Implementation and reassessment of the Perdew-Zunger self-interaction correction

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IMPLEMENTATION AND REASSESSMENT OF THE PERDEW-ZUNGER SELF-INTERACTION CORRECTION

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Fyrir Rebekku Rós.

"Time changes everything."

"That's what people say, it's not true. Doing things changes things. Not doing things leaves things exactly as they were."

House M.D.

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Abstract

Density functional theory (DFT) using semi-local functional approximations can describe many chemical properties to high accuracy, but in some cases large and even qualitative errors emerge. Some of these errors are ascribed to an unphysical interaction of each electron with itself, which is present as a result of the approximations made in the exchange-correlation functional. The Perdew-Zunger self-interaction correction (PZ-SIC) attempts to remove this spurious interaction from approximate functionals and does so for systems that include only a single electron. For many-electron systems, PZ-SIC had previously been found to result in an overcorrection in many cases. But, most previous applications of PZ-SIC restricted the orbitals to be real functions and did not take into account that orbitals are in general complex.

The implications of the restriction to real orbitals were explored in detail in this thesis project and it was found that the effect on the total energy and on the structure of molecules can be large. Generally available electronic structure software could not be used for the calculations as this orbital-density dependent functional form is significantly different from common density functional approximations and a special optimization algorithm is needed. The electronic structure software QUANTICE was developed as part of this thesis project. It includes an efficient new algorithm for minimizing the energy of orbital-density dependent functionals, in particular PZ-SIC, as well as the option of using complex orbitals. The present reassessment of PZ-SIC including complex orbitals has extended and in some cases revised the results from previous studies. The total energy of atoms is found to be improved by PZ-SIC when applied to a suitable density gradient dependent functional. The overcorrection found in molecular properties is in many cases less severe when complex orbitals are used. The molecular structure of the CH_3 radical, which had previously been found to become incorrect by the application of PZ-SIC, is shown here to be predicted correctly when complex orbitals are used. A scaled down version of PZ-SIC can give improved results on average but large, unsystematic errors still remain. While PZ-SIC does not turn out to give the desired overall accuracy, the methodology and software developed in this thesis project for the efficient implementation of orbital-density dependence in the functional form, can help in the development of a significantly more accurate energy functional for electronic systems.

Útdráttur

Þéttnifellafræði (DFT) byggð á nær staðbundnum nálgunum á fellinu geta gefið góða nákvæmni í mörgum tilfellum en í sumum tilfellum koma í ljós stórar og jafnvel eigindlegar skekkjur. Talið er að sumar þessar skekkjur stafi af sjálf-víxlverkun rafeindanna sem er ranglega til staðar vegna nálgana í víxlunar-fylgni fellinu. Perdew-Zunger leiðréttingin (PZ-SIC) leitast við að fjarlægja þessa villu í víxlverkuninni og virkar vel fyrir kerfi með aðeins einni rafeind. Fyrir kerfi með mörgum rafeindum hefur verið sýnt fram á að PZ-SIC gefi gjarnan of stóra leiðréttingu. En, í flestum tilfellum hafa reikningar með PZ-SIC gert ráð fyrir því að svigrúmin séu raunföll og ekki tekið til greina að almennt eru svigrúm tvinnföll.

Þessi takmörkun hefur verið könnuð í doktorsverkefninu og sýnt fram á að áhrifin á heildar orku og lögun sameinda geti verið veruleg. Hugbúnað sem almennt er aðgengilegur er ekki hægt að nota í slíka reikninga því fellið er háð svigrúma þéttni sem er ólíkt venjulegum rafeindafellum og nauðsynlegt er að nota sérstakar bestunaraðferðir. Hugbúnaðurinn QUANTICE var þróaður sem hluti af þessu verkefni til að innleiða nýja bestunaraðferð fyrir svigrúmaþéttniháð felli, þar með PZ-SIC, og eiga möguleika á að nota tvinnfalla svigrúm. Það endurmat á PZ-SIC með tvinnfalla svigrúmum sem hér kemur fram bætir við og í sumum tilfellum leiðréttir niðurstöður fyrri reikninga. Í ljós kom að mat á heildarorku atóma verður nákvæmara með PZ-SIC þegar aðferðinni er beitt á viss felli sem háð eru stigli rafeindaþéttninnar. Leiðréttingin á eiginleikum sameinda er síður ofmetin þegar tvinnfalla svigrúm eru notuð. Lögun CH_3 stakeindarinnar er rétt þegar tvinnfalla sigrúm eru notuð en áður hafði verið bent á að PZ-SIC spái rangri lögun, en þá með raunfalla svigrúmum. Sköluð PZ-SIC leiðrétting getur bætt reiknuð gildi að jafnaði, en stórar og ókerfisbundnar skekkjur verða samt eftir.

Þótt PZ-SIC hafi ekki gefið þá nákvæmni sem sóst er eftir, þá getur sú þróun á aðferðafræði og hugbúnaði sem fram hefur farið í doktorsverkefninu

og gert það kleift að nota svigrúmaþéttniháð felli hjálpað til við að þróa verulega nákvæmari orkufelli fyrir rafeindakerfi í framtíðinni.

List of Publications

Publications included in the thesis

- **Importance of complex orbitals in calculating the self-interaction-corrected ground state of atoms**
  Simon Klüpfel, Peter Klüpfel, and Hannes Jónsson
  Physical Review A ***84****, 050501(R) (2011).*
- **Optimization of functionals of orthonormal functions in the absence of unitary invariance**
  Peter Klüpfel, Simon Klüpfel, Kiril Tsemekhman, and Hannes Jónsson
  Applied Parallel and Scientific Computing, Lecture Notes in Computer Science, Vol. 7134, edited by K. Jónasson (Springer Berlin / Heidelberg, 2012), pp. 23–33.
- **The effect of the Perdew-Zunger self-interaction correction to density functionals on the energetics of small molecules**
  Simon Klüpfel, Peter Klüpfel, and Hannes Jónsson
  Journal of Chemical Physics ***137****, 124102 (2012).*

