Implementation of Modern Density Functional Methods

Gradients for Local Hybrid Functionals and SCF for Local Range-Separated Hybrid Functionals

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Abstract

Local hybrid functionals are a relatively new and promising tool in the widely used Kohn-Sham density functional theory, but they have been lacking the capability for structure optimization and vibrational spectroscopic calculations. To close that gap, this thesis is concerned with the implementation and assessment of energy derivatives w.r.t. nuclear displacements (gradients) for local hybrids. The new implementation in the quantum chemical program package Turbomole is then used in the evaluation of a new benchmark set of small, gas phase mixed-valence systems. One of the local hybrid functionals is among the best performing functionals in that evaluation.

In the second part, the concept of making a previously constant parameter position-dependent is transferred to the competing approach of range-separated hybrid functionals. Expanding on previous preliminary work with this method, the first self-consistent implementation of local range-separated functionals into Turbomole is described, followed by an assessment of a new functional on molecular properties of selected test sets. We use a semi-empirical range-separation function in combination with PBE-type exchange and the standard PBE correlation functionals. Even with this simple approach, the functionals with *local* range separation are superior to those with constant parameters for thermochemistry and kinetics.

Zusammenfassung

Lokale Hybridfunktionale sind ein relativ neues und vielversprechendes Werkzeug in der weit verbreiteten Kohn-Sham-Dichtefunktionaltheorie, jedoch waren Strukturopimierungungen und schwingungsspektroskopische Berechnungen bislang nicht möglich. Um diese Lücke zu schließen, befasst sich diese Dissertation mit der Implementierung und Validierung von Ableitungen der Energie bzgl. der Kernpositionen (Gradienten) für lokale Hybridfunktionale. Die neue Implementierung im quantenchemischen Programmpaket Turbomole wird anschließend bei der Evaluierung eines neuen Benchmark-Testsatzes genutzt, der aus kleinen, gemischtvalenten Systemen in der Gasphase besteht. Eines der lokalen Hybridfunktionale ist unter den besten Funktionalen in dieser Untersuchung.

Im zweiten Teil wird das Konzept, einen zuvor konstanten Parameter positionsabhängig zu machen, auf den konkurrierenden Ansatz der Hybridfunktionale mit *Reichenweitenseparierung* übertragen. Aufbauend auf vorigen anfänglichen Bemühungen zu dieser Methode beschreiben wir die erste selbstkonsistente Implementierung lokaler Reichenweitenseparierungsfunktionale in Turbomole und validieren ein neues Funktional für molekulare Eigenschaften an ausgewählten Testsätzen. Es wird eine semiempirische Reichweitenseparierungsfunktion in Kombination mit einem Austauschfunktional des PBE-Typs und dem üblichen PBE-Korrelationfunktional genutzt. Selbst mit diesem einfachen Ansatz sind die Funktionale mit *lokaler* Reichweitenseparierung solchen mit konstanten Parametern für Thermochemie und Kinetik überlegen.

List of Publications

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- [2] S. Klawohn, M. Kaupp, and A. Karton. J. Chem. Theory Comput. 14 (2018). PMID: 29874463, 3512. DOI: 10.1021/acs.jctc.8b00289.
- [3] S. Klawohn and H. Bahmann. "Self-Consistent Implementation of Local Range-Separated Hybrid Functionals (preliminary title)". 2019. To be Submitted.

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A cronyms

Acronyms

AE	atomization energy
AO	atomic orbital
BH	barrier height
CBS	complete basis set
CF	calibration function
COSX	chain-of-spheres exchange
CPU	central processing unit
DFT	density functional theory
EA	electron affinity
FDO	functional derivative w.r.t. the orbitals
GGA	generalized gradient approximation (functional)
GH	global hybrid (functional)
GKS	generalized Kohn-Sham
GRSH	global range-separated hybrid (functional)
GTO	Gaussian-type orbital
HF	Hartree-Fock (method)
HK	Hohenberg-Kohen (theorem)
HOMO	highest occupied molecular orbital
IP	ionization potential
IR	infrared
IRC	intrinsic reaction coordinate
IRMPD	infrared multiphoton dissociation
KS	Kohn-Sham (method)
KS-DFT	Kohn-Sham density functional theory
LC	long-range correction
LCAO	linear combination of atomic orbitals
LDA	local density approximation (functional)
LH	local hybrid (functional)
LHG	local hybrid gradient
LMF	local mixing function
LR	long-range
LRSH	local range-separated hybrid (functional)
LSDA	local spin-density approximation (functional)
LUMO	lowest unoccupied molecular orbital
MAE	mean absolute error

Basis Sets

MAX	maximum error
mGGA	meta-GGA (functional)
MLSL	multi-level single linkage (algorithm)
MO	molecular orbital
MP	Møller-Plesset (perturbation theory)
MSE	mean signed error
MV	mixed valence
RHF	restricted Hartree-Fock (method)
RI	resolution of the identity
RMSE	root mean square error
RS	range separation
RSF	range-separation function
RSH	(global or local) range-separated hybrid
SCF	self-consistent field
SIE	self-interaction error
SL	semi-local
SR	short-range
STO	Slater-type orbital
TDDFT	time-dependent density functional theory
UHF	unrestricted Hartree-Fock (method)
wMAE	weighted MAE
XC	exchange-correlation
XX	exact exchange

Basis Sets

Triple- ζ basis set with implicit diffuse functions on
non-H and explicit additional ones (Pople family). ^{4–14}
Correlation-consistent triple- ζ basis set with polar-
ization and diffuse functions (Dunning family). ¹⁵
Correlation-consistent quintuple- ζ basis set with po-
larization and diffuse functions, and weighted core-
valence (Dunning family). ¹⁵
Correlation-consistent quadruple- ζ basis set with po-
larization and diffuse functions (Dunning family). ¹⁵
Quadruple- ζ basis set (Ahlrichs family). ¹⁶
Basis set with split-valence polarization (Ahlrichs
family). ^{17,18}

def2-TZVP	Triple-ζ basis set (Ahlrichs family). ^{18,19}
MG3	Basis set introduced for modifications of the
	Gaussian-3 method (modified $G3$). ^{20,21}
MG3S	Variant of MG3 without diffuse functions on hydro-
	gen $(semi-diffuse)$. ²²

Test Sets

ABDE4	Subset of <i>alkyl bond dissociation energies</i> from AECE.
AE6/11	Subset of AEs from DBH24/08.
AEĆE	Combination of DBH24/08 and four test sets of bond energies/AEs for systems of catalytic interest (<i>aver-</i> <i>aged error for catalytic energies</i>). ²³
AL2X	Subset of dimerization energies of AlX_3 compounds from GMTKN30.
ALK6	Subset of <i>reactions of alkaline and alkaline-cation-</i> <i>benzene complexes</i> from GMTKN30.
BH76	Subset of various <i>barrier heights</i> from GMTKN30.
BH76RC	Reaction energies of BH76 from GMTKN30.
BHPERI	Subset of <i>barrier heights of pericyclic reactions</i> from GMTKN30.
BSR36	Subset of <i>bond separation reactions of saturated hy-</i> <i>drocarbons</i> from GMTKN30.
DARC	Subset of <i>Diels-Alder reaction energies</i> from GMTKN30.
DBH24/08	Collection of four small test sets for diverse BHs. ²⁴
DC9	Subset of <i>nine difficult cases for DFT</i> from GMTKN30.
F2	Vibrational data of small second-period molecules. ²⁵
G2	Collection of test sets for multiple properties. ²⁶
G2-1	Subset of 55 AEs from G2. ^{27,28}
G21EA	Subset of <i>adiabatic electron affinities</i> from G2, used in GMTKN30.
G21IP	Subset of <i>adiabatic ionization potentials</i> from G2, used in GMTKN30 (except for two excited states).
G2RC	Subset of reaction energies of selected G2/97 systems from GMTKN30.

Methods and Functionals

GMTKN30	Collection of 30 test sets, split into three property categories. ²⁹
HATBH6	Subset of DBH24/08.
HTBH38/08	Subset of <i>H</i> -transfer BHs from Minnesota Databases $2.0^{24,30}$
HTBH6	Subset of BHs from HTBH38/08.
ISO34	Subset of <i>isomerization energies of small and</i> <i>medium-sized organic molecules</i> from GMTKN30.
ISOL22	Subset of <i>isomerization energies of large organic</i> molecule from GMTKN30.
MB08-165	Subset of <i>decomposition energies of artificial molecules</i> from GMTKN30.
MGAE109/11	Subset of AEs from Minnesota Databases 2.0. ^{30,31}
MGBL19	Test set of main-group bond lengths. ³²
MVO-10	Benchmark test set of ten MV oxides. ²
NBPRC	Subset of NH_3/BH_3 reactions from GMTKN30.
NSBH6	Subset of <i>BHs for nucleophilic substitution</i> from AECE.
O3ADD6	Subset of various energies for addition of O_3 from GMTKN30.
PA	Subset of <i>adiabatic proton affinities</i> from GMTKN30.
RSE43	Subset of <i>radical stabilization energies</i> from GMTKN30.
SIE11	Subset of <i>self-interaction error related problems</i> from
	GMTKN30.
UABH6	Subset of <i>BHs for unimolecular and association re</i> - <i>actions</i> from AECE.
W4-08	Subset of <i>atomization energies of small molecules</i> from GMTKN30.

Methods and Functionals

$\mathrm{G}_{0}\mathrm{W}_{0}$	Perturbational method based on Green's function
	G with screened Coulomb interaction W to zeroth-
	order. ³³
$\omega B97M-V$	GRSH functional with XX at LR, mGGA at SR and
	full-range NL mGGA correlation. ^{34,35}
$\omega B97X$	GRSH functional with B97 at short-range (SR) and
	XX at long-range (LR) . ³⁶

ωB97X-D	ω B97X with DFT-D1 dispersion correction. ³⁷
B3LYP	GH functional combining XX, B88, VWN, and LYP;
	adjusted by three parameters. $^{38-40}$
B88	GGA exchange functional by Becke. ⁴¹
B97	GH functional by Becke with gradient expansion of
	exchange and correlation, empirically optimized on
	G2. ^{42,43}
BHLYP	GH functional combining B88 exchange and 50% XX
	with LYP correlation. ⁴⁴
BLYP35	Variant of BHLYP with 35% XX, developed for MV
	systems. ^{45,46}
BMK	GH mGGA functional by Boese and Martin for ki-
	netics. ⁴⁷
BP86	GGA functional with B88 exchange and P86 correla-
	tion. ⁴¹
CAM-B3LYP	GRSH variant of B3LYP. ⁴⁸
CC	Coupled cluster; post-HF method with varying de-
	grees of excited states.
CCSD	CC with single and double excitations.
CCSD(T)	CCSD with perturbative triple excitations.
CCSDT(Q)	CCSD with triple and perturbative quadruple exci-
	tations.
CI	Configuration interaction; post-HF method with
	varying degrees of excited states.
DFT-D1	First version of Grimme's empirical dispersion cor-
	rection. ⁴⁹
GRS-oPBE	GRSH functional investigated in Section 4.3.
GRS-sPBE	GRSH functional investigated in Section 4.3.
GRS-SVWN	GRSH functional investigated in Section 4.3.
HISS	GRSH functional employing PBE at SR and LR, and
	XX at mid-range by Henderson, Izmaylov, Scuseria
	and Savin. ⁵⁰
HSE	GRSH variant of PBE0 by Heyd, Scuseria and Ernz-
	erhof. ^{51,52}
LC-ωPBE	GRSH functional based on PBE with XX at LR. 53
LH-sifPW92	LH functional with Slater exchange and PW92 cor-
	relation, with <i>full</i> self-interaction correlation correc-
	tion. ⁵⁴

LH-sirPW92	LH-sifPW92 with partial (<i>reduced</i>) self-interaction correlation correction. ⁵⁴
LH-SVWN	LH functional with Slater exchange and VWN corre-
LH646-SVWN	LH functional with t-LMF ($b = 0.646$) used in Section 3.4
LH670-SVWN	LH functional with t-LMF ($b = 0.670$) used in Section 3.4.
LRS-oPBE	LRSH functional investigated in Section 4.3.
LRS-sPBE	LRSH functional investigated in Section 4.3.
LRS-SVWN	LRSH functional investigated in Section 4.3.
LYP	GGA correlation functional by Lee, Yang and Parr. ⁵⁵
M06	GH mGGA functional from Minnesota. ⁵⁶
M06-2X	Variant of M06 with double XX (54%) . ⁵⁶
MN15	GH functional from Minnesota. ⁵⁷
MR-ACPF	Multi-Reference method using averaged coupled pair
	functional. ⁵⁸
oPBE	sPBE scaled to equate for non-RS limit.
OT-oPBE	PBE-based functional recreated with GRS-oPBE for comparison in Section 4.3.
OT-RSH	Category of GRSHs functionals adjusted to exact constraints (e.g. Koopmans' theorem) for each sys- tem separately.
P86	GGA correlation functional by Perdew. ⁵⁹
PBE	GGA exchange and correlation functionals by Perdew Burke and Ernzerhof 60,61
PBE0	GH functional version of PBE with a quarter XX admixture. 62,63
PBE0-1/3	Variant of PBE0 with a third XX instead of a quar- ter. ⁶⁴
PW92	LDA correlation functional by Perdew and Wang. ⁶⁰
revPBE	Variant of PBE. ⁶⁵
RPBE	Variant of PBE. ⁶⁶
S	LDA exchange functional named after Slater (and/or Dirac). 67,68

- Abbreviation for LH-SVWN with s-LMF (c = 0.22) s-lh used in Section 3.3. LMF with scaled reduced density gradient.⁶⁹ s-LMF sPBE PBE-related GRSH functional with a different non-RS limit than PBE. SVWN LDA functional with Slater exchange and correlation. Abbreviation for LH-SVWN with t-LMF (b = 0.48)t-lh used in Section 3.3. LMF with scaled reduced kinetic energy density.⁷⁰ t-LMF
- TPSSh GH functional by Tao, Perdew, Stanroverov, and
- Scuseria.^{60,71,72} VWN LDA correlation functional by Vosko, Wilk, and Nu-
- VWN LDA correlation functional by Vosko, Wilk, and Nu sair.⁷³
- W2-F12 Predecessor of W3-F12.^{74–76}
- W3-F12 Composite post-HF method based on CC/CBS calculations. 77

1 Introduction

Modern chemistry is ever more reliant on predictions from theoretical electronic structure methods, e.g. for the interpretation of experimental data or the preselection of promising materials. Wave function methods can be highly accurate but tend to be restricted to relatively small systems because of their often unfavorable scaling of computational demands with systems size. As an alternative, density functional theory $(DFT)^{78}$ relies per definition on the electron density only and therefore enables the investigation of larger systems. In practice, the approximate Kohn-Sham density functional theory (KS-DFT)⁷⁹ has become the most widely used quantum chemical method because of its balance between accuracy and efficiency, albeit by introducing more complex ingredients like the gradient of the electron density, and (un)occupied orbitals. Within this method, the difficulty of finding an approximation for the universal density functional is shifted to the notorious exchange-correlation (XC) functional, for which various constraints are known. Starting from the simple model of the uniform electron gas, the sophistication of new XC functionals has increased ever since, ranging from *ab initio* derivations of exact constraints, over highly parametrized approaches optimized for a (possibly large) selection of systems, to combined ansatzes.

One major domain is the inclusion of non-local exact exchange (XX) to mitigate the self-interaction error (SIE), either in a constant way, as in global hybrid (GH) functionals, or at certain interelectronic ranges, as in global range-separated hybrid (GRSH) functionals. In both cases the controlling parameters are constants optimized for sets of properties and systems to get average values. Instead, the constants can also be optimized individually to fulfill certain theoretical conditions (e.g. Koopmans' theorem) for a given system, resulting in optimally tuned rangeseparated hybrid (OT-RSH) functionals.^{80,81} This leads to a (inhomogeneous) collection of range-separated hybrid (RSH) functionals but with favorable description

1 Introduction

of outer valence properties.

To circumvent this one-size-fits-all mentality, using a position- and therefore system-dependent local mixing function (LMF) to replace the constant fraction of XX in GHs gives rise to local hybrid (LH) functionals.⁸² They yield improved results for thermochemical properties and excitation energies.⁶⁹ Computation of structural or vibrational data of LHs have been out of reach so far since the necessary algorithms had not been implemented. Following the prior efficient implementations of self-consistent field (SCF) energy and linear response time-dependent density functional theory (TDDFT) algorithms for LHs,^{83,84} the first part (Chapter 3) of this thesis will provide the theoretical background and implementation of the energy derivatives w.r.t. the displacement of nuclei, i.e. the local hybrid gradients (LHGs),¹ into the quantum chemical program package Turbomole.⁸⁵ These gradients enable structure optimization as well as the (numerical) calculation of vibrational spectroscopic data for comparison with experiment. The implementation is assessed for accuracy and efficiency, especially regarding two screening techniques. Furthermore, LHs are applied to a benchmark set of small, gas phase mixed valence (MV) oxides, which are sensitive to the XX fraction for the correct description of their electronic structure.²

The same principle can also be applied to GRSH functionals by introducing a position-dependent range-separation function (RSF), which leads to local range-separated hybrid (LRSH) functionals. Prior work in this direction yielded improvements in comparison with the fixed approach.⁸⁶ However, those investigations were based only on functionals of the local density approximation (LDA) and were conducted non-self-consistently. Interest in the further development of this method has apparently halted since then. The second part (Chapter 4) of this thesis will be concerned with the derivation and self-consistent implementation of this approach for the LDA as well as a variant based on the generalized gradient approximation (GGA) functional PBE into Turbomole.³ We introduce our first, general RSF, optimize it for a small training set, and assess the resulting LRSH functionals for multiple test sets covering various properties, including the comparison with separately optimized global equivalents of our new functionals.

In preparation of those two main topics, the next chapter (Chapter 2) will give some theoretical foundations. Starting from basic Hartree-Fock (HF) theory, KS- DFT will be introduced, leading to approximations for the XC functionals, including the GH, LH, and GRSH schemes mentioned above. Afterwards the mathematical and algorithmic common ground for both ansatzes will be defined for later reference in the principal results chapters.

This chapter sets the theoretical background for the derivations and implementations. First, some basics of quantum chemical methodology with focus on the HF method is given, followed by an overview of KS-DFT with focus on the global, local and range-separated hybrid functionals. A short overview of the quantities and integration techniques will help in understanding the implementation aspects and changes to existing computer code in later chapters. The program package Turbomole is described to give an impression of how the program parts interact, followed by further details of current implementation details for later reference.

As is common practice in quantum mechanics, we will use atomic units in this work. They are linked to fundamental constants^a and their combinations^b. The upper limit of sums and products will be omitted if they are clear from context.

2.1 Hartree-Fock Method

According to the basic principles of quantum mechanics, every system can be described by a wave function Ψ , which contains all information about the system.⁸⁷ In the non-relativistic, time-independent case, the Schrödinger equation

$$\hat{H}\Psi = E\Psi \tag{2.1.1}$$

holds, where Ψ is the eigenfunction and the energy E is the eigenvalue of the Hamilton operator \hat{H} , which expresses all interactions of the system. Except for the simplest cases, Eq. (2.1.1) cannot be solved analytically. Various methods have been developed to find approximate solutions.

^amass: rest mass of the electron $m_{\rm e}$; charge: elemental charge e; action: Planck constant \hbar . ^blength: Bohr radius a_0 ; energy: Hartree $E_{\rm h}$.

A typical simplification is the Born-Oppenheimer approximation, where the positions of the nuclei (because of their distinctly higher mass) is treated as fixed compared to the electrons. With this, Eq. (2.1.1) reduces to an analogous equation with an *electronic* Hamilton operator \hat{H}_e and an electronic wave function Ψ_e , which depends only parametrically on the coordinates of the nuclei. We will only consider these electronic operators and wave functions from here on and therefore drop the index 'e' for simplicity.

The energy contribution of the nuclei is then limited to the internuclear Coulomb repulsion

$$E_{\rm N} = \sum_{A} \sum_{B>A} \frac{Z_A Z_B}{r_{AB}}.$$
 (2.1.2)

Here Z_A and Z_B are the charges of the nuclei A and B, respectively, and r_{AB} is the distance between them. The (electronic) Hamilton operator

$$\hat{H} = \hat{T} + \hat{V}_{\rm Ne} + \hat{V}_{\rm ee} = -\frac{1}{2} \sum_{i} \nabla_i^2 - \sum_{A} \sum_{i} \frac{Z_A}{r_{Ai}} + \sum_{i} \sum_{j>i} \frac{1}{r_{ij}}, \qquad (2.1.3)$$

therefore contains the remaining electronic energy contributions. The interaction of the electrons with the potential of the nuclei is treated within the operator \hat{V}_{Ne} . Additionally there is the kinetic energy (\hat{T}) and the potential energy due to the interelectronic repulsion (\hat{V}_{ee}) . Again, Z_A is the charge of nucleus A, and r_{Ai} or r_{ij} refer to the distance between an electron i and either a nucleus A or another electron j. The symbol ∇^2 describes the second derivative w.r.t. electronic coordinates.

According to the variational principle, the energy expectation value of an arbitrary trial wave function Ψ_{trial} cannot lie below the true ground state wave function Ψ_0 , i.e. $E_{\text{trial}} \geq E_0$. By minimizing the energy, one therefore tends towards Ψ_0 . Since the inspection of all (infinitely many) possible wave functions is practically impossible, one chooses a subset of functions from which the best one can be determined algorithmically.

In the HF method, the system's wave function Ψ is composed of orthonormal one-electron wave functions $\tilde{\varphi}_i$ for each electron *i*, which are called spin orbitals. They are created by multiplying the spatial orbitals φ_i with an orthonormal spin function α or β (in general σ), which takes the spin $s \in \{-\frac{1}{2}, +\frac{1}{2}\}$ of the electron as an argument,

$$\tilde{\varphi}_i(\boldsymbol{r},s) = \varphi_i(\boldsymbol{r})\sigma(s).$$
 (2.1.4)

The Pauli principle states that the wave function changes sign when fermions (e.g. electrons) are interchanged. To satisfy this condition, one uses an antisymmetric product of spin orbitals, the Slater determinant

$$\Psi = \Phi_{\rm SD} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \tilde{\varphi}_1(\boldsymbol{r}_1, s_1) & \cdots & \tilde{\varphi}_1(\boldsymbol{r}_N, s_N) \\ \vdots & \ddots & \vdots \\ \tilde{\varphi}_N(\boldsymbol{r}_1, s_1) & \cdots & \tilde{\varphi}_N(\boldsymbol{r}_N, s_N) \end{vmatrix}, \qquad (2.1.5)$$

where N is the number of electrons.

Considering a closed-shell system, one can assign a pair of electrons to the same spatial orbital φ_i . Each pair then contains one α and one β spin function. Such a calculation is called restricted Hartree-Fock (RHF). For systems with unpaired electrons, the theory is extended to unrestricted Hartree-Fock (UHF), where each electron is assigned its own spatial orbital, so that open-shell systems can be described as well. A disadvantage of UHF is that the resulting wave function is not an eigenfunction of the total angular momentum operator \hat{S}^2 , whereas this is true for RHF. The deviation of the calculated from the expected value is called spin contamination. In the restricted case (i.e. for closed-shell systems), the spin functions vanish by integration over all spins, so that the equations contain only spatial orbitals and further distinction between α and β is unnecessary.

According to the variational principle, by minimizing the energy of the system's wave function $\Phi_{\rm SD}$ from Eq. (2.1.5) for an infinite (basis) set of orbitals, one reaches the Hartree-Fock limit $E_{\rm HF}$ as the upper limit of the true ground state energy. The minimization is accomplished by variation of the orbitals φ_i , which leads to equations similar to Eq. (2.1.1), named HF equations,

$$\hat{f}_i^{\rm HF}\varphi_i = \varepsilon_i\varphi_i, \qquad (2.1.6)$$

where the eigenvalue ε_i represents the energy of the orbital φ_i and the Fock oper-

ator is defined as

$$\hat{f}_{i}^{\rm HF} = \hat{h}_{i} + \sum_{j} \left[2\hat{J}_{j}(\boldsymbol{r}_{1}) + \hat{K}_{j}(\boldsymbol{r}_{1}) \right].$$
(2.1.7)

The operator \hat{h}_i is the Hamilton operator of an independent system of electron i in the potential of the nuclei. The Coulomb operator

$$\hat{J}_j(\boldsymbol{r}_1)\varphi_i(\boldsymbol{r}_1) = \varphi_i(\boldsymbol{r}_1) \int \varphi_j(\boldsymbol{r}_2)\varphi_j(\boldsymbol{r}_2) \frac{1}{r_{12}} \,\mathrm{d}\boldsymbol{r}_2 \qquad (2.1.8)$$

describes the repulsion of an electron by the average potential of electron j. Because of the sum over j in Eq. (2.1.7), every electron i interacts with the average potential of all other electrons j, even from itself for i = j, which is known as self-interaction. The prefactor 2 in Eq. (2.1.7) stems from the simplification of RHF (the number of orbitals is halfed but each is occupied twice).

The exchange operator

$$\hat{K}_{j}(\boldsymbol{r}_{1})\varphi_{i}(\boldsymbol{r}_{1}) = -\varphi_{j}(\boldsymbol{r}_{1})\int\varphi_{j}(\boldsymbol{r}_{2})\varphi_{i}(\boldsymbol{r}_{2})\frac{1}{r_{12}}\,\mathrm{d}\boldsymbol{r}_{2}$$
(2.1.9)

does not have a classical equivalent. It is non-local and results from the Pauli principle. Furthermore, it exactly compensates the unphysical self-interaction of the Coulomb operator for i = j (see above).

To solve the system of equations depicted by Eq. (2.1.6), it would be necessary to already know the solution because of the sum of Coulomb and exchange terms over all electrons in Eq. (2.1.7). To circumvent this problem, one starts with initial orbitals, e.g. by neglecting the Coulomb and exchange terms at first, and calculates all orbitals anew. These solutions differ from the initial ones and can again be used for the iterative recalculation until the change in energy from one cycle to the next falls below a chosen threshold. Within this threshold, the resulting one-electron wave functions then describe a potential from which they reemerge. Hence, this is named the self-consistent field (SCF) method.

The HF method deals with the interaction of the electrons only in an averaged manner (i.e. it is a mean-field theory). However, in their motion electrons avoid each other due to their Coulomb and exchange interactions, so the Coulomb term in Eq. (2.1.7) is too large and the true energy lies lower. This effect is termed

(Coulomb) electron correlation, and the difference between the true energy E_0 and the HF limit is called the correlation energy $E_{\rm C} = E_0 - E_{\rm HF}$. This quantity will reappear in DFT with a slightly different meaning.

The correlation lacking in HF can be further dissected into dynamic correlation and static (also non-dynamic, or near-degeneracy) correlation. The attribution is inconclusive, though, and other terms are mangled with them, e.g. left-right correlation.⁸⁸ Part of the error stems from the usage of a single Slater determinant to describe a non-interacting reference systems, which is insufficient in general. Cases where this leads to especially erroneous results are called multi-reference systems. A simple example is the hydrogen molecule with stretched bond length, where the single determinant enforces a closed-shell, ionic description instead of the open-shell covalent one with lower energy.

In modern quantum chemistry one tries to incorporate the missing energy as it may amount to the range of binding energies. Next to various post-HF methods like configuration interaction (CI), coupled cluster (CC), or perturbation theoretical ansatzes like Møller-Plesset (MP) theory, DFT is another approach that turned out to be quite successful, especially within the approximation by Kohn and Sham. After a short general introduction in the next section, we will consider only the KS-DFT framework for the remainder of this work.

2.2 Density Functional Theory

The electron density is generally defined as

$$\rho(\boldsymbol{r}_1) = N \int \cdots \int |\Psi|^2 \,\mathrm{d}\boldsymbol{r}_2 \dots \,\mathrm{d}\boldsymbol{r}_N \tag{2.2.1}$$

where Ψ is the electronic wave function of the quantum system of interest.⁸⁹ For a normalized wave function, integrating ρ over the complete space (d \mathbf{r}_1) yields N, the total number of electrons.

A function f(x) = y assigns a number y to another number x. In contrast, a functional F[f] = y assigns a number y to a function f. Formally, every expectation value in quantum mechanics is a functional of the wave function but we will use it to refer to the exchange and correlation functionals of KS-DFT, which depend on the electron density and related quantities at each point in space.

2.2.1 From Hohenberg-Kohn Theory to the Kohn-Sham DFT Method

The first Hohenberg-Kohn (HK) theorem⁷⁸ states that the properties of a system in the ground state can be described fully by the electron density alone (without the wave function). The second HK theorem shows, analogously to the variational principle for wave functions, that there is only one electron density ρ_0 that yields the energy of the ground state; any other electron density ρ_{trial} will give a higher energy: $E[\rho_{\text{trial}}] \geq E[\rho_0]$. This facilitates the application of an SCF method for DFT analogous to HF as described in Section 2.1.

The total energy is, according to Hohenberg and Kohn, a functional of the electron density and is composed of an intrinsic and an extrinsic part,

$$E[\rho] = F_{\rm HK}[\rho] + V_{\rm ext}[\rho].$$
 (2.2.2)

The extrinsic part V_{ext} consists of the potential energy of the electrons in the field of the nuclei A, with charge Z_A at positions A,

$$V_{\rm Ne} = -\sum_{A} \int \frac{Z_A}{|\boldsymbol{r} - \boldsymbol{A}|} \rho(\boldsymbol{r}) \,\mathrm{d}\boldsymbol{r} \,, \qquad (2.2.3)$$

and whatever additional external fields that affect the system under scrutiny, e.g. a magnetic field. The HK functional

$$F_{\rm HK}[\rho] = T[\rho] + V_{\rm ee}[\rho]$$
 (2.2.4)

contains the kinetic energy of the electrons T and the complete potential of interaction between the electrons. There is up to now no good approximative functional known for the kinetic energy of a multi-electron system.

In the Kohn-Sham (KS) ansatz,⁷⁹ one uses a Slater determinant of one-electron wave functions, as with the HF method, which are now called KS orbitals. From

this, one gets

$$T = -\frac{1}{2} \sum_{i} \int \varphi_i(\boldsymbol{r}) \nabla^2 \varphi_i(\boldsymbol{r}) \,\mathrm{d}\boldsymbol{r} \quad .$$
 (2.2.5)

Its value is the correct kinetic energy of a non-interacting reference system with the same density as the actual, interacting system. With this approximation, the predominant portion of the kinetic energy is incorporated. The electron-electron interaction

$$V_{\rm ee}[\rho] = J[\rho] + E_{\rm XC}[\rho],$$
 (2.2.6)

then consists of the Coulomb repulsion J and the exchange-correlation energy $E_{\rm XC}$. The Coulomb energy

$$J = \frac{1}{2} \iint \frac{\rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2)}{r_{12}} \,\mathrm{d}\boldsymbol{r}_1 \,\mathrm{d}\boldsymbol{r}_2 \tag{2.2.7}$$

is given as a functional of the density (cf. Eq. (2.1.8)). The non-interacting kinetic energy and the Coulomb energy can thus be calculated exactly (and, more importantly, *simply*). What is left is $E_{\rm XC}$ in Eq. (2.2.6).

From HF (Section 2.1) we know that the Pauli principle leads to a non-classical exchange contribution to the energy. Furthermore, the correlation energy, defined before as the difference between the HF limit and the true energy, and a small part of the kinetic energy of the fully interacting system all need to be included. This is done via the XC functional. In summary, the quantity $E_{\rm XC}$ is the condensed problem to be solved in KS-DFT to get more accurate results. It is usually split into the exchange energy $E_{\rm X}$ and the correlation energy $E_{\rm C}$,

$$E_{\rm XC} = E_{\rm X} + E_{\rm C}, \qquad (2.2.8)$$

although this splitting is not mandatory. Note that this correlation energy is not equivalent to the correlation energy defined in HF theory since it includes also the missing kinetic energy contribution by definition. Furthermore, we introduce the corresponding energy densities $\varepsilon_{\rm X}$ and $\varepsilon_{\rm C}$ according to

$$E_{\rm XC}[\rho] = \int \varepsilon_{\rm XC}(\boldsymbol{r}) \, \mathrm{d}\boldsymbol{r} = \int \varepsilon_{\rm X}(\boldsymbol{r}) \, \mathrm{d}\boldsymbol{r} + \int \varepsilon_{\rm C}(\boldsymbol{r}) \, \mathrm{d}\boldsymbol{r} \,. \tag{2.2.9}$$

In analogy to HF theory (cf. Eq. (2.1.6)) the orbitals that give the lowest energy

are determined by solving the KS equations

$$\hat{f}_i^{\rm KS}\varphi_i = \varepsilon_i\varphi_i , \qquad (2.2.10)$$

where the KS operator

$$\hat{f}_{i}^{\text{KS}} = -\frac{1}{2}\nabla_{i}^{2} - \sum_{A} \frac{Z_{A}}{r_{iA}} + \int \frac{\rho(\boldsymbol{r}_{2})}{r_{i2}} \,\mathrm{d}\boldsymbol{r}_{2} + v_{\text{XC}}$$
(2.2.11)

includes the kinetic and classical Coulomb contributions (nuclear-electronic and interelectronic), as well as the XC potential

$$v_{\rm XC} = \frac{\delta E_{\rm XC}}{\delta \rho} \,. \tag{2.2.12}$$

From the HK theorem follows that $E_{\rm XC}[\rho(\mathbf{r})]$ can be expressed using the electron density alone. However, a prescription how this dependence looks like is still lacking and may be arbitrarily complicated. Some constraints that the true functional must fulfill are known, however. They may be used in the construction of approximate functionals.

2.2.2 Approximate Functionals

Many approximate density functionals for exchange and correlation have been and still are being proposed. They are the fundamental starting point for improving the predictions of DFT, and they are often grouped by the quantities they depend on. For functionals within the LDA only the electron density is used. For open-shell systems one typically uses the local spin-density approximation (LSDA), which is based on *spin-DFT* with two separate densities ρ_{α} and ρ_{β} , one for each spin. We will refer to both approximations as LDA going onward.

Functionals within the GGA additionally rely on the density gradient $\nabla \rho$. With the term *meta*-GGA one refers to functionals that use the second derivative of the electron density $\nabla^2 \rho$, and/or the KS-kinetic energy density $\tau = \frac{1}{2} \sum_i |\nabla \varphi_i|^2$. This classification, which continues with *hyper*-GGAs, is referred to as *Jacob's ladder* of chemical accuracy⁹⁰ where each "rung" involves more complex ingredients and the prior ones. The aim of ever more accurate results is, however, not assured.

In a different classification⁹¹ the first group contains all functionals with explicit dependence on the electron density and quantities derived from it. The second contains those that also incorporate quantities depending on occupied orbitals, e.g. τ or exact exchange (see below). The third class further includes unoccupied (i.e. virtual) orbitals and promises the highest accuracy but also requires the largest computing effort.

