depends on the exchange treatment. In contrast, the band widths—in particular the valence band width—vary only to a minor extent among the PBE, HSE06, and PBE0 approximations.
6 TTF, TCNQ surfaces

In the following, basic properties of TTF and TCNQ surfaces and their dependence on the chosen cleavage plane are studied. In principle the molecules close to the surface can undergo surface relaxation and reconstruction. However, the present study is purely academic as it will neglect such surface relaxations and reconstructions and only bulk terminated surfaces, that are surfaces that preserve their bulk like atomic geometric configuration, are considered. Focus will be put on the cleavage plane dependence of the cleavage energy and the ionization potential. The latter allows to study the relative alignment of valence band maximum (VBM) and conduction band minimum (CBM) between TCNQ and TTF surfaces and thus represents the periodic pendant in two dimensions to the HOMO and LUMO levels of molecular clusters.

6.1 Modeling crystal surfaces: The super cell approach

Bulk materials which are strictly periodic in three dimensions can be canonically modeled within periodic boundary conditions (PBC). Systems of lower periodicity can be still treated with PBC techniques, by the so-called super cell approach. Within this approach surfaces are approximated by introducing a vacuum and a slab region into the unit cell (Figure 6.1). In the limit of infinite slab and vacuum thickness this construction leads to a description of a surface: it is semi-infinite in the direction of the vacuum and infinite in the remaining directions. This approach can only be computationally successful if a quantity of interest can be converged with respect to both, the slab and vacuum region and therefore introduces two additional convergence parameters.

Convergence with respect to the slab thickness is tested by successively adding 'unit slabs'. Here a unit slab is defined as that slab that can be built from a single bulk unit cell by cutting it apart along a given orientation and being periodic in the remaining ones. This prescription does not uniquely determine the cutting
Figure 6.1: Illustration of the super cell geometry for the [010] TTF surface, where the slab region consists of two mono layers. The black rectangles represent the unit cell which is periodically repeated in three dimensions. The dashed line indicates the work function reference level $z_0$ for the electrostatic potential and the location of the compensating dipole layer which are chosen in the middle of the vacuum.
6.1 Modeling crystal surfaces: The super cell approach

Figure 6.2: Illustration of the unit slabs for the low index surfaces of the TTF (a)-(c) and TCNQ (d)-(f). The shaded area indicates the vacuum region. In the lateral directions the slabs are periodic with respect to their bulk periodicity.

plane yet, as parallel planes have the same orientation. Therefore the chemical constraint is introduced, which requires that bonds within a molecule remain intact upon surface formation. Hence, the individual molecules are not allowed to be ripped apart when the surface is formed. This is reasonable, because the inter-molecular interaction is much weaker than the strong intra-molecular ones. Figure 6.2 shows the low index unit slabs of TTF and TCNQ obtained in this way, where the underlying bulk unit cells were chosen to be the optimized structures on the PBE+vdW level of theory as presented in Chapter 5. The [100] and [010] unit slab of TTF correspond to one mono layer (ML) of TTF molecules whereas the [001] unit slab consists of two mono layers which are arranged in a herringbone fashion. Due to the $C2/c$ bulk symmetry group all TCNQ unit slabs consist of two mono layers.

Although the super cell approach as employed in Chapter 6 is conceptually appealing it also introduces artefacts coming from long-range electrostatic interactions between periodic slab images. This is in particular the case for polar surfaces which have a non-vanishing net dipole moment. These undesired interactions may
be eliminated by the dipole correction.\textsuperscript{294,295} The dipole correction is reviewed in Appendix A.3. Its basic idea is to introduce a compensating dipole layer in the middle of the vacuum (indicated by the dashed line in Figure 6.1).

## 6.2 Cleavage energies

When a bulk crystal is cleaved it leaves two complementary surfaces exposed. The cleavage energy $\gamma$ is an energetic measure for this process. In DFT $\gamma$ is typically calculated at $T = 0$ with the additional approximation in which the contributions from pressure and (zero point) vibration are neglected.\textsuperscript{296} It is then calculated according to\textsuperscript{297}

$$\gamma = \frac{(E_{slab} - nE_{bulk})}{2A}, \quad (6.1)$$

where $A$ is the unit cell surface area, $E_{bulk}$ is the energy of the bulk crystal, $n$ is the number of unit slabs, and $E_{slab}$ is the total energy of the slab. The factor of two comes from the fact that the slab contains two surfaces. The cleavage energy corresponds to the average of both surface energies and corresponds to the surface energy only if both surfaces are equivalent. In general, $\gamma$ is anisotropic as it depends on the facet of the crystal for which it is calculated.

The super cell approach requires convergence with respect to slab and vacuum thickness. For the low index surface energies of TTF and TCNQ this is shown in Figure 6.4 on the PBE+vdW level of theory. For all systems convergence with respect to the vacuum region is already achieved at 20 Å. It should be noted, that for atom centered orbitals a bigger vacuum region does not increase the computational cost as the basis size does not depend on the unit cell size. The dependence of $\gamma$ on the slab thickness is very weak due to weak interaction of the individual slabs. It follows that all considered surface orientations are converged for one unit slab for TCNQ and two unit slabs for TTF.

Table 6.1 summarizes surface energies for standard semi-local functionals including vdW corrected PBE. As geometry the PBE+vdW optimized crystal geometry and its induced surface geometries was chosen. For a given functional, all surface energies of TTF are almost degenerate within $< 1 \text{ meV/Å}^2$ and thus TTF has no clearly preferred cleavage plane along the low index surfaces. Comparing the PBE and PBE+vdW values, Table 6.1 implies that the vdW interactions constitute the dominant contribution to $\gamma$. In particular, PBE would predict the [010] facet to have even negative cleavage energy, which would imply that the system would gain energy upon surface formation. In other words: without vdW forces the bulk crystal would not exist but would rather fall apart.

In contrast to TTF, the TCNQ surfaces do exhibit surface anisotropy of the
cleavage energy, where PBE+vdW and LDA predict the same energy hierarchy of increased cleaved energy in the sequence [010], [001], and [100] of surface orientations. A comparison between PBE and PBE+vdW in Table 6.1 shows that also the TCNQ crystal is predominantly vdW bound. The surface anisotropy of TCNQ may be explained in terms of the different TCNQ crystal packings along the individual directions. The [010] direction with the lowest cleavage energy –Fig. 6.2 (e)– consists of TCNQ monolayers with weak intermolecular interaction between two adjacent monolayers. The [001] direction –Fig. 6.2 (f)– has a similar vdW contribution as the [010] direction but with additional interlayer N···H interactions contributing to \( \gamma \). Due to the \( C2/c \) bulk symmetry group of TCNQ the [100] surface –Fig. 6.2 (d)– consists of two interpenetrating TCNQ layers, which gives
6 TTF, TCNQ surfaces

Table 6.1: Cleavage energy $\gamma$ [meV/A$^2$] for the low-index surfaces of TTF and TCNQ. The geometries were the bulk terminated surfaces of the PBE+vdW optimized crystals and the tier 2 basis was used.

<table>
<thead>
<tr>
<th>Surface</th>
<th>LDA</th>
<th>PBE</th>
<th>PBE+vdW</th>
</tr>
</thead>
<tbody>
<tr>
<td>TTF</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[010]</td>
<td>5.9</td>
<td>4.0</td>
<td>-0.4</td>
</tr>
<tr>
<td>[001]</td>
<td>5.9</td>
<td>9.8</td>
<td>0.5</td>
</tr>
<tr>
<td>TCNQ</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[010]</td>
<td>9.0</td>
<td>6.7</td>
<td></td>
</tr>
<tr>
<td>[001]</td>
<td>8.3</td>
<td>9.9</td>
<td></td>
</tr>
</tbody>
</table>

rise to increased intermolecular vdW contributions and thus the largest cleavage energy.

While it is clear that vdW contribution are important for calculating cleavage energies an ultimate judgment on the accuracy of PBE+vdW for the presented surfaces is not possible, due to the lack of experimental data or higher level calculations. Furthermore, the employed additive, pairwise vdW correction scheme could show deficiencies for cleavage energies. While there exists a surface adapted extension of the TS scheme$^{298}$, this may still not be applicable for calculating cleavage energies, because Eq. (6.1) also depends on the bulk total energy. For finite gap systems one possible way beyond a pairwise vdW scheme that is applicable for infinite and semi-infinite systems has been proposed recently.$^{185}$

6.3 Surface ionization potential

In a 2D-periodic (in $x$ and $y$) slab calculation, the ionization potential (IP) is obtained as the difference between the electrostatic potential at infinity ($z = +\infty$) and the KS eigenstate at the VBM.

$$\text{IP} = v(\infty) - \epsilon_{\text{VBM}}$$

(6.2)

Within the 3D super cell approach, infinity is approximated by a point $z_0$ far away from the surface, and the lateral average over the surface unit cell of the electrostatic potential is considered. For a coordinate system in which the surface normal points in the $z$-direction, this can be written as

$$v(\infty) \to \bar{v}(z_0) := \frac{1}{A} \int_A \int \nu(x, y, z_0) \, dx \, dy,$$

(6.3)

where $A$ is the area of the surface unit cell. By symmetry it is most convenient to place $z_0$ in the middle of the vacuum as illustrated by the dashed line in Figure 6.1.
6.3 Surface ionization potential

![Figure 6.4](image)

Figure 6.4: Convergence of the PBE IP with respect to the slab and vacuum thickness for TTF (a)-(b) and TCNQ (c)-(d). As geometries the bulk terminated surfaces of the PBE+vdW optimized crystals were taken and the tier 2 basis was employed.

The super cell approach requires convergence with respect to both, the slab thickness and the vacuum region (and hence also for the reference point $z_0$ of the electrostatic potential) for the IP. This is illustrated in Figure 6.4 for various TTF and TCNQ surface orientations on the PBE level of theory. Similar to what has been found for surface energies, convergence of the IP with respect to the vacuum is readily achieved at 20 Å. Convergence with respect to the slab thickness is material and orientation dependent. For all TCNQ surfaces, the IP is converged within 15 meV or better for one unit slab, which corresponds to 2 mono layers (cf. Figure 6.2). The [100] and [001] TTF surfaces are converged within 40 meV for one unit slab and within 15 meV for two unit slabs. For the remaining [010] TTF surface, convergence within 20 (50) meV is achieved for 5 (3) unit slabs, while the
error bar for one (two) unit slab is about 0.2 (0.1) eV. As a compromise between accuracy and computational cost one unit slab for all TCNQ surfaces, two unit slabs for the [100] and [001] TTF planes, and three unit slabs for the [010] TTF plane is chosen.