Publications not included in the thesis

- **Using complex degrees of freedom in the Kohn-Sham self-interaction correction**
  Dirk Hofmann, Simon Klüpfel, Peter Klüpfel, and Stephan Kümmel
  Physical Review A ***85****, 062514 (2012).*

Contents

1 Theoretical Background 1
- 1.1 Hohenberg-Kohn Density Functional Theory 4
- 1.2 Kohn-Sham Density Functional Theory 6
- 1.3 Density Functional Approximations 7
- 1.4 Shortcomings of Approximate Functionals 14

2 Perdew-Zunger Self-Interaction Correction 19
- 2.1 Definition 19
- 2.2 Self-Consistent Minimization 20
- 2.3 Previous Assessment 24
- 2.4 Scaled Self-Interaction Correction 25

3 Implementation of Perdew-Zunger Self-Interaction Correction 27
- 3.1 Complex Orbitals 27
- 3.2 Unitary Optimization Algorithm 29
- 3.3 Quantice 32

4 Numerical results 35
- 4.1 Atomic Systems 35
- 4.2 Molecular Systems 42

5 Summary and Outlook 45

List of Figures 49

List of Tables 51

Bibliography 53

Included Publications 65

I Importance of complex orbitals in calculating the self-interaction-corrected ground state of atoms 65

II Optimization of functionals of orthonormal functions in the absence of unitary invariance 67

III The effect of the Perdew-Zunger self-interaction correction to density functionals on the energetics of small molecules 69

1

Theoretical Background

The accurate description of systems on a molecular or atomic level cannot be achieved by means of classical mechanics, as quantum effects have to be accounted for. In the beginning of the 20th century it became apparent that light has both wave- and particle-like characteristics. In 1924, de Broglie postulated in his dissertation [1] that matter had these characteristics as well and proposed a connection of a particle's momentum, p, to its wavelength, λ, through Planck's constant, h, as $\lambda = \frac{h}{p}$. In analogy to classical mechanics, Schrödinger postulated in 1926 a description of the propagation of matter waves from a Hamiltonian principle [2] as

$$\mathrm{i}\hbar \frac{\partial}{\partial t}\Psi(t) = \hat{H}(t)\Psi(t) \; , \tag{1.1}$$

where $\hbar = h/2\pi$ is the reduced Planck constant and $\Psi(t) = \Psi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N, t)$ is the wavefunction of N particles. The Hamiltonian operator $\hat{H}(t)$ is defined as

$$\hat{H}(t) = \sum_{k=1}^{N} -\frac{\hbar}{2m_k}\hat{\Delta}_{r_k} + \hat{V}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N, t) = \hat{T} + \hat{V}(t) \tag{1.2}$$

with the Laplace operator $\hat{\Delta}_{r_k}$depending on the coordinates $\boldsymbol{r}_k$.

In the case of a time independent potential, $\hat{V}(t) = \hat{V}$, a stationary state $\Psi = \Psi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)$ is defined by the stationary Schrödinger equation

$$\hat{H}\Psi = \left(\hat{T} + \hat{V}\right)\Psi = E\Psi \; . \tag{1.3}$$

Systems of chemical interest are built up from negatively charged electrons and positively charged nuclei that interact with each other through electrostatic interaction. The wavefunction $\Psi = \Psi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N, \boldsymbol{R}_1, \ldots, \boldsymbol{R}_M)$ of such systems depends on the coordinates of N electrons, $\{\boldsymbol{r}\}$, and of M nuclei, $\{\boldsymbol{R}\}$. For such a system the potential operator $\hat{V}$ is built up from different contributions: Nucleus-nucleus repulsion ($\hat{V}_{\mathrm{nn}}$), nucleus-electron attraction ($\hat{V}_{\mathrm{ne}}$), electron-electron repulsion ($\hat{V}_{\mathrm{ee}}$) and, possibly, the interaction of the particles with an external electrostatic field ($\hat{V}_0$).

Thus, the Hamiltonian of a system of electrons and nuclei in an external potential reads

$$\hat{H} = \hat{T}_{\mathrm{n}} + \hat{T}_{\mathrm{e}} + \hat{V}_0 + \hat{V}_{\mathrm{nn}} + \hat{V}_{\mathrm{ne}} + \hat{V}_{\mathrm{ee}}. \tag{1.4}$$

For convenience in the formulation of the Hamiltonian, "atomic units" [3] are introduced. The elementary charge, e, electron mass, m_{e}, Bohr radius, a_0, reduced Planck constant, $\hbar$, and the Coulomb constant, $k_e = {}^1/_{4\pi\varepsilon_0}$, are set to unity. By this transformation energy takes the unit of the Hartree energy, E_{h}, and the mass of a particle is defined in units of the electron mass.

In these units, the components of the Hamiltonian are of particularly simple form. The kinetic energy operators are expressed as

$$\hat{T}_{\mathrm{n}} = \sum_{i=1}^{M} -\frac{1}{2m_i}\hat{\Delta}_{\boldsymbol{R}_i} \qquad \text{and} \qquad \hat{T}_{\mathrm{e}} = \sum_{i=1}^{N} -\frac{1}{2}\hat{\Delta}_{\boldsymbol{r}_i} \tag{1.5}$$

and the potential energy operators read

$$\hat{V}_{\mathrm{nn}} = \sum_{i=1}^{M}\sum_{j=i+1}^{M} \frac{Z_i Z_j}{|\boldsymbol{R}_i - \boldsymbol{R}_j|} \tag{1.6}$$

$$\hat{V}_{\mathrm{ne}} = \sum_{i=1}^{M}\sum_{j=1}^{N} -\frac{Z_i}{|\boldsymbol{R}_i - \boldsymbol{r}_j|} \tag{1.7}$$

$$\hat{V}_{\mathrm{ee}} = \sum_{i=1}^{N}\sum_{j=i+1}^{N} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}, \tag{1.8}$$

with Z_i being the charge on the nucleus at R_i.