In search of functionals that give more reliable descriptions of quantum mechanical systems, the number of parameters has increased. Some of them are fixed by exact constraints, others by fitting to a (possibly large) selection of training systems in order to minimize the deviation of several properties compared to experimental or highly accurate theoretical values. Those are often atomization energys (AEs), barrier heights (BHs), and excitation energies. There is criticism that new functionals may diverge from the true path towards the exact one if lowering of energies is the only benchmark, while the density they export does not conform with the correct one.⁹²

LDA Functionals

For the LDA one assumes an artificial uniform electron gas with constant density that exists in an infinite space filled with homogeneously distributed positive charge (for electroneutrality). The Slater functional (S) for exchange was derived from this model. Its energy density is

$$\varepsilon_{\rm X}^{\rm LDA}(\boldsymbol{r}) = \frac{3}{4} \left(\frac{3}{\pi}\right)^{\frac{1}{3}} \rho^{\frac{4}{3}}(\boldsymbol{r}).$$
 (2.2.13)

The corresponding correlation term cannot be stated analytically, but there are analytical fits to accurate Monte-Carlo simulations. Two prominent examples are the functional by Vosko, Wilk, and Nusair $(VWN)^{73}$ and PW92 by Perdew and Wang.⁶⁰

GGA functionals

While a good starting point, LDA is not a sufficient model for molecular systems where the density may vary strongly. The GGA gives rise to a variety of functionals. They are classified as semi-local (SL), even though the gradient is local from a mathematical point of view, to distinguish them from LDA.

For example, there is both the exchange and the correlation functional by Perdew, Burke, and Ernzerhof (PBE).⁶¹ By using several constraints for the low and high varying density limits (i.e. $\nabla \rho \to 0$ and $|\nabla \rho| \to \infty$) they got for exchange

$$E_{\rm X}^{\rm PBE} = \int \varepsilon_{\rm X}^{\rm LDA} F_{\rm X}^{\rm PBE} \,\mathrm{d}\boldsymbol{r} \quad , \qquad (2.2.14)$$

$$F_{\rm X}^{\rm PBE} = 1 + \frac{\mu s^2}{1 + \mu s^2 / \kappa} ,$$
 (2.2.15)

$$s = \frac{|\nabla \rho|}{2(3\pi^2)^{\frac{1}{3}}\rho^{\frac{4}{3}}}, \qquad (2.2.16)$$

where $\kappa = 0.804$ is determined by the Lieb-Oxford bound^{93,94} ($F_X \leq 1.804$), s is the reduced density gradient, and $\mu \approx 0.21951$ is chosen w.r.t. the corresponding PBE correlation functional.⁹⁵ Two examples of many further variations are revPBE⁶⁵ with an adjusted $\kappa = 1.245$, and RPBE,⁶⁶ where F_X^{PBE} includes an exponential term, exp ($-\mu s^2/\kappa$). Both of them improve chemisorption results but may worsen other properties.⁶⁶

Global Hybrid Functionals

In case of GH functionals, part of the DFT exchange is replaced by a quantity that is calculated analogously to the HF exchange. Since the orbitals used for this calculation are not equal to the ones in the HF method, some authors prefer to distinguish them by calling the DFT equivalent exact exchange (XX) instead of HF exchange. For GHs, part of the DFT exchange is replaced by a constant fraction a_0 of XX. The XX is non-local due to the dependence on two independent positions \mathbf{r}_1 and \mathbf{r}_2 (see r.h.s. of Eq. (2.1.9)), therefore all hybrid functionals are also classified as non-local within the generalized Kohn-Sham (GKS) framework.

For example, in PBE0⁹⁶ one mixes 25% XX with 75% PBE exchange, while the

correlation is not adjusted. The widely used functional B3LYP^{38-40,55}

$$E_{\rm XC}^{\rm B3LYP} = a_0 E_{\rm X}^{\rm ex} + (1 - a_0) E_{\rm X}^{\rm S} + a_{\rm X} \Delta E_{\rm X}^{\rm B88} + E_{\rm C}^{\rm VWN} + a_{\rm C} \Delta E_{\rm C}^{\rm LYP}$$
(2.2.17)

contains XX (ex), Slater exchange (LDA), gradient corrections of the B88 exchange, and the correlation functional by Lee, Yang und Parr (LYP) in addition to the VWN correlation functional. The mixing parameters $a_0 = 0.20$, $a_X = 0.72$ und $a_C = 0.81$ are empirical and the differences in Eq. (2.2.17) are $\Delta E_X^{\text{B88}} = E_X^{\text{B88}} - E_X^{\text{LDA}}$ and $\Delta E_C^{\text{LYP}} = E_C^{\text{LYP}} - E_C^{\text{VWN}}$.

Local Hybrid Functionals

For GH functionals a_0 is a constant, for LH functionals it is a space-dependent function, termed the LMF $a(\mathbf{r})$, usually constrained by

$$0 \le a \le 1$$
. (2.2.18)

The exchange energy for LHs is then defined as

$$E_{\rm X} = \int a\varepsilon_{\rm X}^{\rm ex} + (1-a)\varepsilon_{\rm X}^{\rm SL} \,\mathrm{d}\boldsymbol{r} \quad , \qquad (2.2.19)$$

where $\varepsilon_{\rm X}^{\rm SL}$ is an approximate exchange energy density (semi-local (SL) or Slater). The LMF is also a function of the electron density and related quantities. The first proposal⁸² was

$$a = \frac{\tau_{\rm W}}{\tau} = \frac{\left|\nabla\rho\right|^2}{8\rho\tau} \equiv t , \qquad (2.2.20)$$

where $\tau_{\rm W}$ is the von-Weizsäcker kinetic energy density. By this definition the LMF approaches one in one-electron regions so that only exact exchange is taken into account, which is a desired effect: in HF, the Coulomb term includes the unphysical self-interaction, which is canceled exactly by HF exchange. By using the analogous equation for the Coulomb term in DFT (cf. Eqs. (2.1.8) and (2.2.7)) the same effect occurs here as well. Since the corresponding exchange is included in the XC functional only approximately, this leads to the self-interaction error (SIE). It may be compensated, at least in part, by admixture of XX.



Figure 2.1 Two visualizations of a scaled t-LMF with b = 0.48 for carbon monoxide; left: graph along the bond axis; right: contour plot in bond axis plane.

With PBE functionals for exchange and correlation the ansatz yields bad predictions for atomization energies.⁶⁹ An extension of Eq. (2.2.20) is accomplished by scaling with a constant prefactor 0 < b < 1, yielding the t-LMF

$$a = bt = b\frac{\tau_{\rm W}}{\tau} , \qquad (2.2.21)$$

which is visualized in Fig. 2.1 for carbon dioxide. Both near the nuclei and far from them, the LMF values are high (even though scaled down), thereby adding more XX. In a spherical shell some distance from the nuclei and especially inside the bonding region, SL exchange dominates instead.

The optimal value when using the Slater exchange functional and the VWN correlation functional (i.e. an LDA-based LH) is b = 0.48 for the G2-1 test set,⁶⁹ although that reduces the compensation of the SIE. Nevertheless this produces distinctly better results, even in comparison with GGA functionals. One possible reason lies in the error compensation of the LDA functionals used, i.e. Slater and VWN. The exchange energy is too high, the correlation energy too low, reducing the total error.⁹⁷ If one combines, for example, Slater exchange with a GGA correlation functional, that beneficial effect is reduced.

Another cause for bad results when using GGA exchange in LHs is related to the *gauge* problem. In contrast to the energy, the energy density is arbitrary in that

one can add a function to the integrand and get the same energy in Eq. (2.2.9) if that function integrates to zero. This implies that any given energy density could already contain portions of gauge. By multiplying with an LMF such a term may not vanish anymore but distort the results. One can try to compensate the gauge error by addition of a calibration function (CF) to the SL exchange functional, leading to so-called *calibrated* LMFs.⁹⁸ A calibrated t-LMF can improve GGA results for various properties over LDA-based ones.⁹⁹ More sophisticated calibration requires ingredients like second derivatives of the electron density or derivatives of the XX energy density and therefore provides a challenge for developers.

Another family of LMFs transforms the reduced density gradient $0 \le s < \infty$ (Eq. (2.2.16)) to a range between zero and one, e.g. using the error function,

$$a = \operatorname{erf}\left(cs\right) \tag{2.2.22}$$

with an adjustable constant c = 0.22 (also optimized for G2-1). This s-LMF⁶⁹ fulfills the constraint of mixing in full XX in asymptotic regions (low density, high s) due to the error function, in contrast to the scaled down t-LMF, but it performs worse than the latter for thermochemical kinetics.⁶⁹

We have so far assumed restricted calculations of closed-shell systems. For unrestricted cases there are two choices. The LMF may be calculated for each density ρ_{α} and ρ_{β} separately and then multiplied with the exchange energy density of the respective spin (*spin-channel* LMF). Alternatively, one can use the sum $\rho = \rho_{\alpha} + \rho_{\beta}$ for both, resulting in additional cross terms, e.g. the product of mixed-spin density gradients $\nabla \rho_{\alpha} \nabla \rho_{\beta}$ (common LMF). Such terms would violate that only electrons of same spin interact via exchange. They can be justified if the exchange term is interpreted as non-dynamical correlation that is added to the full XX, as can be done by adding and subtracting $\varepsilon_{X}^{\text{ex}}$ in Eq. (2.2.19),

$$E_{\rm X} = \int \varepsilon_{\rm X}^{\rm ex} + (1-a) \left(\varepsilon_{\rm X}^{\rm SL} - \varepsilon_{\rm X}^{\rm ex} \right) \,\mathrm{d}\boldsymbol{r} \quad . \tag{2.2.23}$$

Such *common* LMFs further improve reaction barriers and other properties.⁵⁴

There are also ansatzes to introduce range separation (RS) into the exchange^{100,101} (see next section) or correlation⁵⁴ part of LH functionals. The latter is motivated by

the idea that the SIE is more adverse at SR, i.e. for short interelectronic distances, while it can have beneficial error canceling effects at LR. Thus the LDA correlation functional PW92 was modified at SR to reduce the SIE partially (LH-sirPW92) or fully (LH-sifPW92), in conjunction with Slater exchange and the t-LMF. Full correction yielded better BHs but worse AEs, whereas partial treatment (related to the t-LMF) improved both.⁵⁴

This is only a small glimpse of the developments in recent years. We refer to the review by Maier, Arbuznikov, and Kaupp¹⁰² for a more comprehensive introduction to LH functionals.

Range-Separated Hybrid Functionals

Another hybrid functional approach is the partitioning of the Coulomb operator into a SR and a LR part, usually by applying the (complementary) error function

$$\frac{1}{r_{12}} = \frac{\operatorname{erf}(\omega r_{12})}{r_{12}} + \frac{1 - \operatorname{erf}(\omega r_{12})}{r_{12}} , \qquad (2.2.24)$$

where $r_{12} \ge 0$ is the interelectronic distance and $0 \le \omega < \infty$ (or μ) is the RS parameter controlling the steepness of the partitioning. This facilitates the application of different methods, functionals, or approximations for either or both ranges.

Originally, this separation had been used for wave function methods to smoothly simplify the computationally demanding Coulomb interactions by calculating the LR erf term as a truncated Fourier series.¹⁰³ An adjusted ansatz, termed Coulomb-attenuation, neglected the LR part completely¹⁰⁴ and was also applied to LDA functionals.¹⁰⁵ Then DFT was used at SR within a CI framework to more efficiently describe the correlation cusp of the wave function.¹⁰⁶

A now common use case, labeled long-range correction (LC), applies a semilocal exchange functional at SR and XX at LR to ensure the correct asymptotic behavior of ρ in regions far from the nuclei. For example, in LC- ω PBE this is done for PBE exchange with fitted $\omega = 0.4$, which gives simultaneously good results for enthalpies of formation and BHs.⁵³ In contrast, HSE incorporates XX at SR range while LR has only PBE exchange, which is favorable for solid-state systems.^{51,52,107} Both ansatzes can be combined, as done for the HISS functional, which incorporates XX only at mid-range while PBE is applied at both SR and LR.⁵⁰

The HSE functional mentioned above is in fact a range-separated GH since it reduces to PBE0 for $\omega \to 0$ (and PBE for $\omega \to \infty$). For CAM-B3LYP one applies the RS to the exchange part of B3LYP (cf. Eq. (2.2.17)) to use different mixing parameters for SR ($a_0 = 0.19$) and LR ($a_0 = 0.65$) with $\omega = 0.33$ yielding better charge transfer energies.⁴⁸ Another example is ω B97X, which applies the B97 exchange¹⁰⁸ (with 16% XX) at SR and full XX at LR, and improves on describing the dissociations of radical cations.³⁶

The next step, combining RS and LHs, was taken first for LDA and PBE with a t-LMF and either full XX at LR (i.e. the LC ansatz from above),

$$E_{\rm X} = \int a\varepsilon_{\rm X,SR}^{\rm ex} + (1-a)\varepsilon_{\rm X,SR}^{\rm SL} + \varepsilon_{\rm X,LR}^{\rm ex} \,\mathrm{d}\boldsymbol{r} \,\,, \qquad (2.2.25)$$

or the (semi-)local functional instead (denoted as "screened"),

$$E_{\rm X} = \int a\varepsilon_{\rm X,SR}^{\rm ex} + (1-a)\varepsilon_{\rm X,SR}^{\rm SL} + \varepsilon_{\rm X,LR}^{\rm SL} \,\mathrm{d}\boldsymbol{r} \quad , \qquad (2.2.26)$$

while the LH functional is used at SR in both cases.¹⁰⁰ Later, Haunschild and Scuseria applied both versions (LC and screened) to one of their PBE-based LHs,¹⁰⁹ where the LC variant gave better results for AEs and non-hydrogen BHs than LC- ω PBE.¹⁰¹

The parameter ω is constant system-wide in the above examples. While the overall performance is appreciable, in principle the optimal value for each system varies considerably. This is underlined by the *optimal tuning* procedure for finite systems,^{110,111} in which the parameter ω is optimized ("tuned") for each system individually to fulfill (or minimize the deviation from) an exact condition, e.g. that the negative vertical ionization potential (IP) should be equal to the highest occupied molecular orbital (HOMO) energy (Koopmans' theorem),

$$\epsilon_{\text{HOMO}} = -\text{IP} = E(N) - E(N-1) ,$$
 (2.2.27)

for a system with N electrons. The IP condition could be complemented by connecting the electron affinity (EA) with the lowest unoccupied molecular orbital (LUMO) energy (EA condition) to better describe fundamental gaps but there is no theoretical basis for this. That is why the IP condition is applied to the anion instead. Such OT-RSH functionals give good charge-transfer excitation energies^{110,112} and quasi-particle spectra.^{81,113} It was further shown that they can achieve similar IP and EA results as the computationally more expensive manybody calculations usually used.¹¹⁴ On the downside, the *optimal* ω for a system of two sufficiently separated subsystems can be different than for either subsystem alone, so the sum of their total energies may not coincide. This size inconsistency results in wrong predictions for binding energies, potential energy surfaces, and spin configurations.¹¹¹

As an alternative to individual tuning and in analogy to the relation between global and local hybrids, the parameter ω can be converted to a position-dependent RSF with quantities like the electron density. Such LRSH functionals were investigated non-self-consistently by Krukau et al. for LDA ingredients and improve on the global results.⁸⁶ An extension to self-consistency and GGAs exchange appears promising and will be discussed in Chapter 4.

2.3 Atomic Orbital Basis

This section will give some information on Gaussian basis functions, predominantly used for molecular DFT applications, and the connection to the ingredients for SL functionals to give context and introduce quantities for the derivations and explanations later on. It will be complemented by the following sections giving an overview of the program package Turbomole and some considerations for the implementation thereafter.

2.3.1 Cartesian Gaussian Orbitals

To solve the DFT equations we choose a basis of primitive functions centered on the nuclei, also known as atomic orbitals (AOs). For primitives one may use Slater-type orbitals (STOs), which is the correct form for the hydrogen atom. More commonly,
Gaussian-type orbitals (GTOs) are used since the analytical computation of their integrals is very efficient, even though a larger number of primitives is needed to approximate the correct orbital form. The type and parameters are defined by the chosen basis set.

We will focus on GTOs of the general form

$$G_A = x_A^i y_A^k z_A^m \exp\left(-\alpha r_A^2\right). \tag{2.3.1}$$

The monomial exponents $i, k, m \ge 0$ are integers and define the angular quantum number $\mathcal{L} = i + k + m$. The variable $x_A = x - A_x$ is the *x*-component of the difference vector between the coordinate \mathbf{r} and the position of nucleus A. The quantities y_A and z_A are defined analogously, and $r_A^2 = x_A^2 + y_A^2 + z_A^2$.

These primitives may be contracted,

$$\chi_{\mu} = \sum_{\gamma} d_{\gamma\mu} G_A^{\gamma} , \qquad (2.3.2)$$

with constant contraction coefficients $d_{\gamma\mu}$. Both $d_{\gamma\mu}$ and α from Eq. (2.3.1) are defined by the basis set for each element of the system. The same values are used for different AOs that belong to the same shell with angular quantum number \mathcal{L} , e.g. the three basis functions p_x , p_y , p_z of a *p*-shell ($\mathcal{L} = 1$) use the same parameters. In the special case of an uncontracted basis, the sum in Eq. (2.3.2) includes only one term and the contraction coefficient is one.

We then define the molecular orbitals (MOs) as a linear combination of atomic orbitals (LCAO),

$$\varphi_i = \sum_{\mu} C_{\mu i} \chi_{\mu} , \qquad (2.3.3)$$

with coefficients $C_{\mu i}$, which are optimized in the context of the SCF algorithm.

Interaction of Two GTOs

For the interaction of two primitives we use an additional set of parameters j, l, and n for a second primitive centered on atom B and distinguish the exponential

prefactors as α_A and α_B . The overlap integral is then written as

$$S_{AB} = \int G_A G_B \,\mathrm{d}\boldsymbol{r} = \int x_A^i y_A^k z_A^m \exp\left(-\alpha_A r_A^2\right) x_B^j y_B^l z_B^n \exp\left(-\alpha_B r_B^2\right) \,\mathrm{d}\boldsymbol{r} \quad (2.3.4)$$

Using the Gaussian overlap rule, we can further simplify this to

$$S_{AB} = K_{AB} \int x_A^i x_B^j y_A^k y_B^l z_A^m z_B^n \exp\left(-\alpha_P r_P^2\right) \mathrm{d}\boldsymbol{r} \quad (2.3.5)$$

$$K_{AB} = \exp\left(-\frac{\alpha_A \alpha_B}{\alpha_A + \alpha_B} R_{AB}^2\right), \qquad (2.3.6)$$
$$\mathbf{p} = \alpha_A \mathbf{A} + \alpha_B \mathbf{B} \qquad (2.2.7)$$

$$\boldsymbol{P} = \frac{\alpha_A \boldsymbol{A} + \alpha_B \boldsymbol{B}}{\alpha_A + \alpha_B} , \qquad (2.3.7)$$

where \boldsymbol{P} is called the *center of charge* between A and B (which is closer to the center with greater α), $R_{AB} = |\boldsymbol{A} - \boldsymbol{B}|$, and $\alpha_P = \alpha_A + \alpha_B$.

The more relevant integral for this work is the repulsion integral

$$V_{AB} = V_{AB}(\boldsymbol{G}) = \int G_A G_B \frac{1}{|\boldsymbol{r} - \boldsymbol{G}|} \,\mathrm{d}\boldsymbol{r} \,. \tag{2.3.8}$$

It will be at the center of attention in Sections 2.4, 3.1 and 4.1 as it is needed for the calculation of XX.

Derivative of GTOs

Differentiating a one-dimensional GTO w.r.t. the electronic coordinate

$$\nabla G_i = iG_{i-1} - 2\alpha G_{i+1} , \qquad (2.3.9)$$

results in a sum of two GTOs, one with a lower and one with a higher quantum number *i*, with prefactors. Since $x_A = x - A_x$, the gradient w.r.t. the nuclear coordinates and w.r.t. the electronic coordinates can be converted to each other, whereby the sign changes,

$$\nabla_{\!\!A}G_A = -\nabla G_A \;. \tag{2.3.10}$$

This also applies to the AOs because the contraction coefficients are constants,

$$\nabla_{\!A}\chi_{\mu} = -\nabla\chi_{\mu}.\tag{2.3.11}$$

One should, however, keep in mind that the sums must still only consider AOs χ_{μ} centered on atom A. The identity Eq. (2.3.11) can be exploited for the implementation by reusing intermediate quantities needed for the energy, SCF, and gradient calculations.

2.3.2 From Eigenvalue to Matrix Equations

The AO basis enables us to restate the KS equations as matrix equations. By inserting the MO definition from Eq. (2.3.3) into Eq. (2.2.10), multiplying from the left with another AO χ_{μ} , and integrating we get

$$\sum_{\nu} C_{\nu i} \int \chi_{\mu} \hat{f}_{i}^{\text{KS}} \chi_{\nu} \, \mathrm{d}\boldsymbol{r} = \varepsilon_{i} \sum_{\nu} C_{\nu i} \int \chi_{\mu} \chi_{\nu} \, \mathrm{d}\boldsymbol{r} \quad .$$
(2.3.12)

This is equivalent to

$$\sum_{\nu} F_{\mu\nu} C_{\nu i} = \varepsilon_i \sum_{\nu} S_{\mu\nu} C_{\nu i} , \qquad (2.3.13)$$

$$F_{\mu\nu} = \int \chi_{\mu} \hat{f}_i^{\text{KS}} \chi_{\nu} \,\mathrm{d}\boldsymbol{r} \quad , \qquad (2.3.14)$$

$$S_{\mu\nu} = \int \chi_{\mu} \chi_{\nu} \,\mathrm{d}\boldsymbol{r} \quad , \qquad (2.3.15)$$

where we introduced the KS matrix with elements $F_{\mu\nu}$ and the overlap matrix elements $S_{\mu\nu}$ for AOs (not to be confused with the overlap integrals S_{AB} for primitives from Eqs. (2.3.4) and (2.3.5)). Now the eigenvalue problem can be solved with algebraic tools. We just have to construct the KS matrix.

2.3.3 Density and Related Quantities in the AO Basis

As preparation for the derivations in Chapters 3 and 4 this subsection defines all quantities for the evaluation of semi-local functionals and real-space functions in

the AO basis. For reference, we define a set of those depended-on quantities

$$\mathbb{Q} = \{\rho, \gamma, \tau\} . \tag{2.3.16}$$

Electron Density

The electron density

$$\rho = \sum_{i} \varphi_{i} \varphi_{i} = \sum_{i} \sum_{\mu\nu} C_{\mu i} C_{\nu i} \chi_{\mu} \chi_{\nu} = \sum_{\mu\nu} D_{\mu\nu} \chi_{\mu} \chi_{\nu} \qquad (2.3.17)$$

is the most basic property. Here we expand the MOs in basis functions as described in Section 2.3.1 and introduce the density matrix with elements

$$D_{\mu\nu} = \sum_{i} C_{\mu i} C_{\nu i} . \qquad (2.3.18)$$

Density gradient

The derivative of the density w.r.t. the electronic coordinate is

$$\nabla \rho = 2 \sum_{i} \nabla \varphi_{i} \varphi_{i} = 2 \sum_{\mu\nu} D_{\mu\nu} \nabla \chi_{\mu} \chi_{\nu} . \qquad (2.3.19)$$

The derivative of the coefficients vanishes since they do not depend on the electronic coordinate. The density gradient was mentioned before as the next-step ingredient for GGA functionals. In practice, one also uses the scalar product of this gradient

$$\gamma = \nabla^{\mathrm{T}} \rho \nabla \rho = 4 \sum_{ij} \nabla^{\mathrm{T}} \varphi_i \varphi_i \nabla \varphi_j \varphi_j$$

= $4 \sum_{\mu\nu\kappa\lambda} D_{\mu\nu} D_{\kappa\lambda} \nabla^{\mathrm{T}} \chi_\mu \chi_\nu \nabla \chi_\kappa \chi_\lambda$, (2.3.20)

whose derivative is

$$\nabla \gamma = 8 \sum_{ij} \nabla \nabla^{\mathrm{T}} \varphi_i \varphi_i \nabla \varphi_j \varphi_j + \nabla \varphi_i \nabla^{\mathrm{T}} \varphi_i \nabla \varphi_j \varphi_j$$

= $8 \sum_{\mu\nu\kappa\lambda} D_{\mu\nu} D_{\kappa\lambda} (\nabla \nabla^{\mathrm{T}} \chi_\mu \chi_\nu \nabla \chi_\kappa \chi_\lambda + \nabla \chi_\mu \nabla^{\mathrm{T}} \chi_\nu \nabla \chi_\kappa \chi_\lambda) .$ (2.3.21)

Kinetic Energy Density

The kinetic energy density

$$\tau = \frac{1}{2} \sum_{i} \nabla^{\mathrm{T}} \varphi_{i} \nabla \varphi_{i} = \frac{1}{2} \sum_{\mu\nu} D_{\mu\nu} \nabla^{\mathrm{T}} \chi_{\mu} \nabla \chi_{\nu} \qquad (2.3.22)$$

is similar to the density gradient. Its gradient is

$$\nabla \tau = \sum_{i} \nabla \nabla^{\mathrm{T}} \varphi_{i} \nabla \varphi_{i} = \sum_{\mu\nu} D_{\mu\nu} \nabla \nabla^{\mathrm{T}} \chi_{\mu} \nabla \chi_{\nu} . \qquad (2.3.23)$$

Exact Exchange

For the exact exchange the dependency on either \mathbf{r}_1 or \mathbf{r}_2 is of relevance. For brevity we will use $\varphi_i^1 = \varphi_i(\mathbf{r}_1), \ \chi_\mu^1 = \chi_\mu(\mathbf{r}_1)$, and $a_1 = a(\mathbf{r}_1)$ in such instances.

The XX energy density is defined by

$$\varepsilon_{\mathrm{X}}^{\mathrm{ex}}(\boldsymbol{r}_{1}) = -\frac{1}{2} \sum_{ij} \varphi_{i}^{1} \varphi_{j}^{1} \int \varphi_{i}^{2} \varphi_{j}^{2} \frac{1}{r_{12}} \,\mathrm{d}\boldsymbol{r}_{2}$$

$$= -\frac{1}{2} \sum_{\mu\nu} D_{\mu\kappa} D_{\nu\lambda} \chi_{\mu}^{1} \chi_{\nu}^{1} \int \chi_{\kappa}^{2} \chi_{\lambda}^{2} \frac{1}{r_{12}} \,\mathrm{d}\boldsymbol{r}_{2} \quad .$$

$$(2.3.24)$$

For the SCF method, the KS matrix has to be determined by calculating the functional derivative of the energy w.r.t. the density. However, the XX depends only implicitly on the density through the KS orbitals. In the GKS framework the strict constraint of KS that the XC potential must be a local potential is relaxed.¹¹⁵ Realizing then that

$$\frac{\delta E_{\rm X}^{\rm ex}}{\delta \varphi_i} = \frac{\delta E_{\rm X}^{\rm ex}}{\delta \rho} \frac{\delta \rho}{\delta \varphi_i} = \frac{\delta E_{\rm X}^{\rm ex}}{\delta \rho} 2\varphi_i , \qquad (2.3.25)$$

the XX potential can be expressed as a functional derivative w.r.t. the orbitals

(FDO),

$$v_{\rm X}^{\rm ex}\varphi_i = \frac{\delta E_{\rm X}^{\rm ex}}{\delta\rho}\varphi_i = \frac{1}{2}\frac{\delta E_{\rm X}^{\rm ex}}{\delta\varphi_i} \,. \tag{2.3.26}$$

We therefore apply the FDO to the XX

$$\frac{\delta E_{\rm X}^{\rm ex}}{\delta \varphi_i} = -2 \sum_j \varphi_j^{\rm 1} \int \varphi_i^{\rm 2} \varphi_j^{\rm 2} \frac{1}{r_{12}} \,\mathrm{d}\boldsymbol{r}_2 \tag{2.3.27}$$

but calculate the usual derivative w.r.t. the density for the other parts.

For LHs we have to consider that the integrand includes the LMF, which also depends on \mathbf{r}_1 (cf. first term in Eq. (2.2.19)). The FDO then contains the derivative of the LMF multiplied by the usual XX energy density, and two terms where the derivative was applied to one orbital that depends on either \mathbf{r}_1 or \mathbf{r}_2 , respectively. By swapping the order of integration in one of those two we get

$$\frac{\delta}{\delta\varphi_i} \int a_1 \varepsilon_{\mathbf{X}}^{\mathrm{ex}}(\boldsymbol{r}_1) \,\mathrm{d}\boldsymbol{r}_1 = \int \frac{\delta a_1}{\delta\varphi_i} \varepsilon_{\mathbf{X}}^{\mathrm{ex}}(\boldsymbol{r}_1) \,\mathrm{d}\boldsymbol{r}_1 \tag{2.3.28a}$$

$$+\sum_{j}\varphi_{j}^{1}\int\varphi_{i}^{2}\varphi_{j}^{2}\frac{a_{1}+a_{2}}{r_{12}}\,\mathrm{d}\boldsymbol{r}_{2} \quad (2.3.28\mathrm{b})$$

where both a_1 and a_2 are included in the last term. For the contributions to the KS matrix (see Eq. (2.3.14)) we change into the AO basis. Then we can split the second term again due to the symmetry of the operator and integration, calculate one of the resulting terms including a_1 ,

$$\overline{\mathcal{K}_{\mu\kappa}} = -\int a_1 \sum_{\nu\lambda} D_{\nu\lambda} \chi^1_{\mu} \chi^1_{\nu} \int \chi^2_{\kappa} \chi^2_{\lambda} \frac{1}{r_{12}} \,\mathrm{d}\boldsymbol{r}_2 \,\mathrm{d}\boldsymbol{r}_1 \,\,, \qquad (2.3.29)$$

and add the transposed matrix,

$$\mathcal{K}_{\mu\kappa} = \overline{\mathcal{K}_{\mu\kappa}} + \overline{\mathcal{K}_{\kappa\mu}} \ . \tag{2.3.30}$$

The first term on the r.h.s. in Eq. (2.3.28) contains the derivative of the LMF, which can be calculated and used as for SL energy densities. This also implies derivatives w.r.t. the gradient of the orbitals, which do not occur for the second term.

2.4 Integration Techniques

This section includes some further details on integrals related to XX. Both Chapters 3 and 4 will use it as the basis of their respective implementations. It encompasses the numerical integration on a grid necessary for semi-local KS-DFT functionals as well as the schemes for Gauss-Rys quadrature or via Boys functions for the GTO basis. Finally, we look at prescreenings to avoid some of the costly evaluations.

2.4.1 Numerical Integration

The integrals for semi-local and non-local functionals cannot be solved analytically, so the integration is done numerically on a grid. The integrals over the spatial coordinates are converted to a summation over grid points g,

$$F = \int f(\boldsymbol{r}) \,\mathrm{d}\boldsymbol{r} \approx \sum_{g} f(\boldsymbol{G}) w_{g} \qquad (2.4.1)$$

with spatial vectors $\boldsymbol{G} = \boldsymbol{G}_g$ and weights w_g . The grid points are not necessarily distributed evenly but may be denser in regions where the electron density fluctuates more strongly than where it is nearly constant. The weights are adjusted accordingly and cannot be moved in front of the sum.

In Turbomole the molecular grid¹¹⁶ is constructed by combining atomic grids for all atoms of the system and mitigating the overlaps via Becke partitioning.¹¹⁷ The atomic grids are built from spherical Lebedev¹¹⁸ (or Lobatto¹¹⁹) grid shells placed on radial Chebychev grid points, which are transformed from their defined range [-1, +1] to $[0, \infty]$.

2.4.2 Rephrasing Exact Exchange on the Grid

For easier reference later on we introduce intermediate quantities for the ingredients of the XX energy density on the grid:

$$\mathcal{X}_{\mu g} = \sqrt{w_g} \chi_{\mu}(\boldsymbol{G}) , \qquad (2.4.2)$$

$$\mathcal{F}_{\kappa g} = \sum_{\mu} \mathcal{X}_{\mu g} D_{\mu \kappa} , \qquad (2.4.3)$$

$$\mathcal{G}_{\kappa g} = \sum_{\lambda} \mathcal{F}_{\lambda g} \mathcal{A}_{\kappa \lambda g} , \qquad (2.4.4)$$

$$\mathcal{A}_{\kappa\lambda g} = \int \chi_{\kappa}(\boldsymbol{r}) \chi_{\lambda}(\boldsymbol{r}) \frac{1}{|\boldsymbol{r} - \boldsymbol{G}|} \,\mathrm{d}\boldsymbol{r} \,\,. \tag{2.4.5}$$

For each grid point g the first three quantities $(\mathcal{X}, \mathcal{F}, \mathcal{G})$ are vectors and the last one (\mathcal{A}) is a matrix with components for all AOs (κ, λ) . Applying this to the energy density and KS matrix contributions of XX for LHs (cf. Section 2.3.3) yields

$$\varepsilon_{\mathrm{X}g}^{\mathrm{ex}} = -\frac{1}{2} \sum_{\kappa\lambda} \mathcal{F}_{\kappa g} \mathcal{F}_{\lambda g} \mathcal{A}_{\kappa\lambda g} = -\frac{1}{2} \sum_{\kappa} \mathcal{F}_{\kappa g} \mathcal{G}_{\kappa g} , \qquad (2.4.6)$$

$$\overline{\mathcal{K}_{\mu\kappa}} = -\sum_{g} a_g \sum_{\lambda} \mathcal{X}_{\mu g} \mathcal{F}_{\lambda g} \mathcal{A}_{\kappa\lambda g} = -\sum_{g} a_g \mathcal{X}_{\mu g} \mathcal{G}_{\kappa g} . \qquad (2.4.7)$$

2.4.3 Gaussian Quadrature

Integration can be efficiently simplified under certain conditions using orthogonal polynomials $P_n(x)$, which fulfill

$$\int_{a}^{b} P_{m}(x)P_{n}(x)W(x) \,\mathrm{d}x = h_{n}\delta_{mn} , \qquad (2.4.8)$$

where W(x) is a weighting function, δ_{mn} is the Kronecker delta, and $h_n = 1$ if the polynomials are normalized (i.e. orthonormal). For our integrals we need the weighting function to be the exponential of the GTO primitives, so Hermite polynomials

$$H_n(x) = (-1)^n \exp(-x^2) \frac{d^n}{dx^n} \exp(-x^2) = \left(2x - \frac{d}{dx}\right)^n 1$$
(2.4.9)

are suitable $(W(x) = \exp(-x^2), a = -\infty, b = +\infty)$. Gaussian quadrature reduces the effort of computing electronic integrals (overlap, Coulomb, exchange, etc.) to finding the roots and weights of the polynomials, calculating the value of the GTO monomials at those roots, and adding up the products. For example, the overlap integral from Eq. (2.3.5) then is

$$S_{AB} = \frac{K_{AB}}{\alpha_P^{3/2}} \sum_{\eta_x} w_{\eta_x} x_A^i x_B^j \sum_{\eta_y} w_{\eta_y} y_A^k y_B^l \sum_{\eta_z} w_{\eta_z} z_A^m z_B^n .$$
(2.4.10)

Here η_x is the index for the roots in the x-direction and w_{η_x} is the weight corresponding to the root o_{η_x} within

$$x_A = \frac{1}{\sqrt{\alpha_P}} o_{\eta_x} - X_{AP} , \qquad (2.4.11)$$

where $X_{AP} = A_x - P_x$ is (exemplary) the *x*-component of the difference vector between **A** and **P**. The other quantities are analogous. The roots and weights of the Hermite polynomials are independent of the integration parameters and are given in the code.