If a crystal is cleaved, the two ensuing complementary surfaces could in principle have different IPs due to different vacuum potentials of the individual surfaces \(v(\infty)\) in equation 6.2. Within the super cell approach, the dipole correction then amounts to the difference between the individual vacuum potentials on either side of the slab. However, for the considered surfaces the potential jump across the slab as given by the compensating dipole layers is essentially zero (< 1 meV). Therefore, for a given cleavage plane, the complementary surfaces possess the same IP.

An the other hand, Figure 6.4 reveals that the IP strongly depends on the cleavage plane. For TCNQ the IP of the [100],[010],[001] plane is 7.63, 6.58, 7.97 eV, while for TTF the corresponding values read 2.87, 3.86, 3.05 eV. The surface anisotropy is most pronounced between the [010] and [001] planes for TCNQ yielding an IP difference \(\Delta IP = 1.4\) eV. For TTF the biggest difference can be observed between the [100] and [010] surfaces, for which \(\Delta IP = 1\) eV. For metals the surface anisotropy of the work function is well established. Interestingly, for organic compounds, the orientation dependence of the ionization potential was discussed only recently in the literature and can be attributed to the different surface orientations of the individual molecules. An immediate consequence of the crystal-face dependence of the IP is, that it may not be approximated by the IP of a single molecule. This approximation would imply that the IP is independent of the surface orientation, which contradicts the above results for TTF and TCNQ.

In principle, the calculated IPs allow a comparison with those obtained by UPS measurements, (see Table 5.1). For TTF and TCNQ, the structural properties of the UPS samples have not been addressed so far. Therefore, it is not clear, which of the crystal faces is exposed in a thin film samples, or if the sample exhibits a morphology that is totally different from any crystal surface. In the light of the discussion above, the IP exhibits strong surface anisotropy. Thus, detailed knowledge of the experimental film morphology is indispensable and motivates future experimental work in this direction.

The above results allow to study the TTF/TCNQ interface in the non-interacting limit. In Section 5.4 it has been shown that the TTF and TCNQ single crystals exhibit a finite band gap, and taking into account that PBE Kohn-Sham band gaps are notoriously smaller than fundamental band gaps, they may be essentially regarded as insulators. However, at their mutual interface, new physical phenomena occur which are different from the electronic properties of the individual crystals. Alves et al. have observed that the TTF/TCNQ interface exhibits metallic con-
duction. The origin of this two dimensional electron gas at the interface has eluded a convincing explanation so far. However, it may be suspected that it is strongly related to the question of charge transfer. Modeling charge transfer with DFT is a delicate task, which has been discussed in Section 3.1 for the TTF/TCNQ dimer. This dimer is an important building block of the interface and allowed to identify the failures of standard XC functionals; in particular the relative alignment of the TCNQ-LUMO and TTF-HOMO needs to be described qualitatively correct in order to avoid an erroneous description of charge transfer. For the interface, the periodic pendant is the relative alignment of the TTF valence band maximum (VBM) and the TCNQ conduction band minimum (CBM) of the individual surfaces. For the case of PBE this is illustrated in Figure 6.5, where solid lines indicate the position of the VBM and dashed lines that of the CBM for various surface orientations. The energy zero was set to the common vacuum level, \( v(\infty) \).

The PBE Kohn-Sham band gap of TCNQ amounts to 1.33, 1.33, 1.29 eV for the [100], [010], [001] surface and is thus essentially independent of the surface orientation. As a consequence, the energetic position of the CBMs appear to be rigidly shifted (by the PBE KS gap) with respect to the VBMs. The relative alignment of the TTF VBM and TCNQ CBM depends significantly on surface orientation and may differ by more than 2 eV. The extreme cases are the alignment of [010] TCNQ with [010] TTF and [001] TCNQ with [100] TTF. The former results in a difference between the TTF VBM and the TCNQ CBM of 1.39 eV whereas the in the latter case the difference amounts to 3.81 eV.

PBE puts the TTF CBM above the TCNQ CBM, irrespective of the surface ori-
entation. This would imply that a certain amount of electron density is transferred from the TTF slab to the TCNQ slab. This would further induce a dipole moment that shifts the vacuum level across the interface. Further, the transferred electron density would partially occupy the previously unoccupied conduction band of TCNQ and thereby will leave partially occupied valence bands on the TTF side. This would be one possible mechanism of creating metallic states at the TTF-TCNQ interface. In fact, preliminary PBE calculations for various TTF-TCNQ interface geometries show metallic bands, that emerge from partial charge transfer between the TTF and TCNQ interface layers.

However, in the light of the results of the TTF/TCNQ dimer of Section 3.1, recall that the PBE approximation favors erroneous charge transfer due to a wrong level ordering. This problem could be solved using the PBEh($\alpha^*$) functional from Section 3.1. The inclusion of exact exchange would open the GKS band gap and thus shift the VBM in Figure 6.5 downward and the CBM upward in energy. Whether or not the TCNQ CBM is below the TTF VB und therefore electron transfer induced metallic bands occurs depends then on two parameters: The GKS band gap (determined by $\alpha^*$) and the surface orientation (which determines the IP anisotropy).

It is important to note, that the $\alpha^*$ value for the periodic structures will be different than for molecules, due to additional screening effects of the surrounding molecules. The determination of $\alpha^*$ for the individual surfaces requires periodic $G_0W_0$ calculations, and is subject to potential future work.
Summary and outlook

In this thesis the performance and limitations of DFT with approximate XC functional was studied for prototypical materials in the field of organic electronics. In the following the basic results are summarized in the light of the underlying assumptions and approximations in order to identify potential future steps.

Methodology

In Chapter 3 a consistency requirement for the XC functional with respect to the $G_0W_0$ approach was introduced. This was achieved by requiring that the formally exact IP-HOMO condition of exact DFT is obeyed as closely as possible. For this purpose hybrid functionals were employed, which allowed me to determine the required fraction of exact exchange ($\alpha$), resulting in an improved description of the frontier orbital level. With this functional, I obtained the correct description of the ground-state charge density of the pathological TTF-TCNQ complex. However the proposed scheme, relies on i) the assumption that the parametrization of the PBEh-family is general enough, and ii) on the accuracy of the $GW$ approximation. Numerical results for the G2 data set indicate that the first point does not represent a major limitation. However, there could be materials for which the parametrization of the PBEh-family is too restrictive; in particular the PBEh-family keeps the correlation energy fixed to the PBE approximation. Furthermore, for combined systems, where each sub-systems requires different $\alpha$ values, e.g., molecules on surfaces, it is not clear when a single choice of $\alpha$ may give a satisfactory description for the whole system. For molecules, the PBEh-family of XC functionals may not be the most suitable functional parametrization, since the asymptotic behavior of the associated XC potential goes with $\alpha/r$. In contrast, the exact XC potential must fall off with $1/r$. While the PBEh-family has at least the correct polynomial power law for $\alpha \neq 0$, the long-range XC potential of the HSE-family for $\omega \neq 0$ is given by the PBE approximation, which vanishes exponentially. From this point of view, a range-separation ansatz complementary to HSE could be ben-
eficial, i.e. describing the long-range exchange energy with exact exchange and the short range with semi-local exchange. An example of such a functional has been proposed recently.\textsuperscript{157,303}

The PBEh(\(\alpha^*\)) functional also hinges on the accuracy of the \(GW\) approximation, which is obtained from Hedin’s equation by neglecting vertex corrections. It is known that the \(GW\) approximation neglects important electron-hole diagrams that would increase the screening \(W\).\textsuperscript{304,305} As a consequence, HOMO-LUMO gaps should be smaller than predicted by \(GW\). Thus, if a beyond \(GW\) self-energy were used, it would be expected to yield slightly smaller optimized \(\alpha\) values.

In Section 3.3 the starting point dependence of the \(rPT2\) scheme was assessed by means of comprehensive benchmark calculations. Furthermore, the compatibility of PBEh(\(\alpha^*\)) with the Tkatchenko-Scheffler (TS) van der Waals correction scheme was investigated and a RPA-based total-energy ansatz, EX@PBEh(\(\alpha^*\))+cRPA-PBE, was proposed. EX@PBEh(\(\alpha^*\))+cRPA-PBE turned out to be the most accurate method studied in this thesis for non-covalent interactions (S66 dataset), while it appears to be less accurate for atomization energies and barrier heights. The TS scheme was found to be compatible with the PBEh(\(\alpha^*\)) functional. In fact, the mean absolute percentage error with respect to CCSD(T) reference data of PBEh(\(\alpha^*\))+TS reduces almost by a factor of two as compared to PBE+TS, which was attributed to the damping function present in the TS scheme. The \(rPT2\) scheme exhibits a strong dependence on the fraction of exact exchange in the underlying functional with a clear trend of performance loss upon increasing \(\alpha\). This leads to \(rPT2@PBE\) having the most ‘balanced’ performance over a wide range of different chemical and electronic environments. At the same time, it was shown that \(rPT2@PBE\) qualitatively fails for the prototypical TTF-TCNQ donor acceptor complex, as the \(rPT2\) correction cannot cure the error in the underlying PBE functional. For organic electronics, which often contain donor-acceptor complexes, this is disappointing. This clearly motivates further research in order to extend the \(rPT2\) method such that it becomes accurate and reliable also for these materials.

Materials

Both TTF and TCNQ form molecular crystals with a monoclinic unit cell. In order to compute the equilibrium structure of such low-symmetry unit cell shapes I have implemented the numerical stress tensor and unit cell relaxation in the FHI-aims code (Chapter 4).

In Chapter 5, basic geometric, energetic, and electronic properties of TTF and TCNQ single crystals were investigated. Again, the most fundamental approximation is the choice of the XC functional. For this class of materials, it has been shown that both the correlation and exchange energy contributions have to be
treated with special care. For the correlation part it has been shown that the inclusion of vdw forces is crucial to describe unit cell geometries and cohesive energies properly.

Exact exchange mostly affects the crystalline band gap. The appropriate fraction of exact exchange could be obtained by PBEh(α∗). It can be expected that for crystals the value of α∗ is different (smaller) than for the individual molecules because of additional screening effects in the bulk. Therefore, periodic G0W0 calculations would be beneficial.