The external potential operator can be expressed as an operator acting on the electrons and on the nuclei, respectively, as

$$\hat{V}_0 = \underbrace{\sum_{i=1}^{M} v_0(\boldsymbol{R}_i)}_{\hat{V}_{0,\mathrm{n}}} + \underbrace{\sum_{i=1}^{N} v_0(\boldsymbol{r}_i)}_{\hat{V}_{0,\mathrm{e}}}. \tag{1.9}$$

By this the Hamiltonian can be separated into a purely nuclear component, $\hat{H}_{\mathrm{nuc}}$, and an electronic component, $\hat{H}_{\mathrm{el}}^{\{\boldsymbol{R}\}}$, that depends parametrically on the coordinates of the nuclei,

$$\hat{H} = \underbrace{\hat{T}_{\mathrm{n}} + \hat{V}_{\mathrm{nn}} + \hat{V}_{0,\mathrm{n}}}_{\hat{H}_{\mathrm{nuc}}} + \underbrace{\hat{T}_{\mathrm{e}} + \hat{V}_{\mathrm{ne}} + \hat{V}_{0,\mathrm{e}} + \hat{V}_{\mathrm{ee}}}_{\hat{H}_{\mathrm{el}}^{\{\boldsymbol{R}\}}} = \hat{H}_{\mathrm{nuc}} + \hat{H}_{\mathrm{el}}^{\{\boldsymbol{R}\}} \ . \tag{1.10}$$

Most commonly, electronic systems are treated in the Born-Oppenheimer approximation [4]. The nuclei have a much larger mass than the electrons, so the latter are expected (assuming similar momenta) to instantly adjust to changes in the nuclear positions. Based on this assumption, the wavefunction can be approximated as the product of a nuclear wavefunction, Ψ_{nuc}, and an electronic wavefunction, $\Psi_{\mathrm{el}}^{\{\boldsymbol{R}\}}$, for each configuration of the nuclei, $\{\boldsymbol{R}\}$ [5],

$$\Psi = \Psi_{\mathrm{nuc}} \Psi_{\mathrm{el}}^{\{\boldsymbol{R}\}} \ . \tag{1.11}$$

In this approximation, the electronic Schrödinger equation

$$\hat{H}_{\mathrm{el}}^{\{\boldsymbol{R}\}} \Psi_{\mathrm{el}}^{\{\boldsymbol{R}\}} = E_{\mathrm{el}}(\{\boldsymbol{R}\}) \Psi_{\mathrm{el}}^{\{\boldsymbol{R}\}} \tag{1.12}$$

can be solved for all configurations of the nuclei and produces the electronic energy as a function of nuclear coordinates, $E_{\mathrm{el}}(\{\boldsymbol{R}\})$. As $\hat{V}_{\mathrm{nn}}$ and $\hat{V}_{0,\mathrm{n}}$ depend only on the nuclear coordinates, these terms can be combined with the electronic energy to give the potential energy surface (PES), $E_{\mathrm{PES}}(\{\boldsymbol{R}\})$. Using the potential energy surface, the nuclear Schrödinger equation can be solved by employing the action of the complete Hamiltonian. Here, the nuclear kinetic energy operator also has an action on the electronic wavefunction, as it depends on the nuclear coordinates in a parametric way. If these *non-adiabatic* contributions to the energy can be neglected [5], the nuclear wavefunction and total energy of the system can be found by solving

$$\left(\hat{T}_{\mathrm{n}} + E_{\mathrm{PES}}(\{\boldsymbol{R}\})\right) \Psi_{\mathrm{nuc}} = E \Psi_{\mathrm{nuc}} \ . \tag{1.13}$$

With the introduced approximations, the computation of the wavefunction and energy of a system made up of nuclei and electrons can be separated into an electronic and a nuclear problem. These two are connected via the potential energy surface, whose computation is in most cases a challenging task. Determining the electronic wavefunction for a single nuclear configuration requires solving the electronic Schrödinger equation—a $3N$-dimensional differential equation. This is infeasible, both analytically and even numerically, for most electronic systems.

1.1 Hohenberg-Kohn Density Functional Theory

In 1964, Hohenberg and Kohn proved two theorems [6], which laid the foundation of modern density functional theory (DFT). They showed that the electron density ρ_0 of a non-degenerate electronic ground state of N electrons in an external potential $v(\boldsymbol{r})$ defines the ground state wavefunction Ψ_0 and by this all observables that can be derived from it. This is—in theory—a great simplification, as the electron density is only a 3-dimensional function, while the wavefunction of N electrons is a function in $3N$ dimensions.

First Hohenberg-Kohn theorem

> *The external potential $v(\boldsymbol{r})$ is a unique functional of the ground state density $\rho_{v,0}(\boldsymbol{r})$, apart from a trivial additive constant.* [6]

The Hamiltonian of N electrons in an external potential $v(\boldsymbol{r})$ reads

$$\hat{H}_{v,N} = \sum_{i=1}^{N} -\frac{1}{2}\hat{\triangle}_{r_i} + \sum_{i=1}^{N} v(\boldsymbol{r}_i) + \sum_{i=1}^{N}\sum_{j=1}^{i-1} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} = \hat{T}_N + \hat{v}(\boldsymbol{r}) + \hat{V}_{\mathrm{ee},N} \ , \quad (1.14)$$

in which the number of electrons, N, and the external potential, $v(\boldsymbol{r})$, are the only non-universal, i.e., system specific, dependencies. Given these, the Hamiltonian defines the ground-state wavefunction, $\Psi_{v,0}$, and by this the ground-state electron density, $\rho_{v,0}(\boldsymbol{r})$.