The Coulomb operator can be expressed as the integral of a Gaussian,

$$\frac{1}{|r_G|} = \frac{2}{\sqrt{\pi}} \int_0^\infty \exp\left(-r_G^2 v^2\right) dv \quad . \tag{2.4.12}$$

Adapting this integral by variable transformation (or other integration techniques), the repulsion integral from Eq. (2.3.8) is reformulated to

$$V_{AB} = \frac{2K_{AB}}{\sqrt{\pi}\alpha_P} \sum_{\gamma} w_{\gamma} \sum_{\eta_x} w_{\eta_x} x^i_A x^j_B \sum_{\eta_y} w_{\eta_y} y^k_A y^l_B \sum_{\eta_z} w_{\eta_z} z^m_A z^n_B .$$
(2.4.13)

Here the integration of the additional integral from the operator is done via Gauss-Rys quadrature¹²⁰ ($W(x) = \exp(-\alpha x^2)$, a = 0, b = 1) with the index γ and the weight w_{γ} . The roots and weights of the Rys polynomials must be determined for each exponential prefactor α in contrast to Gauss-Hermite quadrature. The

relative positions are transformed as

$$x_{A} = \sqrt{\frac{1 - t_{\gamma}^{2}}{\alpha_{P}}} o_{\eta} + X_{GP} t_{\gamma}^{2} - X_{AP}$$
(2.4.14a)

$$= \sqrt{\frac{1}{\alpha_P(1+u_{\gamma})}} o_{\eta} + X_{GP} \frac{u_{\gamma}}{1+u_{\gamma}} - X_{AP} , \qquad (2.4.14b)$$

where o_{η_x} and t_{γ} are the roots of the Hermite and Rys polynomials, respectively. The alternative $u_{\gamma} = t_{\gamma}^2/(1-t_{\gamma}^2)$ shown in Eq. (2.4.14b) is used sometimes instead, e.g. in Turbomole. The other positions $(x_B, y_A, \text{ etc.})$ are analogous, and $X_{GP} = G_x - P_x$ is (exemplary) the x-component of the difference vector between \boldsymbol{G} and \boldsymbol{P} .

The number of needed points, i.e. the degree of the underlying polynomial, depends on the angular quantum numbers via

$$\eta_x^{\max} > \frac{i+j}{2}$$
, (2.4.15)

and analogously for y and z. If the integrals for all basis functions of a shell pair are calculated together, the upper limit of all Gauss-Hermite sums can be set to the highest among them without significant overhead,

$$\eta^{\max} > \frac{i+j+k+l+m+n}{2} = \frac{\mathcal{L}_{\mathcal{I}} + \mathcal{L}_{\mathcal{J}}}{2}.$$
 (2.4.16)

The same is true for the Gauss-Rys index γ .

2.4.4 Integration with Boys Functions

As an alternative to Gauss-Rys quadrature, one may express the integrals resulting from Eq. (2.4.12) as Boys functions

$$F_n(x) = \int_0^1 s^{2n} \exp\left(-xs^2\right) \mathrm{d}s \ . \tag{2.4.17}$$

The monomials centered on A and B can be further expanded into monomials on the center of charge P with expansion coefficients C_w^{ij} ,

$$x_A^i x_B^j = \sum_{w=0}^{i+j} C_w^{ij} x_P^w .$$
 (2.4.18)

Combining this and the Gaussian product rule, we can rephrase the product of GTOs as

$$G_i G_j = \sum_{t=0}^{i+j} E_t^{ij} \frac{\partial^t}{\partial P_x^t} \exp\left(-\alpha_P x_P^2\right), \qquad (2.4.19)$$

$$E_{tuv}^{AB} = E_t^{ij} E_u^{kl} E_v^{mn} , (2.4.20)$$

with prefactors E_t^{ij} , E_u^{kl} , and E_v^{mn} for the x, y and z direction, respectively. They can be calculated starting from $E_{t=0}^{00} = K_{AB}^x$ and analogues. The conversions culminate in another expression for the repulsion integral (cf. Eqs. (2.3.8) and (2.4.13))

$$V_{AB} = \frac{2\pi}{\alpha_P} \sum_{tuv} E_{tuv}^{AB} \frac{\partial^t}{\partial P_x^t} \frac{\partial^u}{\partial P_y^u} \frac{\partial^v}{\partial P_z^v} F_0(\alpha_P R_{PG}^2) . \qquad (2.4.21)$$

Differentiating the Boys function results in a Boys function of higher order. They are usually approximated by interpolation and already implemented in the programs. For example, two p_x primitives (i, j = 1; k, l, m, n = 0) yield

$$V_{110000} = \frac{2\pi}{\alpha_P} K_{AB} \left\{ \left(X_{PA} X_{PB} + \frac{1}{2\alpha_P} \right) F_0 - \left[(X_{PB} + X_{PA}) X_{PG} + \frac{1}{2p} \right] F_1 + X_{PG}^2 F_2 \right\}.$$
(2.4.22)

For more details, see [121, Sections 9.4ff].

2.4.5 Prescreening Techniques for Exact Exchange

The computation of the repulsion integrals related to XX is the bottleneck of all the functional implementations we are interested in. Therefore we prescreen pairs of shells, basis functions, or primitives in order to skip any demanding computation

for elements deemed to be negligible.

S-Junctions

The concept of S-junctions follows the chain-of-spheres exchange (COSX) algorithm¹²² for XX in GHs. Starting at an initial distance from the nucleus, estimated from the most diffuse primitive, one probes each basis function of that atom by varying the distance and evaluating its value until it is smaller than a given threshold. Constructing spheres with these distances as radii, only shell pairs whose spheres overlap are evaluated. Accordingly, a lower threshold results in more shell pairs to be evaluated. Thresholds are adjusted in negative powers of ten, e.g. 10^{-5} .

P-Junctions

An additional ansatz for prescreening looks at the multiplication of \mathcal{A} with \mathcal{F} in Eq. (2.4.4). If elements of \mathcal{F} are very small, the corresponding products with \mathcal{A} will be negligible and the evaluation of some elements $\mathcal{A}_{\kappa\lambda g}$ can be skipped. The threshold is adjusted in negative powers of ten, as with S-junctions.

Exponential Overlap

This concept is similar to that of S-junctions but applied to pairs of primitives. The prefactor K_{AB} from Eqs. (2.4.13) and (2.4.21) can be screened using the nuclear positions and basis set information alone. If the exponential is very small, the evaluation of the integral can be skipped.

2.5 Overview of Turbomole

The program package Turbomole⁸⁵ consists of various programs and scripts, collectively called modules. The most important ones in the context of this thesis are listed in Table 2.1. This section gives an overview of the interlocking of those modules to fulfill various tasks so that the changes applied for the LHGs and the LRSHs are easier to comprehend. Modules and subroutines will be set in monospace font and the latter have appended parentheses.

Name	Type	Usage
define	Р	Interactive input for calculation parameters
dscf	Р	SCF calculation
ridft	Р	Same as dscf with RI approximation
grad	Р	Analytical nuclear gradient calculation
rdgrad	Р	Same as grad with RI approximation
statpt	Р	Nuclear stationary point analysis and displacement of nuclei
aoforce	Р	Analytical nuclear Hessian calculation
jobex	\mathbf{S}	Structure optimization
NumForce	\mathbf{S}	Numerical nuclear Hessian calculation

Table 2.1 Some programs (P) and scripts (S) of Turbomole and their usage.

2.5.1 SCF Calculation with dscf and ridft

The programs dscf and ridft both do SCF calculations to converge the groundstate for a fixed configuration of nuclei. In ridft the resolution of the identity (RI) approximation¹⁹ is used for Coulomb (option \$rij) and/or exchange (option \$rik). For both programs, starting orbitals (i.e. MO coefficients) have to be provided. This can be accomplished by an extended Hückel guess¹²³ via the input program define.

Some subroutines of both programs are visualized in Fig. 2.2. For dscf, the nuclear repulsion energy is calculated in nucrep(), then the one-electron integrals of the core Hamiltonian as well as the overlap matrix are handled in symoneint(). The same routine is used by ridft through allone(). The Coulomb repulsion energies are determined in fockbuild() for dscf and in colaux() for ridft. The XC parts are prepared in scf() and riscf() for dscf and ridft, respectively. Both of them call scf_dft(). It splits according to the necessary ingredients between LDA (xcurhf()), GGA (xcrhf()), meta-GGA (mGGA) (xcmrhf()), and LH (xclhyb()), where the XC energy and the corresponding parts of the KS matrix are calculated. The latter is used for the optimization of the MO coefficients via matrix diagonalization in fdiag() for restricted or ufdiag() for unrestricted calculations. The new implementation for LRSHs will be inserted analogously in a new subroutine xclrs(), so it can be used by both programs.



Figure 2.2 Call graph for dscf and ridft and the energy terms calculated therein: nuclear repulsion N, electronic repulsion J, overlap integrals S, kinetic energy T, nucleus-electron attraction V, DFT exchange and correlation XC. The subroutine xclhyb() for LH energy and KS matrix highlighted in blue has already been implemented⁸³ and will be described in Section 2.6. The orange-shaded xclrs() foreshadows the implementation of LRSHs in Chapter 4.

2.5.2 Nuclear Gradient Calculation with grad or rdgrad

Assuming a converged SCF calculation, the program grad (or rdgrad for the RI version) calculates the change in energy w.r.t. a displacement of nuclear coordinates directly from the MO coefficients.

As for the SCF programs, Fig. 2.3 depicts some subroutines of grad and rdgrad. The former delegates to scfder() to call jkder() for the gradient contributions of the electron-electron Coulomb interactions, and dstv() for the nucleus-electron and nucleus-nucleus interactions as well as overlap integrals and kinetic energy. For rdgrad the first part is done in twoder(), and oneder() calls dstv() as well. Both rdgrad and grad (through scfder()) rely on the same routine grdfinp() for the XC contributions. As for the SCF, it splits into grurhf() for LDA, grrhf() for GGA, grmrhf() for mGGA functionals. We can adopt this concept with a new routine grlochyb() for LHG, thereby supporting both programs.



Figure 2.3 Call graph for grad and rdgrad. Gradients of the various energy terms: nuclear repulsion N, electronic repulsion J, overlap integrals S, kinetic energy T, nucleus-electron attraction V, DFT exchange and correlation XC. The orange-shaded grlochyb() is the new subroutine for LH gradients discussed in Chapter 3.

2.5.3 Structure Optimization with jobex

Structure optimizations are conducted using the superordinate script *jobex*. It calls multiple modules sequentially, which depend on the results of the previous one.

The broad structure of the script is shown schematically in Fig. 2.4. After initialization the script enters a loop for structure optimization. First a gradient module (grad or rdgrad) is called to calculate the gradient w.r.t. nuclear coordinates, followed by the computation of the (usually approximated) Hessian by statpt. The latter subroutine also changes the nuclear coordinates, followed by a full SCF calculation (with dscf or ridft) until convergence of the orbitals is reached. If the difference in energy (and some other parameters) compared to the previous (nuclear) iteration lies below the convergence criterion for structure optimization, the script finishes successfully. Otherwise, the next iteration starts with the calculation of a new gradient. To prevent an infinite loop the number of iterations is limited. As soon as a new functional is implemented into grad or rdgrad, this module can use it without further modification.



Figure 2.4 Scheme of structure optimization in the script *jobex*.

2.5.4 Frequency Calculation with NumForce and aoforce

The script NumForce performs gradient calculations with grad or rdgrad for various nuclear positions to get a numerical approximation for the Hessian w.r.t. nuclear displacement within the harmonic approximation. This is used for the calculation of vibrational force constants, i.e. spectroscopic data for the infrared (IR) range. The analytical equivalent is **aoforce**. Because of the complications arising from the second derivatives, they are often not implemented for new functionals. For such cases, NumForce remains a viable alternative. As soon as a new functional is implemented into grad or rdgrad, this module can use it without further modification.

2.6 Implementation Prerequisites

This section will shed some light on how \mathcal{A} (Eq. (2.4.5)) is being constructed for the SCF method of LHs, i.e. we will describe the integration techniques introduced in Section 2.4 in the context of their explicit implementation in Turbomole. This should prove helpful for understanding the changes for the implementation of both LHGs (Section 3.2) and LRSHs (Section 4.2).

0	,	
Subroutine	Input	Output
xclhyb()	D	$E_{\rm XC}, \ \boldsymbol{F}^{\rm XC}$
funct_2()		χ, χ'
ondes_ks()	$\boldsymbol{D},\chi,\chi',$	$ ho, \gamma, \tau$
lmf_1()	$ ho,\gamma, au$	$a, \frac{\partial a}{\partial \rho}, \frac{\partial a}{\partial \gamma}, \frac{\partial a}{\partial \tau}$
calc_ftg()	\boldsymbol{D},χ	${\cal F}$
numpot()	${\cal F}$	${\cal G}$
nlpot_lh()	$\chi, a, \mathcal{F}, \mathcal{G}$	$\varepsilon_{\mathrm{X}}^{\mathrm{ex}},\mathcal{K}$
lochyb_1()	$\boldsymbol{D}, a, \frac{\partial a}{\partial \rho}, \frac{\partial a}{\partial \gamma}, \frac{\partial a}{\partial \tau}, \varepsilon_{\mathrm{X}}^{\mathrm{ex}}$	$E_{\rm XC}, O, O', O''$
onf_k()	$\boldsymbol{D}, O, O', O'', \chi, \chi'$	F^{O}

 Table 2.2 General flow of information for subroutines regarding LH SCF (without grid and junctions).

Storing \mathcal{G} Instead of \mathcal{A}

The matrix \mathcal{A} is symmetrical, and its size depends on the number of AOs, i.e. the number of atoms, the choice of elements and the basis set. To prevent unnecessary memory usage, \mathcal{A} is calculated per shell pair (for all its AOs, primitives and grid points) and immediately multiplied with \mathcal{F} to get \mathcal{G} (see Eq. (2.4.4)). Nonetheless we denote this as calculating \mathcal{A} since its repulsion integrals are the most tedious task.

2.6.1 Calculating LH XC in xclhyb()

The subroutine xclhyb()⁸³ consists prominently of a loop over grid point blocks, which cluster the (possibly millions of) grid points into groups of about a hundred. This is a compromise between not having to calculate intermediate results for each grid point alone and keeping memory requirements at bay. The routine's general flow of information is listed in Table 2.2.

For each block of grid points the values and derivatives of the AOs are calculated in funct_2(). These are used to calculate \mathcal{F} (calc_ftg(), Eq. (2.4.3)) as well as the electron density ρ , its squared derivative γ , and the kinetic energy density τ (ondes_ks(), Section 2.3.3). Then \mathcal{G} is determined in numpot() (Eq. (2.4.4)), and given to nlpot_lh() to calculate $\varepsilon_{\rm X}^{\rm ex}$ (Eq. (2.4.6)) and \mathcal{K} , the non-local XX part

of the KS matrix (Eq. (2.4.7)). The subroutine lochyb_1() is used to calculate the XC energy (Eq. (2.2.9)) as well as the operator terms (O, O', O''). These purely multiplicative potential terms arise from derivatives of the SL quantities $\Theta \in \{a, \varepsilon_{\rm X}^{\rm SL}, \varepsilon_{\rm C}^{\rm SL}\}$ w.r.t. $Q \in \mathbb{Q}$ (Eq. (2.3.16)). They are subsequently contracted with the AOs and their derivatives in onf_k() and added to the KS matrix,

$$\frac{\partial \Theta}{\partial Q} \to \begin{cases} O\chi_{\mu}\chi_{\nu} \\ O'\nabla\chi_{\mu}\chi_{\nu} \\ O''\nabla^{\mathrm{T}}\chi_{\mu}\nabla\chi_{\nu} \end{cases} \to F^{\mathrm{O}}_{\mu\nu} .$$
(2.6.1)

Finally, the non-multiplicative part \mathcal{K} (Eqs. (2.3.30) and (2.4.7)) is added to get the complete XC contribution of the KS matrix,

$$\boldsymbol{F}^{\mathrm{XC}} = \boldsymbol{F}^{\mathrm{O}} + \boldsymbol{\mathcal{K}} \,. \tag{2.6.2}$$

2.6.2 Calculating A in numpot()

The general structure of numpot ()⁸³ can be seen in Algorithm 1. The upper triangle of \mathcal{A} is skipped because it is symmetrical. It is compensated by an additional multiplication for \mathcal{G} using the same (off-diagonal) element $\mathcal{A}_{\kappa\lambda g}$. Because of that the integral routines assert that the second shell is never greater than the first.

The routine is dominated by five nested loops. The first two are the shell pairs, the next two their primitives. The innermost loop discerns the grid points within the current block and calls the integral routine vspdf () to acquire the current part of \mathcal{A} . A mapping for the monomial exponents is prepared before the primitive loops, which is needed for the Gauss-Rys algorithm as will be explained in Section 2.6.3. The integral values of \mathcal{A} are summed up over all primitives of the shell pair, multiplied with \mathcal{F} (twice for the off-diagonal elements) and added to the respective elements of \mathcal{G} .

2.6.3 Calculating V_{AB} in vspdf()

The subroutine vspdf() is used for the repulsion integrals. It applies the Boys algorithm from Section 2.4.4 for shells with angular quantum number $0 \leq \mathcal{L} \leq 3$,

```
for shell \mathcal{I} do
        \mathcal{L}_{\mathcal{I}} \leftarrow angular quantum number of \mathcal{I}
        for shell \mathcal{J} up to \mathcal{I} do
                \mathcal{L}_{\mathcal{J}} \leftarrow angular quantum number of \mathcal{J}
                calculate monomial exponents for \mathcal{L}_{\mathcal{I}}\mathcal{L}_{\mathcal{J}}
                for primitive \mathcal{P}_{\mathcal{I}} do
                        for primitive \mathcal{P}_{\mathcal{J}} do
                                for grid point g do
                                        I_{\gamma} \leftarrow preliminary integrals for up to \mathcal{L}_{\mathcal{I}} \mathcal{L}_{\mathcal{J}}
                                         for roots \gamma do
                                           \qquad \qquad \mathcal{A} \leftarrow \text{combine } I_{\gamma} \text{ for } \mathcal{L}_{\mathcal{I}} \mathcal{L}_{\mathcal{J}} 
                                         end
                                end
                                sum up over all primitives \mathcal{P}_{\mathcal{J}}
                        end
                        sum up over all primitives \mathcal{P}_{\mathcal{I}}
                end
                \mathcal{G} \leftarrow \text{multiply } \mathcal{A} \ (\mathcal{L}_{\mathcal{I}} \mathcal{L}_{\mathcal{J}}) \text{ with } \mathcal{F}
               \mathcal{G} \leftarrow \text{multiply } \mathcal{A} \ (\mathcal{L}_{\mathcal{J}} \mathcal{L}_{\mathcal{I}}) \text{ with } \mathcal{F}
        end
```

 \mathbf{end}

Algorithm 1: Algorithm to calculate elements of \mathcal{A} for a shell pair \mathcal{IJ} .

i.e. from s- to f-shells. For higher shells Gauss-Rys quadrature from Section 2.4.3 is used instead.

Boys Function Quadrature with vcl_??()

For the smallest possible pairs (ss and ps) Boys function quadrature is done completely in specific routines vcl_s() and vcl_p(). For most higher ones, vcl_ll() provides the basic building blocks with the Boys functions F_n , the distances X_{PG} (also for y and z), and the exponential parameter. They are then combined with X_{PA} and X_{PB} (etc.) for the individual case, e.g. do_ll() is used for two (nonidentical) p_x primitives. The last few are handled by specific routines for each case again (with vcl_ffdf(), vcl_fe()).

Gauss-Rys Quadrature with vint()

We can rewrite the repulsion integral from Eq. (2.4.13) as

$$V_{AB} = \frac{2K_{AB}}{\sqrt{\pi}\alpha_P} \sum_{\gamma} w_{\gamma} I_{\gamma}^{ij} I_{\gamma}^{kl} I_{\gamma}^{mn} , \qquad (2.6.3)$$

where we have introduced the Gauss-Hermite sums as preliminary integrals, e.g.

$$I_{\gamma}^{ij} = \sum_{\eta_x} w_{\eta_x} x_A^i x_B^j \ . \tag{2.6.4}$$

They are stored in arrays of batches with ascending γ . Each batch has space for all possible permutations of the underlying quantum numbers *i* and *j* within the system (e.g. from i = 0, j = 0 through i = 0, j = 3 to i = 3, j = 3 if the highest is an *f*-shell)^c. Elements that are not needed for the shell pair at hand are skipped. These integral arrays are computed by subroutine vint().

The preliminary integrals are subsequently combined according to the mapping of monomial exponents established in numpot() to get the \mathcal{A} elements for the current shell pair and summed up over all root batches. This concept is visualized in Fig. 2.5 for two (different) *p*-shell pairs in a system where *p* is the highest shell

^cThe examples use low shell types (s to f) for simplicity although this scheme is only used for shells higher than f in vspdf().



Figure 2.5 Calculating elements of \mathcal{A} arising from a pair of two different *p*-shells. Left: preliminary integrals in *x*, *y* and *z* for multiple Rys roots (only two are shown); top right: two example calculations; bottom right: overview of all results for the *pp* example. The preliminary integrals are multiplied in specific patterns to give the actual integrals, e.g. **pp**, **ss**, and **ss** yield the $(p_x p_x)$ integral (yellow), **ss**, **ps**, and **sp** give $(p_y p_z)$ (blue), and so on. The products have to be calculated for each root, then summed up over those roots, see Eq. (2.6.3).

(thus there are no gaps in the arrays). In case of identical shells $\mathcal{I} = \mathcal{J}$ the upper triangular elements are skipped for efficiency, therefore the ordering is different because of the symmetry of the \mathcal{A} part (not shown).

3 Local Hybrid Gradients

At the beginning of this project, SCF and linear-response TDDFT capabilities for LH functionals had already been implemented.^{83,84} Analytical nuclear gradients, however, were still lacking.

This chapter is the first of the two main topics of this work. It contains the derivation (Section 3.1), implementation (Section 3.2) and assessment (Section 3.3) of nuclear gradients for LH exchange functionals, which we had published previously.¹ Furthermore, a validation and application case is given by the benchmark of gas-phase MV oxides (Section 3.4),² taking advantage of structure optimization and numerical force calculations based on the analytical gradients developed in this work.

3.1 Theoretical Background

Applying the numerical integration from Eq. (2.4.1) to the exchange energy for LHs from Eq. (2.2.19) yields

$$E_X = \sum_g \varepsilon_{Xg} w_g = \sum_g \left[a_g \varepsilon_{Xg}^{ex} + (1 - a_g) \varepsilon_{Xg}^{SL} \right] w_g$$
(3.1.1)

with the index g denoting the evaluation at G. We differentiate w.r.t. nuclear displacement and reorder to get

$$\nabla_{\!A} E_{\mathrm{X}} = \sum_{g} \left[\nabla_{\!A} a_g \left(\varepsilon_{\mathrm{X}g}^{\mathrm{ex}} - \varepsilon_{\mathrm{X}g}^{\mathrm{SL}} \right) + a_g \nabla_{\!A} \varepsilon_{\mathrm{X}g}^{\mathrm{ex}} + (1 - a_g) \nabla_{\!A} \varepsilon_{\mathrm{X}g}^{\mathrm{SL}} \right] w_g + \varepsilon_{\mathrm{X}g} \nabla_{\!A} w_g \,. \tag{3.1.2}$$

In the following subsections, the gradients from Eq. (3.1.2) will be derived.

3.1.1 Nuclear Gradients of the Coefficients

Since the MO coefficients $C_{\mu i}$ (Eq. (2.3.3)) depend on the nuclear positions through the SCF scheme, the gradients of the energy, including $\nabla_{\!\!A} E_{\rm X}$, contain such contributions as well. On the other hand the total energy was minimized w.r.t. the coefficients during the SCF, so the corresponding partial derivatives within the gradients are zero. Hence it is possible to convert all those contributions to a term that does not include partial derivatives w.r.t. the coefficients.

Considering only the coefficient-related gradient terms of the total energy (denoted by the superscript C) within the AO basis, we get¹²⁴

$$\nabla_{\!A}^{\rm C} E = 2 \sum_i \sum_{\mu\nu} \nabla_{\!A} C_{\mu i} F_{\mu\nu} C_{\nu i}$$
(3.1.3)

$$= 2\sum_{i} \varepsilon_{i} \sum_{\mu\nu} \nabla_{\!A} C_{\mu i} S_{\mu\nu} C_{\nu i} , \qquad (3.1.4)$$

where we have used Eq. (2.3.13) to replace the KS matrix elements $F_{\mu\nu}$ with the MO eigenvalues ε_i and the overlap matrix elements $S_{\mu\nu}$ (Eq. (2.3.14)). We then apply the equality

$$2\sum_{\mu\nu} \nabla_{\!A} C_{\mu i} S_{\mu\nu} C_{\nu i} = -\sum_{\mu\nu} C_{\mu i} C_{\nu i} \nabla_{\!A} S_{\mu\nu} , \qquad (3.1.5)$$

which emerges from the orthogonality constraint of the MOs and is derived in Section 3.A.1. Inserting this into Eq. (3.1.4) yields

$$\nabla_{\!A}^{\rm C} E = -\sum_i \varepsilon_i \sum_{\mu\nu} C_{\mu i} C_{\nu i} \nabla_{\!A} S_{\mu\nu}$$
(3.1.6)

$$= -\sum_{\mu\nu} W_{\mu\nu} \nabla_{\!A} S_{\mu\nu} , \qquad (3.1.7)$$

$$W_{\mu\nu} = \sum_{i} \varepsilon_i C_{\mu i} C_{\nu i} , \qquad (3.1.8)$$

with the energy-weighted density matrix W. Thus all the energy derivatives w.r.t. the MO coefficients, including those within E_X , can be converted to one gradient term of the overlap matrix S. This term is calculated outside of our routines and does not need to be changed for different functionals.

3.1.2 Gradients of the Density and Related Quantities in the AO Basis

In analogy to Section 2.3.3, this section gives the explicit nuclear gradients for the quantities the functionals depend on.

Nuclear Gradient of ρ , γ , and τ

The nuclear gradients of the basic quantities are analogous to the electronic ones from Section 2.3.3:

$$\nabla_{\!A}\rho = 2\sum_i \nabla_{\!A}\varphi_i\varphi_i = 2\sum_{\mu\nu} D_{\mu\nu}\nabla_{\!A}\chi_\mu\chi_\nu , \qquad (3.1.9)$$

$$\nabla_{\!A}\gamma = 8\sum_{ij} \nabla_{\!A}\nabla^{\mathrm{T}}\varphi_i\varphi_i\nabla\varphi_j\varphi_j + \nabla_{\!A}\varphi_i\nabla^{\mathrm{T}}\varphi_i\nabla\varphi_j\varphi_j , \qquad (3.1.10)$$

$$= 8 \sum_{\mu\nu\kappa\lambda} D_{\mu\nu} D_{\kappa\lambda} \left(\nabla_{\!A} \nabla^{\mathrm{T}} \chi_{\mu} \chi_{\nu} \nabla \chi_{\kappa} \chi_{\lambda} + \nabla_{\!A} \chi_{\mu} \nabla^{\mathrm{T}} \chi_{\nu} \nabla \chi_{\kappa} \chi_{\lambda} \right) , \qquad (3.1.11)$$

$$\nabla_{\!A}\tau = \sum_{i} \nabla_{\!A} \nabla^{\mathrm{T}} \varphi_{i} \nabla \varphi_{i} = \sum_{\mu\nu} D_{\mu\nu} \nabla_{\!A} \nabla^{\mathrm{T}} \chi_{\mu} \nabla \chi_{\nu} . \qquad (3.1.12)$$

Due to the connection between the two gradients described in Section 2.3.1, the same implementation can be used as for the SCF with changed sign and the restriction to basis functions concerned with atom A.

Nuclear Gradient of a and $\varepsilon_{\rm X}^{\rm SL}$

Both the LMF and the semi-local exchange energy are chosen by the user of the program. Therefore we follow a general ansatz of those principal quantities $\Theta \in \{a, \varepsilon_{\rm X}^{\rm SL}, \varepsilon_{\rm C}^{\rm SL}\}$ with dependencies on all quantities $Q \in \mathbb{Q}$ (Eq. (2.3.16)) via the total differential, which yields

$$\nabla_{\!A}\Theta = \sum_{Q} \frac{\partial \Theta}{\partial Q} \nabla_{\!A}Q . \qquad (3.1.13)$$

The partial derivatives of Θ are the same as for SCF or TDDFT, and can be reused as already implemented. The nuclear gradients of the inner quantities have been given above.

3 Local Hybrid Gradients

Nuclear Gradient of $\varepsilon_{\rm X}^{\rm ex}$

Here we use the abbreviations $\varphi_i^1 = \varphi_i(\mathbf{r}_1), \ \chi_{\mu}^1 = \chi_{\mu}(\mathbf{r}_1)$, and $a_1 = a(\mathbf{r}_1)$. Differentiating the XX energy density (Eq. (2.3.24)) w.r.t. the nuclear positions yields

$$\nabla_{A} \varepsilon_{X}^{ex}(\boldsymbol{r}_{1}) = -\sum_{ij} \nabla_{A} \varphi_{i}^{1} \varphi_{j}^{1} \int \varphi_{i}^{2} \varphi_{j}^{2} \frac{1}{r_{12}} d\boldsymbol{r}_{2}$$

$$-\sum_{ij} \varphi_{i}^{1} \varphi_{j}^{1} \int \nabla_{A} \varphi_{i}^{2} \varphi_{j}^{2} \frac{1}{r_{12}} d\boldsymbol{r}_{2} \qquad (3.1.14a)$$

$$= -\sum_{\mu\nu\kappa\lambda} D_{\mu\kappa} D_{\nu\lambda} [\nabla_{A} \chi_{\mu}^{1} \chi_{\nu}^{1} \int \chi_{\kappa}^{2} \chi_{\lambda}^{2} \frac{1}{r_{12}} d\boldsymbol{r}_{2}$$

$$+ \chi_{\mu}^{1} \chi_{\nu}^{1} \int \nabla_{A} \chi_{\kappa}^{2} \chi_{\lambda}^{2} \frac{1}{r_{12}} d\boldsymbol{r}_{2}] . \qquad (3.1.14b)$$

For GHs one would now swap the order of integration to get only one term. Yet this is prevented by the LMF, which also depends on r_1 and would end up within the inner integral (cf. Eq. (2.3.28b)), complicating its analytical computation. In the AO basis we define the two energy gradient terms (including the LMF) separately,

$$\nabla_{\!A} E_1^{\text{ex}} = -\sum_g a_g w_g \sum_{\mu\nu\kappa\lambda} D_{\mu\kappa} D_{\nu\lambda} \nabla_{\!A} \chi_{\mu g} \chi_{\nu g} \mathcal{A}_{\kappa\lambda g}$$

$$= -\sum_g a_g \sum_{\mu\kappa\lambda} D_{\mu\kappa} \mathcal{X}'_{\mu g} \mathcal{F}_{\lambda g} \mathcal{A}_{\kappa\lambda g} = -\sum_g a_g \sum_{\mu\kappa} D_{\mu\kappa} \mathcal{X}'_{\mu g} \mathcal{G}_{\kappa g} , \qquad (3.1.15a)$$

$$\nabla_{\!A} E_2^{\text{ex}} = -\sum_g a_g w_g \sum_{\mu\nu\kappa\lambda} D_{\mu\kappa} D_{\nu\lambda} \chi_{\mu g} \chi_{\nu g} \mathcal{A}'_{\kappa\lambda g}$$

$$= -\sum_g a_g \sum_{\kappa\lambda} \mathcal{F}_{\kappa g} \mathcal{F}_{\lambda g} \mathcal{A}'_{\kappa\lambda g} = -\sum_g a_g \sum_{\kappa} \mathcal{F}_{\kappa g} \mathcal{G}'_{\kappa g} , \qquad (3.1.15b)$$

where we have applied the numerical grid, reused the matrix and vector elements introduced in Section 2.4.2, and added their gradients

$$\mathcal{X}'_{\mu g} = \sqrt{w_g} \nabla_{\!\!A} \mathcal{X}_{\mu g} , \qquad (3.1.16)$$

$$\mathcal{F}'_{\kappa g} = \sum_{\mu} \mathcal{X}'_{\mu g} D_{\mu \kappa} , \qquad (3.1.17)$$

$$\mathcal{G}'_{\kappa g} = \sum_{\lambda} \mathcal{F}_{\lambda g} \mathcal{A}'_{\kappa \lambda g} , \qquad (3.1.18)$$

$$\mathcal{A}_{\kappa\lambda g}' = \int \nabla_{\!A} \chi_{\kappa} \frac{1}{r_G} \chi_{\lambda} \,\mathrm{d}\boldsymbol{r} \quad . \tag{3.1.19}$$

Note that \mathcal{A}' is not symmetrical, in contrast to \mathcal{A} , because the derivative only applies to the first AO. It also has three components, one each for x, y, and z. The number of elements will therefore be increased by a factor of about seven (one for \mathcal{A} and about six for \mathcal{A}').

3.1.3 Nuclear Gradient of w_q

The grid weights depend as well on the position of the nuclei due to the atomcentered grids mentioned in Section 2.4.1. Consequently, they spawn a gradient term as well. The values are usually small and can be neglected but for some tasks, e.g. frequency calculations, they may be needed for the desired accuracy.

Because we use the DFT grids as provided by the program and there is no dependence on the functional (besides multiplication, see last term in Eq. (3.1.2)), the same routine can be used as in any other gradient implementation and multiplied with our XC energy density.

3.2 Implementation

3.2.1 Calculating LHGs in grlochyb()

The LH gradient subroutine grlochyb() is similar to xclhyb() for LH SCF. It is, however, based on a copy of the gradient routine grmrhf() (cf. Section 2.5.2) for the mGGA case because that uses ingredients up to the kinetic energy density, as does the LH case. The structure can be seen in Table 3.1.

Subroutine	Input	Output
grlochyb()	D	$\nabla_{A}E_{\rm XC}$
<pre>funct_3()</pre>		χ, χ', χ''
<pre>get_ftg_dftg()</pre>	D, χ, χ'	$\mathcal{F}, \mathcal{F}'$
a_matrices()	${\cal F}$	\mathcal{G},\mathcal{G}'
get_hfx1()	$oldsymbol{D},\chi',\mathcal{G}$	$\nabla_A E_1^{\mathrm{ex}}$
get_hfx2()	\mathcal{F},\mathcal{G}'	$\nabla_A E_2^{\mathrm{ex}}$
get_exx()	\mathcal{F},\mathcal{G}	$\varepsilon_{\rm X}^{\rm ex}$
ondes_ks()	D, χ, χ'	ρ, γ, τ
lmf_1()	ρ, γ, τ	$a, \frac{\partial a}{\partial \rho}, \frac{\partial a}{\partial \gamma}, \frac{\partial a}{\partial \tau}$
<pre>lochyb_1()</pre>	$\boldsymbol{D}, \varepsilon_{\mathrm{X}}^{\mathrm{ex}}, a, \frac{\partial a}{\partial \rho}, \frac{\partial a}{\partial \gamma}, \frac{\partial a}{\partial \tau}$	$\varepsilon_{\rm XC}, O, O', O''$
ongrd_k()	$D, O, O', O'', \chi', \chi''$	$\nabla_{A} E_{\rm XC}^{\rm O}$
wmgrd()	$\varepsilon_{ m XC}$	$\nabla_{A} E_{\rm XC}^{\rm w}$

 Table 3.1 General flow of information for subroutines regarding LHGs (without grid and junctions).