In Chapter 6 basic properties of TTF and TCNQ surfaces were considered. The ionization potential was shown to exhibit strong surface anisotropy, and may differ by over one eV between different surface orientations. Unfortunately, in the published experimental UPS data the surface orientation of the measured TTF and TCNQ films has not been addressed so far. Therefore, the results of Chapter 6 motivate further experimental research in this direction. From the level alignment between TTF and TCNQ surfaces, it follows that electron-density transfer from TTF to TCNQ depends on both the mutual surface orientation and a proper description of the valence and conduction band position. The latter can be achieved by the PBEh(α∗) functional, which requires periodic G0W0 calculations for the determination of α∗. This would clarify if the interface of TTF and TCNQ exhibits metallic bands caused by electron transfer.

There’s is plenty of room at the bottom is a well known quote from Richard Feynman. It expresses the basic idea behind organic electronics: designing molecular structures with certain electronic and mechanical properties. Giving the rich world of organic chemistry, theory can have an important role in this field as a screening tool for desired compounds and to provide insight in key properties and physical processes. Since organic compounds are complicated in their structure it is important to describe realistic structures. This limits theoretical approaches by model Hamiltonians and one has to resort to ab initio methods. The contribution of this thesis is to show how and why standard ab initio methods can fail severely and to provide a theoretical framework to overcome these limitations. However, in order to improve the predictive power of DFT methods, it would be desirable to have an error estimate without resorting to high-level quantum-chemical calculations or experiment. Furthermore, their computational cost is still significant. Thus, there is plenty of room at the bottom of theory for a reliable screening tool for potential applicable materials at modest computational cost.
A.1 Basis sets

This appendix serves as an introduction to the basis type that was used in this thesis. The employed basis set is the most important distinctive feature between the many DFT implementations that exist nowadays. Here, focus will be put on the FHI-aims\textsuperscript{132} characteristic numerical atom centered orbitals (for a review of alternative basis set types, see Ref.\textsuperscript{307}). From a mathematical point of view, it is desirable to have a basis set that spans the full one-particle Hilbert space $\mathcal{H}$. However, in practical calculations this is never achieved and the basis has to be truncated. In a DFT calculation one therefore has to assure that the employed basis set is large enough. This can be done by performing a so-called convergence test: one starts with a given set of basis functions and successively adds further basis functions until a quantity of interest changes only within an acceptable error bar. Appendix A.2 shows an example of this procedure. The convergence behavior depends in general on the quantity of interest and on the form of the Hamiltonian for which the eigenvalue problem needs to be solved. For example total energy differences tend to converge faster than total energies. Furthermore, Hamiltonians that depend on the unoccupied spectrum (e.g. RPA or $G_0W_0$) converge worse than those which rely on the occupied spectrum only (e.g. standard KS schemes).

Numerical atom centered orbitals (NAOs)

This type of basis set is of the form\textsuperscript{132}

$$\phi_n = \frac{u_n(r)}{r} Y_{lm}(\Omega), \quad r \in \mathbb{R}, \quad \Omega \in S^2. \quad (A.1)$$

A basis function $\phi_n$ consists of a radial part $u_n(r)$ and an angular part, which is given by the spherical harmonics $Y_{lm}(\Omega)$. The radial shape $u_n(r)$ is numerically
A Appendix

tabulated, and is obtained by a numerical solution of a 1 dimensional Schrödinger like radial equation

\[
\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + v_{\text{shape}}(r) + v_{\text{cut}}(r)\right] u_n(r) = \epsilon_n u_n(r), \tag{A.2}
\]

where \(l\) is the angular quantum number. By Eq. (A.2), \(u_n(r)\) is determined by (i) \(l\), (ii) a potential \(v_{\text{shape}}\) that shall determine the main shape of \(u_n(r)\), and (iii) a confining potential \(v_{\text{cut}}\). The task of \(v_{\text{cut}}\) is to warrant a smooth decay of each radial function \(u_n(r)\) to zero outside a certain region \(r \geq r_{\text{cut}}\). This may be achieved by choosing \(v_{\text{cut}}(r)\) as

\[
v_{\text{cut}}(r) = \begin{cases} 
0 & r \leq r_{\text{onset}}, \\
\frac{s}{(r-r_{\text{onset}})^w} e^{r-r_{\text{onset}}} & r_{\text{onset}} < r < r_{\text{cut}}, \\
0 & r \geq r_{\text{cut}},
\end{cases} \tag{A.3}
\]

where \(s\) and \(w\) are global scaling parameters, and \(r_{\text{onset}}\) determines the onset of the exponential part of \(v_{\text{cut}}\). Equations (A.2-A.3) allow to construct radial NAO basis functions for each species by:

1. Construction of a (functional dependent) minimal basis for the free atom, by setting \(v_{\text{shape}}\) in Eq. (A.2) to the self-consistent radial part of the KS potential (for HF or hybrid functionals, see Ref.127).  

2. Generating a pool of (functional independent) additional ‘candidate’ basis functions, by solving Eq. (A.2) for various choices of \(v_{\text{shape}}\). In FHI-aims these are hydrogen-like, atom-like, or cation-like potentials.

3. Starting with the minimal basis set, generate a hierarchy of additional basis functions. These are obtain by picking out those of the candidate pool of step 2, that contribute most to a pre-defined objective function. In FHI-aims the objective function is chosen to be the LDA total energy of a di-atomic dimer of a given species.

The additional radial basis functions obtained in step 3 are grouped together in different ‘tiers’. Table A.1 summarizes these tiers for the H, C, N and S atoms (these are the species that build TTF and TCNQ).

Once the radial part of the basis function is constructed, its 3 dimensional form is obtained by multiplication of \(2l + 1\) angular momentum functions, according to Equation (A.1).
Table A.1: Standard radial basis functions for H, C, N, and S. The minimal basis consists of free atom radial functions (notation: [noble gas configuration] + additional valence functions). The additional radial functions are of the form \( H(nl, z) \) or \( X^{2+}(nl) \). \( H(nl, z) \) denotes a hydrogen-like radial function for the Coulomb potential in Equation (A.2), \( v_{\text{shape}}(r) = \frac{z}{r}, z \in \mathbb{R} \), with quantum numbers \( n, l \) (using the notation \( s (l = 0), p (l = 1), d (l = 2), \ldots \)). \( X^{2+}(nl) \) labels the \( n, l \) function for the doubly positive charged ion \( X \).

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<th>H</th>
<th>C</th>
<th>N</th>
<th>S</th>
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<td>([\text{He}]+2s2p)</td>
<td>([\text{Ne}]+3s3p)</td>
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<td>(S^{2+}(3d))</td>
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<td>(H(3s, 5.8))</td>
<td>(H(4f, 7))</td>
<td>(S^{2+}(3s))</td>
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<td>(H(4f, 10.8))</td>
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<td>(H(3p, 5.8))</td>
<td>(H(5g, 10.8))</td>
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<td>(H(4f, 11.6))</td>
<td>(H(4p, 10.4))</td>
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<td>(\ldots)</td>
<td>(\ldots)</td>
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</table>
A Appendix

A.2 Convergence tests for the numerical stress tensor

In this appendix the convergence behavior of the numerical stress tensor, $\sigma$, is investigated. Three illustrative examples consisting of a metal (FCC-Al), a semiconductor (diamond-Si) and an insulator (Polyethylene) are considered. Experimental lattice parameters were taken for diamond-Si ($\|a_i\|_2 = 3.84$ Å, $\alpha_i = 60^\circ$, $\forall i$), LDA lattice constants for fcc-Al ($\|a_i\|_2 = 2.814$ Å, $\alpha_i = 60^\circ$, $\forall i$), and for Polyethylene a strained geometry with lattice vectors $a_1 = (8.7, 0.0, 0.0)$, $a_2 = (0.0, 6.1, 0.0)$, $a_3 = (0.0, 0.0, 2.563)$ was considered.

The convergence tests are performed by first fixing all parameters to their default values within tight FHI-aims settings (the k-grid sampling of the Brillouin zone was chosen $20 \times 20 \times 20$ for Al, $8 \times 8 \times 8$ for Si and $7 \times 7 \times 7$ for Polyethylene). Second, one parameter is picked and varied systematically, while keeping the others fixed. All tests were performed for the infinity norm of the stress tensor $\|\sigma\|_\infty := \max_{ij} |\sigma_{ij}|$, using the PBE XC functional. The results are summarized in Fig. A.1 for the following convergence parameters (for a detailed explanation of these parameters, see FHI-aims publication

i) **The step width** $h$ for the evaluation of the numeric derivative as given in Eq. (4.10). Figure A.1 (a) shows that for $h \leq 0.01$ the stress tensor is relatively insensitive with respect to the the choice of $h$. In particular the default value of $h = 10^{-4}$ is converged within $10^{-3}$ eV Å$^{-3}$.

ii) **Basis set.** Figure A.1 (b) shows the basis set convergence (where each higher level includes the lower levels). The most pronounced difference is for Silicon when the basis is increased from tier 1 to tier 2, whereas a further increase of the basis set changes $\sigma$ only within $O(10^{-3})$ eV Å$^{-3}$. Hence, the default choice for the basis set ensures a convergence within $10^{-3}$ eV Å$^{-3}$ for all presented systems.

iii) **k-grid sampling of the Brillouin zone.** For the insulator (Polyethylene) and the semiconductor (Si), the k-grid convergence is unproblematic –Figure A.1 (c). For the metallic system the k-grid needs to be sufficiently dense in order to ensure convergence within $10^{-3}$ eV Å$^{-3}$. This is to be expected since the strongly dispersive electronic band structure of Al requires a denser k-mesh than for systems where electronic bands are flatter.

iv) **Onset of the cutoff radius**, $r_{\text{onset}}$; see Eq. (A.3). Figure A.1 (d) shows, that the default value of $r_{\text{onset}} = 4$ Å already ensures convergence within $10^{-3}$ eV Å$^{-3}$. Increasing $r_{\text{onset}}$ further changes $\sigma$ only slightly.

v) **Maximum angular momentum** $l_{\text{max}}$ in the multipole decomposition of the Hartree potential. Similar to $r_{\text{onset}}$, $l_{\text{max}}$ is converged for the default tight value
A.2 Convergence tests for the numerical stress tensor