The ground state density defines N by integration, but more importantly also the external potential, which can be proven by *reductio ad absurdum* [6]. Hence, the Hamiltonian is completely defined from the density alone, which makes it possible to formulate the energy as a functional of the ground state density by

$$E_{v,0}[\rho_{v,0}] = \int \mathrm{d}\boldsymbol{r}\ \rho_{v,0}(\boldsymbol{r})v(\boldsymbol{r}) + F[\rho_{v,0}] \ , \quad (1.15)$$

with the “universal functional”

$$F[\rho_{v,0}] = \left\langle \Psi_{v,0} \,\middle|\, \hat{T}_N + \hat{V}_{\mathrm{ee},N} \,\middle|\, \Psi_{v,0} \right\rangle \ . \quad (1.16)$$

This functional can be expressed as the sum of the Hartree energy, $E_{\mathrm{H}}[\rho_{v,0}]$, i.e., the classical Coulomb repulsion of the density with itself, and another universal functional, $G[\rho_{v,0}]$, containing the remaining contributions,

$$F[\rho_{v,0}] = \frac{1}{2}\iint \mathrm{d}\boldsymbol{r}\ \mathrm{d}\boldsymbol{r}'\ \frac{\rho_{v,0}(\boldsymbol{r})\rho_{v,0}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + G[\rho_{v,0}] = E_{\mathrm{H}}[\rho_{v,0}] + G[\rho_{v,0}] \ . \quad (1.17)$$

For a known external potential and number of electrons the ground-state energy can be found by a variational procedure, as shown by the second theorem.

Second Hohenberg-Kohn theorem

> *For a given external potential $v(\boldsymbol{r})$ and number of electrons N, the variational relation $E_v[\rho_{v',0}] \geq E_v[\rho_{v,0}] = E_{v,N,0}$ holds for any N-electron ground-state density $\rho_{v',0}(\boldsymbol{r})$ corresponding to a potential $v'(\boldsymbol{r})$.* [6]

Using this variational relation one can find the ground state density and energy for a given external potential and number of electrons. However, two problems arise in this procedure: i) The trial densities must correspond to an N-electron wavefunction (N-representability) and ii) they must be the ground state density of *some* external potential (v-representability).

The N-representability of the trial densities can be ensured. For any non-negative and differentiable density which integrates to N electrons, a corresponding valid wavefunction can be constructed [7, 8]. The necessity of v-representable trial densities can be eliminated by using the constrained search formalism [9]. Here, the universal functional of v-representable densities $F[\rho_{v,0}]$ is replaced by the functional

$$\widetilde{F}[\rho] = \min_{\Psi_\rho \to \rho} \left\langle \Psi_\rho \,\middle|\, \hat{T}_N + \hat{V}_{\mathrm{ee},N} \,\middle|\, \Psi_\rho \right\rangle \,, \tag{1.18}$$

a universal functional of N-representable densities which includes implicit minimization over all valid wavefunctions Ψ_ρ that yield the density ρ.

Variational minimization of the total energy expression with respect to the density yields the ground-state energy, which, in this formulation, also holds for degenerate ground states:

$$\begin{aligned} E_{v,0}[\rho_{v,0}] &= \min_{\rho \to N} \left\{ \int \mathrm{d}\boldsymbol{r}\, \rho(\boldsymbol{r}) v(\boldsymbol{r}) + \widetilde{F}[\rho] \right\} \qquad (1.19) \\ &= \min_{\rho \to N} \left\{ \int \mathrm{d}\boldsymbol{r}\, \rho(\boldsymbol{r}) v(\boldsymbol{r}) + \min_{\Psi_\rho \to \rho} \left[\langle \Psi_\rho \,|\, \hat{T}_N + \hat{V}_{\mathrm{ee},N} \,|\, \Psi_\rho \rangle \right] \right\} \,. \end{aligned}$$

While this procedure gives the exact ground state energy of the system, any application of it requires the variational minimization of $\widetilde{F}[\rho]$. This in turn requires the evaluation and minimization of expectation values of correlated

N-electron wavefunctions. As a consequence, using the exact formulation of DFT involves the same or even more effort than the direct solution of the Schrödinger equation.

Applicability of DFT relies on sufficiently good approximations of the universal functional, which depend explicitly on the density (or properties easily derived from it). Unfortunately, such approximations are often unsuitable to describe inhomogeneous systems such as atoms or molecules. Amongst other deficits, the kinetic energy, in particular, is described poorly.

1.2 Kohn-Sham Density Functional Theory

Based on the Hohenberg-Kohn theorems, Kohn and Sham proposed an alternative, but still exact way to apply DFT to electronic systems [10]. They introduced a reference system that produces the same density as the correlated wavefunction, but consists of non-interacting electrons, i.e., a Slater-determinant of Kohn-Sham (KS) orbitals, $\{\varphi\}$ (or more general, a linear combination of energetically degenerate determinants).

The kinetic energy of this reference system, T_s, can be evaluated exactly and is separated from the universal functional,

$$G[\rho] = T_\mathrm{s}[\rho] + E_\mathrm{xc}[\rho] \ , \tag{1.20}$$

where $E_\mathrm{xc}[\rho]$ is defined as the *exchange-correlation* energy of $\rho(\boldsymbol{r})$. The total energy expression then reads

$$E[\rho] = T_\mathrm{s}[\rho] + V_\mathrm{ext}[\rho] + E_\mathrm{H}[\rho] + E_\mathrm{xc}[\rho] \ , \tag{1.21}$$

with $V_\mathrm{ext}[\rho] = \int \mathrm{d}\boldsymbol{r}\ \rho(\boldsymbol{r})v(\boldsymbol{r})$.

From functional variation under conservation of the number of electrons, the stationary condition of the total energy is given in terms of the KS orbitals φ_i by the Kohn-Sham equations

$$\begin{aligned} \left\{-\frac{1}{2}\hat{\triangle} + v(\boldsymbol{r}) + v_\mathrm{H}[\rho](\boldsymbol{r}) + v_\mathrm{xc}[\rho](\boldsymbol{r})\right\}\varphi_i &= \\ \left\{-\frac{1}{2}\hat{\triangle} + v_\mathrm{eff}[\rho](\boldsymbol{r})\right\}\varphi_i &= \varepsilon_i\varphi_i \ , \end{aligned} \tag{1.22}$$

with the exchange-correlation potential $v_\mathrm{xc}[\rho](\boldsymbol{r}) = \frac{\delta E_\mathrm{xc}[\rho]}{\delta\rho(\boldsymbol{r})}$. These equations can be solved iteratively, in a similar way as is done in the Hartree-Fock

(HF) approximation. Having solved the KS equations, the energy of the system can be obtained from equation (1.21).