For each block of grid points the values and derivatives of the AOs are calculated. In comparison with the LH SCF routine, we need basis function derivatives of higher order for the gradient (i.e. funct_3() instead of funct_2()). These are used to calculate \mathcal{F} and \mathcal{F}' in calc_ftg() (Eqs. (2.4.3) and (3.1.17)), as well as the electron density ρ , its squared derivative γ , and the kinetic energy density τ (ondes_ks(), Section 2.3.3). Then \mathcal{G} and \mathcal{G}' (Eqs. (2.4.4) and (3.1.18)) are determined in a_matrices() and used to calculate $\varepsilon_X^{\text{ex}}$ (Eq. (2.4.6)) and the gradient parts $\nabla_A E_1^{\text{ex}}$ and $\nabla_A E_2^{\text{ex}}$ of the XX energy (Eqs. (3.1.15a) and (3.1.15b)) in get_hfx1() and get_hfx2(), respectively. For the gradients from SL quantities $\Theta \in \{a, \varepsilon_X^{\text{SL}}, \varepsilon_C^{\text{SL}}\}$ we use the same operator terms as in the SCF implementation (O, O', O'', cf. Section 2.6.1), which are calculated in lochyb_1(). They are handed over to ongrd_k() to be multiplied with the AOs and their derivatives, yielding $\nabla_A E_{\text{XC}}^{\text{O}}$,

$$\frac{\partial \Theta}{\partial Q} \rightarrow \begin{cases} O \nabla_{\!A} \chi_{\mu} \chi_{\nu} \\ O' \left(\nabla_{\!A} \chi'_{\mu} \chi_{\nu} + \nabla_{\!A} \chi_{\mu} \chi'_{\nu} \right) \\ O'' \nabla_{\!A} \chi'_{\mu} \chi'_{\nu} \end{cases} \rightarrow \nabla_{\!A} E^{O}_{\rm XC} . \tag{3.2.1}$$

If desired, the gradient of the grid weights (see Section 3.1.3) is computed in

wmgrd(). Finally, all the contributions are added up to the XC energy gradient

$$\nabla_{\!A} E_{\rm XC} = \nabla_{\!A} E_{\rm XC}^{\rm O} + \nabla_{\!A} E_1^{\rm ex} + \nabla_{\!A} E_2^{\rm ex} + \nabla_{\!A} E_{\rm XC}^{\rm w} . \qquad (3.2.2)$$

Note that in get_hfx1() χ' and **D** have to be used instead of \mathcal{F}' because the mapping from the AO to the atom for which the gradient is being computed was lost by summing up over the relevant index μ .

3.2.2 Calculating A and A' in a_matrices()

The structure of a_matrices() is more convoluted than that of numpot() (cf. Section 2.6.2) because of the additional \mathcal{G}' . As described in Section 3.1.2 the complete \mathcal{A}' is needed for the gradient.

We could either extend the shell loops to go through all shell pairs (and skip \mathcal{A} for the upper triangle), or we keep the structure but calculate both $\mathcal{A}'_{\kappa\lambda g}$ and $\mathcal{A}'_{\lambda\kappa g}$ together. In the former case, the number of subroutine calls for the integral routines is almost doubled. In the latter, the angular quantum number of both shells is effectively increased by one, thereby also increasing the number of roots by one, but the number of calls remains the same. Choosing the latter, the Gauss-Rys quadrature (see Section 2.6.3) is a potent tool because of its modularity: We can use all but one (the highest) elements of the intermediate integral elements and combine them in different ways (see below). To do that, we need five mapping arrays for the monomial exponents ($\mathcal{L}_{\mathcal{I}}\mathcal{L}_{\mathcal{J}}$; $\mathcal{L}_{\mathcal{I}}^{-}\mathcal{L}_{\mathcal{J}}$; $\mathcal{L}_{\mathcal{I}}\mathcal{L}_{\mathcal{J}}^{-}$, $\mathcal{L}_{\mathcal{I}}\mathcal{L}_{\mathcal{J}}^{+}$), where in numpot () we used just one ($\mathcal{L}_{\mathcal{I}}\mathcal{L}_{\mathcal{J}}$). Here we use the abbreviations $\mathcal{L}_{\mathcal{I}}^{+} = \mathcal{L}_{\mathcal{I}} + 1$, $\mathcal{L}_{\mathcal{I}}^{-} = \mathcal{L}_{\mathcal{I}} - 1$, and analogues.

To get the current parts of \mathcal{A}' for two primitives of a given shell pair, we multiply the intermediate integrals $\mathcal{L}_{\mathcal{I}}^{-}\mathcal{L}_{\mathcal{J}}$ and $\mathcal{L}_{\mathcal{I}}^{+}\mathcal{L}_{\mathcal{J}}$ with their appropriate prefactors and subtract one from the other according to Eq. (2.3.9). This is depicted on the r.h.s. of Fig. 3.1. The same is done with the pair $\mathcal{L}_{\mathcal{I}}\mathcal{L}_{\mathcal{J}}^{-}$ and $\mathcal{L}_{\mathcal{I}}\mathcal{L}_{\mathcal{J}}^{+}$. For this we need a reversed mapping for the monomial exponents to find the correct elements to combine, which is prepared together with the normal mapping. The remaining integrals ($\mathcal{L}_{\mathcal{I}}\mathcal{L}_{\mathcal{J}}$) already represent the parts of \mathcal{A} , as in numpot(). Outside the primitive loops, all of those calculated elements are multiplied with \mathcal{F} to get both \mathcal{G} and \mathcal{G}' . This is illustrated in Algorithm 2.

 $\mathcal{L}_{\mathcal{I}} \leftarrow \text{angular quantum number of shell } \mathcal{I}$ $\mathcal{L}_{\mathcal{J}} \leftarrow angular quantum number of shell <math>\mathcal{J}$ calculate mapping of monomial exponents for $\mathcal{L}_{\mathcal{I}}\mathcal{L}_{\mathcal{J}}$ calculate mappings of monomial exponents for $\mathcal{L}_{\mathcal{I}}^{-}\mathcal{L}_{\mathcal{J}}, \mathcal{L}_{\mathcal{I}}^{+}\mathcal{L}_{\mathcal{J}}, \mathcal{L}_{\mathcal{I}}\mathcal{L}_{\mathcal{J}}^{-}, \mathcal{L}_{\mathcal{I}}\mathcal{L}_{\mathcal{J}}^{+}$ for primitive $\mathcal{P}_{\mathcal{I}}$ do for primitive $\mathcal{P}_{\mathcal{J}}$ do $I_{\gamma} \leftarrow$ preliminary integrals for up to $\mathcal{L}_{\mathcal{I}}^+ \mathcal{L}_{\mathcal{I}}^+$ for roots γ do $\mathcal{A} \leftarrow \text{combine } I_{\gamma} \text{ for } \mathcal{L}_{\mathcal{I}} \mathcal{L}_{\mathcal{J}}$ combine I_{γ} for $\mathcal{L}_{\mathcal{I}}^{-}\mathcal{L}_{\mathcal{J}}$ sum up each product over all roots end $\mathcal{A}' \leftarrow \text{combine products of } \mathcal{L}_{\mathcal{I}} \mathcal{L}_{\mathcal{J}}^{-} \text{ and } \mathcal{L}_{\mathcal{I}} \mathcal{L}_{\mathcal{J}}^{+}$ sum up over all primitives $\mathcal{P}_{\mathcal{J}}$ end $\mathcal{A}' \gets \text{combine products of } \mathcal{L}_{\mathcal{I}}^{-} \mathcal{L}_{\mathcal{J}} \text{ and } \mathcal{L}_{\mathcal{I}}^{+} \mathcal{L}_{\mathcal{J}}$ sum up over all primitives $\mathcal{P}_{\mathcal{I}}$ end $\mathcal{G} \leftarrow \text{multiply } \mathcal{A} \ (\mathcal{L}_{\mathcal{I}} \mathcal{L}_{\mathcal{J}}) \text{ with } \mathcal{F}'$ $\mathcal{G} \leftarrow \text{multiply } \mathcal{A} \ (\mathcal{L}_{\mathcal{J}} \mathcal{L}_{\mathcal{I}}) \text{ with } \mathcal{F}'$ $\mathcal{G}' \leftarrow \text{multiply } \mathcal{A}' \ (\mathcal{L}_{\mathcal{I}}^{-} \mathcal{L}_{\mathcal{J}} \text{ and } \mathcal{L}_{\mathcal{I}}^{+} \mathcal{L}_{\mathcal{J}}) \text{ with } \mathcal{F}$ $\mathcal{G}' \leftarrow \text{multiply } \mathcal{A}' \ (\mathcal{L}_{\mathcal{I}} \mathcal{L}_{\mathcal{J}}^{-} \text{ and } \mathcal{L}_{\mathcal{I}} \mathcal{L}_{\mathcal{J}}^{+}) \text{ with } \mathcal{F}$ Algorithm 2: Algorithm to calculate elements of \mathcal{G} and \mathcal{G}' for a shell pair \mathcal{IJ} (without consideration of P-junctions, see Fig. 3.2). Compare with Algorithm 1

(shell loops were left out for simplicity).

Calculating V_{AB} in a_matrices_integrals()

The subroutine a_matrices_integrals() is based on vspdf() (cf. Section 2.6.3). As explained above, the Boys function part was removed because of the modularity of the Gauss-Rys implementation. In Fig. 3.1 an example is given for a pp shell pair, in comparison to Fig. 2.5. The routine is called as if it was a dd shell pair $(\mathcal{L}_{\mathcal{I}} = 2, \mathcal{L}_{\mathcal{J}} = 2)$. This gives rise to the preliminary integrals for ss, sp, sd, ps, pp, pd, ds, dp and dd for multiple Rys roots, see l.h.s. of Fig. 3.1. They are multiplied and summed up over all Rys roots for each of the five shell type pairs listed before, as given by the mappings prepared in a_matrices(). These intermediate integrals are returned to a_matrices() for further processing as explained above.

3.2.3 Prescreening with S- and P-Junctions

To speed up the gradient calculations, S-junctions were implemented as explained for LH SCF (see Section 2.4.5) without adjustments.

For P-junctions the procedure had to be extended to \mathcal{F}' (cf. Section 2.4.5). For each shell the values of \mathcal{F} and \mathcal{F}' are compared to a given threshold and if any elements are above that threshold for the current block of grid points, the shell is marked as mandatory. This results in two lists of junctions that indicate non-negligible elements of \mathcal{A} and \mathcal{A}' upon multiplication with \mathcal{F} or \mathcal{F}' .

The modularity of the calculation enables us to further refine the prescreening. For each shell pair to be calculated the combination of primary (\mathcal{I}) and secondary (\mathcal{J}) shell is evaluated to see if the pair can be skipped, or at least if the virtual quantum number \mathcal{L} of the integral routine call can be lowered for this pair. The procedure is illustrated in Fig. 3.2.

3.3 Assessment

During and after implementation of the new gradients, some tests were run to check its correctness and efficiency. In addition to coinciding with numerical gradients, the analytical gradient should give comparable structures and vibrational frequencies.



Figure 3.1 Calculating elements of \mathcal{A}' arising from a pair of two different p shells. Left: preliminary integrals in x, y and z (only x is shown) for multiple roots (only one is shown); center: intermediate integrals; top right: example calculations; bottom right: overview of all results for the pp example (∂ summarizes ∂_x , ∂_y and ∂_z). The intermediate integrals sp, pp and dp are crafted from the preliminary integrals as in Fig. 2.5. The intermediate integrals of pp (gray) represent the elements of \mathcal{A} . Those from sp and dp are combined according to Eq. (2.3.9) to yield the gradient of pp in all three directions, including the exponential factor α and the Cartesian quantum number as a prefactor, here 1. For example, each of $(d_{xx}p_z), (d_{xy}p_z)$ and $(d_{xz}p_z)$ is combined with (sp_z) to give the gradients $(\partial_x p_x p_z), (\partial_y p_x p_z),$ and $(\partial_z p_x p_z)$, which can be denoted as a vector $(\partial p_x p_z)$. This example only depicts the calculation of elements $\mathcal{A}'_{\kappa\lambda g}$ but with the remaining preliminary integrals the $\mathcal{A}'_{\lambda\kappa g}$ elements (e.g. $(p_x \partial p_z)$) can also be created.



Figure 3.2 Scheme for P-junctions. \mathcal{F} and \mathcal{F}' for primary (\mathcal{I}) and secondary (\mathcal{J}) shells are compared to the threshold (th) to possibly skip all for a primary shell (skip \mathcal{I}), all for a secondary shell (skip \mathcal{J}), or to lower the virtual angular quantum number for the integral routine by one $(\mathcal{L}_{\mathcal{I}}^{+}\mathcal{L}_{\mathcal{J}} \text{ or } \mathcal{L}_{\mathcal{I}}\mathcal{L}_{\mathcal{J}}^{+}$ instead of $\mathcal{L}_{\mathcal{I}}^{+}\mathcal{L}_{\mathcal{J}}^{+}$). Horizontal arrows (orange) denote that all values of a shell are below the threshold, vertical ones (blue) that at least one is not.

3.3.1 Comparing Analytical and Numerical Gradients

The smallest system to check the correctness of the gradients is a molecule of two atoms, e.g. LiH. By calculating the total energy for two different distances and dividing their difference by the change in that distance, we get a viable approximation for the gradient. The smaller the change in distance the more accurate this will be. The approximation is also better if one compares with the gradient at average distance.

For example, we calculated the gradient of LiH with LH-SVWN (t-LMF with b = 0.5, cf. Eq. (2.2.21)) for an atomic distance of 2.4000 and the energy for displacements of ± 0.0001 . The approximate numerical gradient

$$\nabla_{A}^{\text{app}}E = \frac{\Delta E}{\Delta d} = \frac{-7.657\,339\,710\,539 - (-7.657\,322\,442\,382)}{0.0002} = -0.086\,340\,785 \quad (3.3.1)$$

is quite close to the analytical $-0.086\,340\,797$. Such tests were used during development but we will instead look at more practical cases in the following sections.

3.3.2 Main-Group and Transition-Metal Structure Test Sets

Computational Details

For structure optimizations we used a set of small molecules of main group elements by Zhao and Truhlar³² (MGBL19 test set) and a 3*d* transition-metal test set by Bühl and Kabrede.¹²⁵ We used def2-TZVP basis sets and a large grid size¹¹⁶ of 5. S- and P-junctions were not used for these calculations.

To be consistent with two LHs previously optimized for thermochemistry and kinetics,^{70,126} we used Slater exchange, VWN correlation and set the constant prefactors b = 0.48 and c = 0.22 for the t-LMF and s-LMF (cf. Eqs. (2.2.21) and (2.2.22)). Within this section we will refer to these specific LHs as "t-lh" and "s-lh". For comparison we used the following functionals: BP86⁴¹ and PBE^{60,61} as GGAs; TPSSh,^{60,71,72} B3LYP,^{38–40} PBE0,^{62,63} and BHLYP⁴⁴ as GHs.

Results

Figure 3.3 shows mean signed errors (MSEs) and mean absolute errors (MAEs) of computed bond lengths for LHs and some other functionals, compared to the experimental values of the MGBL19 set.

The results of t-lh are comparable to the B3LYP ones, with MAEs of 0.58 pm and 0.59 pm and maximum errors (MAXs) of -2.68 pm (F₂) and -2.65 pm (Cl₂), respectively. The s-lh results are slightly worse with MAE 0.64 pm and MAX 3.05 pm (F₂). TPSSh performs somewhat better and PBE0 slightly worse. BH-LYP, chosen as its large XX admixture of 50 % is close to the maximum of 48 % in the selected t-LMF, exhibits the largest errors (with generally negative MSE), whereas the GGA functionals perform moderately well.

Figure 3.4 shows the results for the set of 3d transition-metal complexes. Here TPSSh has also the lowest MAE. The MAEs of t-lh and B3LYP are similar (1.73 pm vs. 1.68 pm). The GGA functionals perform well for this test set, as had been noted before,¹²⁵ whereas PBE0 and in particular BHLYP are slightly inferior. The MAE of s-lh (1.93 pm) lies between t-lh and PBE0. In summary, the selected LHs have a similar accuracy for molecular structures as other commonly used functionals like B3LYP for the chosen test sets while they have been shown to be more accurate for a larger range of properties.^{69,70,91,127}



Figure 3.3 MSEs and MAEs for bond lengths (in pm) of main-group structure test set MGBL19, comparing two local hybrids (t-lh, s-lh) and a few other functionals.

3.3.3 Main-Group Vibrational Frequencies

Computational Details

As an even more critical test, we computed vibrational frequencies for a set of small molecules (the F2 subset by Scott and Radom²⁵). The structures were optimized and the frequencies calculated with def2-TZVP basis sets and a grid size m5 (i.e. a medium grid size 3 during the SCF but a large grid size 5 for the last iteration and the gradient). Furthermore the SCF convergence criterion was set to 10^{-9} , and the gradient threshold to 10^{-5} during the structure optimization.

In some cases, frequencies from different irreducible representations are very close and the order may thus differ from one functional to another. We have therefore compared the calculated to experimental frequencies in numerical order without attempting to match representations. This avoids favoring a given method that is used for the initial assignment. Since analytical second derivatives so far are not available for LH functionals, we used the numerical differentiation of analytical gradients, that is provided by Turbomole's NumForce module (see Sec-

3 Local Hybrid Gradients



Figure 3.4 MSEs and MAEs for bond lengths (in pm) of the set of 3d transitionmetal complexes, comparing two local hybrids (t-lh, s-lh) and a few other functionals.

tion 2.5.4), to obtain the second derivatives. For consistency, this was also done for the reference calculations with other functionals. Additional calculations with fully analytical second derivatives (for available functionals), computed using the **aoforce** module within the RI approximation,^{116,128–131} were performed to gauge the accuracy of numerical differentiation. The impact on mean errors is, however, marginal (below 1 cm^{-1} for any GGA and GH functional) and only results with numerical derivatives will be compared below. S- and P-junctions were not used for these calculations.

Results

As is commonly done, for each functional we determined a scaling factor $\lambda = \sum \nu_{\rm th} \nu_{\rm expt} / \sum \nu_{\rm th}^2$ that minimizes the root mean square error (RMSE) between calculated and experimental frequencies. The scaling factor compensates for a general overestimation in calculated frequencies, which is only in part caused by a given functional and to a larger extent by the harmonic approximation.²⁵
	(/				
Functional	λ	MSE	MAE	MAX	SMSE	SMAE	SMAX
BHLYP	0.934339	111.3	113.2	319.8	-0.8	20.4	179.3
PBE0	0.960138	60.0	63.5	216.6	-6.0	24.9	169.5
t-lh	0.960182	60.9	64.6	215.8	-5.1	22.1	170.6
s-lh	0.967318	48.0	52.4	206.5	-5.7	23.1	169.7
B3LYP	0.967821	47.5	52.1	210.4	-5.4	20.3	174.1
TPSSh	0.968549	45.4	51.6	210.7	-6.2	20.6	175.2

Table 3.2 Scaling factor λ and errors (in cm⁻¹) for the F2 vibrational frequency test set. SMSE, SMAE, SMAX: The scaled results for the corresponding errors (without prefix S).

Table 3.2 lists the scaling factors and the statistics without and with scaling. Overall, scaling factors, and errors before and after scaling are very similar for t-lh, s-lh, and most of the GHs. Only BHLYP requires notably more scaling, while after scaling performance is comparable to the other functionals. These preliminary results suggest that both LHs perform similarly for main-group vibrational frequencies as established GHs. The IR intensities (not shown) of t-lh and B3LYP are also similar.

3.3.4 Timings for Linear Alkanes and Adamantane

Computational Details

To evaluate computational efficiency aspects, we measured the application of Sand P-junctions by timing gradient calculations for unoptimized linear alkanes $(C_nH_{2n+2} \text{ with } n \in \{1, \ldots, 20\})$ with t-lh. All timings were done using a single central processing unit (CPU) core (Intel i3-4130 CPU @ 3.40 GHz). We used the general timing output of the Turbomole programs. The initial structures were created with C-C distances of 145.0 pm, H-C distances of 108.9 pm and angles of 109.471°. A single SCF was run on each structure. Afterwards the gradient was calculated with thresholds for S-junctions and P-junctions varying from 10^{-4} to 10^{-8} , or without any junction screening. Grid size 1 and def2-TZVP basis sets were used for these calculations.

Subsequently, the timing measurements were extended to adamantane $(C_{10}H_{16})$

as a more compact case. The initial structure parameters are the same as for the linear alkanes above. Here we also investigated the time for a complete structure optimization to an energy threshold of 10^{-6} . For the LH functional we tested different P-junction thresholds between 10^{-4} and 10^{-6} , and also distinct ones for SCF and gradient calculations. In one case both S- and P-junction thresholds were set to 10^{-5} . For comparison we also measured the CPU time for gradients of the semi-numerical XX senex algorithm¹³² for GHs in Turbomole, with grid size 1 and its default S- and P-junction thresholds (which are not directly comparable to ours). To estimate the influence of basis set size we compared def2-SVP, def2-TZVP, and def2-QZVP basis sets, using the same computer as above and grid size 1. For all calculations with def2-QZVP basis sets, a grid point batch size of 70 was used, otherwise it was 100.

Results for Linear Alkanes

Figure 3.5 provides timings for the computation of the LHG as a function of alkane chain length, and with different thresholds for S- and P-junctions, respectively. While the overall appearance of the two graphs is similar, the magnitude of the time savings due to prescreening by S- and P-junctions is notably different. In both cases, the percentage saving increases with chain length and thus with system size. However, S-junctions are less efficient for prescreening in this case than P-junctions.

Taking reasonably conservative and accurate (see below) thresholds of 10^{-5} for both cases, S-junction savings converge to about 7% for longer chains, whereas the reduction in computation time due to P-junctions does not seem to level off much even at 20 carbon atoms, where it amounts already to almost 40%. With tighter thresholds, the savings are less and they start at larger chain lengths.

Turning to the effects of S- and P-junctions on numerical accuracy, we note that the errors of the gradients with S- and P-junctions relative to calculations without prescreening remain approximately constant with chain length. Table 3.3 provides MAEs for all alkanes studied. These depend appreciably on the thresholds used. Considering an accuracy of 10^{-6} for the gradient as reasonable for most purposes, we see that thresholds of 10^{-5} for both S- and P-junctions provide sufficient accuracy but still allow for favorable timings (see above). If we want to be even more



Figure 3.5 Relative CPU time of a local hybrid gradient calculation for *n*-alkanes as function of chain length, with different thresholds for S-junction (above) and P-junctions (below) in negative powers of ten, compared to results without S- or P-junctions. The kink of graph 5 and 6 for C_4H_{10} are artifacts caused by rounding the timings to seconds for times longer than a minute.

Table 3.3 Mean absolute error (MAE) of local hybrid alkane molecular gradients (averaged over all alkanes) for different thresholds (th) of S- and P-junctions. The reference values are gradients without prescreening.

th	$MAE(\nabla$	$_4E)/a.u.$
	S	Р
10^{-4}	$6 \cdot 10^{-05}$	$5 \cdot 10^{-05}$
10^{-5}	$9 \cdot 10^{-09}$	$4 \cdot 10^{-07}$
10^{-6}	$2\cdot 10^{-09}$	$1\cdot 10^{-09}$
10^{-7}	$4\cdot 10^{-12}$	$2 \cdot 10^{-12}$
10^{-8}	$2 \cdot 10^{-14}$	$1 \cdot 10^{-15}$

conservative, thresholds of 10^{-6} may be used.

Results for Adamantane

Figure 3.6 provides timings for a single gradient calculation of adamantane. In addition to an LH with the present implementation (t-lh), we have chosen TPSSh as an example of a GH and PBE as an example GGA functional (timings for functionals of the same family are very similar). The timings are given relative to those of TPSSh using the efficient analytical gradient of Turbomole's rdgrad module. We additionally provide data for TPSSh obtained with the *senex* option, which also uses a semi-numerical treatment of the XX energy integrals (prefix sx).

As expected, the GGA gradient calculation is much faster than that with the GH, which in turn is faster than the current implementation for LHs. However, the semi-numerical implementation for LHs and for GHs scales better with basis set size than the analytical implementation for GHs. Thus, while the LH gradient takes 7.5 times longer than a standard TPSSh calculation with the small def2-SVP basis sets, the factor decreases to 3.3 with def2-TZVP and to 2.6 with def2-QZVP. We also confirm that the effect of using P-junctions (shaded area on the bar) becomes more notable with increasing basis set size. The senex algorithm for GHs (provided with default settings for S- and P-junctions) performs even better, with factors of 1.5 (def2-SVP), 0.64 (def2-TZVP) and 0.62 (def2-QZVP). Due to the additional integrals needed for \mathcal{A}' with LHs (see Section 3.2.2), the corresponding factor decreases less quickly for this system size.



- Figure 3.6 Relative CPU times for a gradient calculation of adamantane with def2-SVP, def2-TZVP and def2-QZVP basis sets, respectively. The time of TPSSh is set to 1 with each basis set. The shaded part of t-lh depicts the time savings obtained with S- and P-junction thresholds of 10^{-5} . sxTPSSh stands for a TPSSh calculation using the *senex* option with default parameters.
- Table 3.4 Absolute CPU time for a full structure optimization (excluding the initial SCF) of adamantane with a local hybrid using def2-QZVP and different P-junction thresholds (no S-junctions). The energy difference and timing ratio refer to the optimization without P-junctions. For comparison, timings with both the recommended value of S- and P-junctions (10^{-5}) are given as well.

P the SCF	reshold grad	Cy SCF	cles Struc	$t/{ m h}$	$\Delta E \ {\rm kJ/mol}$	t/t_0
		50	10	13.7		
1	0^{-4}	116	15	13.8	10^{+0}	+1%
10^{-4}	10^{-5}	84	11	12.3	10^{+0}	-10%
10^{-5}	10^{-4}	72	17	12.6	10^{-1}	-8%
1	0^{-5}	50	10	10.4	10^{-2}	-24%
10^{-5}	10^{-6}	50	10	12.3	10^{-2}	-10%
10^{-6}	10^{-5}	47	9	10.1	10^{-3}	-26%
1	0^{-6}	50	10	12.8	10^{-4}	-6%
S,P th	$. = 10^{-5}$	50	10	9.8	10^{-2}	-28%

Table 3.4 lists the computation times and cycles of a complete structure optimization of adamantane using t-lh with varying P-junction thresholds (no Sjunctions), plus one result with both S- and P-junction thresholds set to 10^{-5} . While the computation time of a single SCF cycle and gradient calculation decreases with looser thresholds, for thresholds of 10^{-4} the overall time for a structure optimization increases due to inaccuracies in the intermediate gradients. The error in total energy after structure convergence decreases to 0.01 kJ/mol upon using P-junction thresholds of 10^{-5} or lower, and the computation time decreases by 24 %. If S-junction thresholds are additionally set to 10^{-5} , the error remains the same but the time is lowered further by about 4%, resulting in an absolute CPU time of 9.8 h compared to 13.7 h without prescreening. This also confirms previous findings that P-junctions are more important than S-junctions. Additional variations with tighter thresholds than 10^{-5} for either the SCF or the gradient are likely insignificant within our measurement accuracy for a full optimization process. Finally our value of 10^{-5} for both S- and P-junctions suggested above is confirmed as a good compromise between accuracy and efficiency for most applications.

3.4 Application to a Gas-Phase Mixed-Valence Oxide Benchmark Set

We have applied the gradients for LH functionals to optimize structures and calculate vibrational data in a study on a new benchmark set for gas-phase mixed valence (MV) oxides consisting of small molecules (MVO-10),² which followed an extensive prior investigation on $Al_2O_4^{-}$.¹³³

3.4.1 Theoretical Background

Chemical systems with two or more formally identical redox centers sharing a number of valence electrons, that do not allow the same integer number of them assigned to all centers, may be considered to be in a mixed valence (MV) state. Such systems are crucial in many technological applications or in biocatalysis and have thus been studied by a wide range of experimental methods^{134–142} and increasingly also by quantum-chemical approaches.¹⁴³ The classification by Robin and Day¹⁴⁴

distinguishes three main classes for MV systems based on the electronic coupling of their redox centers and the resulting (de)localization of the charge: I) decoupled with full localization, II) moderately coupled with partial delocalization, and III) strongly coupled with full delocalization. The distinction between class II and III systems can be challenging for quantum-chemical models since several aspects must be addressed simultaneously: (a) Exchange, as well as dynamical and nondynamical correlation need to be treated in a balanced way.^{45,46,143,145,146} (b) As most (spectroscopy) experiments on the (often charged) MV systems are performed in polar solvents, a good treatment of environmental effects also becomes crucial. Moreover, many of the MV systems of chemical or technological interest may have appreciable size, rendering the most accurate post-HF methods to treat point (a) too computationally demanding at present.

Small MV systems in the gas phase could alleviate part of this complication and allow for the evaluation of DFT functionals by comparison with high-level CC methods at the complete basis set (CBS) limit. The radical anion $Al_2O_4^$ is such a system and was identified previously as class II¹³³ in agreement with experiment.¹⁴⁷ Interestingly, the computations confirmed not only the localized C_{2v} minima representing terminal oxyl radicals but also provided a high-lying further local minimum with D_{2h} symmetry that may be characterized as a bridgelocalized state with the electron hole distributed over the two bridging oxygen atoms.¹³³ The initially surprising localized character of such a small MV system has been rationalized by the relatively ionic Al–O bonding, which explains the relatively weak electronic coupling between the terminal oxygen redox centers.



Figure 3.7 Systems included in the MVO-10 benchmark set.

Based on that study, we extended the investigation to ten systems of both main group (Al, Si) and transition metal (Sc, Ti, V, Cr) oxides, shown in Fig. 3.7. For details on the selection of systems, see [2, Section 2].

The performance of a given functional will be determined by the balance between a minimization of so-called delocalization errors arising from incomplete cancellation of Coulomb self-interaction¹⁴⁸ on the one hand and covering important left–right correlation contributions in the covalent bonds on the other hand.

3.4.2 Computational Details

The calculations have been performed with the Turbomole (revision 7.2),^{85,116,149} Gaussian (version 09, revisions A.02 and D.01; version 16, revision A.03),¹⁵⁰ as well as with the MOLPRO (revision 2012.1)^{151,152} and MRCC¹⁵³ program suites. We have ensured that the programs usually provide identical energies (to within less than 0.5 mH) and structures (to within less than 0.5 pm at a given computational level). High-level benchmark data with an approximate energy accuracy of about 1 kJ/mol have been obtained by our collaborator Dr. Amir Karton at the University of Western Australia² using W3-F12 theory⁷⁷ for systems containing first- and second-row atoms, and truncated levels of theory for systems containing first-row transition metals. For more details on those benchmark calculations, see [2, Sections 3 and 4].

The benchmark data have been used to evaluate the performance of a variety of different DFT approaches. In all cases, the structures of minima and transition states were fully optimized using the given functional with def2-TZVP basis sets.¹⁸ Previous tests, e.g. against def2-QZVP results, showed that this basis set provides essentially converged structures and energies¹³³ (we confirmed this by some further test calculations that generally exhibited changes in energy differences that were less than 2 kJ/mol).

We have evaluated the following functionals: a) global hybrids (B3LYP,³⁸⁻⁴⁰ BH-LYP,⁴⁴ BLYP35,^{45,46} M06,⁵⁶ M06-2X,⁵⁶ MN15,⁵⁷ PBE0,^{62,63} PBE0–1/3,⁶⁴ BMK⁴⁷), b) global range-separated hybrids (CAM-B3LYP,⁴⁸ ω B97X-D³⁷), and c) local hybrids: t-LMF⁷⁰ with SVWN and b = 0.646 (LH646-SVWN) or b = 0.670 (LH670-SVWN), LH-sifPW92⁵⁴ (b = 0.709), and LH-sirPW92⁵⁴ (b = 0.646), see Section 2.2.2. The prefactors of the two LH-SVWN functionals have been chosen either to be equal to that of LH-sirPW92 (b = 0.646), to probe the effects of the correlation functional, or as b = 0.670 since this is above the threshold value where the structural details of Al₂O₄⁻ are correctly reproduced (see below). For the other functionals, we will report data obtained with Gaussian 09 (and Gaussian 16 for MN15),¹⁵⁰ after having made sure that all programs provide essentially identical results for functionals available in both.

With Gaussian we mostly used default options for convergence of structure optimizations and for vibrational frequency calculations. In some critical cases the superfinegrid and tight or verytight options were used, or the more robust quadratic convergence SCF procedure (QC) was employed. Because of its small energy difference to the high-lying D_{2h} minimum, we applied further options to converge the transition state of $Si_2O_4^+$ with $\omega B97X$ -D (maxstep=5) and the associated intrinsic reaction coordinate (IRC) (maxpoints=200, stepsize=1, iop(1/7=10)). For Turbomole, the SCF convergence threshold was generally set to 10^{-8} to be on par with the default value of Gaussian. In some tests, gridsize was set to 3 or 5, the option gcart to 4 or 5 for the structure optimization, or the S- and P-junctions were disabled. In particular, for frequency calculations we employed derivatives of integral grid weights to improve numerical Hessians. The ground-state structure of $Al_2O_4^-$ with LH-SVWN was a borderline case where stricter thresholds were not reliably resulting in the lowest energy. We therefore started optimizations from both delocalized and localized structures, choosing the result with the lowest energy. Use of this scheme when varying the prefactor for the LMF led to a crossing point between b = 0.664 and b = 0.665. This established the safe value of b = 0.670mentioned above.

Based on these data, structures and spin-density distributions were visualized using the Chemcraft (v1.8) software.¹⁵⁴

3.4.3 Results and Discussion

Evaluation of XC Functionals for Energies and Minimum Structures

We compare the performance of different XC functionals in reproducing both energetics and structures obtained at CC levels. Figure 3.9 shows the spin-density



Figure 3.8 Spin-density distributions of different stationary points of Si_2O_4^+ (ω B97X-D, ± 0.01 isosurfaces). Left: C_{2v} low-lying minimum; middle: transition state (C_{2v}); right: D_{2h} bridge-localized high-lying minimum.

distributions (at ω B97X-D/def2-TZVP level) for both localized and delocalized structures of all species (and for the bridge state of Al₂O₄⁻; Si₂O₄⁺ is given in Fig. 3.8) to give a better impression of the electronic-structure situation. Table 3.5 summarizes relevant energy differences for all complexes studied here. In most cases, a positive number denotes the energy barrier in going from a localized, symmetry-broken minimum to a delocalized transition state. Al₂O₄⁻ and Si₂O₄⁺ are exceptions, as here the structure at higher energy represents another minimum, with the spin density delocalized over the two bridging oxygen ligands (a "bridgelocalized minimum" and bond-stretch isomer, as discussed in detail in [133] for Al₂O₄⁻).

We start with these two isoelectronic main-group species. For $Al_2O_4^-$ we add further results for LH functionals as well as for the GH MN15 to the data from previous work.¹³³ While the energy differences for all four LHs are very similar and overestimate the best reference data only slightly, the ground-state structure depends very sensitively on minuscule details of the functional (Table 3.A.1). That is, LH-sifPW92, LH-sirPW92, and LH646-SVWN do not give the correct symmetry breaking but converge to a ground-state structure close to D_{2h} symmetry, where the spin density is almost symmetrically delocalized over the two terminal oxygen atoms (preliminary calculations for LH646-SVWN had suggested more symmetry breaking, but for large grids and tight convergence criteria, the structure also remains close to D_{2h}). We had found similar behavior for several GHs with intermediate XX admixtures between 25% and 32% (see also PBE0 data in Table 3.A.1). Notably, for this system the extreme sensitivity of the ground-state



Figure 3.9 Spin-density distributions (± 0.01 isosurfaces) of localized and delocalized structures of the benchmark models ($\omega B97X$ -D/def2-TZVP level). For Si₂O₄⁺ see Fig. 3.8. Designations of transition states and minima obtained at the same level (inconsistent for V₄O₁₀⁻ with a delocalized D_{2d} structure deduced from experimental spectra).