Figure A.1: Convergence tests of the numeric stress tensor for FCC-Al, cubic-polyethylene and diamond-Si crystals. The figures on the top illustrate the individual unit cell geometries (see text for unit cell parameters).
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of $l_{\text{max}} = 6$ within $10^{-3}$ eVÅ$^{-3}$. The stress tensor of the Al and Polyethylene crystals is insensitive to a further increase of $l_{\text{max}}$, whereas it changes slightly for Si.

vi) Integration grid. Integration in FHI-aims is performed on real space grid that is built from atom-centered grids around each atom. An integration is performed by integrating first individually over all atom-centered grids, and then ‘gluing’ them together by employing partition of unity. Each single-atom integral is split into angular and radial parts, by introducing $N_r$ integration spheres. On each integration sphere, a modified Lebedev grid$^{132,308}$ is used as angular grid. The accuracy of the integration grid can be improved, by increasing the radial and angular grid densities. The radial grid density can be increased by placing additional integration spheres in between the $N_r$ given ones. The number $(N_r + 1)(N_{r, \text{div}} - 1)$ of these additional integration shells is determined by the integer $N_{r, \text{div}}$, which is called ‘radial multiplier’ in the code. The angular grid density can be increased by adding additional grid points $N_{\text{ang, max}}$ on the integration spheres. The index ‘max’ refers to the fact that, the number of angular grid points depends on the respective integration sphere (less angular points are needed for small spheres near the nucleus than for larger spheres, cf. Ref$^{132}$). The convergence test for $N_{\text{ang, max}}$ and $N_{r, \text{div}}$ is illustrated in Fig. A.1 (g) and (f), respectively. The default integration grid settings, $(N_{\text{ang, max}}, N_{r, \text{div}}) = (434, 2)$, provide an accuracy of $O(10^{-3})$ eVÅ$^{-3}$. Increasing the grid density further, gives only small changes to $\sigma$.

In summary, the numerical stress tensor is converged within $O(10^{-3})$ eVÅ$^{-3}$ for default tight settings in the presented test cases. This accuracy is similar to the analytic force implementation, which is accurate within $O(10^{-2}) - O(10^{-3})$ eVÅ$^{-1}$, depending on the system$^{107}$. For local structure relaxation schemes such an accuracy is sufficient, since these methods use a typical force convergence criterion of $10^{-2}$ eVÅ$^{-1}$ ($\epsilon$ in Algorithms 4 or 5).

A.3 Dipole correction for slab calculations

Although the super cell approach as employed in Chapter 6 is conceptually appealing it also introduces artefacts coming from long-range electrostatic interactions between periodic slab images. This is in particular the case for polar surfaces which have a non-vanishing net dipole moment. There are two ways to eliminate these undesired interactions: one approach introduces a compensating dipole field$^{294,295}$ into the vacuum region, and the other modifies the coulomb potential$^{309,310}$ by applying a spatial cutoff in the direction of the vacuum region. The former approach is also called dipole correction and is applicable only for surfaces whereas the latter
A.3 Dipole correction for slab calculations

can be also applied for systems with lower than two dimensional periodicity. While both schemes differ in their basic ideas it has been shown that both schemes yield very similar results\textsuperscript{311}.

In order to illustrate the dipole correction (which is implemented in FHI-aims\textsuperscript{132}), introduce a coordinate system in which the lateral directions of the slab are in the $x$-$y$ plane and the surface normal points in the the $z$-direction. First consider an isolated slab which is not repeated in the $z$-direction yet. Let $\rho$ be the total charge density and consider the planar averaged charge density

$$\bar{\rho}(z) = \frac{1}{A} \int \int_{A} \rho \, dx \, dy,$$

(A.4)

where $A$ is the area of the surface unit cell. The corresponding electrostatic potential $\bar{v}$ due to $\bar{\rho}$ solves the Poisson equation $\partial_{zz} \bar{v}(z) = -4\pi \bar{\rho}(z)$. In particular, for a point well above (below) the slab where $\bar{\rho}$ vanishes, $\bar{v}$ is of the form\textsuperscript{294} $2\pi \mu (-2\pi \mu)$, with the dipole moment

$$\mu = \int_{R} \bar{\rho}(z) z \, dz.$$  

(A.5)

The potential of the isolated slab thus exhibits a constant jump across the slab. However, in the super cell approach the slab is additionally repeated periodically in the $z$-direction with lattice vector $L_z$. Therefore the potential must be adapted\textsuperscript{a} in order to obey periodic boundary conditions\textsuperscript{295},

$$\bar{v}(z) \to \bar{v}^{\text{PBC}}(z) = \bar{v}(z) - 4\pi \mu \left( \frac{z}{L_z} - \Theta(z_0 - z) \right), \quad 0 < z \leq L_z,$$  

(A.6)

where $\Theta$ is the step function. In Eq. (A.6) the additional term in the bracket accounts for PBC. It changes the physics of the system as it introduces a constant electric field. The idea of the dipole correction is then to approximate the isolated slab within PBC by introducing a correcting potential $v^{\text{dip}}$ that exactly removes

\textsuperscript{aFix a point $z_0$ below the surface which is not contained in the support of $\bar{\rho}$, $z_0 \notin \text{supp}(\bar{\rho})$. For a sufficient small $\delta > 0$ the potential is of the form $\bar{v}(z_0 + \delta) = -2\pi \mu$, $\bar{v}(z_0 + L_z - \delta) = 2\pi \mu$. As the potential is only fixed up to a linear term by the Poisson equation, make the following ansatz for the periodic solution: $v^{\text{PBC}}(z) = \bar{v}(z) + \alpha z$. Imposing PBC and taking the limit from above, determines $\alpha$ on the open interval $(z_0, z_0 + L_z)$: $\lim_{\delta \to 0^+} \bar{v}(z_0 + \delta) = \lim_{\delta \to 0^+} \bar{v}(z_0 + L_z - \delta) \Rightarrow \alpha = -4\pi \mu / L_z$. For this value of $\alpha$ consider the boundary of the interval by taking the limit $\lim_{\delta \to 0^+} \bar{v}(z_0 + L_z + \delta) = \lim_{\delta \to 0^+} \bar{v}(z_0 + \delta) - 4\pi \mu$. This gives raise to an additional step function $4\pi \mu \Theta(z_0 - z)$.}
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this additional term

\[ v_{\text{dip}} = +4\pi \mu \left( \frac{z}{L_z} - \Theta(z_0 - z) \right), \quad 0 < z \leq L_z, \tag{A.7} \]

and has to be added to the Hartree potential\textsuperscript{312}. The potential jump due to the \( \Theta \)-function must be placed outside the charge density. In practice it is put in the middle of the vacuum as indicated by the dashed line in Figure 6.1.
A.4 Detailed results for benchmark calculations

This appendix contains detailed results of molecular benchmark calculations for ionization potentials, binding energies, atomization energies, and barrier heights. The PBE, PBE0, and PBEh(α*) functionals were employed within the generalized Kohn-Sham (GKS) framework and as starting points for various approximations within many body perturbation theory.

For PBEh(α*), the fraction of exact exchange (α*) was determined by first performing single point calculations $G_0W_0@PBEh(\alpha)$ for $\alpha = 0.0, 0.25, 0.5, 0.75, 1.0$ followed by a quadratic fit for the difference of the KS and QP HOMO energies. The minimum of the quadratic fit function is then determined analytically on the compact interval [0, 1].
Table A.2: Ionization potentials [eV] for a subset of 50 molecules of the G2 test set. The IPs were obtained by taking the negative of the (G)KS HOMO-level, the $G_0W_0$, and $\Delta$-SCF method as well as by the Slater-Janak model (SJM). The results were obtained for three XC functionals within the PBE-hybrid family, which are labeled by their amount of exact exchange (0 for PBE, 1/4 for PBE0, and $\alpha^*$ for PBEH($\alpha^*$)). A tier 4 basis set augmented with diffuse functions from aug-cc-pV5Z (tier 4 + a5Z-d) was used. Also tabulated are experimental reference data taken from the NIST database and the $\alpha^*$ values.

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<th>(G)KS 1/4</th>
<th>(G)KS $\alpha^*$</th>
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<th>$G_0W_0$@ 1/4</th>
<th>$G_0W_0$@ $\alpha^*$</th>
<th>$\Delta$-SCF 0</th>
<th>$\Delta$-SCF 1/4</th>
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<th>SJM $\alpha^*$</th>
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ME [eV]  
MAE [eV]  
MAPE [%]
### A Appendix

Table A.3: Mean absolute percentage error (MAPE) and mean absolute error (MAE in meV, parenthesis) of different total energy methods for the S66 database. The errors are relative to results obtained by CCSD(T) results extrapolated to the complete basis set limit\textsuperscript{167}.

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<th>Other</th>
<th>Total</th>
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<td>22.8% (28)</td>
<td>31.9% (49)</td>
<td>33.1% (81)</td>
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<tr>
<td>PBE</td>
<td>11.6% (37)</td>
<td>105.3% (159)</td>
<td>56.8% (88)</td>
<td>57.9% (95)</td>
</tr>
<tr>
<td>PBE0</td>
<td>10.8% (32)</td>
<td>109.4% (156)</td>
<td>53.1% (82)</td>
<td>56.4% (90)</td>
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<tr>
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<td>100.5% (146)</td>
<td>43.0% (66)</td>
<td>51.1% (80)</td>
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<tr>
<td><strong>TS-vdW</strong></td>
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<tr>
<td>PBE</td>
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<td>21.9% (27)</td>
<td>8.1% (12)</td>
<td>12.1% (20)</td>
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<tr>
<td>PBE0</td>
<td>5.0% (20)</td>
<td>14.5% (18)</td>
<td>6.9% (10)</td>
<td>8.9% (16)</td>
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<tr>
<td>PBEh(\alpha^*)</td>
<td>6.2% (30)</td>
<td>6.0% (9)</td>
<td>7.4% (12)</td>
<td>6.5% (17)</td>
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<td><strong>EX+cRPA</strong></td>
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<td>PBE</td>
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<td>23.5% (33)</td>
<td>16.0% (24)</td>
<td>17.0% (32)</td>
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<tr>
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<td>28.7% (41)</td>
<td>16.0% (25)</td>
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<td>PBEh(\alpha^*)</td>
<td>6.7% (19)</td>
<td>40.5% (58)</td>
<td>21.0% (32)</td>
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<tr>
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<td>7.1% (11)</td>
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<td>23.6% (34)</td>
<td>11.2% (17)</td>
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<td>45.6% (65)</td>
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<td>10.8% (18)</td>
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<td>8.8% (12)</td>
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<tr>
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<tr>
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Table A.4: S66 binding energies [meV] for the (G)KS, TS-vdW, and EX+cRPA total energy methods. The results were obtained for three XC functionals within the PBE-hybrid family, which are labeled by their amount of exact exchange (0 for PBE, 1/4 for PBE0, and $\alpha^*$ for PBEh($\alpha^*$)). A tier 4 basis set augmented with diffuse functions from aug-cc-pV5Z (tier 4 + a5Z-d) was used (except for TS-vdW and the LDA results: tier 3) and a counterpoise correction performed. Also tabulated are reference CCSD(T) results extrapolated to the complete basis set limit\(^{167}\), the $\alpha^*$ values, and the LDA results.