The KS equations in this form are derived for the case of a closed shell system, i.e., for each spin-up orbital, a spatially identical spin-down orbital exists. For open-shell systems, this is not the case, but the Hohenberg-Kohn and Kohn-Sham formalism could be extended to spin-polarized densities [11]. With σ indicating the spin, i.e.,either $\uparrow$ or $\downarrow$, the total density is the sum of the spin-densities, $\rho = \rho^{\uparrow} + \rho^{\downarrow}$, which are defined by the spin orbitals as $\rho^{\sigma}(\boldsymbol{r}) = \sum_{i=1}^{N_\sigma} |\varphi_i^{\sigma}(\boldsymbol{r})|^2$. The *unrestricted Kohn-Sham* equations read

$$\left\{-\frac{1}{2}\hat{\triangle} + v_{\text{eff}}^{\sigma}[\rho^{\uparrow},\rho^{\downarrow}](\boldsymbol{r})\right\}\varphi_i^{\sigma} = \varepsilon_i^{\sigma}\varphi_i^{\sigma}\ , \tag{1.23}$$

with the spin-dependent effective potential,

$$v_{\text{eff}}^{\sigma}[\rho^{\uparrow},\rho^{\downarrow}](\boldsymbol{r}) = v(\boldsymbol{r}) + v_{\text{H}}[\rho](\boldsymbol{r}) + v_{\text{xc}}^{\sigma}[\rho^{\uparrow},\rho^{\downarrow}](\boldsymbol{r})\ , \tag{1.24}$$

in which the exchange-correlation potential is defined as

$$v_{\text{xc}}^{\sigma}[\rho^{\uparrow},\rho^{\downarrow}](\boldsymbol{r}) = \frac{\delta E_{\text{xc}}[\rho^{\uparrow},\rho^{\downarrow}]}{\delta\rho^{\sigma}(\boldsymbol{r})}\ . \tag{1.25}$$

KS-DFT is an exact treatment of the electronic systems, as E_{xc}, per definition, contains all contributions to the energy not covered by the remaining terms. This, however, only holds if the ground state density is *non-interacting v representable*, i.e., if there exists an effective potential for which the ground state of the non-interacting reference system produces the correct density. This is not the general case [12], but it is commonly assumed to hold in practical applications of KS-DFT.

As in the case of Hohenberg-Kohn DFT, the exchange-correlation functional has to be approximated to make applications practical. The non-interacting kinetic energy usually contains a large part of the total kinetic energy, so that errors due to approximation of E_{xc} turn out to be not as severe as for approximation of $G[\rho]$ as a whole.

1.3 Density Functional Approximations

Several methods of constructing a density functional approximation are possible. It can be constructed empirically to best reproduce experimental data, less empirically to best reproduce properties obtained theoretically, or non-empirically trying to fulfill as many known properties of the exact functional as possible.

Exchange-correlation functionals can be categorized by their level of approximation. Perdew described the different levels as the rungs of "Jacob's ladder of density functional approximations" [13, 14].

This ladder has five rungs and stepping up from one to the next, the functionals become more complex, but by this they also have the potential to be more accurate.

The functionals on the first rung only depend on the value of the spin density and are described by the *local spin-density* (LSD) approximation. The second rung consists of the *generalized gradient approximation* (GGA), where dependencies on the gradient of the spin-density are included in the functional as well. On the third rung, the orbital kinetic-energy density and optional also Laplacians of the density are included, which defines the *meta generalized gradient approximation* (meta-GGA). While the lowest three rungs merely use semi-local information, the *hyper generalized gradient approximation* (hyper-GGA) on the fourth rung also takes the fully non-local exact exchange energy density into account. The functionals on the fifth rung, the *generalized random phase approximation*, also include the unoccupied orbitals.

Local Spin Density Approximation

The most essential model system of electronic structure theory is the homogeneous electron gas (HEG), an infinite number of electrons distributed over all space with a constant, spin-unpolarized density ρ. For this system, the exchange energy is known analytically as a functional of the density in the local density approximation (LDA),

$$E_{\mathrm{x}}[\rho] = \int \mathrm{d}\boldsymbol{r}\; \epsilon_{\mathrm{x}}^{\mathrm{LDA}}(\rho(\boldsymbol{r}))\;, \tag{1.26}$$

with the exchange energy density, $\epsilon_{\mathrm{x}}^{\mathrm{LDA}}$, defined as

$$\epsilon_{\mathrm{x}}^{\mathrm{LDA}}(\rho) = -\frac{3^{4/3}}{4\pi^{1/3}}\rho^{4/3} = -C_{\mathrm{x}}^{\mathrm{LDA}}\rho^{4/3}\;. \tag{1.27}$$

The energy density of a spin polarized HEG, $E_{\mathrm{x}}[\rho^{\uparrow},\rho^{\downarrow}]$ can be evaluated by the fundamental scaling relation of the exchange energy,

$$E_{\mathrm{x}}[\rho^{\uparrow},\rho^{\downarrow}] = \frac{1}{2}\left(E_{\mathrm{x}}[2\rho^{\uparrow}] + E_{\mathrm{x}}[2\rho^{\downarrow}]\right)\;. \tag{1.28}$$

The correlation energy of the HEG is known analytically only in the asymptotic limits of high [15, 16] and low density [17] for the polarized and unpolarized case [18]. The correlation energy for several densities has been evaluated by a quantum Monte Carlo study [19] and several interpolating parametrizations for intermediate densities and spin-polarizations exist, e.g., VWN [20], PZ81 [21] or PW92 [22].

The local spin-density (LSD) approximation of the exchange-correlation energy has the general form,

$$E_{\mathrm{xc}}^{\mathrm{LSD}}[\rho^{\uparrow},\rho^{\downarrow}] = \int \mathrm{d}\boldsymbol{r}\; \varepsilon_{\mathrm{xc}}^{\mathrm{LSD}}\left(\rho^{\uparrow}(\boldsymbol{r}),\rho^{\downarrow}(\boldsymbol{r})\right) \;, \tag{1.29}$$

where $\varepsilon_{\mathrm{xc}}^{\mathrm{LSD}}$ is derived from equations (1.27) and (1.28). When applied to a homogenous electron gas, the LSD approximation gives the exact exchange-correlation energy. For varying electron density, the underlying assumptions are less valid and the error increases with the inhomogeneity of the systems. While the electronic structure of valence states in solid metals is accurately described by LSD, the method usually fails to give a proper description of atoms and molecules, where the valence density has large spatial variations.