тарте	J.J COIII	parison o	relevant	t energy	differenc	es (in kJ	(moi) at	different	computat	tonal leve
System	$Al_2O_4^-$	$\mathrm{Si}_{2}\mathrm{O}_{4}^{+}$	$\rm Si_2O_4^-$	$Ti_2O_4^-$	$\mathrm{Ti}_{2}\mathrm{O}_{4}^{+}$	ScO_2	TiO_{2}^{+}	$Cr_2O_6^-$	$V_2O_4^+$	$V_4O_{10}^{-}$
Character	O hole	O hole	Si el.	Ti el.	O hole	O hole	0 hole	Cr el.	V el.	V el.
Symmetries	D_{2h}, C_{2v}	D_{2h}, C_{2v}	C_{2v}, C_s	C_{2h}, C_s	C_{2h}, C_s	C_{2v}, C_s	C_{2v}, C_s	D_{2h}, C_{2v}	C_{2h}, C_s	D_{2d}, C_s
CCSD(T)	69.5	120.5	48.1	-2.5	59.4	10.7	-6.9	-1.1	31.5	-25 d
CCSDT(Q)	67.9	112.2	47.8	e	e	6.2	-0.6	 e	 e	-5 ⁵
B3LYP	19.1 ^b	0.0	49.1	0.3	55.0	0.5	0.1	9.5	18.8	1.1
BHLYP	98.6	158.4	64.6	33.6	124.9	32.7	11.4	51.2	68.4	62.1
BLYP35	76.6	133.3	57.6	13.3	91.5	16.3	5.5 5	30.4	44.4	26.4
M06	19.4 b	134.5	47.2	0.6	67.7	9.6	4.3	4.3	12.4	0.1
M06-2X	85.2	140.9	52.7	23.3	114.8	25.6	16.0	53.9	66.1	60.9
PBE	0.0	0.0	36.1	0.3	0.1	0.1	0.1	0.0	0.1	0.7
PBE0	80.3 ^c	127.6	48.5	3.2	67.2	5.6	1.6	13.0	24.7	0.6
PBE0-1/3	74.5	136.0	52.1	11.0	87.0	14.8	4.9	24.0	38.3	18.3
BMK	77.8	134.5	50.1	10.1	101.0	13.9	10.2	36.7	56.7	31.0
MN15	76.2	131.7	39.0	5.9	85.1	12.8	6.7	13.0	27.7	6.7
CAM-B3LYP	68.7	124.4	58.2	15.2	89.4	14.4	4.1	23.0	36.5	18.7
ωB97X-D	67.1	125.6	54.8	16.7	69.4	14.9	5.2	21.1	34.8	13.3
LH-sir $PW92$	76.9°	126.3	51.4	6.6	54.1	1.1	3.7	10.0	24.3	0.1
LH-sifPW92	74.5 c	129.1	51.0	8.8	60.0	3.0	5.0	12.3	27.7	2.7
LH646-SVWN	76.5 $^{ m c}$	131.0	56.4	11.4	63.3	7.0	6.2	14.6	29.7	5.7
LH670-SVWN	76.3	133.2	60.2	13.3	66.8	8.7	7.3	16.3	32.2	8.2
^a DFT/def2-TZ	VP with st	ructures of	ptimized <i>e</i>	at the sar	ne level, a	and CC si	ngle-point	energies v	with BLYF	35/CBS-
artifact of the s	tructure on	timization.	c Low-	lving mini	mum with	spin dens	ity at the	terminal o	xvgen aton	ns almost
		T L	• bo			in the second				

delocalized to D_{2h} symmetry. ^d No benchmark computations available. The preference for a delocalized structure is inferred from the experimental gas-phase vibrational spectra of [147], which are thought to correspond to a tempera-ture below 50 K. ^e The highest-level W3-F12 computations corresponding to the CCSDT(Q)/CBS level have not been possible with the available computational resources.

structure may lead to convergence to different structures depending on the starting point within a rather wide range of LMF prefactors around this borderline value. MN15 provides also good structures and energy differences similar to those of the better-performing functionals (Table 3.5). We note that GHs with lower XX admixtures, such as B3LYP or M06 (as well as GGA or mGGA functionals), do not allow the bridge-localized D_{2h} structure to be located and inevitably give a "terminal-oxo delocalized" D_{2h} structure only (Table 3.A.1). GHs with too large XX admixture (e.g. BHLYP or M06-2X) give good structures but overestimate the energy difference.

For the isoelectronic $Si_2O_4^+$ (Fig. 3.8) the overall electronic and molecular structure is very similar but the energy difference between bridge-hole and terminal-hole states is much higher, ca. 112 kJ/mol compared to about 68 kJ/mol.¹³³ Locating the barrier for transformation from the high-lying D_{2h} minimum to the ground state turned out to be difficult in several cases, likely due to its extreme smallness: with ω B97X-D we found it to be 4kJ/mol (supported by a CCSD(T)/CBS// ω B97X-D/def2-TZVP single-point value of 4.3 kJ/mol obtained from W2-F12 theory), even smaller than the one found for the isoelectronic $Al_2O_4^{-}$ (ca. 10 kJ/mol¹³³). Otherwise, results for $Si_2O_4^+$ show less sensitivity to the functional than observed for $Al_2O_4^{-}$. PBE and B3LYP delocalize and fail to provide the bridge state, PBE0 and M06 give the high-lying bridge state (in contrast to its absence in case of $Al_2O_4^{-}$ for M06¹³³) but a delocalized ground-state structure (Table 3.A.2). Notably, in contrast to $Al_2O_4^{-}$ (see above) all LHs tested give the correct C_{2v} groundstate minimum. Interestingly, all functionals that provide the qualitatively correct minimum structures overestimate the benchmark CCSDT(Q)/CBS energy difference at least by about $15 \, \text{kJ/mol}$. However, this could be related to the unusually large effect of the post-CCSD(T) contributions for this system (cf. [2, Tab. 1]). We note in this context that the high-lying D_{2h} minimum involves a higher degree of non-dynamical correlation effects relative to the C_{2v} structure. This is reflected, for example, in relative contributions of perturbative triples to the total atomization energies^{74,76,77} of 4.9% and 6.8% for the C_{2v} and D_{2h} structures, respectively. This means that all qualitatively reasonable functionals provide energy differences only 4 kJ/mol to 14 kJ/mol larger than the CCSD(T)/CBS data (Table 3.5), with noticeably good performance of ω B97X-D and CAM-B3LYP.

The anion $Si_2O_4^{-}$ has a C_s minimum structure with pyramidalization and partial silicon radical-anion character at one of the two silicon centers (the second Si center is almost planar, Table 3.A.3; computations on the dianion $Si_2O_4^{2-}$ gave a similar C_s structure for one isomer¹⁵⁵), whereas the C_{2v} transition state shows a delocalized distribution (Fig. 3.9). This anion differs from all other systems in this study by exhibiting an unexpectedly small dependence of the activation barrier on the XC functional (Table 3.5): only PBE as our single example for a GGA functional underestimates the barrier noticeably, and surprisingly the GH MN15 (with 44%XX admixture) also gives a low barrier. The B3LYP and M06 hybrids, which featured clearly too low XX admixture and consequently too high delocalization errors for $Al_2O_4^{-}$ and $Si_2O_4^{+}$ (see above), now provide the best agreement with the ca. 48 kJ/mol benchmark CC barrier (together with ωB97M-V, PBE0, and some LHs). Moderately overestimated barriers are found with the other functionals, with somewhat unexpected trends (Table 3.5). For example, M06-2X with 54%XX admixture, which clearly over-localizes the other species in this study, provides a lower barrier than some functionals performing better for other systems.

Leaving these main-group radicals, we start with the smallest transition-metal complexes, the isoelectronic ScO_2 and TiO_2^+ (Table 3.5). The very small benchmark $C_{2v} - C_s$ energy differences render these systems particularly challenging. Given the remaining error margins of the benchmark data, any functional giving an energy difference of only a few kJ/mol and reasonable structural data should be considered adequate (some functionals do not give an imaginary frequency at the C_{2v} structure, even though it is higher in energy than the C_s minimum; for TiO_2^+ , this holds with PBE, for ScO_2 with PBE, B3LYP, and with some of the LHs, consistent with CC data¹⁵⁶). Most functionals reproduce small energy differences, possibly with the exception of BHLYP and M06-2X (i.e. for the highest XX admixtures of the GHs screened) for ScO_2 (Table 3.5). Structural differences are not very pronounced (Tables 3.A.4 and 3.A.5): variations of the M–O distances in the C_{2v} structures are small, the O-M-O angles vary over a range of ca. 20° for ScO_2 (with the CCSD(T) value in the middle) but only over less than 5° for TiO₂⁺ (with the CC value at the lower end). Differences between the short and long M–O distances at the C_s structure are fairly similar for ScO₂ (with the exception of PBE, which does not give a distorted structure), whereas those for

 TiO_2^+ vary between 0 pm (PBE) and 22 pm (M06-2X), with the CC data (10 pm) in the middle. While functionals with elevated XX admixtures agree best with the CCSD(T) data for this difference in ScO₂, the smaller CC distortion in TiO_2^+ is best reproduced by B3LYP (8 pm, Table 3.A.5). In view of the extreme shallowness of the potential-energy surfaces, these structural comparisons have to be viewed with caution. We can thus draw only limited conclusions from these two systems.

It is therefore best to jump from the two smallest systems to the largest complex of the present study, $V_4O_{10}^{-}$. In the absence of high-level quantum-chemical benchmark data, we take the low-temperature experimental gas-phase vibrational frequencies as indication for a D_{2d} -symmetrical delocalized structure, with small uncertainties in the energetics arising from thermal fluctuations and zero-point vibrations. Getting right simultaneously the molecular and electronic structure of $Al_2O_4^-$ as the most clear-cut localized gas-phase MV system, and of $V_4O_{10}^-$ as a delocalized counterpoint, provides a challenge for any approximate functional. While functionals with low or zero XX admixture (PBE, B3LYP, M06) correctly describe $V_4O_{10}^{-}$ as delocalized,¹⁵⁷ they clearly fail to capture the correct localized ground-state structure and high-lying bridge-hole structure of Al₂O₄⁻. Functionals like PBE0 and the local hybrids LH-sirPW92, LH-sifPW92, LH646-SVWN provide an almost but not quite delocalized situation for $V_4O_{10}^{-}$ and get the high-lying bridge-hole structure for $Al_2O_4^{-}$, but they give a too delocalized ground-state structure for the latter anion. Functionals that are already too localized for the aluminum system (BHLYP, M06-2X) are obviously far from adequate for the vanadium complex and give a large bias towards a localized C_s minimum (see also Table 3.A.6 for structural data). But even GHs like BLYP35 and BMK, which have performed reasonably well in previous studies on class II MV systems,^{143,145,146} still give sizeable stabilizations of above 25 kJ/mol to 30 kJ/mol to the C_s minimum of $V_4O_{10}^{-}$ (Table 3.5). Focusing on the best-performing functionals for the localized $Al_2O_4^-$ (see above¹³³), we see that for $V_4O_{10}^-$ the global range-separated hybrids ω B97X-D and CAM-B3LYP give an artificial barrier of only about 13 kJ/mol and 19 kJ/mol, respectively. The local hybrid LH670-SVWN gives 8 kJ/mol. Interestingly, the recent MN15 global hybrid, which has been presented as a particularly good compromise between single- and multireference situations,⁵⁷ gives ca. $7 \, \text{kJ/mol}$. The latter two functionals may thus be considered to provide the overall

best combined performance for these two extreme localized and delocalized cases.

The two d^1d^0 dinuclear systems $\operatorname{Cr}_2\operatorname{O}_6^-$ and $\operatorname{Ti}_2\operatorname{O}_4^-$ are electronically similar to $\operatorname{V}_4\operatorname{O}_{10}^-$, as the benchmark data characterize them as close to a delocalized class III situation. We should keep in mind, however, that higher-order corrections beyond $\operatorname{CCSD}(T)/\operatorname{CBS}$ might still give non-negligible barriers for both systems. Similar to $\operatorname{V}_4\operatorname{O}_{10}^-$, functionals with lower XX admixtures (PBE, B3LYP, M06, PBE0) obviously give small or zero "delocalization barriers". Variations for $\operatorname{Cr}_2\operatorname{O}_6^-$ are larger than for $\operatorname{Ti}_2\operatorname{O}_4^-$. Even ω B97X-D and LH670-SVWN give barriers of 21 kJ/mol and 16 kJ/mol, respectively, for the chromium complex, slightly lower ones for the titanium complex (Table 3.5). The low barrier (6 kJ/mol) for MN15 is again notable. Overall the trends are similar as for $\operatorname{V}_4\operatorname{O}_{10}^-$, suggesting that appreciably delocalized d^1d^0 MV cases exhibit closely comparable dependencies. Structural deviations from a symmetrical arrangement for $\operatorname{Cr}_2\operatorname{O}_6^-$ in cases where a C_{2v} structure is more stable than the D_{2h} one are rather small (Table 3.A.7), a fraction of a pm and a few degree in distances and angles, respectively. Differences in M–M distances and M–M–O angles for Ti₂O₄⁻ are more pronounced (Table 3.A.8).

The last of the d^1d^0 MV systems studied is the cationic V₂O₄⁺, which has substantially more localized character according to the benchmark data. Here B3LYP, M06 or PBE0 still provide localized minima (see also previous B3LYP data¹⁵⁸), but with too low barriers compared to the ca. 32 kJ/mol CCSD(T)/CBS//BLYP35 benchmark and the previous ca. 27 kJ/mol MR-ACPF/B3LYP energies¹⁵⁸ (PBE is the only functional tested that gives a delocalized structure). Among the bestperforming functionals for Al₂O₄⁻ (see above), LH670-SVWN, MN15, ω B97X-D, and CAM-B3LYP provides the best agreement with the reference data for V₂O₄⁺ (Table 3.5). LH-sifPW92 and LH646-SVWN approach the reference barrier for V₂O₄⁺ closely from below, but they do not provide the correct ground-state structure for the aluminum anion (see above). BHLYP or M06-2X overshoot strongly, and even BLYP35 or BMK give clearly too large barriers. Structures are closely comparable with all functionals (Table 3.A.9), except for the delocalized minimum structure at PBE level.

Finally, we return to a localized terminal oxyl-hole system, Ti_2O_4^+ (cf. Fig. 3.9), for which the benchmark data provide an appreciable $C_{2h} - C_s$ barrier of ca. 60 kJ/mol for the more stable trans isomer. Interestingly, this value is bracketed quite well by the B3LYP and M06 data (Table 3.5), while several of the functionals performing well for the aluminum case (BLYP35, PBE0–1/3, BMK, and even CAM-B3LYP and MN15) overestimate the reference value appreciably. Keeping in mind again possible effects of the missing "beyond CCSD(T)" corrections, ω B97X-D and the LH670-SVWN local hybrid perform again well, underscoring the overall good performance of these two functionals for the overall test set, with the LH avoiding somewhat better over-localization in delocalized cases. Structurally, the distortions of the C_s structure tend to be similar for most functionals (Table 3.A.10). For example, the differences between the oxyl and oxo M–O bonds vary between 22 pm (B3LYP) and 25 pm (e.g. M06-2X, BHLYP), except for the PBE GGA (3 pm).

Comparison of Vibrational Frequencies with Experimental Data

While the aim was mainly to establish a benchmark set for (de)localization errors in small gas-phase MV systems, some comparison with available experimental data seems in order, in particular regarding vibrational spectra, where available. Because of the new implementation this is also possible for the used LH functionals. For $Al_2O_4^-$, previous work showed that the infrared multiphoton dissociation (IRMPD) spectra were reproduced by several functionals that provide the correct symmetry breaking of the C_{2v} ground-state minima,^{133,147} albeit the exact frequencies, and in particular the intensities were a challenge. For the isoelectronic $Si_2O_4^+$, so far no vibrational data are available, and thus the data provided in Table 3.A.11, which are closely analogous to the corresponding data for $Al_2O_4^$ but naturally shifted to higher frequencies, are predictions.

In case of Si_2O_4^- , the broad photoelectron detachment spectrum has been interpreted¹⁵⁹ as consistent with a C_s type structure (cf. Table 3.A.3), similar to a previous suggestion for the diamon.¹⁵⁵ No vibrational structure could be extracted, and thus the data in Table 3.A.12 are also predictions in this case.

We used the experimental IRMPD spectra for $V_4O_{10}^-$ as evidence for the D_{2d} structure, as its very few features (one V=O stretching frequency near 990 cm⁻¹ and V-O-V stretches below 750 cm⁻¹) are consistent with a delocalized high-symmetry structure.¹⁵⁷ When comparing different functionals and structures (Ta-

ble 3.A.13), it is clear that D_{2d} structures reproduce the spectra well, possibly with some downscaling needed, while C_s minima do not, even if they are only very slightly more stable than the D_{2d} transition state (e.g. for LH670-SVWN or for MN15). That is, C_s structures always give additional bands in the region between 800 cm^{-1} to 900 cm^{-1} , which are absent in the experimental spectra,¹⁵⁷ even if a given functional provides only a very small energetic penalty to the D_{2d} structure (Table 3.A.13). This holds also for the mentioned LH, albeit interestingly it does not give any imaginary frequency for the D_{2d} -optimized structure in spite of its energy being about 8 kJ/mol above the C_s structure (cf. Table 3.5). This suggests on one hand that for this type of functional the potential energy surface is already very shallow in the decisive region. On the other hand we may even question if a zero-point vibration would fit into the computed well of the C_s structure. The observed high-symmetry spectrum might thus also be consistent with a very weakly stabilized C_s structure.

Another ion for which gas-phase vibrational spectra are available is $V_2O_4^{+,160}$ Here the overall five bands at 594, 776, 794 (shoulder), 1029, and 1049 cm⁻¹ had been clearly interpreted in terms of a localized symmetry-broken structure.¹⁶⁰ Indeed, only calculations using a localized C_s structure provide these five bands (Table 3.A.14), while computations for the delocalized C_{2h} structure (e.g. favored at PBE level; Table 3.5) give only two bands. All functionals would require downscaling of the frequencies to agree better with experiment. Additionally, while all functionals (except PBE, see above) correctly give higher intensity to the asymmetric V=O stretch at 1029 cm⁻¹ than to the symmetric one at 1049 cm⁻¹, some of them provide very low intensity to the symmetric band (Table 3.A.14). Additionally, the experimental spectra would suggest that the band at 794 cm⁻¹, which is a shoulder to the 776 cm⁻¹ band, should thus have much less intensity than the latter. This lower intensity is not correctly reproduced by most functionals (Table 3.A.14). We keep in mind, however, that intensities may depend on anharmonicities, which are neglected in the computations.

More limited information from photodetachment spectra is available for $\text{Ti}_2\text{O}_4^$ and Cr_2O_6^- . The resolution does not allow full vibrational analyses. Thus, for Ti_2O_4^- the major information taken from the photoelectron spectra is that of a localized extra electron.¹⁶¹ As we saw above, the energy differences between localized and delocalized structures are so small in this case that even the benchmark data do not unequivocally decide between these two cases. Hence we provide computed vibrational data for both C_{2h} and C_s structures in Tables 3.A.15 and 3.A.16 for future reference (we note, however, that other photoelectron spectra suggest a mixture of *cis* and *trans* isomers¹⁶²). The only vibrational information that may be extracted from the photoelectron spectra of Cr_2O_6^- is a mode at 780 cm⁻¹ (50). A band in this area is present in the computed spectra both for delocalized and localized structures, and thus no information on the structure of this borderline case may be obtained from this comparison. No experimental vibration spectroscopic data are available for ScO₂ or TiO₂⁺ (but note high-level CC data¹⁵⁶), nor for Ti₂O₄⁺.

3.4.4 Summary

Starting from the previous example $Al_2O_4^-$, we have collected a benchmark set of ten relatively small main-group and transition-metal MV oxo systems (MVO-10). For these systems we have obtained high-level CC benchmark energy data (CCSD(T)/CBS or CCSDT(Q)/CBS, depending on system size), taking into account also experimental observations (e.g. for $V_4O_{10}^-$) on the relative stabilities of localized and delocalized MV situations. These benchmark data have been used to evaluate a range of DFT XC functionals, in particular GH, GRSH, and LH functionals. The goal has been to provide guidelines to screen for minimal delocalization vs. localization errors for gas-phase MV systems, i.e. without the added complication of environmental effects that usually affect studies of MV systems.

Pinning $Al_2O_4^-$ and $V_4O_{10}^-$ against each other as the most extreme counter points of a strongly localized class II main-group oxyl system and a delocalized early transition-metal d^1d^0 case provides already a substantial challenge that is not fully met by any of the functionals tested. Functionals with relatively high XX admixtures get the proper structures and energetics of the aluminum system right (albeit too high admixtures overestimate the energy differences). However, these functionals tend to artificially localize the spin/charge in $V_4O_{10}^-$. The overall best performers simultaneously for these two extreme cases are the highly parameterized MN15 global hybrid, the much less empirical LH670-SVWN local hybrid, and the ω B97X-D global range-separated hybrid (all three functionals exhibit weak symmetry breaking for the vanadium system but with energy differences that may be insignificant compared to zero-point vibrational energies). Other systems in the benchmark set encompass both delocalized and localized d^1d^0 cases, as well as oxyl cases on both sides of the divide between localized and delocalized. The three functionals mentioned provide the overall best performance across these cases, with the notable exception of the silicon-centered Si₂O₄⁻⁻, which exhibits a pattern of relative energies that is difficult to rationalize, and the oxyl-centered Ti₂O₄⁻⁻, where MN15 clearly over-localizes. The systems studied cover an appreciable number but certainly not all potential electronic situations we may encounter in MV systems. The data set provided should thus at least constitute a good starting point for further evaluations.

3.5 Conclusions and Outlook

Up to now implementations of LH functionals had been lacking gradients w.r.t. nuclear displacement, hindering structure optimization and the calculation of vibrational force constants. This gap has now been closed by the implementation of those gradients into the program package Turbomole. We employed a seminumeric integration scheme with the Gauss-Rys and Gauss-Hermite formalisms, reusing auxiliary integrals in the simultaneous calculation of the XX-related matrices \mathcal{A} and \mathcal{A}' for efficiency. This is accompanied by adjusted screening techniques of S- and P-junctions from the LH SCF routines.

The implementation was initially assessed for test sets of main-group and transition metal compounds yielding structures and vibrational data on par with commonly used GGA and GH functionals. The effectiveness of the screenings was evaluated on timings and error estimates for unbranched alkanes and the threedimensional adamantane, resulting in recommended values of 10^{-5} (or 10^{-6}) for both S- and P-junctions.

Finally, the gradients were applied to a new benchmark test set consisting of ten small, gas-phase molecules that lie on the verge between the mixed valence classes II and III. One LH (t-LMF, b = 0.670 with SVWN) performed especially well, even though the transition state between the low- and high-lying minima of $\rm{Si}_2O_4{}^+$ could only be determined with another functional and program because of its shallowness.

The gradient implementation may in the future be extended to further ingredients, e.g. the Laplacian and Hessian of the electron density. The efficiency could be increased by adapting the Boys-function based integration for low angular quantum numbers used by the energy calculations. Alternatively, the Obara-Saika scheme¹⁶³ could yield even better timings by utilizing recurrence relations. The P-junction scheme would have to be adapted accordingly.

Parts of the code can be reused in other implementations, e.g. for gradients of excited states (work along this line is in $\operatorname{progress}^{164}$). An extension to second derivatives (i.e. aoforce) is probably not worthwhile at this time as the second derivatives of \mathcal{A} would exhibit a very high demand for processing and memory, while the numerical approximation (NumForce) already offers usable results.

3.A Appendix

3.A.1 Connection Between Gradient and Overlap

Assuming orthonormal MOs, the overlap matrix is defined as¹²⁴

$$\int \varphi_i \varphi_j \,\mathrm{d}\boldsymbol{r} = \sum_{\mu\nu} C_{\mu i} S_{\mu\nu} C_{\nu j} = \delta_{ij} \;, \qquad (3.A.1)$$

with coefficients $C_{\mu i}$ and $C_{\nu i}$, overlap matrix elements $S_{\mu\nu}$ and the Kronecker delta δ_{ij} . If one differentiates the equation w.r.t. nuclear coordinates, the product rule yields

$$\sum_{\mu\nu} \nabla_{\!A} C_{\mu i} S_{\mu\nu} C_{\nu j} + C_{\mu i} \nabla_{\!A} S_{\mu\nu} C_{\nu j} + C_{\mu i} S_{\mu\nu} \nabla_{\!A} C_{\nu j} = 0 . \qquad (3.A.2)$$

The first and last summand can be combined by interchanging the indices. Moving the second summand to the other side gives

$$2\sum_{\mu\nu}\nabla_{\!A}C_{\mu i}S_{\mu\nu}C_{\nu j} = -\sum_{\mu\nu}C_{\mu i}C_{\nu j}\nabla_{\!A}S_{\mu\nu} \qquad (3.A.3)$$

and for i = j the used identity

$$2\sum_{\mu\nu}\nabla_{\!A}C_{\mu i}S_{\mu\nu}C_{\nu i} = -\sum_{\mu\nu}C_{\mu i}C_{\nu i}\nabla_{\!A}S_{\mu\nu} . \qquad (3.1.5)$$

3.A.2 Additional Tables for MVO-10

The following pages include tables of structural and vibrational data for the MV systems discussed and referenced in Section 3.4. They were given as supporting information for the original paper.²

omparison of key s	tructure	parameter	s (in pm	and o) for	Al_2U_4 at	various com	putati
		d(MM)	d(MM)	$d(MO_t)$	$d(\mathrm{MO_t})$	$\Delta d(\mathrm{MO_t})$	
Functional	ΔE	D_{2h}	C_{2v}	D_{2h}	$\left[C_{2v}\right]_{\mathrm{s}}$	$[C_{2v}]_{1-s}$	
CCSD(T) /aug-cc-VQZ	69.0	282.8	243.3	162.6	163.6	12.1	
B3LYP	19.1	242.5	242.1	168.3	167.5	0.0	
BHLYP	98.6	279.0	240.7	159.8	160.8	13.0	
BLYP35	76.6	279.9	241.7	160.8	161.9	12.0	
M06	19.4	240.1	239.6	167.2	166.5	0.0	
M06-2X	85.2	279.7	241.1	160.8	161.8	12.6	
PBE	0.0	242.8	242.8	168.9	168.9	0.0	
PBE0	80.3	278.1	240.7	161.5	167.2	0.0	
PBE0-1/3	77.4	279.3	240.6	160.7	162.0	11.8	
BMK	77.8	278.6	239.9	160.6	161.7	12.3	
MN15	76.2	280.7	242.2	161.0	162.0	12.7	
CAM-B3LYP	68.7	280.1	241.6	160.8	161.7	12.7	
ωB97X-D	67.1	280.5	241.6	161.0	162.0	12.9	
LH-sirPW92	76.9	281.0	242.7	161.8	167.8	0.0	
LH-sifPW92	74.5	281.9	242.7	161.7	167.8	0.1	
LH646-SVWN	76.5	282.1	243.0	161.8	167.7	0.5	
LH670-SVWN	76.3	282.5	243.9	161.8	162.9	13.7	
^a Results with	local hy	brids from	[2], the o	ther data	from [133].		

utational levels.^a -; \langle ĽV ح 0 7 4 ר ו-ד Table 3.A.1 Co

_	Ι	Ι	Ι	6		1	H	н	H	Π	1	7	H	Η	Ŧ			
JH670-SVWN	JH646-SVWN	JH-sifPW92	JH-sirPW92	bB97X-D	CAM-B3LYP	MN15	BMK	$^{9}\mathrm{BE0-1/3}$	BEO	BE	M06-2X	A06	3LYP35	3HLYP	33LYP	OCSD(T) aug-cc-VQZ	runctional	
133.2	131.0	129.1	126.3	125.6	124.4	131.7	134.5	136.0	127.6	0.0	140.9	134.5	133.3	158.4	0.0	116.7	ΔE	
269.9	269.8	269.4	269.4	267.7	267.9	267.5	267.6	266.8	267.6	233.8	267.4	266.0	267.8	266.3	233.4	269.9	D_{2h}	d(MM)
234.8	235.3	234.4	234.2	232.6	233.3	233.2	232.3	232.0	231.8	233.8	232.6	231.0	233.4	232.3	233.5	234.3	C_{2v}	d(MM)
148.8	148.8	148.8	148.8	148.4	148.3	148.1	148.2	148.1	148.8	155.8	148.2	148.1	148.2	147.1	154.2	150.0	D_{2h}	$d(\mathrm{MO}_{\mathrm{t}})$
149.2	149.3	149.3	149.8	148.7	148.6	148.5	148.5	148.5	153.8	155.8	148.5	153.3	148.5	147.5	154.2	150.2	$\left[C_{2v}\right]_{\rm s}$	$d(\mathrm{MO}_{\mathrm{t}})$
13.4	13.3	12.4	10.7	12.5	12.5	12.2	12.3	12.2	0.0	0.0	12.5	0.1	12.3	12.7	0.0	12.0	$[C_{2v}]_{l-s}$	$\Delta d(\mathrm{MO_t})$

Table 3.A.2 Comparison of key structure parameters (in pm and °) for $Si_2O_4^+$ at various computational levels.

Table 3.A.3 Con	ıpariso	in of key s	tructure p	arameters	(in pm a	nd °) for S	i_2O_4 at var	ious comput ⁸	tional levels.
		d(MM)	d(MM)	$d(\mathrm{MO_t})$	$d(MO_t)$	$d(MO_t)$	$\angle(\mathrm{MMO}_{\mathrm{t}})$	$\angle(\mathrm{MMO}_{\mathrm{t}})$	$\angle(\rm MMO_t)$
Functional	ΔE	C_{2v}	\tilde{C}_s	C_{2v}	$\left[C_s\right]_{\rm s}$	$\left[C_{s}\right]_{1}$	$\left[C_{2v}\right]$	$\left[C_s\right]_{\rm s}$	$\left[C_{s} ight]_{1}$
CCSD(T) /aug-cc-VQZ	47.7	236.2	242.9	153.2	152.9	154.8	170.0	134.6	177.5
B3LYP	49.1	238.5	243.5	153.0	152.4	154.6	163.9	133.5	177.0
BHLYP	64.6	230.2	240.8	150.9	150.5	152.7	171.6	132.8	177.8
BLYP35	57.6	234.4	242.3	152.0	151.4	153.7	168.0	133.0	177.5
M06	47.2	233.8	240.7	152.0	151.4	153.5	166.8	133.3	177.1
M06-2X	52.7	232.6	241.3	151.9	151.4	153.5	169.5	133.0	177.8
PBE	36.1	239.6	244.1	154.7	154.0	155.9	162.9	135.1	175.6
PBE0	48.5	231.1	241.4	152.4	152.0	154.0	171.0	133.8	177.1
PBE0-1/3	52.1	229.0	240.6	515.8	151.4	153.5	172.7	133.5	177.4
BMK	50.1	230.0	240.9	151.9	151.6	153.8	172.4	133.0	177.4
MN15	39.0	235.3	241.4	151.9	151.5	153.3	167.1	134.5	176.2
CAM-B3LYP	58.2	232.1	242.2	152.0	151.5	153.7	170.9	133.0	177.6
ωB97X-D	54.8	229.2	241.7	152.1	151.6	153.9	173.3	133.2	177.6
LH-sirPW92	51.4	233.3	243.1	152.8	152.2	154.3	170.5	133.7	177.6
LH-sifPW92	51.0	232.2	243.0	152.7	152.2	154.3	171.4	133.9	177.4
LH646-SVWN	56.4	233.9	244.0	152.8	152.3	154.5	170.4	132.4	178.1
LH670-SVWN	60.2	237.0	243.7	152.7	152.3	154.2	167.9	134.1	178.2

		d(MO)	d(MO)	$\Delta d(MO)$	∠(OMO)	∠(OMO)
	ΔE	C_{2v}	$\left[C_s\right]_{ m s}$	C_s	C_{2v}	C_s
CCSD(T) /aug-cc-VQZ	9.8	180.1	171.5	29.4	146.5	123.4
B3LYP	0.5	177.0	169.9	20.2	134.3	119.9
BHLYP	32.74	176.0	166.6	30.2	140.1	120.9
BLYP35	16.3	176.6	167.7	28.0	137.6	119.3
M06	9.6	176.9	167.9	26.1	127.6	117.7
M06-2X	25.6	175.7	166.9	30.4	147.6	119.5
PBE	0.1	177.3	177.3	0.1	129.7	129.3
PBE0	5.6	175.6	167.5	25.1	136.1	118.0
PBE0-1/3	14.8	175.2	166.6	27.7	137.6	118.6
BMK	13.9	176.4	168.1	27.8	138.6	120.1
MN15	128.8	181.1	167.1	27.9	142.8	121.3
CAM-B3LYP	14.4	175.7	167.2	27.6	138.0	119.1
ωB97X-D	14.9	175.7	167.0	28.2	136.0	119.1
LH-sirPW92	1.1	175.8	167.5	27.4	144.2	123.1
LH-sifPW92	3.0	175.6	167.1	28.9	145.9	122.0
LH646-SVWN	7.0	176.6	167.6	29.9	146.1	120.7
LH670-SVWN	8.7	176.7	167.6	30.9	147.5	121.9

Table 3.A.4 Comparison of key structure parameters (in pm and $^{\circ}$) for ScO_2 at various computational levels.