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<th>$\alpha^*$</th>
<th>TS-vdW@</th>
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<th>1/4</th>
<th>$\alpha^*$</th>
<th>EX+cRPA@</th>
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<tr>
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Table A.5: S66 binding energies [meV] for various RPA-based total energy methods. The results were obtained for three XC functionals within the PBE-hybrid family, which are labeled by their amount of exact exchange (0 for PBE, 1/4 for PBE0, and $\alpha^*$ for PBEh($\alpha^*$)). A tier 4 basis set augmented with diffuse functions from aug-cc-pV5Z (tier 4 + a5Z-d) was used and a counterpoise correction performed. Also tabulated are reference CCSD(T) results extrapolated to the complete basis set limit.$^{167}$

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<td>-192 -162 -135</td>
<td>-172 -159 -136</td>
<td>-162 -159 -146</td>
<td>-182 -166 -140</td>
<td>-184</td>
</tr>
<tr>
<td>61 pentane · AcOH</td>
<td>-126</td>
<td>-143 -107 -74</td>
<td>-122 -102 -74</td>
<td>-105 -95 -79</td>
<td>-130 -107 -77</td>
<td>-133</td>
</tr>
<tr>
<td>64 peptide · ethene</td>
<td>-130</td>
<td>-129 -111 -86</td>
<td>-120 -109 -87</td>
<td>-119 -113 -99</td>
<td>-134 -120 -93</td>
<td>-133</td>
</tr>
<tr>
<td>65 pyridine · ethyne</td>
<td>-173</td>
<td>-184 -174 -164</td>
<td>-172 -171 -164</td>
<td>-174 -177 -175</td>
<td>-190 -184 -172</td>
<td>-184</td>
</tr>
<tr>
<td>ME [meV]</td>
<td>0</td>
<td>-7 16 41 9 20 41</td>
<td>15 17 28 -9 7 32</td>
<td>-5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MAE [meV]</td>
<td>0</td>
<td>17 19 41 10 21 41</td>
<td>18 23 34 17 22 38</td>
<td>9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MAPE [%]</td>
<td>0.0</td>
<td>9.1 12.3 25.9 6.1 13.4 25.7 10.8 13.8 20.9 7.0 11.8 23.7</td>
<td>4.3</td>
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</table>
Table A.6: G2-1\textsuperscript{168} atomization energies [eV] for the (G)KS, EX+cRPA, and EX+cRPA+SE total energy methods. The results were obtained for three XC functionals within the PBE-hybrid family, which are labeled by their amount of exact exchange (0 for PBE, 1/4 for PBE0, and $\alpha^*$ for PBEh($\alpha^*$)). The Gaussian cc-pV6Z basis set was used and a counterpoise correction was performed. Zero-point corrected experimental reference data are taken from Ref. 189.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Ref</th>
<th>GKS</th>
<th>EX+cRPA @</th>
<th>EX+cRPA +SE @</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
<td>1/4</td>
<td>$\alpha^*$</td>
</tr>
<tr>
<td>1 BeH</td>
<td>2.160</td>
<td>2.406</td>
<td>2.420</td>
<td>2.432</td>
</tr>
<tr>
<td>6 CH$_2$ ($^1A_1$)</td>
<td>7.845</td>
<td>7.763</td>
<td>7.648</td>
<td>7.289</td>
</tr>
<tr>
<td>7 CH$_2$ ($^3B_1$)</td>
<td>8.248</td>
<td>8.439</td>
<td>8.405</td>
<td>8.223</td>
</tr>
<tr>
<td>17 Cl$_2$</td>
<td>2.515</td>
<td>2.846</td>
<td>2.565</td>
<td>1.639</td>
</tr>
<tr>
<td>18 ClF</td>
<td>2.667</td>
<td>3.142</td>
<td>2.618</td>
<td>1.517</td>
</tr>
<tr>
<td>19 ClO</td>
<td>2.801</td>
<td>3.570</td>
<td>2.934</td>
<td>1.400</td>
</tr>
<tr>
<td>20 F$_2$</td>
<td>1.657</td>
<td>2.293</td>
<td>1.513</td>
<td>0.036</td>
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</table>

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<table>
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<tr>
<th>Molecule</th>
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<th>EX+cRPA+SE@</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
<td>1/4</td>
<td>α*</td>
</tr>
<tr>
<td>28</td>
<td>HF</td>
<td>6.119</td>
<td>6.160</td>
<td>5.929</td>
</tr>
<tr>
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<td>0.836</td>
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<tr>
<td>31</td>
<td>LiF</td>
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<td>6.007</td>
<td>5.703</td>
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<tr>
<td>36</td>
<td>NH\text{\textsubscript{2}}</td>
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<td>8.185</td>
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<tr>
<td>39</td>
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<td>0.761</td>
<td>0.679</td>
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<td>47</td>
<td>SO</td>
<td>5.421</td>
<td>6.107</td>
<td>5.458</td>
</tr>
<tr>
<td>50</td>
<td>Si\text{\textsubscript{2}}H\text{\textsubscript{6}}</td>
<td>23.009</td>
<td>22.568</td>
<td>22.700</td>
</tr>
<tr>
<td>51</td>
<td>SiH\text{\textsubscript{2}} (\textsuperscript{1}A\textsubscript{1})</td>
<td>6.578</td>
<td>6.416</td>
<td>6.390</td>
</tr>
<tr>
<td>52</td>
<td>SiH\text{\textsubscript{2}} (\textsuperscript{3}B\textsubscript{1})</td>
<td>5.676</td>
<td>5.713</td>
<td>5.742</td>
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Continued on next page
<table>
<thead>
<tr>
<th>Molecule</th>
<th>Ref</th>
<th>GKS</th>
<th>( \text{EX+cRPA@} )</th>
<th>( \text{EX+cRPA +SE@} )</th>
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<tr>
<td>ME [eV]</td>
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<td>MAPE [%]</td>
<td>0.0</td>
<td>6.1</td>
<td>2.7</td>
<td>16.3</td>
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Table A.7: G2-1$^{168}$ atomization energies [eV] for various RPA-based total energy methods. The results were obtained for three XC functionals within the PBE-hybrid family, which are labeled by their amount of exact exchange (0 for PBE, 1/4 for PBE0, and α* for PBEh(α*)). The Gaussian cc-pV6Z basis set was used and a counterpoise correction was performed. Zero-point corrected experimental reference data are taken from Reference 189.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Ref</th>
<th>EX+cRPA +rSE®</th>
<th>EX+cRPA +SOSEX®</th>
<th>rPT2®</th>
<th>EX@PBEh(α*) +cRPA @PBE</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0 1/4 α*</td>
<td>0 1/4 α*</td>
<td>0 1/4 α*</td>
<td></td>
</tr>
<tr>
<td>1 BeH</td>
<td>2.160</td>
<td>2.211 2.320 2.465</td>
<td>2.213 2.303 2.400</td>
<td>2.248 2.322 2.401</td>
<td>2.230</td>
</tr>
<tr>
<td>6 CH₂ (1A₁)</td>
<td>7.845</td>
<td>7.618 7.517 7.376</td>
<td>7.844 7.608 7.326</td>
<td>7.894 7.635 7.332</td>
<td>7.609</td>
</tr>
<tr>
<td>7 CH₂ (1B₁)</td>
<td>8.248</td>
<td>7.813 7.973 8.031</td>
<td>8.297 8.211 8.057</td>
<td>8.321 8.226 8.065</td>
<td>7.808</td>
</tr>
<tr>
<td>12 CH₄</td>
<td>18.217</td>
<td>17.604 17.638 17.410</td>
<td>18.206 17.949 17.450</td>
<td>18.262 17.985 17.466</td>
<td>17.572</td>
</tr>
<tr>
<td>17 Cl₂</td>
<td>2.515</td>
<td>2.219 2.330 2.352</td>
<td>2.429 2.298 2.247</td>
<td>2.543 2.356 2.247</td>
<td>2.242</td>
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<tr>
<td>18 CIF</td>
<td>2.687</td>
<td>2.472 2.505 2.111</td>
<td>2.359 2.201 1.949</td>
<td>2.591 2.328 1.954</td>
<td>2.479</td>
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<tr>
<td>19 CIO</td>
<td>2.801</td>
<td>2.844 2.699 2.591</td>
<td>2.328 2.268 2.283</td>
<td>2.653 2.454 2.312</td>
<td>3.197</td>
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<tr>
<td>20 F₂</td>
<td>1.657</td>
<td>1.461 1.418 1.493</td>
<td>1.049 0.829 0.846</td>
<td>1.243 0.938 0.883</td>
<td>1.462</td>
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Table A.7 – continued from previous page