Generalized Gradient Approximation

Local spin density functionals only depend on the value of the spin densities and are hence incapable of properly describing strongly varying densities. As an extension to LSD functionals, the generalized gradient approximation (GGA) [23–28] also depends on the gradient of the density. By this some *non-locality* is introduced into the functional as the gradient of the density at some point in space is directly connected to density variations in its vicinity. As these functionals still exclusively depend on properties of the density at each individual point in space, they are usually classified as *semi-local* functionals rather than *non-local*.

A GGA exchange functional can be constructed by scaling the LSD exchange energy density with an enhancement factor, $F(s)$, that depends on the density and its gradient. This dependency is usually expressed by a dimensionless reduced gradient in the form of

$$s(\boldsymbol{r}) = \frac{1}{\sqrt[3]{24\pi^2}} \frac{|\nabla\rho(\boldsymbol{r})|}{\rho(\boldsymbol{r})^{4/3}} \;. \tag{1.30}$$

The general structure of the GGA exchange energy is

$$E_{\mathrm{x}}^{\mathrm{GGA}}[\rho, \nabla\rho] = \int \mathrm{d}\boldsymbol{r}\ \varepsilon_{\mathrm{x}}^{\mathrm{LDA}}(\rho(\boldsymbol{r}))F_{\mathrm{x}}(s(\boldsymbol{r})) \tag{1.31}$$

and several different forms of $F_{\mathrm{x}}(s)$ have been proposed. For $s \to 0$ the enhancement factor should approach unity, to ensure the correct description of the HEG. The GGA correlation functionals can take significantly different forms, but again a desirable feature is to produce the correct correlation energy of the HEG if the gradient of the density is zero.

B88 Exchange Functional

The B88 exchange functional [29] is inspired by deficits of LSD exchange as an approximation for HF exchange. In the HF approximation of a closed shell atom, the exchange energy density, $\varepsilon_{\mathrm{x}}^{\mathrm{HF}}(\boldsymbol{r})$, far from the nucleus is given by [30]

$$\lim_{r\to\infty} \varepsilon_{\mathrm{x}}^{\mathrm{HF}}(\boldsymbol{r}) \simeq -\frac{1}{2|r|}\rho(\boldsymbol{r}) \ . \tag{1.32}$$

In this region, the electron density is decaying exponentially [18] as

$$\lim_{r\to\infty} \rho(\boldsymbol{r}) \simeq 2e^{-\alpha r} \ , \tag{1.33}$$

with α being a factor related to the largest eigenvalue of the occupied orbitals. Application of the LDA exchange functional to this density gives an exchange energy density of

$$\lim_{r\to\infty} \varepsilon_{\mathrm{x}}^{\mathrm{LDA}}(\boldsymbol{r}) \simeq -C_{\mathrm{x}}^{\mathrm{LDA}} 2^{4/3} e^{-\frac{4}{3}\alpha r} \ , \tag{1.34}$$

which decays much faster with r than equation (1.32).

Becke proposed a GGA form for the exchange functional which reproduces the HF exchange-energy density for atomic cases [29]. This functional has one free parameter, which was fit to the exchange energy of the six noble gas atoms from helium through radon. The B88 functional was found to improve the exchange energy over the local approximation with a remarkable accuracy.

LYP Correlation Functional

Colle and Salvetti developed a formula to approximate the correlation energy of a system based on the Hartree-Fock wavefunction [31]. Four free parameters in this formula were fit to best reproduce the correlation energy of the helium atom. Lee, Yang and Parr reformulated the Colle-Salvetti formula as a functional of the the density and local kinetic-energy density. The LYP GGA correlation functional was then obtained by a gradient expansion of the kinetic-energy density [32].

BLYP Exchange-Correlation

In the BLYP exchange-correlation functional, LYP correlation accompanies the B88 exchange functional. This functional greatly improves the description of atomic and molecular systems over the LSD approximation. This remarkable, as the theoretical considerations for the construction of the functional components stem from the Hartree-Fock approximation and adjustable parameters were fit to a very limited test set of rare gas atoms.

PW91 Exchange-Correlation Functional

Perdew and Wang constructed exchange and correlation functionals [33–35] that obey a number of known properties of the exact functional.

The exchange-correlation energy can be expressed as the electrostatic interaction of the density $\rho(\boldsymbol{r})$ with the density of an "exchange-correlation hole" [18, 36] around an electron at $\boldsymbol{r}$, $\rho_{\mathrm{xc}}(\boldsymbol{r},\boldsymbol{r}')$,

$$E_{\mathrm{xc}}[\rho] = \frac{1}{2}\int \mathrm{d}\boldsymbol{r}\,\rho(\boldsymbol{r})\int \mathrm{d}\boldsymbol{r}'\,\frac{\rho_{\mathrm{xc}}(\boldsymbol{r},\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\,. \tag{1.35}$$

The exchange-correlation hole is the sum of the exchange hole and the correlation hole, $\rho_{\mathrm{xc}} = \rho_{\mathrm{x}} + \rho_{\mathrm{c}}$, which have the properties

$$\begin{aligned} E_{\mathrm{x}}[\rho] &= \frac{1}{2}\int \mathrm{d}\boldsymbol{r}\,\rho(\boldsymbol{r})\int \mathrm{d}\boldsymbol{r}'\,\frac{\rho_{\mathrm{x}}(\boldsymbol{r},\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}, \quad \int \mathrm{d}\boldsymbol{r}'\,\rho_{\mathrm{x}}(\boldsymbol{r},\boldsymbol{r}') = -1, \quad \rho_{\mathrm{x}}(\boldsymbol{r},\boldsymbol{r}') < 0 \\ E_{\mathrm{c}}[\rho] &= \frac{1}{2}\int \mathrm{d}\boldsymbol{r}\,\rho(\boldsymbol{r})\int \mathrm{d}\boldsymbol{r}'\,\frac{\rho_{\mathrm{c}}(\boldsymbol{r},\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}, \quad \int \mathrm{d}\boldsymbol{r}'\,\rho_{\mathrm{c}}(\boldsymbol{r},\boldsymbol{r}') = 0\,. \end{aligned} \tag{1.36}$$

Other known properties of the exact functional are limits for the exchange-correlation energy under uniform and non-uniform density scaling [37], a bound for the magnitude of exchange and exchange-correlation energy [38] and the gradient expansion of the HEG energy [10, 39–41].