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rious comp	∠(OMO)	C_s	94.1	96.0	102.4	100.2	98.7	103.1	94.2	97.1	99.1	101.9	100.1	99.0	99.7	100.2	100.6	101.6	102.3
LIU2 at Va	∠(OMO)	C_{2v}	92.8	95.2	96.6	95.7	95.3	95.1	94.1	94.1	94.4	95.8	94.9	94.6	95.1	96.5	96.7	96.9	97.2
and ') ior	$\Delta d(\mathrm{MO})$	C_s	9.9	7.7	21.7	18.5	17.5	22.2	0.1	14.1	17.9	19.2	18.7	17.1	18.0	17.3	18.4	19.8	20.5
ers (in pm	d(MO)	$\begin{bmatrix} C_s \end{bmatrix}_{\mathbf{s}}$	161.2	161.4	154.3	156.4	156.9	154.5	165.7	157.5	155.6	155.9	155.7	156.5	156.0	156.4	155.8	156.2	156.1
paramete	d(MO)	C_{2v}	165.9	164.9	164.0	164.4	164.2	163.4	165.7	163.6	163.2	164.6	163.5	163.7	163.5	163.7	163.5	164.4	164.5
structure		ΔE	-3.8	0.1	11.4	5.5	4.3	16.0	0.1	1.6	4.9	10.2	6.7	4.1	5.2	3.7	5.0	6.2	7.3
comparison or key			CCSD(T) /aug-cc-pwCV5Z	B3LYP	BHLYP	BLYP35	M06	M06-2X	PBE	PBE0	PBE0-1/3	BMK	MN15	CAM-B3LYP	ωB97X-D	LH-sirPW92	LH-sifPW92	LH646-SVWN	LH670-SVWN

iputational levels. and °) for TiOa⁺ at various com i.j f l, . Table 3.A.5 Co

		d(MM)	d(MM)	d(MM)	d(MM)	$d(MO_t)$	$d(MO_t)$	$d(MO_b)$	$d(\mathrm{MO}_\mathrm{b})$
Functional	ΔE	$\left[D_{2d}\right]_{\min}$	$[D_{2d}]_{\max}$	$[C_s]_{\min}$	$[C_s]_{\max}$	D_{2d}	$[C_s]_{\max}$	$[D_{2d}]^{\text{mean}}_{\text{all}}$	$[C_s]_{\mathrm{mean,max}}$
B3LYP	1.1	309.0	312.9	309.0	312.6	158.8	158.8	180.2	180.2
BHLYP	62.1	307.8	310.6	305.7	317.9	156.0	156.5	178.3	190.3
BLYP35	26.4	308.6	312.0	306.7	318.5	157.4	157.7	179.3	190.2
M06	0.1	306.0	310.6	306.0	310.5	157.8	157.7	179.4	179.4
M06-2X	60.9	308.6	311.2	306.1	317.7	156.1	156.5	179.2	191.3
PBE	0.7	307.6	312.9	307.6	312.8	160.4	160.4	181.1	181.1
PBE0	0.6	305.7	310.2	305.6	310.1	157.5	157.5	178.9	178.9
PBE0-1/3	18.3	305.2	309.3	303.7	315.3	156.6	156.9	178.2	188.5
BMK	31.0	308.7	311.9	307.0	317.6	157.3	157.7	179.5	190.0
MN15	6.7	305.3	310.1	304.2	315.3	150.7	157.2	178.5	187.8
CAM-B3LYP	18.7	307.1	311.0	305.9	317.1	157.3	157.5	178.9	189.3
ωB97X-D	13.3	307.1	311.0	305.9	316.8	157.1	157.2	179.3	189.5
LH-sirPW92	0.1	306.9	311.0	306.1	315.1	157.4	157.6	179.3	187.1
LH-sifPW92	2.7	306.7	310.6	305.7	315.7	157.2	157.3	179.2	188.1
LH646-SVWN	5.7	308.6	312.2	307.5	317.9	157.8	158.0	180.0	189.9
LH670-SVWN	8.2	308.8	312.4	307.6	318.3	157.8	158.0	180.1	190.4

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Table 3.A.7	Compa	rison of k	sey structur	e parame	sters (in pm <i>s</i>	and °) for Cr_2	$_{2}O_{6}^{-}$ at var.	ious comput _é	utional levels.
Dunational	∠ 	$d(\mathrm{MM})$	$\Delta d(\mathrm{MM})$	$d(\mathrm{MO_t})$	$\Delta d(\mathrm{MO_t})$	$\Delta d(\mathrm{MO_t})$	$\angle(\mathrm{MMO_t})$	$\Delta \angle (\mathrm{MMO}_{\mathrm{t}})$	$\Delta \angle (\text{MMO}_{t})$
r ulicuoliai	75	D_{2h}	$ \nabla 2v = D2h $	$ u_{2h}$	$\left[\nabla 2v - D2h \right]_{\rm S}$	$\left[\bigcup_{n=1}^{\infty} \mathcal{D}_{n} \right]_{n=1}$	D_{2h}	$\left[\nabla 2v - D2h \right]_{\rm S}$	$\left[C_{2v} - \mathcal{U}_{2h} \right]_{1}$
B3LYP	9.5	252.4	6.5	158.6	-0.1	0.3	123.4	-1.8	1.3
BHLYP	51.2	250.9	8.9	155.8	-0.5	0.5	123.2	-2.3	1.5
BLYP35	30.4	251.6	8.5	157.2	-0.3	0.6	123.2	-2.1	1.4
M06	4.3	249.9	4.8	157.7	-0.1	0.4	123.4	-1.4	1.1
M06-2X	53.9	251.8	9.5	156.0	-0.4	0.7	123.1	-2.3	1.5
PBE	0.0	252.5	0.0	160.3	0.0	0.0	123.4	0.0	0.0
PBE0	13.0	249.6	7.1	157.2	-0.1	0.4	123.3	-1.9	1.4
PBE0-1/3	24.0	249.0	8.3	156.4	-0.2	0.6	123.3	-2.1	1.4
BMK	36.7	251.5	7.9	157.0	-0.2	0.6	123.2	-2.2	1.4
MN15	13.0	248.5	7.7	156.7	-0.1	0.4	123.3	-1.8	1.3
CAM-B3LYP	23.0	249.9	8.7	157.0	-0.1	0.5	123.3	-1.9	1.4
ωB97X-D	21.1	249.6	8.3	157.0	-0.1	0.5	123.3	-1.9	1.4
LH-sir $PW92$	10.0	250.0	6.9	157.2	-0.1	0.4	123.3	-1.7	1.3
LH-sifPW92	12.3	249.7	7.4	156.9	-0.1	0.5	123.3	-1.8	1.3
LH646-SVWN	14.6	251.7	7.5	157.7	-0.2	0.6	123.3	-1.9	1.3
LH670-SVWN	16.3	251.9	7.8	157.6	-0.2	0.6	123.3	-1.9	1.3

Table 3.A.8 ()	ompari	son of key	structure	paramete	rs (in pm ar	id ") for Ti_2	O_4^- at vario	us computat:	ional levels.
		d(MM)	d(MM)	$d(\mathrm{MO}_{\mathrm{t}})$	$\Delta d(\mathrm{MO}_{\mathrm{t}})$	$\Delta d(\mathrm{MO_t})$	$\angle(\mathrm{MMO}_{\mathrm{t}})$	$\angle(\mathrm{MMO}_{\mathrm{t}})$	$\angle(\mathrm{MMO}_{\mathrm{t}})$
Functional	ΔE	C_{2v}	C_s	C_{2v}	$\left[C_{s}\right]_{\mathrm{s}}$	$[C_s]_1$	$[C_{2v}]$	$\left[C_{s} ight]_{\mathrm{s}}$	$[C_s]_1$
$CCSD(T)_{a}$ //B3LYP	0.8			169.4					
B3LYP	0.3	269.5	269.6	167.1	0.1	0.1	144.8	144.6	146.0
BHLYP	33.6	266.6	273.3	165.8	0.0	1.6	156.1	149.2	162.4
BLYP35	13.3	268.3	272.2	166.5	0.2	1.1	150.1	148.3	153.0
M06	0.6	266.9	266.8	166.3	0.0	0.0	146.2	146.8	146.9
M06-2X	23.3	265.7	272.9	165.7	-0.2	1.5	163.6	146.5	162.1
PBE	0.3	270.4	270.4	167.7	0.0	0.0	138.0	137.9	138.3
PBE0	3.2	267.4	269.0	165.8	0.2	0.4	144.0	141.7	145.8
PBE0-1/3	11.0	266.5	269.7	165.4	0.2	0.8	146.5	145.7	146.2
BMK	10.1	268.2	272.1	167.2	0.1	1.3	151.7	147.0	150.6
MN15	5.9	265.4	268.7	166.0	-0.1	0.6	154.5	151.0	153.4
CAM-B3LYP	15.2	266.6	271.1	166.3	0.0	0.6	151.4	147.1	149.7
ωB97X-D	16.7	266.8	271.3	166.2	-0.1	0.5	150.3	145.5	145.9
LH-sirPW92	6.6	267.7	270.8	166.3	0.1	0.4	148.4	145.7	147.8
LH-sifPW92	8.8	267.4	270.8	166.1	0.1	0.5	149.5	146.3	148.3
LH646-SVWN	11.4	269.1	272.8	166.9	0.0	0.7	150.6	147.8	149.0
LH670-SVWN	13.3	269.1	273.3	167.0	0.0	0.8	151.4	149.1	150.7
^a CCSD(T)//B:	3LYP re	esults from	ı [165].						

3 Local Hybrid Gradients

Table 3.A.9 C	omparis	son of key	structure	e parameto	ers (in pm a	nd °) for V_2C	$)_4^+$ at vario	us computat	cional levels.
		d(MM)	d(MM)	$d(\mathrm{MO_t})$	$\Delta d(\mathrm{MO_t})$	$\Delta d(\mathrm{MO_t})$	$\angle(\mathrm{MMO}_{\mathrm{t}})$	$\angle(\mathrm{MMO}_{\mathrm{t}})$	$\angle(\mathrm{MMO_t})$
Functional	ΔE	C_{2h}	C_s	C_{2h}	$\left[C_s - C_{2h}\right]_{\rm s}$	$\left[C_s - C_{2h}\right]_1$	$[C_{2h}]$	$[C_s]_{\mathrm{small}}$	$[C_s]_{ m large}$
MR-ACPF ^a	27.4 ^b			159.0			123.8		
$CCSD(T)^{c}$	31.6								
B3LYP	18.8	258.4	264.3	155.0	-0.4	0.5	123.6	121.7	123.2
BHLYP	68.4	256.6	264.3	152.3	-0.2	0.4	125.7	122.8	123.9
BLYP35	44.4	257.5	264.8	153.7	-0.3	0.5	124.7	122.8	123.0
M06	12.4	255.4	260.8	154.0	-0.3	0.25	121.8	118.6	123.5
M06-2X	66.1	257.1	265.2	152.5	-0.3	0.5	125.3	122.1	123.7
PBE	0.1	258.7	258.7	156.6	0.0	0.0	121.8	121.8	121.8
PBE0	24.7	255.5	262.1	153.7	-0.3	0.5	122.8	120.7	122.6
PBE0-1/3	38.3	254.8	262.1	152.8	-0.3	0.5	123.2	121.0	122.4
BMK	56.7	257.1	264.2	153.7	-0.3	0.6	125.2	122.8	124.0
MN15	27.2	254.3	261.4	153.3	-0.3	0.4	123.3	120.4	123.4
CAM-B3LYP	36.5	256.0	263.4	153.6	-0.3	0.5	123.8	121.9	122.8
ωB97X-D	34.8	255.6	263.1	153.5	-0.3	0.6	123.5	121.6	124.1
LH-sirPW92	24.3	256.1	263.0	153.5	-0.3	0.6	123.5	121.6	124.1
LH-sifPW92	27.7	255.8	263.0	153.2	-0.3	0.6	123.7	121.7	124.2
LH646-SVWN	29.7	257.3	264.2	153.9	-0.2	0.5	124.7	122.9	125.8
LH670-SVWN	32.2	257.9	264.9	154.0	-0.3	0.5	124.8	123.5	123.8
^a MR-ACPF re	sults fro	m [158].	^b Single-J	point energ	gies at B3LY.	P-optimized s ¹	tructures.		
^c CCSD(T)/CB	S) at B]	LYP35-opt	imized str	uctures fro	m [2].				

Table 3.A.10	Comparis	son of key	structure	paramet	ers (in pm an	d °) for Ti_2C	D_4^+ at vario	us computat	ional levels.
Functional	ΛE	$d({ m MM})$	d(MM)	$d(\mathrm{MO_t})$	$\Delta d(\mathrm{MO_t})$	$\Delta d(\mathrm{MO}_{\mathrm{t}})$	$\angle (\mathrm{MMO}_{\mathrm{t}})$	$\angle (MMO_t)$	$\angle (\mathrm{MMO}_{\mathrm{t}})$
B3LYP	55.0	272.5	272.2	164.5	158.2	180.8	109.2	113.9	117.3
BHLYP	124.9	269.7	270.1	164.5	155.6	181.0	109.4	115.4	121.7
BLYP35	91.5	271.2	271.2	164.3	156.9	181.3	109.3	114.7	120.0
M06	67.7	270.4	270.1	163.8	157.1	180.9	108.6	113.2	115.4
M06-2X	114.8	272.0	270.8	161.4	155.8	181.2	110.8	115.5	119.9
PBE	0.1	273.9	274.0	165.3	163.8	167.0	108.5	107.8	109.3
PBE0	67.2	270.2	269.8	163.3	156.9	180.2	108.5	113.2	117.4
PBE0-1/3	87.0	269.3	269.0	163.0	156.1	180.2	108.5	113.5	117.8
BMK	101.0	272.5	270.9	163.1	156.8	182.0	111.2	115.6	121.2
MN15	85.1	269.8	269.3	162.5	156.4	180.3	108.7	114.0	118.1
CAM-B3LYP	89.4	271.4	270.4	162.4	156.7	180.7	108.7	114.3	118.4
ωB97X-D	69.4	272.3	270.6	161.6	156.6	181.8	108.8	112.7	118.1
LH-sirPW92	54.1	273.5	270.8	162.5	156.7	181.4	109.5	114.9	120.2
LH-sifPW92	60.0	273.6	270.6	162.1	156.4	181.3	109.6	115.1	120.8
LH646-SVWN	63.3	274.3	271.8	163.5	157.0	182.7	110.3	115.3	121.6
LH670-SVWN	66.8	274.4	271.9	163.6	157.0	182.9	110.4	115.6	121.9

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Tab	le 3.4	N.11 (Comp	uted v	vibratio	nal free	quencies	inten	sities) fo	or $\rm Si_2O_4$	е. +	
Functional				fr	equencie	s in cm ⁻	⁻¹ (intens	sities in l	km/mol)			
B3LYP	117	192	254	260	442	482	591	717	872	899	905	1267
BHLYP	(21) 115	$(43) \\ 196$	$^{(0)}_{260}$	$^{(0)}_{278}$	(115) 467	$^{(0)}_{496}$	(1785) 668	(0) 765	$(0) \\ 919$	$(1786) \\ 1049$	(237) 1206	(0) 1425
	(24)	(38)	(0)	(8)	(138)	(0)	(22)	(187)	(2)	(205)	(230)	(118)
BLYP35	112	189	252	267	449	482	642	732	887	1016	1139	1378
	(22)	(35)	0	(-1)	(122)	(1)	(71)	(137)	(1)	(186)	(45)	(32)
M06	116	195	259	266	271	455	491	756	879	904	945	1310
M06-2X	(22) 113	(44) 194	(0) 253	(0) 267	(7169) 445	(121) 487	(0) 646	(0) 740	(1516) 896	(0) 10.32	(240) 1182	(0) 1393
	(21)	(35)	(0)	8	(126)	0	(73)	(182)	(0)	(189)	(203)	(101)
PBE	111	179	241	245	409	463	683	688	821	868	9999	1215
	(17)	(36)	0	(0)	(88)	(0)	(0)	(2)	(0)	(191)	(447)	(0)
PBE0	117	192	256	260	296	445	487	736	865	883	926	1287
	(22)	(44)	(0)	0	(6608)	(117)	(0)	(0)	(1630)	(0)	(239)	(0)
PBE0-1/3	111	188	252	266	445	483	653	735	887	1026	1141	1384
	(21)	(35)	(0)	(2)	(118)	(1)	(68)	(126)	(3)	(180)	(29)	(24)
BMK	118	201	264	280	448	487	708	770	906	1055	1182	1499
	(20)	(37)	(0)	(9)	(122)	(1)	(64)	(159)	(0)	(188)	(66)	(99)
MN15	108	184	246	260	441	479	655	744	894	1026	1157	1391
	(21)	(34)	(0)	(2)	(118)	(0)	(68)	(148)	(0)	(184)	(72)	(48)
CAM-B3LYP	111	187	252	266	445	480	368	732	884	1014	1156	1382
	(21)	(33)	(0)	(2)	(119)	(0)	(20)	(171)	(0)	(179)	(125)	(73)
ωB97X-D	109	189	253	276	442	477	641	723	881	1042	1161	1370
	(20)	(35)	0)	(9)	(114)	0)	(65)	(175)	(0)	(172)	(146)	(81)
LH-sirPW92	111	1965	254	272	446	473	638	714	864	1002	1050	1355
	(22)	(37)	0)	(9)	(125)	(10)	(65)	(40)	(09)	(193)	(69)	(1)
LH-sifPW92	112	191	253	269	446	452	604	652	827	935	984	1328
	(22)	(39)	(0)	(5)	(125)	(373)	(883)	(57)	(864)	(564)	(198)	(83)
LH646-SVWN	110	196	254	274	446	473	626	719	868	1001	1099	1361
	(22)	(36)	(0)	(9)	(124)	(1)	(22)	(128)	(2)	(194)	(26)	(24)
LH670-SVWN	109	197	249	267	445	475	627	722	872	1009	1122	1368
	(22)	(37)	(0)	(9)	(125)	(0)	(70)	(153)	(0)	(193)	(74)	(45)
^a With def2-TZ	VP bas	is, afte	r optin	nization	ı in C_{2v}	symmet	ry.					

3.A Appendix

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Table 3	B.A.12	2 Com	pute	l vibri	ationa	l freq	uencie	s (inte	nsities) for S	$i_2 O_4^- a$	
Functional				freque	encies i	n cm ⁻¹	(inten	usities in	km/m	ol)		
B3LYP	109	228	304	307	411	499	546	646	872	919	1134	1284
	(15)	(17)	(0)	(8)	(39)	(27)	(80)	(133)	(7)	(146)	(216)	(213)
BHLYP	117	247	326	329	452	536	592	712	934	977	1197	1356
	(18)	(23)	(1)	(11)	(50)	(48)	(85)	(194)	(12)	(174)	(257)	(268)
BLYP35	113	238	315	318	433	517	568	679	903	948	1163	1320
	(17)	(20)	(0)	(10)	(45)	(37)	(77)	(166)	(10)	(160)	(235)	(241)
M06	111	235	311	314	422	510	573	673	000	949	1177	1327
	(15)	(19)	(0)	(9)	(41)	(31)	(71)	(146)	(8)	(152)	(243)	(232)
M06-2X	110	243	320	322	436	524	585	695	914	963	1184	1339
	(17)	(22)	(1)	(10)	(50)	(41)	(78)	(176)	(11)	(172)	(260)	(247)
PBE	100	213	287	289	366	471	528	598	821	878	1098	1230
	(12)	(14)	(0)	(6)	(24)	(13)	(51)	(79)	(2)	(122)	(195)	(166)
PBE0	109	233	310	313	416	508	572	669	$\frac{1}{2}$	940	1157	1303
	(15)	(19)	(1)	(9)	(39)	(27)	(67)	(143)	(8)	(148)	(230)	(218)
PBE0-1/3	112	239	316	320	429	518	586	680	904	958	1176	1325
	(16)	(20)	(1)	(9)	(43)	(33)	(72)	(162)	(10)	(156)	(242)	(235)
BMK	111	240	318	319	430	517	602	700	907	963	1185	1343
	(17)	(22)	(1)	(10)	(46)	(36)	(72)	(173)	(12)	(163)	(239)	(246)
CAM-B3LYP	113	236	313	318	432	516	568	681	901	946	1167	1318
	(16)	(19)	(0)	(9)	(45)	(38)	(75)	(177)	(11)	(157)	(238)	(239)
ωB97X-D	112	237	319	322	429	512	583	683	897	965	1148	1321
	(16)	(20)	(9)	(1)	(42)	(35)	(67)	(180)	(13)	(155)	(234)	(246)
LH-sifPW92	118	245	319	323	430	516	567	673	892	939	1164	1310
	(16)	(20)	(0)	(9)	(43)	(41)	(74)	(167)	(10)	(164)	(248)	(244)
LH-sir $PW92$	123	250	323	324	434	518	567	673	891	939	1164	1309
	(16)	(21)	(8)	(0)	(42)	(43)	(74)	(166)	(10)	(165)	(248)	(243)
LH646-SVWN	112	237	314	321	430	515	556	669	891	940	1152	1303
	(16)	(19)	(0)	(10)	(45)	(41)	(77)	(179)	(13)	(165)	(241)	(253)
LH670-SVWN	120	246	319	323	434	515	561	673	892	935	1167	1308
	(17)	(20)	(0)	(9)	(45)	(45)	(77)	(180)	(12)	(171)	(262)	(247)
^a With def2-TZV	VP bas	is, afte	r optin	nizatio	n in C_{ε}	, symm	etry $(t$	rans isoi	mer).			
		ing our our	- open		()		00-0 (0	- 00100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 -				

	Tał	ole 3.	A.15	Con	npute	d vibra	ationa]	frequ	lencies	inte	nsities) for V	$^{/}_{4}O_{10}^{-}$	е.		
Functional						freque	ncies ir	cm^{-1}	(intens	ities in	km/me	ol)				
B3LYP	466 (23)	522 (90)	(20)	551	567	596 (30)	596 (30)	632 (98)	(148)	650 (148)	(0)	675	1062	1062	1062	1091
BHLYP	467	513	(20) 552	(0) 558	(0) (0)	(06)	(nc) 688	(<i>3</i> 0) 739	752	000 000	910	(u) 943	(1123)	(1137)	(1139)	(0) 1171
	(4)	(6)	(0)	(11)	(15)	(130)	(50)	(111)	(269)	(618)	(020)	(917)	(609)	(664)	(653)	(23)
BLYP35	457	502	535	541	629	665	665	715	727	866	869	888	1090	1100	1101	1131
	(4)	(6)	$\begin{pmatrix} 1 \\ \ddots \end{pmatrix}$	(10)	(14)	(107)	(42)	(91)	(230)	(620)	(516)	(554)	(000)	(604)	(593)	(13)
M06	498	549	549	565	583	621	621	649	672	672	680 (a)	705	1079	1079	1079	1110
VC SUM	(16)	(13)	(13)	(0) 652	(0)	(27)	(27)	(100)	(174)	(174)	(0)	(0)	(582)	(531)	(530)	(0)
X77-00141	(5)	(3)	(0)	(13)	(24)	(139)	(47)	(85)	(248)	(705)	(538)	(937)	(616)	(644)	(627)	(21)
PBE	535	546	561	561	591	614	614	(33)	641	652	(666)	666	1014	1014	1014	1038
	(0)	(0)	(0)	(0)	(2)	(10)	(10)	(0)	(173)	(0)	(243)	(243)	(441)	(393)	(393)	(0)
PBE0	410	502	502	566	580	606	606	647	668	668	679	696	1090	1090	1090	1121
	(17)	(20)	(20)	(0)	(0)	(22)	(22)	(92)	(142)	(142)	(0)	(0)	(590)	(532)	(532)	(0)
PBE0-1/3	476	512	546	548	636	676	677	727	735	863	874	886	1103	1113	1115	1144
	(4)	(8)	(11)	(1)	(12)	(35)	(107)	(85)	(225)	(626)	(502)	(442)	(609)	(602)	(587)	(13)
BMK	359	493	522	544	603	613	631	703	713	872	907	976	1114	1138	1139	1166
	(13)	(19)	(33)	(26)	(140)	(44)	(29)	(409)	(388)	(370)	(249)	(687)	(909)	(592)	(595)	(42)
CAM-B3LYP	455	504	529	542	630	668	668	716	727	860	870	882	1097	1104	1106	1135
	(2)	(-)	(1)	(10)	(13)	(112)	(36)	(78)	(227)	(637)	(510)	(451)	(605)	(598)	(586)	(8)
ωB97X-D	437	498	504	533	619	657	658	705	712	840	849	866	1091	1097	1099	1129
	0	0	(4)	(12)	(15)	(32)	(122)	(81)	(232)	(628)	(499)	(439)	(615)	(591)	(578)	(5)
LH-sifPW92	455	492	531	535	606	662	664	702	705	731	816	819	1085	1091	1093	1122
	(4)	(3)	(1)	(11)	(5)	(35)	(109)	(184)	(56)	(254)	(324)	(419)	(621)	(594)	(567)	(3)
LH-sirPW92	482	485	527	530	616	665	666	710	711	776	838	840	1090	1098	1099	1129
	(3)	(9)	(1)	(12)	(6)	(39)	(111)	(80)	(192)	(390)	(457)	(357)	(633)	(605)	(577)	(4)
LH646-SVWN	464	484	516	524	612	656	658	702	706	791	834	840	1074	1085	1086	1115
	(3)	(-	(1)	(12)	(10)	(42)	(111)	(74)	(212)	(476)	(459)	(364)	(000)	(590)	(573)	(10)
LH670-SVWN	476	489	517	524	614	656	658	703	709	809	839	847	1076	1086	1087	1116
	(4)	(9)	(0)	(12)	(11)	(39)	(113)	(84)	(218)	(547)	(472)	(376)	(604)	(590)	(580)	(10)
^a With def2-T2 $400 \mathrm{cm^{-1}}$ are sl	ZVP Ł 10wn.	asis a	fter c	ptimiz	ation	withou	t symm	letry (d	converg	ing to	C_s syl	mmetry	r). Onl	y vibra	ations a	bove

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Functional			upuve	frequi	encies i	n cm ⁻	$\frac{1}{1}$ (inter	nsities ir	km/m		204.	
B3LYP	112	194	208	328	353	389	442	639	789	852	1126	1145
	(24)	(14)	(2)	(1)	(38)	(19)	(3)	(237)	(147)	(141)	(324)	(59)
BHLYP	118	197	211	346	380	420	450	681	839	930	1203	1220
	(28)	(18)	(4)	(1)	(56)	(16)	(2)	(305)	(212)	(289)	(512)	(0)
BLYP35	114	195	209	337	366	406	441	662	813	896	1166	1183
	(26)	(16)	(3)	(1)	(48)	(17)	(3)	(274)	(179)	(230)	(419)	(31)
M06	111	191	217	337	349	386	431	636	799	852	1139	1155
	(25)	(16)	(2)	(1)	(36)	(26)	(6)	(228)	(167)	(105)	(395)	(14)
M06-2X	134	215	220	346	376	414	432	659	822	806	1202	1222
	(23)	(13)	(3)	(1)	(58)	(16)	(1)	(297)	(206)	(282)	(470)	(45)
PBE	115	201	202	294	313	407	443	520	733	748	1080	1092
	(19)	(8)	(0)	(42)	(0)	(0)	(63)	(0)	(106)	(0)	(262)	(0)
PBE0	115	198	212	337	360	401	454	658	812	881	1159	1176
	(24)	(14)	(2)	(1)	(40)	(18)	(3)	(250)	(162)	(178)	(370)	(45)
PBE0-1/3	116	199	214	342	368	411	456	671	827	906	1183	1199
	(25)	(15)	(3)	(1)	(45)	(17)	(3)	(269)	(181)	(229)	(425)	(27)
BMK	116	197	214	343	371	410	554	735	885	971	1168	1193
	(28)	(18)	(3)	(1)	(46)	(19)	(6)	(260)	(189)	(276)	(420)	(79)
CAM-B3LYP	115	197	211	337	363	404	446	666	817	897	1171	1190
	(25)	(14)	(3)	(1)	(45)	(17)	(2)	(275)	(176)	(218)	(393)	(55)
ωB97X-D	115	198	216	341	364	404	468	682	821	894	1178	1200
	(26)	(15)	(2)	(1)	(42)	(21)	(2)	(267)	(180)	(213)	(388)	(72)
LH-sifPW92	103	199	215	343	363	404	446	653	822	889	1173	1189
	(25)	(14)	(3)	(1)	(45)	(21)	(3)	(268)	(180)	(196)	(410)	(64)
LH-sir $PW92$	102	195	214	341	361	401	448	651	818	882	1165	1182
	(25)	(15)	(3)	(1)	(44)	(21)	(3)	(262)	(174)	(180)	(391)	(68)
LH646-SVWN	108	202	209	339	363	402	446	650	810	878	1157	1170
	(24)	(15)	(4)	(1)	(49)	(19)	(3)	(272)	(179)	(192)	(447)	(10)
LH670-SVWN	124	210	212	340	365	402	436	646	812	882	1157	1172
	(24)	(15)	(3)	(1)	(48)	(21)	(3)	(272)	(181)	(206)	(452)	(1)
^a With def2-TZ	VP bas	is after	optim:	iizatior	$1 in C_s$	symme	etry (tr	ans isor	ner).			
	1	10 01001	Porte		() 5		101 J 101	WICO IDOI	. (

Table 3.A.14 Computed vibrational frequencies (intensities) for $V_2O_4^+$.^a
Tab	le 3.A	15 C	ompute	ed vibra	ational	freque	encies	(intens	ities) fo	or Ti_2C	\mathbf{a}^{-} .a	
Functional				freque	encies in	cm^{-1} (intensi	ties in k	m/mol)			
B3LYP	09	106	132	167	248	295	346	499	684	698	938	070
	(85)	(321)	(390)	(27)	(0)	(140)	(27)	(1)	(9)	(214)	(958)	(2)
BHLYP	52	107	166	264	271	325	455	551	775	802	957	1014
	(40)	(23)	(39)	(0)	(100)	(5)	(11)	(263)	(316)	(311)	(1137)	(116)
BLYP35	00	116	166	258	260	323	458	532	749	771	943	989
	(28)	(26)	(35)	(64)	(0)	(3)	(8)	(192)	(273)	(182)	(1079)	(88)
M06	80	123	169	200	238	338	498	517	695	716	949	984
	(23)	(0)	(28)	(108)	(0)	(0)	(99)	(0)	(0)	(218)	(1023)	(0)
M06-2X	51	115	159	255	261	322	462	551	747	777	951	1009
	(26)	(25)	(35)	(74)	(0)	(4)	(5)	(259)	(309)	(313)	(1091)	(135)
PBE	71	132	165	246	248	338	494	516	662	664	913	937
	(9)	(0)	(21)	(0)	(43)	(0)	(0)	(207)	(0)	(162)	(020)	(0)
PBE0	76	124	168	252	258	332	479	491	735	741	953	986
	(20)	(32)	(30)	(38)	(0)	(22)	(4)	(30)	(234)	(33)	(666)	(71)
PBE0-1/3	70	124	168	260	263	336	472	543	754	777	958	1000
	(22)	(31)	(34)	(41)	(0)	(5)	(9)	(192)	(265)	(175)	(1017)	(121)
BMK	69	130	149	247	257	318	324	475	616	684	998	1036
	(24)	(22)	(23)	(0)	(50)	(16)	(10)	(278)	(292)	(247)	(1106)	(12)
CAM-B3LYP	67	120	165	258	259	329	464	546	751	775	952	995
	(24)	(28)	(33)	(53)	(1)	(4)	(9)	(213)	(267)	(202)	(1049)	(91)
ωB97X-D	80	133	174	263	267	335	456	551	739	768	957	998
	(23)	(27)	(32)	(49)	(1)	(4)	(4)	(270)	(268)	(236)	(983)	(127)
LH-sifPW92	87	132	175	267	268	329	458	540	750	764	950	993
	(26)	(25)	(32)	(45)	(0)	(9)	(2)	(190)	(275)	(161)	(1043)	(107)
LH-sirPW92	84	134	173	265	266	329	461	538	746	758	948	989
	(28)	(20)	(31)	(42)	(0)	(6)	(9)	(161)	(266)	(126)	(1025)	(66)
LH646-SVWN	84	127	174	265	265	327	445	534	743	761	938	982
	(23)	(28)	(33)	(56)	(0)	(4)	(8)	(221)	(276)	(186)	(1008)	(112)
LH670-SVWN	68	115	172	259	262	322	439	526	743	761	935	982
	(26)	(26)	(34)	(09)	(0)	(3)	(8)	(229)	(283)	(198)	(1037)	(108)
^a With def2-TZ ^A	VP bas	is after a	optimiza	tion in 6	\mathcal{C}_s symn	netry $(t$	<i>rans</i> isc	omer).				

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3.A Appendix

^a With def2-TZV 400 cm^{-1} are sh		LH670-SVWN		LH646-SVWN		LH-sirPW92		LH-sifPW92		ωB97X-D		CAM-B3LYP		MN15		BMK		PBE0-1/3		PBE0		PBE		M06-2X		M06		BLYP35		BHLYP		B3LYP	Functional
VP bas own.	(1)	447	(1)	445	(1)	444	(1)	445	(0)	445	(0)	443	(0)	434	0	452	(0)	450	(1)	438	(7)	397	(1)	459	(2)	423	(0)	448	(1)	467	(1)	426	
sis afte	(2)	452	(2)	454	(2)	464	(2)	464	(1)	481	(2)	465	(1)	463	(0)	558	(2)	476	(2)	470	(0)	437	(1)	461	(1)	467	(2)	464	(2)	477	(2)	455	
r optim	(184)	622	(179)	621	(161)	619	(175)	627	(190)	651	(199)	644	(170)	631	(202)	721	(197)	648	(167)	627	(0)	490	(231)	645	(89)	571	(204)	642	(236)	659	(148)	604	frequen
ization ii	(163)	778	(160)	779	(157)	787	(161)	791	(159)	793	(163)	786	(156)	791	(168)	799	(163)	799	(147)	788	(0)	727	(188)	772	(6)	777	(165)	779	(191)	799	(138)	762	cies in ci
n C_{2v} sy	(101)	811	(88)	808	(51)	803	(73)	814	(123)	831	(137)	834	(81)	819	(174)	852	(141)	844	(72)	812	(104)	729	(253)	848	(135)	783	(162)	837	(239)	873	(41)	781	m^{-1} (int
mmetry.	(435)	1022	(446)	1023	(510)	1039	(510)	1047	(515)	1034	(502)	1049	(496)	1053	(519)	1128	(450)	1053	(472)	1035	(382)	961	(402)	1053	(440)	1017	(430)	1036	(288)	1040	(458)	1006	ensities
Only vi	(232)	1036	(223)	1037	(190)	1055	(209)	1061	(226)	1042	(206)	1065	(223)	1062	(260)	1152	(246)	1066	(194)	1054	(0)	995	(299)	1056	(202)	1030	(244)	1050	(280)	1044	(154)	1031	in km/r
brations	(118)	1067	(106)	1067	(49)	1079	(59)	1088	(60)	1075	(63)	1090	(67)	1093	(72)	1169	(113)	1099	(65)	1075	(0)	866	(167)	1109	(72)	1059	(124)	1082	(270)	1121	(48)	1044	nol)
above	(396)	1075	(399)	1074	(443)	1082	(442)	1091	(430)	1077	(441)	1095	(408)	1097	(453)	1185	(407)	1106	(409)	1082	(438)	1006	(438)	1114	(366)	1065	(396)	1091	(388)	1128	(402)	1053	

Table 3.A.16 Computed vibrational frequencies (intensities) for $Cr_2O_6^-$.^a

The idea of replacing the system-wide RS parameter by a function is straightforward in light of the analogous global vs. local hybrid functionals. A first step was the non-self-consistent implementation in combination with LDA at SR and full LDA correlation by Krukau et al.⁸⁶ A full self-consistent implementation within this scheme, however, was considered too costly¹⁶⁶ and the concept has been abandoned since then, despite promising first results.

This chapter is the second of the two main topics of this work. It contains the derivation (Section 4.1), implementation (Section 4.2) and assessment (Section 4.3) of self-consistent energy calculations for LRSH exchange functionals with common ingredients from semi-local functionals.

4.1 Theoretical Background

Applying the position-dependent RSF $\omega = \omega(\mathbf{r})$ in the split Coulomb operator from Eq. (2.2.24) yields

$$\frac{1}{r_{12}} = \frac{\operatorname{erf}\left(\omega(\boldsymbol{r}_1) \cdot r_{12}\right)}{r_{12}} + \frac{1 - \operatorname{erf}\left(\omega(\boldsymbol{r}_1) \cdot r_{12}\right)}{r_{12}} .$$
(4.1.1)

We do not adjust the correlation functionals, therefore the XC energy is

$$E_{\rm XC}^{\rm LRS} = E_{\rm X}^{\rm LR} + E_{\rm X}^{\rm SR} + E_{\rm C}^{\rm SL} = \int \varepsilon_{\rm X}^{\rm LR} + \varepsilon_{\rm X}^{\rm SR} + \varepsilon_{\rm C}^{\rm SL} \,\mathrm{d}\boldsymbol{r} \quad . \tag{4.1.2}$$

We use XX in the LR regime and DFT functionals at SR. In the following subsections, the energy terms and the contributions to the KS matrix will be derived.