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<tr>
<th>Molecule</th>
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<th>EX+cRPA</th>
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<th>rPT2@</th>
<th>EX@PBEh(α*)</th>
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<td>+rSE@</td>
<td>+SOSEX@</td>
<td></td>
<td>+cRPA@PBE</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0/1</td>
<td>α*</td>
<td>0/1</td>
<td>α*</td>
</tr>
<tr>
<td>HF</td>
<td>28</td>
<td>6.119</td>
<td>5.744</td>
<td>5.830</td>
<td>5.918</td>
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<td>0.749</td>
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<tr>
<td>LiF</td>
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<td>6.023</td>
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<td>5.683</td>
<td>5.969</td>
</tr>
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<td>LiH</td>
<td>32</td>
<td>2.515</td>
<td>2.353</td>
<td>2.319</td>
<td>2.175</td>
</tr>
<tr>
<td>Na₂</td>
<td>39</td>
<td>0.737</td>
<td>0.642</td>
<td>0.542</td>
<td>0.502</td>
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<tr>
<td>SiH₂ (ⅡA₁)</td>
<td>52</td>
<td>5.676</td>
<td>5.574</td>
<td>5.615</td>
<td>5.577</td>
</tr>
</tbody>
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<table>
<thead>
<tr>
<th>Molecule</th>
<th>Ref</th>
<th>EX+cRPA +rSE@</th>
<th>EX+cRPA +SOSEX@</th>
<th>rPT2@</th>
<th>EX@PBEh(α*) +cRPA@PBE</th>
</tr>
</thead>
<tbody>
<tr>
<td>ME [eV]</td>
<td>0.000</td>
<td>-0.328 -0.356 -0.561</td>
<td>-0.251 -0.412 -0.713</td>
<td>-0.094 -0.325 -0.698</td>
<td>-0.094</td>
</tr>
<tr>
<td>MAE [eV]</td>
<td>0.000</td>
<td>0.342 0.364 0.576</td>
<td>0.273 0.418 0.722</td>
<td>0.167 0.333 0.707</td>
<td>0.355</td>
</tr>
<tr>
<td>MAPE [%]</td>
<td>0.0</td>
<td>4.2 5.1 7.7</td>
<td>4.3 6.5 10.2</td>
<td>2.8 5.2 10.0</td>
<td>4.5</td>
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</table>
Table A.8: Hydrogen-transfer barrier heights for the HTBH38 test set [eV] for the (G)KS, EX+cRPA, and EX+cRPA+SE total energy methods (using the Gaussian cc-pV6Z basis set). The results were obtained for three XC functionals within the PBE-hybrid family, which are labeled by their amount of exact exchange (0 for PBE, 1/4 for PBE0, and α* for PBEh(α*)). Reference data are from Ref. 169.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Ref</th>
<th>GKS</th>
<th>EX+cRPA@</th>
<th>EX+cRPA+SE@</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
<td>1/4</td>
<td>α*</td>
</tr>
<tr>
<td>1 H + HCl $\rightarrow$ H$_2$ + Cl</td>
<td>Fwd</td>
<td>0.247</td>
<td>0.023</td>
<td>0.127</td>
</tr>
<tr>
<td>2 OH + H$_2$ $\rightarrow$ H + H$_2$O</td>
<td>Rev</td>
<td>0.377</td>
<td>−0.057</td>
<td>0.100</td>
</tr>
<tr>
<td>3 CH$_3$ + H$_2$ $\rightarrow$ H + CH$_4$</td>
<td>Fwd</td>
<td>0.247</td>
<td>−0.265</td>
<td>0.011</td>
</tr>
<tr>
<td>4 OH + CH$_4$ $\rightarrow$ CH$_3$ + H$_2$O</td>
<td>Rev</td>
<td>0.919</td>
<td>0.590</td>
<td>0.748</td>
</tr>
<tr>
<td>5 H + H$_2$ $\rightarrow$ H$_2$ + H</td>
<td>Fwd</td>
<td>0.525</td>
<td>0.168</td>
<td>0.302</td>
</tr>
<tr>
<td>7 OH + CH$_4$ $\rightarrow$ CH$_3$ + H$_2$O</td>
<td>Rev</td>
<td>0.663</td>
<td>0.403</td>
<td>0.516</td>
</tr>
<tr>
<td>9 H + H$_2$ $\rightarrow$ H$_2$ + H</td>
<td>Fwd</td>
<td>0.416</td>
<td>0.159</td>
<td>0.246</td>
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<tr>
<td>10 OH + NH$_3$ $\rightarrow$ H$_2$O + NH$_2$</td>
<td>Fwd</td>
<td>0.139</td>
<td>−0.500</td>
<td>−0.078</td>
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<tr>
<td>12 HCl + CH$_3$ $\rightarrow$ Cl + CH$_4$</td>
<td>Rev</td>
<td>0.551</td>
<td>−0.025</td>
<td>0.329</td>
</tr>
<tr>
<td>14 OH + C$_2$H$_6$ $\rightarrow$ H$_2$O + C$_2$H$_5$</td>
<td>Rev</td>
<td>0.343</td>
<td>−0.087</td>
<td>0.098</td>
</tr>
<tr>
<td>16 F + H$_2$ $\rightarrow$ HF + H</td>
<td>Fwd</td>
<td>0.078</td>
<td>−0.544</td>
<td>−0.193</td>
</tr>
<tr>
<td>19 O + CH$_4$ $\rightarrow$ OH + CH$_3$</td>
<td>Rev</td>
<td>1.448</td>
<td>1.075</td>
<td>1.216</td>
</tr>
<tr>
<td>21 H + PH$_3$ $\rightarrow$ PH$_2$ + H$_2$</td>
<td>Fwd</td>
<td>0.134</td>
<td>−0.073</td>
<td>0.020</td>
</tr>
<tr>
<td>23 H + OH $\rightarrow$ H$_2$ + O</td>
<td>Rev</td>
<td>1.006</td>
<td>0.793</td>
<td>0.890</td>
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Continued on next page
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Ref</th>
<th>GKS</th>
<th>Ex+cRPA@</th>
<th>Ex+cRPA+SE@</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 H + H₂S → H₂ + HS</td>
<td>Fwd</td>
<td>0.152</td>
<td>-0.049</td>
<td>0.051</td>
</tr>
<tr>
<td>26 O + HCl → OH + Cl</td>
<td>Rev</td>
<td>0.750</td>
<td>0.409</td>
<td>0.537</td>
</tr>
<tr>
<td>27 NH₂ + CH₃ → CH₄ + NH</td>
<td>Fwd</td>
<td>0.425</td>
<td>-0.438</td>
<td>0.116</td>
</tr>
<tr>
<td>28 NH₂ + C₂H₅ → C₂H₆ + NH</td>
<td>Rev</td>
<td>0.451</td>
<td>-0.289</td>
<td>0.147</td>
</tr>
<tr>
<td>29 NH₂ + CH₃ → CH₄ + NH</td>
<td>Fwd</td>
<td>0.347</td>
<td>0.038</td>
<td>0.228</td>
</tr>
<tr>
<td>30 NH₂ + C₂H₅ → C₂H₆ + NH</td>
<td>Rev</td>
<td>0.971</td>
<td>0.465</td>
<td>0.721</td>
</tr>
<tr>
<td>31 NH₂ + C₂H₅ → C₂H₆ + NH</td>
<td>Fwd</td>
<td>0.325</td>
<td>0.135</td>
<td>0.311</td>
</tr>
<tr>
<td>32 C₂H₆ + NH₂ → NH₃ + C₂H₅</td>
<td>Rev</td>
<td>0.794</td>
<td>0.334</td>
<td>0.605</td>
</tr>
<tr>
<td>33 C₂H₆ + NH₂ → NH₃ + C₂H₅</td>
<td>Fwd</td>
<td>0.451</td>
<td>0.070</td>
<td>0.325</td>
</tr>
<tr>
<td>34</td>
<td>Rev</td>
<td>0.755</td>
<td>0.444</td>
<td>0.640</td>
</tr>
<tr>
<td>35 NH₂ + CH₄ → CH₃ + NH₃</td>
<td>Fwd</td>
<td>0.629</td>
<td>0.197</td>
<td>0.437</td>
</tr>
<tr>
<td>36 C₅H₈ → C₅H₈</td>
<td>Rev</td>
<td>0.772</td>
<td>0.342</td>
<td>0.553</td>
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<tr>
<td>37 C₅H₈ → C₅H₈</td>
<td>Fwd</td>
<td>1.665</td>
<td>1.354</td>
<td>1.545</td>
</tr>
<tr>
<td>38</td>
<td>Rev</td>
<td>1.665</td>
<td>1.354</td>
<td>1.545</td>
</tr>
<tr>
<td>ME</td>
<td>0</td>
<td>-0.410</td>
<td>-0.189</td>
<td>0.309</td>
</tr>
<tr>
<td>MAE</td>
<td>0</td>
<td>0.410</td>
<td>0.189</td>
<td>0.326</td>
</tr>
<tr>
<td>MAPE</td>
<td>0.0</td>
<td>128.8</td>
<td>57.6</td>
<td>100.0</td>
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</table>
Table A.9: Hydrogen-transfer barrier heights for the HTBH38 test set [eV] for various RPA-based total energy methods (using the Gaussian cc-pV6Z basis set). The results were obtained for three XC functionals within the PBE-hybrid family, which are labeled by their amount of exact exchange (0 for PBE, 1/4 for PBE0, and α* for PBEh(α*)). Reference data are from Ref.169.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Ref</th>
<th>EX+cRPA +rSE@</th>
<th>EX+cRPA +SOSEX@</th>
<th>rPT2@</th>
<th>EX@PBEh(α*) +cRPA@PBE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 H + HCl $\rightarrow$ H$_2$ + Cl</td>
<td>Fwd</td>
<td>0.247</td>
<td>0.188</td>
<td>0.194</td>
<td>0.396</td>
</tr>
<tr>
<td>2</td>
<td>Rev</td>
<td>0.377</td>
<td>0.264</td>
<td>0.004</td>
<td>0.402</td>
</tr>
<tr>
<td>3 OH + H$_2$ $\rightarrow$ H + H$_2$O</td>
<td>Fwd</td>
<td>0.247</td>
<td>0.177</td>
<td>0.258</td>
<td>0.486</td>
</tr>
<tr>
<td>4</td>
<td>Rev</td>
<td>0.919</td>
<td>1.055</td>
<td>1.147</td>
<td>0.760</td>
</tr>
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<td>5 CH$_3$ + H$_2$ $\rightarrow$ H + CH$_4$</td>
<td>Fwd</td>
<td>0.525</td>
<td>0.605</td>
<td>0.651</td>
<td>0.517</td>
</tr>
<tr>
<td>6</td>
<td>Rev</td>
<td>0.663</td>
<td>0.736</td>
<td>0.808</td>
<td>0.685</td>
</tr>
<tr>
<td>7 OH + CH$_4$ $\rightarrow$ CH$_3$ + H$_2$O</td>
<td>Fwd</td>
<td>0.291</td>
<td>0.226</td>
<td>0.058</td>
<td>0.376</td>
</tr>
<tr>
<td>8</td>
<td>Rev</td>
<td>0.850</td>
<td>0.688</td>
<td>0.724</td>
<td>0.888</td>
</tr>
<tr>
<td>9 H + H$_2$ $\rightarrow$ H$_2$ + H</td>
<td>Fwd</td>
<td>0.416</td>
<td>0.540</td>
<td>0.575</td>
<td>0.459</td>
</tr>
<tr>
<td>10</td>
<td>Rev</td>
<td>0.416</td>
<td>0.540</td>
<td>0.575</td>
<td>0.459</td>
</tr>
<tr>
<td>11 OH + NH$_3$ $\rightarrow$ H$_2$O + NH$_2$</td>
<td>Fwd</td>
<td>0.139</td>
<td>0.685</td>
<td>0.754</td>
<td>0.443</td>
</tr>
<tr>
<td>12</td>
<td>Rev</td>
<td>0.551</td>
<td>1.148</td>
<td>1.165</td>
<td>0.848</td>
</tr>
<tr>
<td>13 HCl + CH$_3$ $\rightarrow$ Cl + CH$_4$</td>
<td>Fwd</td>
<td>0.074</td>
<td>0.105</td>
<td>0.068</td>
<td>0.074</td>
</tr>
<tr>
<td>14</td>
<td>Rev</td>
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<td>0.254</td>
<td>0.104</td>
<td>0.244</td>
</tr>
<tr>
<td>15 OH + C$_2$H$_6$ $\rightarrow$ H$_2$O + C$_2$H$_4$</td>
<td>Fwd</td>
<td>0.147</td>
<td>0.139</td>
<td>0.173</td>
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<td>16</td>
<td>Rev</td>
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<td>0.937</td>
</tr>
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<td>17 F + H$_2$ $\rightarrow$ HF + H</td>
<td>Fwd</td>
<td>0.078</td>
<td>0.327</td>
<td>0.339</td>
<td>0.183</td>
</tr>
<tr>
<td>18</td>
<td>Rev</td>
<td>1.448</td>
<td>1.575</td>
<td>1.750</td>
<td>1.523</td>
</tr>
<tr>
<td>19 O + CH$_4$ $\rightarrow$ OH + CH$_3$</td>
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<td>0.594</td>
<td>0.421</td>
<td>0.748</td>
<td>0.720</td>
</tr>
<tr>
<td>20</td>
<td>Rev</td>
<td>0.351</td>
<td>0.436</td>
<td>0.415</td>
<td>0.047</td>
</tr>
<tr>
<td>21 H + PH$_3$ $\rightarrow$ PH$_2$ + H$_2$</td>
<td>Fwd</td>
<td>0.134</td>
<td>0.131</td>
<td>0.204</td>
<td>0.151</td>
</tr>
<tr>
<td>22</td>
<td>Rev</td>
<td>1.006</td>
<td>1.130</td>
<td>1.123</td>
<td>1.006</td>
</tr>
<tr>
<td>23 H + OH $\rightarrow$ H$_2$ + O</td>
<td>Fwd</td>
<td>0.650</td>
<td>0.596</td>
<td>0.750</td>
<td>0.676</td>
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<tr>
<td>24</td>
<td>Rev</td>
<td>0.568</td>
<td>0.489</td>
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<td>0.318</td>
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Continued on next page
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<th>Ref</th>
<th>EX+cRPA +rSE@</th>
<th>EX+cRPA +SOSEX@</th>
<th>rPT2@</th>
<th>EX@PBEh(α*) +cRPA@PBE</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 H + H₂S →→ H₂ + HS</td>
<td></td>
<td>0.152</td>
<td>0.108</td>
<td>0.183</td>
<td>0.166</td>
</tr>
<tr>
<td>26</td>
<td>Rev</td>
<td>0.750</td>
<td>0.726</td>
<td>0.725</td>
<td>0.612</td>
</tr>
<tr>
<td>27 O + HCl →→ OH + Cl</td>
<td></td>
<td>0.425</td>
<td>-0.384</td>
<td>0.255</td>
<td>0.578</td>
</tr>
<tr>
<td>28</td>
<td>Rev</td>
<td>0.451</td>
<td>-0.301</td>
<td>0.205</td>
<td>0.328</td>
</tr>
<tr>
<td>29 NH₂ + CH₄ →→ CH₄ + NH</td>
<td></td>
<td>0.347</td>
<td>0.208</td>
<td>0.325</td>
<td>0.265</td>
</tr>
<tr>
<td>30</td>
<td>Rev</td>
<td>0.971</td>
<td>0.804</td>
<td>0.934</td>
<td>0.743</td>
</tr>
<tr>
<td>31 NH₂ + C₂H₅ →→ C₂H₆ + NH</td>
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<td>0.325</td>
<td>0.263</td>
<td>0.307</td>
<td>0.192</td>
</tr>
<tr>
<td>32</td>
<td>Rev</td>
<td>0.794</td>
<td>0.698</td>
<td>0.828</td>
<td>0.463</td>
</tr>
<tr>
<td>33 C₂H₆ + NH₂ →→ NH₃ + C₂H₅</td>
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<td>0.451</td>
<td>0.370</td>
<td>0.484</td>
<td>0.071</td>
</tr>
<tr>
<td>34</td>
<td>Rev</td>
<td>0.755</td>
<td>0.555</td>
<td>0.690</td>
<td>0.479</td>
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<tr>
<td>35 NH₂ + CH₄ →→ CH₄ + NH₃</td>
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<td>0.629</td>
<td>0.484</td>
<td>0.596</td>
<td>0.380</td>
</tr>
<tr>
<td>36</td>
<td>Rev</td>
<td>0.772</td>
<td>0.508</td>
<td>0.654</td>
<td>0.582</td>
</tr>
<tr>
<td>37 C₅H₈ →→ C₅H₈</td>
<td></td>
<td>1.665</td>
<td>1.776</td>
<td>1.839</td>
<td>1.752</td>
</tr>
<tr>
<td>38</td>
<td>Rev</td>
<td>1.665</td>
<td>1.776</td>
<td>1.839</td>
<td>1.752</td>
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</table>