The functional was derived from a gradient expansion of the electron holes, where cutoff radii were introduced to fulfill the exact properties of the holes. The PW91 exchange functional was proposed as a "modified Becke form" with a decay as s^{-2} for large reduced gradients to fulfill exact bounds [33].

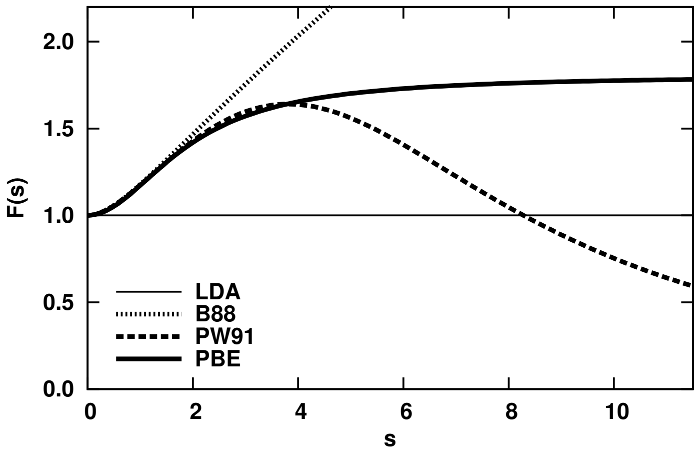

Figure 1.1: *The enhancement factor for exchange, $F(s)$, as a function of the reduced density gradient, s, for B88, PW91 and PBE. LSD corresponds to a constant factor of one.*

The correlation functional was first obtained numerically and then fitted with an analytical expression.

By the introduced cutoffs, the long-range contributions of the exchange and correlation holes are not accounted for. These, however, are expected to cancel each other [42]. Due to this, an accurate description of the energy can still be achieved with this approximate exchange-correlation functional, while the exchange or correlation functional by themselves might give inferior results.

PBE Exchange-Correlation Functional

In 1996, Perdew, Burke and Ernzerhof presented a "GGA made simple" functional [43], which was derived non-empirically, i.e., all parameters in the GGA are fundamental constants. The structure of the functional is much simpler than that of PW91, but PBE does not satisfy all the exact requirements described above. This, however, seems to have a minor effect on its performance for many practical applications, where it performs similar to PW91. Also for PBE, the exchange and correlation functionals complement each other and should not be used individually.

Figure 1.1 shows the enhancement factors of exchange for the three functionals described above.

Hybrid Functionals

Based on the adiabatic connection formula [44], Becke proposed to combine a fraction of exact exchange, i.e., HF-like exchange, with semi-local functionals. He first proposed and tested a "half-and-half" form based on LSD [45],

$$E^{\text{hyb}} = a_1 E_{\text{x}}^{\text{exact}} + a_2 E_{\text{xc}}^{\text{LSD}} \,, \tag{1.37}$$

with $a_1 = a_2 = 0.5$, resembling a linear approximation of the adiabatic connection. This hybrid could describe atomization energy of several molecules more accurately than LSD, but could be improved further by a numerical fit of the two parameters [45].

Perdew, Ernzerhof, and Burke proposed the form of a general hybrid functional [46],

$$E^{\text{hyb}} = E_{\text{xc}} + \frac{1}{n}\left(E_{\text{x}}^{\text{exact}} - E_{\text{x}}\right) \,, \tag{1.38}$$

and argued that the integer n should be the lowest order of perturbation theory which reproduces the integrand of the adiabatic connection reasonably well. They suggested a value of $n = 4$ for a reasonable description of most molecules.

B3LYP

The B3LYP hybrid functional is the most frequently used functional in calculations on molecules [47]. Becke constructed the hybrid functional B3PW91 [48] of the form

$$\begin{aligned} E_{\text{xc}}^{\text{B3PW91}} &= E_{\text{xc}}^{\text{LSD}} + a_0\left(E_{\text{x}}^{\text{exact}} - E_{\text{x}}^{\text{LSD}}\right) \\ &+ a_{\text{x}}\left(E_{\text{x}}^{\text{B88}} - E_{\text{x}}^{\text{LSD}}\right) + a_{\text{c}}\left(E_{\text{c}}^{\text{PW91}} - E_{\text{c}}^{\text{LSD}}\right) \,, \end{aligned} \tag{1.39}$$

with three adjustable parameters, a_0, a_{x}, and a_{c}. The optimal parameters were determined by a linear least-squares fit to atomization energies, ionization potentials, and proton affinities of a selection of molecules as well as the total energy of atoms. The optimized parameters were obtained as $a_0 = 0.20$, $a_{\text{x}} = 0.72$, and $a_{\text{c}} = 0.81$.

Based on this functional, Stephens *et al.* created the B3LYP [49] hybrid functional, which differs from B3PW91 in the correlation functional. The LYP functional replaced PW91 correlation and the VWN functional was used as the local component of correlation. Even though the parameters determined by Becke had not been refit to the different functional form, the B3LYP functional gives remarkably accurate results for calculations on molecular systems.

PBE0

Adamo and Barone [50] used this functional form of equation (1.38) with $n = 4$ to construct the non-empirical hybrid functional PBE0,

$$E^{\mathrm{PBE0}} = E_{\mathrm{xc}}^{\mathrm{PBE}} + \frac{1}{4}\left(E_{\mathrm{x}}^{\mathrm{exact}} - E_{\mathrm{x}}^{\mathrm{PBE}}\right) . \tag{1.40}$$

The PBE0 functional improved agreement with experiment over PBE for equilibrium geometry, binding energy, dipole moment and harmonic frequency of a selection of molecules [50].