4.1.1 Long-Range Exact Exchange

Here we use the abbreviations $\varphi_i^1 = \varphi_i(\mathbf{r}_1)$, $\chi_{\mu}^1 = \chi_{\mu}(\mathbf{r}_1)$, and $\omega_1 = \omega(\mathbf{r}_1)$. The error function is introduced to the repulsion integrals of the LR XX energy (cf. Eq. (2.3.24))

$$E_{\rm X}^{\rm LR} = -\frac{1}{2} \sum_{ij} \int \varphi_i^{\mathbf{1}} \varphi_j^{\mathbf{1}} \int \varphi_i^{\mathbf{2}} \varphi_j^{\mathbf{2}} \frac{\operatorname{erf}(\omega_1 r_{12})}{r_{12}} \, \mathrm{d}\boldsymbol{r}_2 \, \mathrm{d}\boldsymbol{r}_1 \, ,$$

$$= -\frac{1}{2} \sum_{\mu\nu\kappa\lambda} D_{\mu\kappa} D_{\nu\lambda} \int \chi_{\mu}^{\mathbf{1}} \chi_{\nu}^{\mathbf{1}} \int \chi_{\kappa}^{\mathbf{2}} \chi_{\lambda}^{\mathbf{2}} \frac{\operatorname{erf}(\omega_1 r_{12})}{r_{12}} \, \mathrm{d}\boldsymbol{r}_2 \, \mathrm{d}\boldsymbol{r}_1 \, .$$
(4.1.3)

Applying the FDO (cf. Eq. (2.3.26)) yields

$$\frac{\delta E_{\mathbf{X}}^{\mathrm{LR}}}{\delta \varphi_i^{\mathbf{1}}} = -\sum_j \varphi_j^{\mathbf{1}} \int \varphi_i^{\mathbf{2}} \varphi_j^{\mathbf{2}} \frac{\operatorname{erf}(\omega_1 r_{12}) + \operatorname{erf}(\omega_2 r_{12})}{r_{12}} \,\mathrm{d}\boldsymbol{r}_2 \tag{4.1.4a}$$

$$-\frac{2}{\sqrt{\pi}}\frac{\delta\omega_1}{\delta\varphi_i^1}\sum_{jk}\varphi_j^1\varphi_k^1\int\varphi_j^2\varphi_k^2\exp\left(-\omega_1^2r_{12}^2\right)\mathrm{d}\boldsymbol{r}_2 \quad (4.1.4b)$$

The first term originates from the derivation w.r.t. the MOs, and subsequent renaming and regrouping. It is a non-local LR XX potential term (cf. Eq. (2.3.28b)).

As for LHs in Section 2.3.3, we change into the AO basis, calculate just the term with ω_1 , and add the transposed matrix for the KS matrix contributions (cf. Eqs. (2.3.14) and (2.3.29))

$$\mathcal{K}_{\mu\kappa}^{\mathrm{erf}} = \overline{\mathcal{K}_{\mu\kappa}^{\mathrm{erf}}} + \overline{\mathcal{K}_{\kappa\mu}^{\mathrm{erf}}} , \qquad (4.1.5)$$

$$\overline{\mathcal{K}_{\mu\kappa}^{\mathrm{erf}}} = -\int \sum_{\nu\lambda} D_{\nu\lambda} \chi_{\mu}^{1} \chi_{\nu}^{1} \int \chi_{\kappa}^{2} \chi_{\lambda}^{2} \frac{\mathrm{erf}(\omega_{1}r_{12})}{r_{12}} \,\mathrm{d}\boldsymbol{r}_{2} \,\mathrm{d}\boldsymbol{r}_{1} \,\,. \tag{4.1.6}$$

The last term in Eq. (4.1.4) stems from differentiating the error function, where the denominator r_{12} is canceled by factors of the chain rule. Hence, the inner integral contains an overlap integral instead of the repulsion integral, adjusted by an exponential function. These contributions to the KS matrix are local and multiplicative. They are similar those containing the derivative of the LMF in Eq. (2.3.28) and can be treated together with the SL exchange energy density.

4.1 Theoretical Background

Assuming that the RSF depends only on the density, the result would be

$$\mathcal{K}_{\mu\kappa}^{\exp} = -\frac{2}{\sqrt{\pi}} \int \frac{\partial \omega_1}{\partial \rho} \chi_{\mu}^{\mathbf{1}} \chi_{\kappa}^{\mathbf{1}} \sum_{\nu \lambda \gamma \eta} D_{\nu \lambda} D_{\gamma \eta} \chi_{\nu}^{\mathbf{1}} \chi_{\gamma}^{\mathbf{1}} \int \chi_{\lambda}^{\mathbf{2}} \chi_{\eta}^{\mathbf{2}} \exp\left(-\omega_1^2 r_{12}^2\right) \mathrm{d}\boldsymbol{r}_2 \, \mathrm{d}\boldsymbol{r}_1 \quad .$$

$$(4.1.7)$$

For other quantities like derivatives of the density, this must be adjusted accordingly. Rephrasing (cf. Section 2.4.2) both expressions yields

$$\overline{\mathcal{K}_{\mu\kappa}^{\mathrm{erf}}} = -\sum_{g} \sum_{\lambda} \mathcal{X}_{\mu g} \mathcal{F}_{\lambda g} \mathcal{A}_{\kappa\lambda g}^{\mathrm{erf}} = -\sum_{g} \mathcal{X}_{\mu g} \mathcal{G}_{\kappa g}^{\mathrm{erf}}$$
(4.1.8)

$$\mathcal{K}_{\mu\kappa}^{\exp} = -\sum_{g} \frac{\partial \omega_{g}}{\partial \rho} \chi_{\mu}^{1} \chi_{\kappa}^{1} \sum_{\eta\lambda} \mathcal{F}_{\eta g} \mathcal{F}_{\lambda g} \mathcal{A}_{\eta\lambda g}^{\exp} = \sum_{g} \frac{\partial \omega_{g}}{\partial \rho} \chi_{\mu}^{1} \chi_{\kappa}^{1} \sum_{\eta} \mathcal{F}_{\eta g} \mathcal{G}_{\eta g}^{\exp} \qquad (4.1.9)$$

$$= -\sum_{g} \frac{\partial \omega_g}{\partial \rho} \chi^1_{\mu} \chi^1_{\kappa} \mathcal{E}_g^{\text{exp}}$$
(4.1.10)

with the intermediate quantities

$$\mathcal{A}_{\kappa\lambda g}^{\mathrm{erf}} = \int \chi_{\kappa}^{2} \chi_{\lambda}^{2} \frac{\mathrm{erf}\left(\omega_{g} r_{g2}\right)}{r_{g2}} \,\mathrm{d}\boldsymbol{r}_{2} \,\,, \qquad (4.1.11)$$

$$\mathcal{G}_{\kappa g}^{\mathrm{erf}} = \sum_{\lambda} \mathcal{F}_{\lambda g} \mathcal{A}_{\kappa \lambda g}^{\mathrm{erf}} , \qquad (4.1.12)$$

$$\mathcal{A}_{\eta\lambda g}^{\exp} = \frac{2}{\sqrt{\pi}} \int \chi_{\kappa}^{2} \chi_{\lambda}^{2} \exp\left(-\omega_{g}^{2} r_{g2}^{2}\right) \mathrm{d}\boldsymbol{r}_{2} \quad , \qquad (4.1.13)$$

$$\mathcal{G}_{\eta g}^{\exp} = \sum_{\lambda} \mathcal{F}_{\eta g} \mathcal{A}_{\eta \lambda g}^{\exp} , \qquad (4.1.14)$$

$$\mathcal{E}_{g}^{\exp} = \sum_{\eta} \mathcal{F}_{\eta g} \mathcal{G}_{\eta g}^{\exp} . \qquad (4.1.15)$$

4.1.2 Short-Range Semi-Local Exchange

The exact expression for the (global) LDA exchange at SR has been derived (among others) by Gill, Adamson, and Pople,¹⁰⁵

$$E_{\rm X}^{\rm LDA} = \int \varepsilon_{\rm X}^{\rm LDA} \,\mathrm{d}\boldsymbol{r} = \frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \int \rho^{4/3} F_{\rm X}^{\rm LDA}(\lambda) \,\mathrm{d}\boldsymbol{r} \quad , \tag{4.1.16}$$

$$F_{\rm X}^{\rm LDA}(\lambda) = 1 - \frac{2}{3}\lambda \left[2\sqrt{\pi} \operatorname{erf}\left(\frac{1}{\lambda}\right) - 3\lambda + \lambda^3 + (2\lambda - \lambda^3) \exp\left(-\frac{1}{\lambda^2}\right) \right], \quad (4.1.17)$$

with the reduced RS parameter $\lambda = \omega/k_{\rm F}$ and the Fermi wave vector $k_{\rm F} = (3\pi^2 \rho)^{\frac{1}{3}}$.

We further use a GGA variant proposed by Toulouse, Colonna, and Savin,¹⁶⁷

$$E_{\rm X}^{\rm PBE} = \int \varepsilon_{\rm X}^{\rm PBE} \,\mathrm{d}\boldsymbol{r} = \int \varepsilon_{\rm X}^{\rm LDA} F_{\rm X}^{\rm PBE}(\lambda) \,\mathrm{d}\boldsymbol{r} \quad , \qquad (4.1.18)$$

$$F_{\rm X}^{\rm PBE}(\lambda) = 1 + \kappa - \frac{\kappa}{1 + b(\lambda)s^2/\kappa} , \qquad (4.1.19)$$

where $\kappa = -C\rho^{4/3}/\varepsilon_{\rm X}^{\rm LDA}$ is determined by the Lieb-Oxford bound with $C = 1.6358.^{94}$ The parameter

$$b(\lambda) = \frac{-c_1 + c_2 \exp(\lambda^{-2})}{c_3 + 54c_4 \exp(\lambda^{-2})}, \qquad (4.1.20a)$$

$$c_1 = 1 + 22\lambda^2 + 144\lambda^4 , \qquad (4.1.20b)$$

$$c_2 = 2\lambda^2 \left(-7 + 72\lambda^2\right),$$
 (4.1.20c)

$$c_3 = -864\lambda^4 (-1+2\lambda^2)$$
, (4.1.20d)

$$c_4 = \lambda^2 \left[-3 - 24\lambda^2 + 32\lambda^4 + 8\lambda\sqrt{\pi} \operatorname{erf}\left(\lambda^{-1}\right) \right], \qquad (4.1.20e)$$

has been obtained from the second-order gradient coefficient for the SR exchange hole. This does, however, not reduce to the commonly employed PBE exchange for $\omega \to 0$ because the constraints used here are different. By introducing a constant prefactor $C_b = 2.5401$ for $b(\lambda)$ the resulting $b(\lambda \to 0) = \frac{7}{81}$ can be scaled up to the "original" $\mu = 0.21852$. We refer to the exchange given by the above equations as sPBE, and the rescaled version as oPBE.

We choose those two exchange functionals (LDA and PBE) as the first targets for our LRSH implementation, changing their constant RS parameter into an RSF.

LRSH for LDA

The functional derivative results in partial derivatives of the exchange energy density. If we consider only the density, we get for LDA

$$\frac{\partial \varepsilon_{\rm X}^{\rm LDA}}{\partial \rho} = \frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \left(\frac{4}{3} \rho^{1/3} F_{\rm X}^{\rm LDA} + \rho^{4/3} \frac{\partial F_{\rm X}^{\rm LDA}}{\partial \lambda} \frac{\partial \lambda}{\partial \rho}\right), \qquad (4.1.21)$$

$$\frac{\partial F_{\rm X}^{\rm LDA}}{\partial \lambda} = -\frac{4}{3} \left[\sqrt{\pi} \operatorname{erf}\left(\frac{1}{\lambda}\right) - 3\lambda + 2\lambda^3 + \left(\lambda - 2\lambda^3\right) \exp\left(-\frac{1}{\lambda^2}\right) \right], \quad (4.1.22)$$

$$\frac{\partial \lambda}{\partial \rho} = -\frac{1}{3\rho k_{\rm F}} \frac{\partial \omega}{\partial \rho} + \frac{1}{k_{\rm F}} \frac{\partial \omega}{\partial \rho} \,. \tag{4.1.23}$$

But the (reduced) RSF may also depend on other quantities $Q \in (\mathbb{Q} \setminus \rho)$, cf. Eq. (2.3.16), implying

$$\frac{\partial \varepsilon_{\rm X}^{\rm LDA}}{\partial Q} = \frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \left(\rho^{4/3} \frac{\partial F_{\rm X}^{\rm LDA}}{\partial \lambda} \frac{\partial \lambda}{\partial Q}\right), \qquad (4.1.24)$$

$$\frac{\partial \lambda}{\partial Q} = \frac{1}{k_{\rm F}} \frac{\partial \omega}{\partial Q} \,. \tag{4.1.25}$$

LRSH for PBE

The PBE functional builds upon the results from last section since $\varepsilon_{\rm X}^{\rm LDA}$ appears both explicitly in the integral of Eq. (4.1.18) and implicitly within κ (Eq. (4.1.19)), thus all of those may depend on $Q \in \mathbb{Q}$ through λ in $\varepsilon_{\rm X}^{\rm LDA}$. The derivatives are

$$\frac{\partial \varepsilon_{\rm X}^{\rm PBE}}{\partial Q} = \frac{\partial \varepsilon_{\rm X}^{\rm LDA}}{\partial Q} F_{\rm X}^{\rm PBE} + \varepsilon_{\rm X}^{\rm LDA} \frac{\partial F_{\rm X}^{\rm PBE}}{\partial Q} , \qquad (4.1.26)$$

$$\frac{\partial F_{\rm X}^{\rm PBE}}{\partial Q} = \left(\frac{bs^2}{\kappa + bs^2}\right)^2 \frac{\partial \kappa}{\partial Q} + \left(\frac{\kappa^2 s^2}{\kappa + bs^2}\right)^2 \frac{\partial b}{\partial \lambda} \frac{\partial \lambda}{\partial Q} + \left(\frac{\kappa^2 b}{\kappa + bs^2}\right)^2 \frac{\partial s^2}{\partial Q} \,. \tag{4.1.27}$$

The derivative of b is a bit unwieldy:

$$\frac{\partial b}{\partial \lambda} = \frac{d_1}{d_2} + \frac{d_3 d_4}{d_2^2} , \qquad (4.1.28a)$$

$$d_{1} = -2\lambda^{-3} \left(-7\lambda^{2} + 18\lambda^{4} \right) e^{\lambda^{-2}} - 22\lambda - 72\lambda^{3} + \left(-14\lambda + 72\lambda^{3} \right) e^{\lambda^{-2}} , \quad (4.1.28b)$$

$$d_2 = 27\lambda^2 d_5 e^{\lambda^2} + 54\lambda^4 (2 - \lambda^2) , \qquad (4.1.28c)$$

$$d_3 = -11\lambda^2 - 18\lambda^4 + (-7\lambda^2 + 18\lambda^4)e^{\lambda^{-2}} - 2, \qquad (4.1.28d)$$

$$d_4 = 54\lambda^{-1}d_5e^{\lambda^{-2}} - 54\lambda d_5e^{\lambda^{-2}} - 27\lambda^2 d_6 - 216\lambda^3 (2-\lambda^2) + 108\lambda^5 , \quad (4.1.28e)$$

$$d_5 = 4\sqrt{\pi\lambda}\operatorname{erf}\left(\lambda^{-1}\right) - 6\lambda^2 + 2\lambda^4 - 3, \qquad (4.1.28f)$$

$$d_6 = -12\lambda + 8\lambda^3 + 4\sqrt{\pi} \operatorname{erf}(\lambda^{-1}) - 8e^{-\lambda^{-2}}.$$
(4.1.28g)

4.1.3 Range-Separation Function

The RSF ω is an inverse length that screens the interelectronic distance r_{12} within the error function. Therefore we use the inverse Wigner-Seitz radius $1/r_{\rm WS} = \left[\frac{4}{3}\pi\rho\right]^{1/3}$ for the length scale. Starting from a gradient expansion in previous work by Krukau et al.,⁸⁶ the best results were obtained with $\omega = \beta \frac{\nabla\rho}{r_{\rm WS}}$. A more general ansatz is obtained by adding the reduced kinetic energy density t (cf. Eqs. (2.2.16) and (2.2.20)) to the reduced density gradient s,

$$\omega = C_0 + \frac{C_1 + C_2 \cdot s + C_3 \cdot t}{r_{\rm WS}} , \qquad (4.1.29)$$

where C_0 through C_3 are adjustable parameters. This form allows for simpler variants to be investigated as well, e.g. a constant $\omega = C_0$, or the truncated gradient expansion $\omega = C_1 \cdot s/r_{\rm WS}$ mentioned above.

Now we can take the derivative of the chosen RSF w.r.t. the quantities it depends

on (\mathbb{Q} in Eq. (2.3.16)),

$$\frac{\partial\omega}{\partial\rho} = C_1 \left(\frac{4\pi}{81\rho^2}\right)^{1/3} - C_2 \frac{\gamma^{1/2}}{(18\pi)^{1/3}\rho^2} - C_3 \frac{\pi^{1/3}\gamma}{1296^{1/3}\rho^{5/3}\tau} , \qquad (4.1.30)$$

$$\frac{\partial\omega}{\partial\gamma} = C_2 \frac{1}{\left(144\pi\right)^{1/3} \rho \gamma^{1/2}} + C_3 \frac{\pi^{1/3}}{384^{1/3} \rho^{2/3} \tau} , \qquad (4.1.31)$$

$$\frac{\partial\omega}{\partial\tau} = -C_3 \frac{\pi^{1/3}\gamma}{384^{1/3}\rho^{2/3}\tau^2} \,. \tag{4.1.32}$$

4.2 Implementation

4.2.1 Calculating XC in xclrs()

The LRSH SCF subroutine xclrs() is similar to xclhyb() for LHs (Section 2.6.1). The structure can be seen in Table 4.1. For each block of grid points the values and derivatives of the AOs are calculated in funct_2(). These are used to calculate the electron density, its squared derivative, and τ (ondes_3()), as well as the RSF (rsf_1(), Eq. (4.1.29)) and \mathcal{F} (calc_ftg(), Eq. (2.4.3)). Then \mathcal{G}^{erf} and \mathcal{G}^{exp} (Eqs. (4.1.12) and (4.1.14)) are determined in lrs_a() and used in get_exx() to calculate both $\varepsilon_{\text{X}}^{\text{ex}}$ and \mathcal{E}^{exp} (Eqs. (4.1.3) and (4.1.15)). They are combined in lrs_1() with the RSF and its derivatives to get the XC energy as well as the operator terms (O, O', O'', cf. Section 2.6.1). As for LHs (Eq. (2.6.1)), the operators include the derivatives of the SL quantities $\Theta \in \{\omega, \varepsilon_{\text{X}}^{\text{SL}}, \varepsilon_{\text{C}}^{\text{SL}}\}$ w.r.t. $Q \in \mathbb{Q}$ (Eq. (2.3.16)). They are multiplied with the basis functions and their derivatives to get part of the KS matrix (onf_3()),

$$\frac{\partial \Theta}{\partial Q} \rightarrow \begin{cases} O\chi_{\mu}\chi_{\nu} \\ O'\nabla\chi_{\mu}\chi_{\nu} \\ O''\nabla^{\mathrm{T}}\chi_{\mu}\nabla\chi_{\nu} \end{cases} \rightarrow F^{\mathrm{O}}_{\mu\nu} .$$
(4.2.1)

The routine get_kmat() provides the other part, \mathcal{K}^{erf} , stemming from the symmetric multiplication of \mathcal{G}^{erf} with the basis functions (Eqs. (4.1.5) and (4.1.8)).

Together they give the full XC contribution to the KS matrix,

$$\boldsymbol{F}^{\mathrm{XC}} = \boldsymbol{F}^{\mathrm{O}} + \mathcal{K}^{\mathrm{erf}} \,. \tag{4.2.2}$$

 Table 4.1 General flow of information for subroutines regarding LRSH SCF (without grid). See Section 4.2.1.

Subroutine	Input	Output
xclrs()	D	$E_{\rm XC}, \ \boldsymbol{F}^{\rm XC}$
funct_2()		χ, χ'
ondes_3()	D, χ, χ'	$\rho, \nabla \rho, \tau$
rsf_1()	$\rho, \nabla \rho, \tau$	$\omega, \frac{\partial \omega}{\partial Q}$
calc_ftg()	$oldsymbol{D},\chi$	\mathcal{F}^{-1}
lrs_a()	\mathcal{F},ω	$\mathcal{G}^{ ext{erf}},\mathcal{G}^{ ext{exp}}$
get_exx()	${\cal F},{\cal G}^{ m erf},{\cal G}^{ m exp}$	$arepsilon_{\mathrm{X}}^{\mathrm{ex}},\mathcal{E}^{\mathrm{exp}}$
lrs_1()	$oldsymbol{D},\omega,rac{\partial\omega}{\partial Q},arepsilon_{\mathrm{X}}^{\mathrm{ex}},\mathcal{E}^{\mathrm{exp}}$	$E_{\rm XC}, O, O', O''$
onf_2()	$\boldsymbol{D}, O, O', O'', \chi, \chi'$	F^{O}
get_kmat()	$\chi, \mathcal{G}^{\mathrm{erf}}$	$\mathcal{K}^{ ext{erf}}$

4.2.2 Calculating $\mathcal{A}^{\mathrm{erf}}$ and $\mathcal{A}^{\mathrm{exp}}$ in lrs_a()

The structure of $lrs_a()$ is shown in Algorithm 3. It is similar to numpot() (cf. Section 2.6.2) but extended because the RSF is used directly, whereas the multiplicative LMF was applied afterwards. While the shell and primitive loops are used as before, the grid point loop now includes the preparation of the RSF and the additional calculation of \mathcal{A}^{exp} (cf. Eq. (4.1.13)). It is an overlap integral between the primitives for atoms A and B, and a third, *s*-type primitive at G with the squared RSF as the exponential coefficient. We apply the Gaussian product rule twice, first to merge A and B to the center of charge P, then P and G to C. We then use Gauss-Hermite quadrature (see Section 2.4.3) to calculate the necessary overlap integrals for the shell types of A and B resulting in elements $\mathcal{A}_{\kappa\lambda g}^{exp}$.

The RSF is provided to lrs_v() as a "reduced mass"-like coefficient

$$\frac{1}{\alpha_{\omega}} = \frac{1}{\alpha_P} + \frac{1}{\omega^2} \tag{4.2.3}$$

and within the prefactor as $\sqrt{\alpha_{\omega}/\alpha_{P}}$, where $\alpha_{P} = \alpha_{A} + \alpha_{B}$ as in Eq. (2.3.5). The returned elements $\mathcal{A}_{\kappa\lambda g}^{\text{erf}}$ and $\mathcal{A}_{\eta\lambda g}^{\text{exp}}$ are summed up for all primitive pairs within the shell pair and multiplied with \mathcal{F} to get $\mathcal{G}_{\kappa g}^{\text{erf}}$ and $\mathcal{G}_{\eta g}^{\text{exp}}$ (Eqs. (4.1.12) and (4.1.14)).

 $\mathcal{L}_{\mathcal{I}} \leftarrow angular quantum number of \mathcal{I}$ $\mathcal{L}_{\mathcal{J}} \leftarrow angular quantum number of \mathcal{J}$ for primitive $\mathcal{P}_{\mathcal{I}}$ do for primitive $\mathcal{P}_{\mathcal{J}}$ do for grid point g do $\omega^2, \alpha_\omega \leftarrow \text{preparation of RSF } \omega$ $\mathcal{A}^{\exp} \leftarrow \text{overlap integrals for } \boldsymbol{A}, \, \boldsymbol{B} \text{ and } \boldsymbol{G} \text{ with } \omega^2$ $\mathcal{A}^{\text{erf}} \leftarrow \text{repulsion integrals via Boys functions with } \alpha_{\omega}$ end sum up over all primitives $\mathcal{P}_{\mathcal{J}}$ end sum up over all primitives $\mathcal{P}_{\mathcal{I}}$ end $\mathcal{G}^{\mathrm{erf}} \gets \mathrm{multiply} \ \mathcal{A}^{\mathrm{erf}} \ (\mathcal{L}_{\mathcal{I}} \mathcal{L}_{\mathcal{J}}) \ \mathrm{with} \ \mathcal{F}$ $\mathcal{G}^{\mathrm{erf}} \leftarrow \mathrm{multiply} \ \mathcal{A}^{\mathrm{erf}} \ (\mathcal{L}_{\mathcal{J}} \mathcal{L}_{\mathcal{I}}) \ \mathrm{with} \ \mathcal{F}$ $\mathcal{G}^{exp} \leftarrow \text{multiply } \mathcal{A}^{exp} (\mathcal{L}_{\mathcal{I}} \mathcal{L}_{\mathcal{J}}) \text{ with } \mathcal{F}$ $\mathcal{G}^{\exp} \leftarrow \text{multiply } \mathcal{A}^{\exp} (\mathcal{L}_{\mathcal{J}} \mathcal{L}_{\mathcal{I}}) \text{ with } \mathcal{F}$ Algorithm 3: Algorithm to calculate elements of \mathcal{G}^{erf} and \mathcal{G}^{exp} for a shell pair IJ.

Calculating V_{AB} in lrs_v()

The subroutine $lrs_v()$ is based on vspdf() presented in Section 2.6.3. The Boys function part was adjusted for LRSHs. Initially, the Gauss-Rys part was removed but the necessary changes will be explained here as well in prospect of future implementations.

We recall from Section 2.4.4 that the Coulomb integrals can be described as a Boys function $F_0(\alpha_P R_{PG}^2)$ that is differentiated w.r.t. the center of charge \boldsymbol{P} with coefficients E_{tuv}^{AB} (Eq. (2.4.21)). For RS this scheme is updated by adjusting the prefactor and the argument of the Boys function, yielding

$$V_{AB} = \frac{2\pi}{\alpha_P} \sqrt{\frac{\alpha_\omega}{\alpha_P}} \sum_{tuv} E^{AB}_{tuv} \frac{\partial^t}{\partial P^t_x} \frac{\partial^u}{\partial P^u_y} \frac{\partial^v}{\partial P^v_z} F_0(\alpha_\omega R^2_{PG}) . \tag{4.2.4}$$

Due to the chain rule the derivatives of the Boys function introduces α_{ω} (cf. Eq. (4.2.3)) to the polynomials in front it. It combines with α_P in E_{tuv}^{AB} in such a way that there is always a power of α_{ω}/α_P equal to the order of the corresponding Boys function. For example, the integral for two p_x primitives (cf. Eq. (2.4.22)) is

$$V_{110000} = \frac{2\pi}{\alpha_P} \sqrt{\frac{\alpha_\omega}{\alpha_P}} K_{AB} \left\{ \left(X_{PA} X_{PB} + \frac{1}{2\alpha_P} \right) F_0 - \frac{\alpha_\omega}{\alpha_P} \left[(X_{PB} + X_{PA}) X_{PC} + \frac{1}{2p} \right] F_1 + \frac{\alpha_\omega^2}{\alpha_P^2} X_{PC}^2 F_2 \right\}$$

$$(4.2.5)$$

This vanishes for small ω ,

$$\lim_{\omega \to 0} \alpha_{\omega} = \omega^2 = 0 , \qquad (4.2.6)$$

$$\lim_{\alpha_{\omega}\to 0} F_n(\alpha_{\omega} R_{PG}^2) = \int_0^1 s^{2n} \, \mathrm{d}s = \frac{1}{2n+1} \,, \tag{4.2.7}$$

$$\lim_{\alpha_{\omega}\to 0} V_{110000} = \frac{2\pi}{\alpha_P^3/\alpha_{\omega}} \sum_t E_{t00}^{AB} \frac{\partial^t}{\partial P_x^t} F_n(\alpha_{\omega} R_{PG}^2) = 0 , \qquad (4.2.8)$$

and reduces to full XX for large ω ,

$$\lim_{\omega \to \infty} \alpha_{\omega} = \alpha_P , \qquad (4.2.9)$$

$$\lim_{\alpha_{\omega} \to \alpha_{P}} \frac{\alpha_{\omega}}{\alpha_{P}} = 1 .$$
 (4.2.10)

For the implementation the subroutines vcl_??() used in vspdf() were copied to lrs_v??(). The prefactor was adjusted by $\alpha_{\omega}/\alpha_{P}$, the argument for the Boys function calculation (i.e. interpolation) was changed to $\alpha_{\omega}R_{PG}^{2}$ and the result multiplied by $\alpha_{\omega}/\alpha_{P}$ to the power according to the order of the Boys function. The rest of the code, including the do_??() routines, were kept as is.

This limits the calculations with LRSHs up to f-type shells for now. One solution would be the extension of the given algorithm to higher angular quantum numbers. This gets, however, more and more complex. As an alternative, one could resort to the Rys scheme and adapt **vint()**, which employs a generic ansatz instead of specific routines for each case.

The necessary adjustments are given here to prepare the extension of the current

implementation to basis sets with higher angular quantum numbers. For that the prefactor would change (cf. Eq. (2.4.13)), yielding

$$V_{AB} = \frac{2K_{AB}}{\sqrt{\pi}\alpha_P} \sqrt{\frac{\alpha_\omega}{\alpha_P}} \sum_{\gamma} w_\gamma \sum_{\eta} w_\eta x_A^i x_B^j \sum_{\eta} w_\eta y_A^k y_B^l \sum_{\eta} w_\eta z_A^m z_B^n , \qquad (4.2.11)$$

as would the transformation of the coordinates (cf. Eq. (2.4.14)), e.g.

$$x_A = \frac{\sqrt{\alpha_P - \alpha_\omega t_\gamma^2}}{\alpha_P} o_{x,\eta} + \frac{\alpha_\omega t_\gamma^2}{\alpha_P} X_{GP} - X_{AP}$$
(4.2.12a)

$$= \sqrt{\frac{\alpha_P + (\alpha_P - \alpha_\omega)u_\gamma}{\alpha_P^2(1 + u_\gamma)}} o_{x,\eta} + \frac{\alpha_\omega u_\gamma}{\alpha_P(1 + u)} X_{GP} - X_{AP} .$$
(4.2.12b)

4.2.3 Calculating DFT Exchange in lrs_1()

Both enhancement factors, $F_{\rm X}^{\rm LDA}$ and $F_{\rm X}^{\rm PBE}$ (Eqs. (4.1.17) and (4.1.19)), are subject to numerical instabilities for small and large λ due to the exponential and error functions in conjunction with the higher powers of λ . To avoid errors the Maclaurin series expansion (i.e. a Taylor series at zero)

$$f(x) \approx \sum_{m} \frac{1}{n!} \left. \frac{\mathrm{d}^{n} f(x)}{\mathrm{d} x^{n}} \right|_{x=0} x^{n} = \sum_{n} \frac{f^{(n)}(0)}{n!} x^{n} = \sum_{n} c_{n} x^{n}$$
(4.2.13)

was applied for the functions themselves (for small λ) and for exp and erf (for large λ). The latter is possible because the argument is the reciprocal of λ in both functions.

To estimate the deviation of those approximations and the numerical problems with double precision (64 bit) calculations, we used the Python module $sympy^{168}$ (version 1.1.1) for results of arbitrary precision.

Approximations for the LDA Enhancement Factor

For the lower limit (small arguments) of F_X^{LDA} only the coefficients for $n \in [0, 1, 2, 4]$ are non-zero. The series gives deviations below 10^{-16} for $0 < \lambda < 0.15$. At the upper limit (large arguments) the square within the exponential and error functions (cf. Eqs. (4.1.17) and (4.1.20a)) mean that only the even powers appear. We mapped

the coefficients according to those expansions up to 2n = 18 and accomplished a deviation of 10^{-16} for $4 < \lambda$. In between $(0.15 \le \lambda \le 4)$ the plain formula was used with deviations up to 10^{-10} . The derivative of $F_{\rm X}^{\rm LDA}$ was approximated in the same way. The coefficients of all four series are given in Table 4.A.1.

Approximations for the PBE Enhancement Factor

For $F_{\rm X}^{\rm PBE}$ the inaccuracies lie within the function $b(\lambda)$. The lower $(0 < \lambda < 0.04)$ and upper limit $(6 < \lambda)$ were in principle applied as for $F_{\rm X}^{\rm LDA}$. The lower limit was accomplished with terms of $0 \le n \le 6$ and had a deviation below 10^{-10} .

Because of the polynomial division the upper limit is not as compact as for LDA. The series for the exponential function was truncated after n = 6, for the error function after 11. The derivatives were applied directly to those approximations. Moreover, the derivative is less stable and requires an additional approximation for $0.085 \leq \lambda \leq 0.6$. A minimax approximation¹⁶⁹ using Mathematica¹⁷⁰ in that range yielded a function of the form

$$F_{\rm X}^{\rm PBE} \approx \sum_{n=0} p_n \lambda^n / \sum_{n=0} q_n \lambda^n$$
 (4.2.14)

with a maximal error estimate of 10^{-8} , which we eventually used in the interval [0.006, 0.6]. The coefficients for all three cases can be found in Tables 4.A.2 to 4.A.4.

4.3 Assessment

4.3.1 Optimizing the RSF

We combined the RSF from Eq. (4.1.29) with our LRSH-adjusted exchange functionals for LDA and PBE, together with standard correlation functionals VWN and PBE, respectively. With all four parameters adjustable we denote the corresponding functionals as LRS-SVWN, LRS-sPBE, and LRS-oPBE. To compare with global variations we also defined GRS-SVWN, GRS-sPBE, and GRS-oPBE, for which $C_1 = C_2 = C_3 = 0$.

Functional	C_0	C_1	C_2	C_3	MAE
GRS-oPBE	0.166				6.8
GRS-sPBE	0.559				3.9
GRS-SVWN	0.612				6.7
LRS-oPBE	0.000	0.252	0.000	0.000	4.5
LRS-sPBE	0.362	0.000	0.098	0.055	3.3
LRS-SVWN	0.160	0.000	0.264	0.149	3.7

Table 4.2 Parameters of separation schemes for SVWN and PBE, optimized for
AE6/11 and HTBH6, see text. Energies in kcal/mol.

The parameters were globally optimized by minimizing the MAE of two small test sets via a multi-level single linkage (MLSL) algorithm.¹⁷¹ The first test set, AE6/11, includes atomization energies and is a subset of MGAE109/11. The second, HTBH6, consists of barrier heights for hydrogen transfer reactions and is part of the superset HTBH38/08. The optimized values were rounded to three decimal places as given in Table 4.2.

The RSFs are depicted in Fig. 4.1 for carbon monoxide along the molecule axis. All those RSFs have maxima at the nuclei, i.e. there they mix in XX even at short interelectronic distances r_{12} . The bonding and asymptotic regions feature small values below 0.5. The magnitude of the GRSH parameters decreases with SVWN >sPBE > oPBE. The functions for both oPBE and SVWN feature relatively high peaks up to 3.0 at the nuclei, which are sharper (i.e. steeper) for oPBE than for SVWN or sPBE. The peaks of sPBE are smaller (up to 1.5) and their steepness resembles those for SVWN. The RSF of oPBE levels off towards zero in the outer regions since the optimization reduced to the function $\omega = \frac{C_1}{r_{\rm WS}}$, which depends only on the density. The optimized RSFs for sPBE and SVWN, on the other hand, approach a constant in the asymptotic region, due to the parameter C_0 and the $\frac{C_{2s}}{r_{\rm WS}}$ terms. This is physically more meaningful as it ensures the correct asymptotic decay of the XC potential through the remaining XC contribution at long range. Overall the RSF of sPBE stays about constant with a slightly lower value in the bonding region. For SVWN the RSF behaves similarly but with lower value, which is consistent with the respective base parameters ($C_0 = 0.160$ for SVWN, $C_0 = 0.362$ for sPBE). The lack of distinct features may indicate that the



Figure 4.1 Two visualizations of optimized RSFs for carbon monoxide with oPBE (top), sPBE (middle), and SVWN (bottom); left: graph along the bond axis (z) with dotted global values; right: contour plot in bond axis plane (white denotes values above 0.5).

optimized RSFs are not yet sensitive enough for the electronic structure.