| ME | 0  | -0.181 | -0.053 | -0.043 | 0.232 | 0.188 | 0.115 | 0.061 | 0.102 | 0.102 | -0.330 |
| MAE| 0  | 0.193  | 0.083  | 0.190  | 0.233 | 0.188 | 0.141 | 0.073 | 0.105 | 0.133 | 0.347 |
| MAPE| 0.0| 55.9  | 24.2  | 60.1  | 76.9 | 60.7 | 46.6 | 24.1 | 32.7 | 44.4 | 108.6 |
Table A.10: Non-hydrogen-transfer barrier heights for the NHTBH38 test set [eV] for the (G)KS, EX+cRPA, and EX+cRPA+SE total energy methods (using the Gaussian cc-pV6Z basis set). The results were obtained for three XC functionals within the PBE-hybrid family, which are labeled by their amount of exact exchange (0 for PBE, 1/4 for PBE0, and $\alpha^*$ for PBEh($\alpha^*$)). Reference data are from Ref. 170.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Ref</th>
<th>GKS</th>
<th>EX+cRPA@</th>
<th>EX+cRPA+SE@</th>
</tr>
</thead>
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<tr>
<td>1 $\text{H} + \text{N}_2\text{O} \rightarrow \text{OH} + \text{N}_2$</td>
<td>Fwd</td>
<td>0.787</td>
<td>0.436</td>
<td>0.608</td>
</tr>
<tr>
<td>3 $\text{H} + \text{FH} \rightarrow \text{HF} + \text{H}$</td>
<td>Fwd</td>
<td>1.829</td>
<td>1.191</td>
<td>1.480</td>
</tr>
<tr>
<td>4</td>
<td>Rev</td>
<td>1.829</td>
<td>1.191</td>
<td>1.480</td>
</tr>
<tr>
<td>5 $\text{H} + \text{CH} \rightarrow \text{HCl} + \text{H}$</td>
<td>Fwd</td>
<td>0.781</td>
<td>0.416</td>
<td>0.578</td>
</tr>
<tr>
<td>6</td>
<td>Rev</td>
<td>0.781</td>
<td>0.416</td>
<td>0.578</td>
</tr>
<tr>
<td>7 $\text{H} + \text{FCH}_3 \rightarrow \text{HF} + \text{CH}_3$</td>
<td>Fwd</td>
<td>1.317</td>
<td>0.799</td>
<td>1.112</td>
</tr>
<tr>
<td>8</td>
<td>Rev</td>
<td>2.609</td>
<td>1.784</td>
<td>2.167</td>
</tr>
<tr>
<td>9 $\text{H} + \text{F}_2 \rightarrow \text{HF} + \text{F}$</td>
<td>Fwd</td>
<td>0.098</td>
<td>-0.406</td>
<td>-0.174</td>
</tr>
<tr>
<td>11 $\text{CH}_3 + \text{FCl} \rightarrow \text{CH}_3\text{F} + \text{Cl}$</td>
<td>Fwd</td>
<td>0.222</td>
<td>-0.235</td>
<td>0.086</td>
</tr>
<tr>
<td>13 $\text{F}^- + \text{CH}_3\text{F} \rightarrow \text{FCH}_3 + \text{F}^-$</td>
<td>Fwd</td>
<td>-0.015</td>
<td>-0.360</td>
<td>-0.111</td>
</tr>
<tr>
<td>14</td>
<td>Rev</td>
<td>-0.015</td>
<td>-0.360</td>
<td>-0.111</td>
</tr>
<tr>
<td>15 $\text{F}^- \cdot \cdot \cdot \text{CH}_3\text{F} \rightarrow \text{FCH}_3 \cdot \cdot \cdot \text{F}^-$</td>
<td>Fwd</td>
<td>0.580</td>
<td>0.297</td>
<td>0.501</td>
</tr>
<tr>
<td>16</td>
<td>Rev</td>
<td>0.580</td>
<td>0.297</td>
<td>0.501</td>
</tr>
<tr>
<td>17 $\text{Cl}^- + \text{CH}_3\text{Cl} \rightarrow \text{ClCH}_3 + \text{Cl}^-$</td>
<td>Fwd</td>
<td>0.134</td>
<td>-0.172</td>
<td>0.037</td>
</tr>
<tr>
<td>18</td>
<td>Rev</td>
<td>0.134</td>
<td>-0.172</td>
<td>0.037</td>
</tr>
<tr>
<td>19 $\text{Cl}^- \cdot \cdot \cdot \text{CH}_3\text{Cl} \rightarrow \text{ClCH}_3 \cdot \cdot \cdot \text{Cl}^-$</td>
<td>Fwd</td>
<td>0.590</td>
<td>0.306</td>
<td>0.487</td>
</tr>
<tr>
<td>20</td>
<td>Rev</td>
<td>0.590</td>
<td>0.306</td>
<td>0.487</td>
</tr>
<tr>
<td>21 $\text{F}^- + \text{CH}_3\text{Cl} \rightarrow \text{FCH}_3 + \text{Cl}^-$</td>
<td>Fwd</td>
<td>-0.544</td>
<td>-0.834</td>
<td>-0.655</td>
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<tr>
<td>22</td>
<td>Rev</td>
<td>0.872</td>
<td>0.524</td>
<td>0.841</td>
</tr>
<tr>
<td>23 $\text{F}^- \cdot \cdot \cdot \text{CH}_3\text{Cl} \rightarrow \text{FCH}_3 \cdot \cdot \cdot \text{Cl}^-$</td>
<td>Fwd</td>
<td>0.125</td>
<td>-0.032</td>
<td>0.071</td>
</tr>
<tr>
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<td>1.284</td>
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<td>1.225</td>
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Table A.10 – continued from previous page