4.3.2 Computational Details

For the assessment of the new functionals we used subsets of the categories basic properties and reaction energies from the large test set GMTKN30²⁹ with def2-TZVP^{18,19} basis sets. We also included the subsets ABDE4, AE6/11, HATBH6, HTBH6, NSBH6, and UABH6 from the AECE test set,²³ which was developed for relevance in catalysis. For ABDE4 the 6-311+G(3df,2p)⁴⁻¹⁴ basis sets were used, MG3S²² basis sets for the other subsets in AECE. Following the procedure of the electron affinities (subset G21EA) outlined in [29], we augmented the def2-TZVP basis sets with diffuse *s*- and *p*-type basis functions from aug-cc-pVTZ¹⁵ (only *s*-type for hydrogen) for that subset.

To verify Koopmans' theorem, the HOMO energies were compared to the IPs obtained as energy differences between the neutral and the cationic species of several small systems from [172] and two heterocyclic aromatic systems (pyridine and pyrimidine).¹⁷³

To gauge the performance of LRSH functionals for electronic eigenvalue spectra, we calculated the orbital energies for benzene, pyridine and pyrimidine from the IP test above. For comparison we adjusted our RS parameter in combination with the oPBE functional to each molecule according to the IP-tuning¹⁷³ procedure: $\omega = 0.287$ for benzene, 0.312 for pyridine, 0.353 for pyrimidine.

All calculations were carried out using grid size 1 and an SCF convergence threshold of 10^{-6} . The results are discussed in terms of (partly weighted) MAEs and MAXs.

4.3.3 Basic Properties and Reaction Energies (GMTKN30)

The largest test set considered in this work is GMTKN30,²⁹ which consists of 30 subsets grouped into three categories. We calculated the *basic properties* with twelve subsets and the *reaction energies* with eight subsets, which are shown in Tables 4.3 and 4.4. First, we discuss a summary given by the weighted MAEs (wMAEs) from Table 4.5 that are calculated according to [29, SI] for each category and both categories together. Although we focus mainly on the comparison

Functional	BH76	BHPERI	G21EA	G21IP	PA	SIE11	W4-08	MB08-165	wMAE
GRS-oPBE	5.4	5.8	6.5	4.1	3.8	8.3	7.7	12.1	8.4
GRS-sPBE	4.1	7.0	7.0	5.5	2.5	4.9	9.1	16.2	10.1
GRS-SVWN	6.1	16.3	5.9	14.2	2.9	7.1	12.9	15.6	12.4
LRS-oPBE	3.5	5.8	8.7	3.9	4.8	6.7	6.3	10.4	7.2
LRS-sPBE	3.1	5.1	7.4	4.3	1.7	4.8	7.2	12.1	7.8
LRS-SVWN	3.1	9.7	4.6	6.8	1.4	5.6	8.3	11.3	8.1
PBE	9.8	3.0	6.6	3.9	2.0	12.2	12.6	9.2	8.8
PBE0	4.6	2.2	8.7	5.3	2.6	11.2	4.8	9.2	6.5

Table 4.3 MAEs of basic properties subsets from the test set GMTKN30 and theirweighted mean in kcal/mol.

Table 4.4 MAEs of *reaction energies* subsets from the test set GMTKN30 and
their weighted mean in kcal/mol.

		0			/								
Functional	AL2X	ALK6	BH76RC	BSR36	DARC	DC9	G2RC	ISO34	ISOL22	NBPRC	O3ADD6	RES43	wMAE
GRS-oPBE	9.0	3.9	2.9	9.6	13.0	13.6	5.8	2.2	7.7	5.1	4.5	2.8	6.7
GRS-sPBE	1.4	1.3	3.3	3.2	16.4	16.5	10.9	3.2	7.4	5.2	9.3	0.9	5.5
GRS-SVWN	7.1	8.9	3.9	8.1	2.7	12.9	7.1	1.9	5.2	4.0	9.1	0.9	5.1
LRS-oPBE	6.7	3.4	2.4	10.7	8.8	13.0	4.8	1.9	6.2	3.7	1.6	2.7	6.0
LRS-sPBE	0.9	1.2	2.9	3.2	12.0	13.5	8.5	2.8	5.9	3.8	6.8	1.2	4.5
LRS-SVWN	9.1	10.5	3.1	7.5	8.0	11.0	3.0	1.5	5.4	4.8	3.9	1.6	5.1
PBE	4.0	2.3	4.2	6.6	6.0	10.3	7.4	2.0	6.8	2.6	4.4	3.7	5.1
PBE0	2.6	1.6	2.9	7.1	3.2	9.6	7.0	1.9	4.2	2.5	4.8	2.1	4.3

Functional	BP	RE	BP+RE
GRS-oPBE	8.4	6.7	7.6
GRS-sPBE	10.1	5.5	8.0
GRS-SVWN	12.4	5.1	9.1
LRS-oPBE	7.2	6.0	6.7
LRS-sPBE	7.8	4.5	6.3
LRS-SVWN	8.1	5.1	6.8
PBE	8.8	5.1	7.2
PBE0	6.5	4.3	5.5

Table 4.5 Weighted MAEs for subsets of categories *basic properties* (BP) and *reaction energies* (RE) from the test set GMTKN30, and weighted mean in kcal/mol.

between global and local RSHs and the different SR exchange functionals, PBE^{60,61} and PBE0^{62,63} values are shown as a reference for standard GGA and GH functionals. The widely used GH B3LYP gave generally worse or similar results than PBE0 in our tests.

The wMAEs confirm that the LRSH functionals are on average superior to their global counterparts. Interestingly, the GRSH scheme with oPBE does not improve upon the parent GGA functional. But LRS-oPBE is significantly better than PBE for *basic properties* and slightly worse for *reaction energies*. When comparing global and local RSHs with the same SR exchange energy density functional, the improvement is most notable with LDA exchange and correlation. PBE0 has the lowest average wMAE in both categories, and in total (5.5 kcal/mol). For the combined subsets, LRSH functionals perform best after that (6.3 kcal/mol to 6.8 kcal/mol). The functionals with global RS parameters exhibit the highest wMAEs (up to 9.1 kcal/mol for GRS-SVWN), and PBE gives an wMAE between those two groups (7.2 kcal/mol). For reaction energies the LRSHs are especially effective with an wMAE of 4.5 kcal/mol for LRS-sPBE close to that of PBE0 (4.3 kcal/mol). The largest wMAE among the listed functionals belongs to GRS-oPBE (6.7 kcal/mol). PBE (5.1 kcal/mol) is comparable with the GRS-SVWN results. For basic properties oPBE exchange seems more suitable than sPBE in an RSH scheme. With a slightly higher wMAE of 7.2 kcal/mol than PBE0 (6.5 kcal/mol) LRS-oPBE performs second best, followed by LRS-sPBE with 7.8 kcal/mol. In this category,

GRS-SVWN exhibits the highest wMAE (12.4 kcal/mol), followed by GRS-sPBE with 10.4 kcal/mol and PBE with 8.8 kcal/mol.

The slightly worse performance of RS functionals for *basic properties* as compared to *reaction energies* is primarily due to the subset MB08-165 (decomposition energies of artificial molecules). Therein the MAEs range from 16.2 kcal/mol with GRS-sPBE down to 10.4 kcal/mol with LRS-oPBE, which is still higher than PBE0 and PBE (both 9.2 kcal/mol). Nevertheless, the good performance of LRS-sPBE is additionally supported by the fact that it yields the lowest error for five of the 20 subsets (AL2X, ALK6, BH76, BSR36, SIE11) and never the largest. While LRS-SVWN also performs best for five subsets (BH76, G21EA, G2RC, ISO34, PA), it yields the largest MAEs for two others (AL2X, ALK6). Six smallest MAEs are accomplished by PBE0 (BHPERI, DC9, ISOL22, NBPRC, W4-08, MB08-165), two each by GRS-SVWN (DARC, RSE43), GRS-SVWN (DARC, RSE43), and LRSoPBE (BH76RC, O3ADD6). One should keep in mind that in some cases the next best values are very close, so the total performance of a functional may be good despite a low number of peak performances. The size and weights of the subsets also vary as seen in the overall wMAE performance discussed before.

It is notable that the GRSH functionals are sometimes better than their local siblings. Within our GMTKN30 results this occurs six times with SVWN (AL2X, ALK6, DARC, ISOL22, NBPRC, RSE43), three times with oPBE (BSR36, G21EA, PA), and two times with sPBE (G21EA, RSE43). This might be due to an overtraining effect of the four-parameter LRSHs to the quite small AE6/11 and HTBH6 test sets compared to the more rigid one-parameter GRSH. The outstanding performance of PBE0 is probably caused by the fixed 25 % XX admixture, which is also done for some GRSH functionals at SR and should be considered for our LRSH functionals in future investigations.

4.3.4 AECE

Additionally to the Grimme test set, we assessed the LRSH functionals for the AECE database²³ by Truhlar. It was assembled as a small, representative set with relevance to catalysis and is thus of interest for new functionals that are by design more flexible and should cover a broad range of properties. We have omitted two

Functional	ABDE4	AE6/11	HATBH6	HTBH6	NSBH6	UABH6	Mean
GRS-oPBE	11.0	8.7	7.3	4.8	3.2	1.8	6.1
GRS-sPBE	1.7	6.1	4.3	1.7	5.4	3.0	3.7
GRS-SVWN	5.9	10.5	7.1	3.0	7.0	4.1	6.3
LRS-oPBE	9.1	5.1	4.4	3.9	1.0	1.6	4.2
LRS-sPBE	2.3	5.2	3.0	1.4	4.0	2.5	3.1
LRS-SVWN	7.5	5.5	1.9	1.9	3.4	2.4	3.8
PBE	3.9	15.1	13.7	9.3	7.0	2.9	8.7
PBE0	4.9	5.9	5.9	4.6	2.1	1.9	4.2

Table 4.6 MAEs for the test set AECE (without transition metals) in kcal/mol.

subsets containing transition metal compounds, due to the current restriction of our implementation up to f-functions (see Section 4.2). The results for the subsets are shown in Table 4.6. Among the functionals tested in the original paper, the GRSH functional ω B97X-D³⁷ (MAE of 1.9 kcal/mol for our selection) was one of the best along with the mGGA GH M06⁵⁶ (2.3 kcal/mol).

The LRSH functionals yield overall better results than the corresponding GRSH ones. One exception are the alkyl bond dissociation energies (ABDE4), where the MAEs are slightly smaller with the GRSH versions of sPBE and SVWN. For these systems we also observe a significant difference between the two PBE flavors. Also confirming our findings for the GMTKN30 subsets, all optimized RSH functionals yield better results for barriers than for bond energies. Again, this may originate from the choice of training set. According to the MAEs (Table 4.6) it favors a better description of barriers. Investigating larger training sets will possibly resolve this issue. Note that neither PBE nor its variations RPBE⁶⁶ or revPBE,⁶⁵ which are popular in catalysis, perform very well for this data base.²³ Here PBE0 gives also mediocre results, except for NSBH6 and UABH6. A different exchange functional at SR, e.g. based on the B97 scheme,^{42,43} should thus be considered in the future to add more flexibility to our functional form. LRS-sPBE performs best on average with a total MAE of 3.1 kcal/mol, underlining the good performance for the GMTKN30 subsets. We also observe a significant improvement with global and local RSHs based on oPBE (6.1 kcal/mol and 4.2 kcal/mol) over the parent GGA (8.7 kcal/mol). We should keep in mind, however, that two of the

six test sets (AE6/11 and HTBH6) are exactly the training sets of our RSFs.

4.3.5 Koopmans' Theorem (IP)

For molecular properties, the LRSH scheme is clearly superior to the associated GRSHs. We further investigate its potential to replace optimal tuning of GRSHs to specific systems. While this procedure is particularly successful for the calculation of quasiparticle spectra, the optimized parameters depend heavily on the system. This was shown for a selection of nine molecules,¹⁷² where the optimal value of the RS parameter varies between 0.25 for the largest molecule (anthracene) and 0.73 for the smallest (F_2). We evaluate the IP condition

$$\epsilon_{\text{HOMO}} = -\text{IP} = E(N) - E(N-1) \tag{4.3.1}$$

with our previously optimized GRSH and LRSH functionals for the same set of molecules and two aromatic heterocycles (pyridine, pyrimidine), which were also studied in the context of photoelectron spectra¹⁷³ with OT-RSH functionals. The deviations between the HOMO energies and the vertical IPs from Δ SCF calculations

$$\Delta IP = \epsilon_{\text{HOMO}} - [E(N) - E(N-1)]$$
(4.3.2)

for all eleven molecules are given in Table 4.7.

As expected for GGAs, the HOMO energies are consistently too high (i.e. not negative enough) for PBE. Introducing 25% XX in PBE0 reduces the error for all molecules in this test set. The functionals with global and local RSHs are distinctly better than PBE0 and PBE. The smallest MAEs are obtained with GRS-sPBE (0.5 eV), LRS-sPBE (0.4 eV), and LRS-SVWN (0.3 eV). On average the functionals with LRSH perform better than their GRSH counterparts: with SVWN and oPBE the MAE is reduced significantly from 1.9 eV and 0.8 eV to 1.2 eV and 0.4 eV, respectively. LRS-sPBE improves upon the global scheme by merely 0.1 eV, which is similar to the values observed for the GMTKN30 subsets.

A general trend for sPBE (with two exceptions) and SVWN is a shift of the deviations to more positive values with LRSHs. GRS-sPBE and GRS-SVWN feature solely (except for F_2 with the former) negative deviations (i.e. the HOMO energy

		GRS			LRS			
	oPBE	sPBE	SVWN	oPBE	sPBE	SVWN	PBE	PBE0
CH2O	2.2	-0.5	-0.9	1.4	-0.1	0.1	4.5	3.2
F2	3.9	0.2	-0.4	1.5	0.6	0.3	6.0	4.3
H2O	3.2	-0.2	-0.7	2.2	0.3	1.0	5.8	3.9
HCOOH	2.1	-0.7	-1.2	1.1	-0.4	0.0	4.4	3.0
N2	2.9	-0.2	-0.7	1.9	0.2	0.3	5.2	4.0
NH3	3.3	-0.5	-0.8	2.0	0.0	0.6	4.9	3.4
anthracene	0.3	-0.7	-0.9	0.2	-0.8	-0.5	2.0	1.7
naphtalene	0.8	-0.8	-0.9	0.8	-0.7	-0.1	2.9	1.9
benzene	-0.4	-0.7	-0.9	0.4	-0.7	-0.4	2.4	1.9
pyrimidine	1.1	-0.7	-0.7	0.6	-0.3	0.0	3.3	2.1
pyridine	1.2	-0.8	-0.8	0.8	-0.5	-0.1	3.4	2.0
MAE	1.9	0.5	0.8	1.2	0.4	0.3	4.1	2.9

Table 4.7 Deviation from the IP condition, Eq. (4.3.2), for several molecules and
functionals.

is more negative than the total energy difference), while their local versions feature mixed signs. In contrast, GRS-oPBE already has quite large positive values (esp. for the small molecules), which are shifted down in the local variant.

Concerning Koopmans' theorem the RS and especially the local variant with sPBE give quite good results, while its scaled sibling oPBE falls behind considerably. Both PBE and PBE0 are at a disadvantage, confirming the need for LR XX for a better description of frontier orbital energies.

4.3.6 Outer-Valence Electron Spectra

Our self-consistent implementation of LRSH functionals allows the calculation of electronic eigenvalues that are frequently used to simulate or complement experimental photoelectron spectra. OT-RSHs in particular have been shown to yield outer-valence spectra of representative organic molecules with an accuracy comparable to G_0W_0 results.^{173,174} The tuning procedure of the RS parameter can be ambiguous concerning the definition of the target function (band gap, pure IP-tuning or Koopmans' condition for the anion, neutral and cationic) as well as the

choice of optimal parameters for open-shell species.¹⁷⁵ It has further been pointed out that the lower valence spectra are not necessarily well represented since the optimization procedure favors the HOMO and similar orbitals while retaining larger SIEs for the other orbitals.¹¹³

Following the approach used with OT-RSHs, we approximated the outer-valence electron spectra by applying Gaussian broadening to the calculated eigenvalues of occupied orbitals.¹⁷³ Since LRS-sPBE was so far the best functional, its resulting spectra for benzene, pyridine and pyrimidine are shown in Fig. 4.2 in comparison to the spectra with GRS-sPBE, the oPBE-based OT-RSH (OT-oPBE) and PBE0. The spectra are not shifted. We checked that OT-oPBE indeed fulfills the target condition $\Delta IP = 0^{173}$ for the reference parameters (see Section 4.3.2), and that the spectra resemble those from [173], where they were shown to be close to G₀W₀ and experimental ones. We give them here as a guidance, considering that OT-RSH functionals are currently the best available option to calculate electronic spectra in the KS framework.

For all three systems, the LRS-sPBE spectra recreate the OT-oPBE shape quite faithfully but they are shifted down to more negative energies (ca. 1.0 eV for benzene, 0.5 for pyrimidine). The resemblance decreases with the introduction of more nitrogen atoms, which can be seen most prominently for pyrimidine in the merging of the two peaks around -11 eV and the increased gap at -17 eV. With GRS-sPBE the differences are more pronounced, starting with a further downshift in all systems (from 1.5 to 1 eV). For pyridine the peaks around -11 eV appear to switch places and the two peaks in pyrimidine merge to one. In fact, the order of the two HOMOs ($11A_1$ and $1A_2$) in pyridine changes for both local and global sPBE in comparison with OT-oPBE. The spectrum at PBE0 level shows significantly less resemblance and is shifted to higher energies by about 2 eV to 3 eV but nonconsistently as can be seen for the peaks around -12 and -9 eV (cf. OT-oPBE at -17 eV and -11 eV).

Given the simple form of our LRSH functional, the overall agreement with the spectra obtained from RSH functionals that are specifically tuned to the systems is remarkable, even more so considering that our parameters were optimized for total energies rather than orbital energies. Apart from more sophisticated RSFs and SR exchange functionals, improved eigenvalue spectra may be obtained by

 $4.3 \ Assessment$



Figure 4.2 Calculated outer-valence electron spectra for benzene (top), pyridine (middle), and pyrimidine (bottom) with Gaussian broadening (FWHM = 1.0 eV for benzene and 0.5 eV otherwise). Energy in eV.

adding a fixed constant percentage of XX at SR, as inferred for the GMTKN30 tests.

4.4 Conclusions and Outlook

As an alternative to GH functionals with globally fixed admixture of XX, GRSH functionals partition the Coulomb interaction in SR and LR, modifying the exchange functional in either or both ranges by inclusion of XX. The ansatz of LH functionals was transferred to GRSHs by replacing the constant parameter with the RSF ω for two functionals, the LDA exchange (Slater) and the PBE variant (GGA) by Toulouse, Colonna, and Savin¹⁶⁷ denoted sPBE, which can be made equal to the original PBE by adding a prefactor for the limit $\omega \rightarrow 0$ (oPBE). These RSH exchange functionals are combined with unadjusted correlation functionals VWN and the original PBE, respectively. Our self-consistent implementation employs a semi-numerical integration scheme based on Boys functions, limited up to *f*-shells at this time. To mitigate numerical inaccuracies in both semi-local functionals they are approximated for small and large input values by truncated series and a minimax algorithm.

We proposed a generic RSF with a constant parameter as well as a scaled dependence on the density, its gradient, and the KS kinetic energy density, and optimized it globally for two small test sets of atomization energies and barrier heights, separately for the three functionals (LRSH) and their global versions (GRSH). The resulting functionals were assessed for reaction barriers and relative energies in a selection of sub test sets from GMTKN30²⁹ and AECE,²³ for Koopmans' theorem in a set of main-group molecules¹⁷² as well as two heterocyclic, aromatic systems.¹⁷³ For the latter we also compared outer electron spectra (from orbital energies with Gaussian broadening) to reproduce OT-RSH results.

Despite the small training set and the (especially for sPBE) unadjusted correlation functional, the LRSH functionals fare quite well in comparison with the GGA PBE or the GH PBE0, although the latter was clearly more suited for GMTKN30 (less so for AECE). They also give similar orbital energies as shown for the outer valence electron spectra against a recreated OT-RSH for PBE (OT-oPBE), without the need to adjust the prefactor for each system. Further development should include the extension to higher shells, e.g. by adaptation of the Gauss-Rys/Gauss-Hermite implementation or the Obara-Saika algorithm.¹⁶³ The recent implementation of known GRSH functionals into Turbomole could help in this, by improving efficiency and the addition of more LRSH-based exchange and correlation functionals (e.g. using B97^{42,43}). Integral screening techniques like S- and P-junctions should be considered as well. Moreover, larger training sets may yield more generally applicable variants of the already implemented LRSH functionals and give insight into the influence of the distinct parts of the functional on various properties. This should lead to more sophisticated RSFs. The restriction to XX only at LR could be easily mitigated in a first step by mixing in a constant XX fraction to the SR functional part as was done for some GRSH functionals and is inspired by the good performance of PBE0 for the GMTKN30 subsets. This can later be complemented by an RSF-dependent contribution of its own, resulting in a three-fold partitioning. Lastly, the combination of LRSHs with LHs should be considered as well.

4.A Appendix

4.A.1 Approximations for LRSH Functionals

To circumvent the numerical instabilities of LRSH enhancement factors and their derivatives, approximations for different ranges of the argument were necessary (see Section 4.2.3). We used Maclaurin series (Eq. (4.2.13)) for the LDA factor $F_{\rm X}^{\rm LDA}$ and its derivative (Eqs. (4.1.17) and (4.1.22)) with small, i.e. near-zero, arguments (*lower* limit). Their coefficients are given in Table 4.A.1 as $l_n^{(0)}$ and $l_n^{(1)}$. For large arguments (*upper* limit), the exponential and error functions were approximated by such series instead, and inserted into the original equations. This yielded polynomial equations with coefficients given as $u_{-2n}^{(0)}$ and $u_{-2n-1}^{(1)}$ in Table 4.A.1.

The same principle was applied to the function $b(\lambda)$ (Eq. (4.1.20a)) and its derivative (Eq. (4.1.28a)) for the PBE-based SR exchange functional. The coefficients for small arguments are given as $l_n^{(0)}$ and $l_n^{(1)}$ in Table 4.A.2.

For large arguments of b itself, inserting the Maclaurin series of exp and erf yielded the quotient of two even polynomials $u^{(0)}/v^{(0)}$. Their coefficients are given

Table 4.A.1 Coefficients for approximated F_X^{LDA} and its derivative, with $\sum_n c_n x^n$, based on Maclaurin series up to degree n = 9 for near-zero (lower) and large (upper) arguments.

n	0	1	2	3	4	5	6	7	8	9
$l_n^{(0)}$	1	$\frac{-4\sqrt{\pi}}{3}$	2	0	$\frac{-2}{3}$	0	0	0	0	0
$u_{-2n}^{(0)}$	0	$\frac{1}{9}$	$\frac{-1}{60}$	$\frac{1}{420}$	$\frac{-1}{3240}$	$\frac{1}{27720}$	$\frac{-1}{262080}$	$\frac{1}{2721600}$	$\frac{-1}{4626720}$	$\frac{1}{2585520}$
$l_n^{(1)}$	$\frac{-4\sqrt{\pi}}{3}$	4	0	$\frac{-8}{3}$	0	0	0	0	0	0
$u_{-2n-1}^{(1)}$	0	$\frac{-2}{9}$	$\frac{1}{15}$	$\frac{-1}{70}$	$\frac{1}{405}$	$\frac{-1}{2772}$	$\frac{1}{21840}$	$\frac{-1}{194400}$	$\frac{1}{4626720}$	$\tfrac{-1}{2585520}$

Table 4.A.2 Coefficients for approximated b from $F_{\rm X}^{\rm PBE}$ and its derivative, with $\sum_n l_n x^n$, based on Maclaurin series up to degree n = 6 and n = 5, respectively, with near-zero arguments.

n	$l_n^{(0)}$	$l_n^{(1)}$
0	$\frac{7}{81}$	$\frac{56\sqrt{\pi}}{243}$
1	$\frac{2\overline{8}\sqrt{\pi}}{243}$	$\frac{16(-18+17\pi)}{729}$
2	$\frac{16(-18+7\pi)}{729}$	$\frac{8(-207+56\pi)\sqrt{\pi}}{729}$
3	$\frac{8(-207+56\pi)\sqrt{\pi}}{2187}$	$\frac{8(2781 - 4320\pi + 896\pi^2)}{6561}$
4	$\frac{2(2781 - 4320\pi + 896\pi^2)}{6561}$	$\frac{320(837 - 666\pi + 112\pi^2)\sqrt{\pi}}{19683}$
5	$\frac{64(837 - 666\pi + 112\pi)\sqrt{\pi}}{19683}$	$\frac{8\left(28917+93960\pi-50688\pi^2+7168\pi^3\right)}{19683}$
6	$\frac{4\left(-28917+93960\pi-50688\pi^2+7168\pi^3\right)}{59049}$	10000

Table 4.A.3 Coefficients for approximated *b* from $F_{\rm X}^{\rm PBE}$, with $\sum_n u_n x^n / \sum_n v_n x^n$, based on Maclaurin series for exp and erf up to degree n = 22, with large arguments. The derivatives are used via the quotient rule, see Eq. (4.A.1).

n	$u_n^{(0)}$	$v_n^{(0)}$	$u_{n-1}^{(1)}$	$v_{n-1}^{(1)}$
0		63		
2		56		112
4		1931		7724
6		2604		15624
8		24738		197904
10	2695	43953	26950	439530
12	11935	126945	143220	1523340
14	64680	435330	905520	6094620
16	274890	1926540	4398240	30824640
18	808500	6486480	14553000	116756640
20	970200	14844060	19404000	296881200
22		17463600		384199200

in Table 4.A.3 as $u_n^{(0)}$ and $v_n^{(0)}$. The derivative was taken directly from this approximation via the quotient rule

$$\frac{\partial b}{\partial \lambda} \approx \frac{u^{(1)} - bv^{(1)}}{v^{(0)}} . \tag{4.A.1}$$

Thus, the coefficients of these odd polynomials $u^{(1)}$ and $v^{(1)}$ are closely related to the former ones and also given in Table 4.A.3

The derivative of *b* required an additional approximation around $\lambda \approx 0.07$. For this we applied a minimax approximation¹⁶⁹ within $0.085 \leq \lambda \leq 0.6$, which yielded the quotient of two polynomials, $\sum_n p_n \lambda^n / \sum_n q_n \lambda^n$, whose coefficients p_n and q_n are listed in Table 4.A.4.

Table 4.A.4 Coefficients for approximated derivative of b from $F_{\rm X}^{\rm PBE}$, with $\sum_n p_n \lambda^n / \sum_n q_n \lambda^n$, using a minimax algorithm within $0.085 \le \lambda \le 0.6$.

$n p_n$	q_n
0 + 0.20423336553555649	+1.0
1 - 0.41492105854350596	-2.8894177391350542
2 - 0.35605859294397825	+3.6943201135864023
3 - 0.34138199734535602	-1.7635611733984347

5 Conclusions and Outlook

The aim of this thesis was the advancement of modern KS-DFT methods by implementing novel approaches for more flexible hybrid functionals into the quantum chemical program package Turbomole, and by evaluating these implementations in numerical computations.

One of the modern ansatzes is LH functionals⁶⁹ (Section 2.2.2), which use a position-dependent LMF to determine the amount of XX combined with approximate SL exchange in order to mitigate the SIE, whereas widely-used GHs apply a constant fraction everywhere and are based on theoretical or empirical considerations for the choice of that value. Building on prior efficient implementations of SCF⁸³ and linear-response TDDFT,⁸⁴ the up-to-now missing energy derivatives w.r.t. nuclear displacement, i.e. local hybrid gradients,¹ were derived and implemented (Sections 3.1 and 3.2) using a semi-numerical Gauss-Rys/Gauss-Hermite quadrature scheme. Those gradients enable structure optimizations as well as the (numerical) calculation of vibrational frequencies but require additionally the matrices \mathcal{A}' , i.e. the (Cartesian) derivatives of the repulsion integral \mathcal{A} for XX. The quadrature scheme was adapted to reuse intermediate integrals so that all necessary matrix elements are calculated together, for the cost of calling the integral subroutines with an increased quantum number and more quadrature roots. This scheme was complemented by the addition of the S-junction and P-junction prescreenings⁸³ in order to skip the time-consuming evaluation of some of the XX repulsion integrals. The former relies on the diffuseness of basis functions and their relative distances,¹²² the latter on the product of the density matrix and basis functions.

Both screenings were evaluated for linear alkanes and the three-dimensional adamantane to determine their effectiveness for different thresholds (Section 3.3). The savings for S-junctions are less pronounced (up to 7%) for the inspected chain

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lengths compared to those for P-junctions (up to about 40%) for a threshold of 10^{-5} . This setting leads to absolute deviations up to ca. 10^{-7} relative to the results without junctions. For the structure optimization of adamantane this threshold was optimal, yielding 28% less computing time and a merely 10^{-2} kJ/mol deviation in total energy. While the prefactor for the new implementation is higher in comparison with the mGGA GH TPSSh, the scaling is more favorable with increasing basis set size because of our semi-numeric scheme. In terms of accuracy, the LHGs were about en par with GHs as tested for interatomic distances on the test sets of main group and 3d transition metal molecules, and slightly worse for frequency calculations on small main group molecules. In both cases we used Slater exchange and VWN correlation in conjunction with LMFs depending on either the reduced KS kinetic energy density (t-LMF) or the reduced electron density gradient (s-LMF), with a prefactor optimized for a small set of AEs and BHs.

Moreover, the gradient implementation was used to optimize the structure and calculate the vibrational frequencies of ten small, gas phase MV oxo systems containing either main group or transition metal centers (Section 3.4).² The goal was to find functionals that can distinguish between different Robin/Day MV classes¹⁴⁴ simultaneously, which can be difficult since it requires varying amounts of XX in different systems for the description of localization/delocalization. As reference we used high-level coupled cluster benchmark data and experimental spectroscopic results. The t-LMF with SVWN and a prefactor of b = 0.670 was one of the best-performing in this study, along with the highly parametrized MN15 and the GRSH functional ω B97X-D. Yet none of the tested functionals accomplished the correct description in all test cases.

For a better description, more sophisticated ingredients of the LMF may be necessary, e.g. the Laplacian or the Hessian of the density (Section 3.5). Such additions would require further development of the accompanying gradient subroutines, while for ingredients already in use (density, its gradient, kinetic energy density) any new functional implementation can apply the gradient as is. The available code can also be built upon for further implementations like LHGs for excited states. The extension to derivatives of second order w.r.t. nuclear displacement (Hessian) does not seem worthwhile at this time because of the even larger demands on memory and processing for the new matrices from the second derivatives of \mathcal{A} . A speedup of the current gradient algorithm could be a first step in that direction. One possible avenue to this is the adaptation of the Boys function quadrature scheme for low quantum numbers as employed for the SCF calculation, although this implies a significant rewrite of existing routines (full \mathcal{A}' vs. half \mathcal{A}). The Obara-Saika scheme¹⁶³ may provide an efficient alternative and reduce code repetition because of its use of recurrence relations. Because of the integration grid, parallelization should be straightforward and decrease the effective run time appreciably (while processing time increases due to multiple processors).

As a competing ansatz to GH and LH functionals, the GRSH functionals split the Coulomb operator into LR and SR parts (most often) via an error function and may mix in XX in either or both regions (Section 2.2.2). In analogy to the LH approach, the RS parameter can be replaced by a position-dependent RSF ω . Preliminary investigations were promising¹⁰¹ but had been abandoned afterwards. As detailed in Section 4.1 we derived the necessary equations for the self-consistent implementation of LRSH functionals. The energy expression and KS matrix contributions for LRSH functionals were subsequently implemented into Turbomole. For the XX integrals, a scheme with Boys functions up to *f*-shells was adapted. As SR exchange, we used LDA¹⁰⁵ and a variant of the GGA exchange functionals PBE¹⁶⁷ (sPBE). Numerical instabilities have to be considered for small and large values of the RSF. We circumvented them by series expansions for small and large arguments, and a minimax approximation for an intermediate interval.

The applied RSF depends on the electron density, its reduced gradient and the reduced kinetic energy density, including four scaling parameters. They were optimized for LDA, sPBE, and oPBE (a modified sPBE, which reduces to the original PBE^{60,61} for $\omega \to 0$) separately for global (GRSH, one parameter) and local (LRSH, four parameters) test functionals on two small sets of AEs and BHs. They were then assessed (Section 4.3) in a selection of sub test sets of GMTKN30²⁹ and AECE²³ containing AEs and BHs, where especially LRS-sPBE gave good results on average (weighted MAE of 3.1 kcal/mol for GMTKN30 without *non-covalent interactions*). We further tested how well the six functionals fulfill Koopmans' IP theorem for some small molecules and aromatic systems. Despite their optimization against AEs and BHs, the functionals with sPBE and SVWN yielded good results with slight improvement for the LRSH variant (MAEs 0.4 eV and 0.3 eV, respectively). The rescaled oPBE fared worse (1.2 eV), and both PBE and PBE0 are at a disadvantage for this property (4.1 eV and 3.0 eV, respectively). Finally, we tested the global and local version of our so far best-performing sPBE for the outer electron spectra of three aromatic systems (benzene, pyridine, pyrimidine) by visual comparison of their orbital energies with Gaussian broadening. The reference was a rebuilt OT-RSH, i.e. our GRS-oPBE with an adjusted RS constant for each system to fulfill Koopmans' theorem for the first IP. The resemblance for LRS-sPBE was very good but slightly shifted towards lower energies, which increased with each additional nitrogen atom. The corresponding GRSH showed an even larger shift, while the GH PBE0 gave pronounced shifts towards more positive energies and less resemblance for the peaks.

Overall the results are quite promising (Section 4.4), especially considering the simple form of our RSF and the optimization on small, specific test sets. Further development should consider more sophisticated RSFs as well as RS-adapted exchange and correlation functionals (e.g. using B97^{42,43}). The latter may be simplified by the recent implementations of GRSH functionals into Turbomole. Larger training sets should prevent an overtraining to specific systems and could reveal some relations between the LRSH ingredients and system properties, leading to improved RSFs. Also, training sets for Koopmans' theorem (i.e. for IPs and EA) should be tested, given that OT-RSH functionals are a often used for these properties. While the current implementation only provides XX at LR, this could be amended in a first step by a constant fraction of XX at SR (GH / LRSH) and later by an SR implementation of LRSH of its own. A combination of LH and LRSH functionals should be considered as well.

Prior to those extensions, however, it is essential to eliminate the current limitations. To enable the calculation of higher shells than f, one may adapt the Gauss-Rys/Gauss-Hermite scheme used for LHG also for the LRSH calculations as given in Section 4.2. A subsequent (or alternative) step could be the usage of the Obara-Saika algorithm mentioned above, especially if it is planned for the LHG implementation as well. For efficiency, S- and P-junctions should be straightforward to implement.

In conclusion, two modern DFT methods have been advanced by derivation, implementation, and assessment of gradients for LH functionals, and SCF energies for LRSH functionals. First results were promising, and the new capabilities due to the gradient were used in a benchmark test set for MV systems, revealing one of the LH functionals to give compelling results albeit not succeeding perfectly for all systems. Still, a lot can be done by increasing efficiency and extending to yet unavailable functionality. This work represents a stepping stone for such an endeavor.
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