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<tr>
<th>Reaction</th>
<th>Ref</th>
<th>GKS</th>
<th>Ex+cRPA@</th>
<th>Ex+cRPA+SE@</th>
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<tr>
<td></td>
<td></td>
<td>0 1/4 α⁺</td>
<td>0 1/4 α⁺</td>
<td>0 1/4 α⁺</td>
</tr>
<tr>
<td>25 OH⁻ + CH₃F → HOCH₃ + F⁻</td>
<td>Fwd</td>
<td>-0.121 -0.484 -0.233 0.221</td>
<td>-0.238 -0.190 -0.608</td>
<td>-1.124 -0.548 -0.691</td>
</tr>
<tr>
<td>26</td>
<td>Rev</td>
<td>0.752 0.408 0.702 1.207</td>
<td>0.616 0.699 0.513</td>
<td>-0.307 0.317 0.436</td>
</tr>
<tr>
<td>27 OH⁻ ... CH₃F → HOCH₃ ... F⁻</td>
<td>Fwd</td>
<td>0.475 0.141 0.365 0.639</td>
<td>0.376 0.439 0.522</td>
<td>-0.193 0.154 0.474</td>
</tr>
<tr>
<td>28</td>
<td>Rev</td>
<td>2.047 1.873 2.124 2.493</td>
<td>1.962 2.059 1.888</td>
<td>1.307 1.772 1.821</td>
</tr>
<tr>
<td>29 H + N₂ → HN₂</td>
<td>Fwd</td>
<td>0.637 0.228 0.372 0.618</td>
<td>0.617 0.674 1.146</td>
<td>0.397 0.564 1.141</td>
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<tr>
<td>30</td>
<td>Rev</td>
<td>0.465 0.390 0.501 0.718</td>
<td>0.486 0.522 0.954</td>
<td>0.446 0.483 0.960</td>
</tr>
<tr>
<td>31 H + CO → HCO</td>
<td>Fwd</td>
<td>0.137 -0.075 0.012 0.142</td>
<td>0.190 0.198 0.399</td>
<td>-0.083 0.085 0.394</td>
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<tr>
<td>32</td>
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<td>0.983 1.063 1.100 1.111</td>
<td>1.062 1.064 1.356</td>
<td>0.898 1.000 1.364</td>
</tr>
<tr>
<td>33 H + C₂H₄ → CH₃CH₂</td>
<td>Fwd</td>
<td>0.075 -0.006 0.030 0.138</td>
<td>0.138 0.153 0.043</td>
<td>-0.075 0.068 0.031</td>
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<tr>
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<td>1.810 1.746 1.916 2.122</td>
<td>1.836 1.897 2.163</td>
<td>1.641 1.806 2.160</td>
</tr>
<tr>
<td>35 CH₃ + C₂H₄ → CH₃CH₂CH₂</td>
<td>Fwd</td>
<td>0.297 0.070 0.181 0.578</td>
<td>0.334 0.346 -0.158</td>
<td>-0.047 0.193 -0.186</td>
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<td>1.425 1.503 1.558</td>
<td>1.152 1.384 1.545</td>
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<tr>
<td>37 HCN → HNC</td>
<td>Fwd</td>
<td>2.088 1.976 2.008 2.090</td>
<td>2.038 2.089 1.861</td>
<td>1.973 2.065 1.851</td>
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<td>ME</td>
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<td>0 -0.370 -0.134 0.313</td>
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<tr>
<td>MAE</td>
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<td>0 0.374 0.155 0.355</td>
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<td>0.0 195.6 65.3 206.8</td>
<td>65.3 37.1 335.8</td>
<td>519.3 221.4 384.0</td>
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</table>
Table A.11: Non-hydrogen-transfer barrier heights for the NHTBH38 test set [eV] for various RPA-based total energy methods (using the Gaussian cc-pV6Z basis set). The results were obtained for three XC functionals within the PBE-hybrid family, which are labeled by their amount of exact exchange (0 for PBE, 1/4 for PBE0, and $\alpha^*$ for PBEh($\alpha^*$)). Reference data are from Ref. 170.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Ref</th>
<th>EX+cRPA +rSE@</th>
<th>EX+cRPA +SOSEX@</th>
<th>rPT2@</th>
<th>EX@PBEh($\alpha^*$) +cRPA@PBE</th>
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<tr>
<td>$\cdot$</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>H + N$_2$O $\rightarrow$ OH + N$_2$</td>
<td>Fwd</td>
<td>0.787</td>
<td>0.676</td>
<td>0.783</td>
</tr>
<tr>
<td>3</td>
<td>H + ClH $\rightarrow$ HCl + H</td>
<td>Fwd</td>
<td>1.829</td>
<td>1.643</td>
<td>1.782</td>
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<tr>
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<td>H + ClH $\rightarrow$ HCl + H</td>
<td>Rev</td>
<td>1.829</td>
<td>1.643</td>
<td>1.782</td>
</tr>
<tr>
<td>5</td>
<td>H + FCH$_3$ $\rightarrow$ HF + CH$_3$</td>
<td>Fwd</td>
<td>0.781</td>
<td>0.675</td>
<td>0.776</td>
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<tr>
<td>6</td>
<td>H + FCH$_3$ $\rightarrow$ HF + CH$_3$</td>
<td>Rev</td>
<td>0.781</td>
<td>0.675</td>
<td>0.776</td>
</tr>
<tr>
<td>7</td>
<td>H + F$_2$ $\rightarrow$ HF + F</td>
<td>Fwd</td>
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<td>H + F$_2$ $\rightarrow$ HF + F</td>
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<td>4.151</td>
<td>4.378</td>
</tr>
<tr>
<td>9</td>
<td>CH$_3$ + FCl $\rightarrow$ CH$_3$F + Cl</td>
<td>Fwd</td>
<td>0.322</td>
<td>0.073</td>
<td>0.208</td>
</tr>
<tr>
<td>10</td>
<td>CH$_3$ + FCl $\rightarrow$ CH$_3$F + Cl</td>
<td>Rev</td>
<td>2.609</td>
<td>2.363</td>
<td>2.480</td>
</tr>
<tr>
<td>11</td>
<td>F$^-$ + CH$_3$F $\rightarrow$ FCH$_3$ + F$^-$</td>
<td>Fwd</td>
<td>-0.015</td>
<td>-0.549</td>
<td>-0.307</td>
</tr>
<tr>
<td>12</td>
<td>F$^-$ + CH$_3$F $\rightarrow$ FCH$_3$ + F$^-$</td>
<td>Rev</td>
<td>-0.015</td>
<td>-0.549</td>
<td>-0.307</td>
</tr>
<tr>
<td>13</td>
<td>F$^-$ + CH$_3$F $\rightarrow$ FCH$_3$ + F$^-$</td>
<td>Fwd</td>
<td>0.580</td>
<td>0.236</td>
<td>0.393</td>
</tr>
<tr>
<td>14</td>
<td>F$^-$ + CH$_3$F $\rightarrow$ FCH$_3$ + F$^-$</td>
<td>Rev</td>
<td>0.580</td>
<td>0.236</td>
<td>0.393</td>
</tr>
<tr>
<td>15</td>
<td>Cl$^-$ + CH$_3$Cl $\rightarrow$ ClCH$_3$ + Cl$^-$</td>
<td>Fwd</td>
<td>0.134</td>
<td>-0.250</td>
<td>-0.072</td>
</tr>
<tr>
<td>16</td>
<td>Cl$^-$ + CH$_3$Cl $\rightarrow$ ClCH$_3$ + Cl$^-$</td>
<td>Rev</td>
<td>0.134</td>
<td>-0.250</td>
<td>-0.072</td>
</tr>
<tr>
<td>17</td>
<td>Cl$^-$ + CH$_3$Cl $\rightarrow$ ClCH$_3$ + Cl$^-$</td>
<td>Fwd</td>
<td>0.590</td>
<td>0.304</td>
<td>0.438</td>
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<td>Cl$^-$ + CH$_3$Cl $\rightarrow$ ClCH$_3$ + Cl$^-$</td>
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<td>Cl$^-$ + CH$_3$Cl $\rightarrow$ ClCH$_3$ + Cl$^-$</td>
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<td>Cl$^-$ + CH$_3$Cl $\rightarrow$ ClCH$_3$ + Cl$^-$</td>
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<td>Cl$^-$ + CH$_3$Cl $\rightarrow$ ClCH$_3$ + Cl$^-$</td>
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<td>Cl$^-$ + CH$_3$Cl $\rightarrow$ ClCH$_3$ + Cl$^-$</td>
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Table A.11 – continued from previous page

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</table>
Curriculum Vitae

2008-2013 Fritz-Haber Institute of the Max-Planck Society, Germany
PhD in physics

2005-2007 University of Technology Vienna, Austria
Diploma thesis *Superfields and Supersymmetry*
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