The energy of hybrid functionals is commonly found by using the KS-equations (1.23) with a non-local exchange-correlation operator $\hat{v}_{\mathrm{xc}}^{\sigma}$. The non-locality is introduced by variation of the non-local exact exchange with respect to the orbitals. This way of treating hybrid functionals is referred to as *generalized Kohn-Sham*, as a true KS method involves a local potential derived from variation with respect to the spin density. A true KS treatment of hybrid functionals can be achieved by means of the optimized effective potential (OEP) method [51–53].

1.4 Shortcomings of Approximate Functionals

Approximations of the exact exchange-correlation functional introduce errors into DFT. These errors can be minor, i.e., within an acceptable tolerance for the particular observable, or severe, which indicates that the particular functional approximation is inappropriate to describe the property of interest. Semi-local functionals often predict the atomization energy of molecules, i.e., the energy needed to split the molecule into individual atoms, to be too high, but are usually in significantly better agreement with experiment for GGA functionals than for LSD. Chemical bonds are usually predicted to be too long, but here GGA functionals give slightly worse results than LSD. Reaction barriers, i.e., the energy difference between the saddle points on the potential energy surface and the minima corresponding to reactants, are usually predicted to be too low by semi-local functionals. In the last years, a large number of functionals has been developed to improve the accuracy of DFT. These are often able to reproduce a certain chemical property very well, while they usually give suboptimal accuracy for many others [54].

Some of the errors of semi-local functionals are expected to be due to a delocalization error, i.e., the tendency to predict a too low energy of delocalized electron densities. The delocalization error becomes evident in the dissociation of diatomic molecules. Homonuclear diatomic cations, X_2^+, are expected to dissociate into two $X^{\frac{1}{2}+}$ fragments. The total energy should be identical to the sum of the energy of X and X^+. For H_2^+, the simplest system of this kind, the energy of the separated $H^{\frac{1}{2}+}$ systems is lower than that of a hydrogen atom and a single proton [55]. Heteronuclear molecules, on the other hand, should dissociate into fragments with integer charges. The dissociation of NaCl predicted by the LSD approximation, however, results in $Na^{0.4+}$ and $Cl^{0.4-}$ [56]. The equilibrium structure of molecules can also be affected by the delocalization error, as illustrated by alkynyl radicals. The PBE equilibrium geometry of the ethynyl radical is not linear, but bent with an angle of 165° [57]. Too strong delocalization of the electron density is expected to cause this effect. Semi-local functionals can also fail to properly describe localized electronic defects in solid state systems where the density becomes too delocalized [58].

The delocalization error is closely related to the self-interaction error (SIE) in approximate functionals. The Hartree energy is the classical Coulomb interaction of the electron density with itself,

$$E_{\mathrm{H}}[\rho] = \frac{1}{2} \iint \mathrm{d}\boldsymbol{r}\, \mathrm{d}\boldsymbol{r}' \, \frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}, \tag{1.41}$$

which includes a spurious interaction of each electron with itself. This, however, is compensated by equally large terms of opposite sign in the exact exchange functional, as is the case for the Hartree-Fock approximation. In the common formulation of the Hartree-Fock total energy, both the Coulomb and the exchange energy expression contain terms of orbital self-interaction, $E_{\mathrm{SI,H}}$ and $E_{\mathrm{SI,x}}$, with opposite signs,

$$E_{\mathrm{SI,H}}[\varphi^N] = \frac{1}{2} \sum_{i=1}^{N} \iint \mathrm{d}\boldsymbol{r}\, \mathrm{d}\boldsymbol{r}' \, \frac{\rho_i(\boldsymbol{r})\rho_i(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} = -E_{\mathrm{SI,x}} \, , \tag{1.42}$$

where φ^N represents the set of N orbitals and $\rho_i(\boldsymbol{r}) = |\varphi_i(\boldsymbol{r})|^2$ is the single-particle density of orbital φ_i.

In contrast to HF, the cancellation of these terms is usually incomplete when approximate exchange-correlation functionals are used in DFT. For systems of a single electron, the conditions for a self-interaction free functional can be expressed as

$$E_{\mathrm{x}}[\rho^1] = -E_{\mathrm{H}}[\rho^1] \qquad \text{and} \qquad E_{\mathrm{c}}[\rho^1] = 0\,, \tag{1.43}$$

which can be used to define a measure for the one-electron self-interaction error of a functional by

$$E_{\mathrm{SIE}}[\rho^1] = E_{\mathrm{xc}}[\rho^1] + E_{\mathrm{H}}[\rho^1]\,. \tag{1.44}$$

It is possible to construct semi-local correlation functionals that return zero energy for any one-electron density and non-zero energy for many-electron densities, e.g., LYP or by a meta-GGA construction. The main problem is to construct an exchange functional that will be self-interaction free for one electron densities: The electrostatic interaction has a strong long-range character which makes the Hartree energy fully non-local. This, however, has to be compensated by a functional that has only local information of the density. Given a particular one-electron density, a semi-local exchange functional can be constructed so that equation (1.43) will hold. It is, however, most likely impossible to create a functional at this level of approximation which is self-interaction free for *all* possible one-electron densities.

The effect of the self-interaction error can be illustrated with the example of hydrogen-like systems, where the ground state wavefunction, density, and total energy are known analytically. For these systems the exact Kohn-Sham equations are equivalent to a one-electron Schrödinger equation and the exact KS-eigenvalue of the orbital is equal to the total energy. Table 1.1 lists the energy and eigenvalue of the atomic one-electron systems of H throughout Ne^{9+}, calculated with the exact density using the LSD and PBE functionals.

Comparison of the total energy shows that the deviations for LSD increase with the nuclear charge, giving the largest error for neon, 0.39 Ha. For PBE, the deviation is much smaller, only 0.06 Ha, so this functional is nearly one-electron self-interaction free for these systems.

It was shown by Janak [59] that the highest eigenvalue of the KS-orbitals obtained from the exact functional corresponds to the change in total energy with respect to variation of the occupation of this orbital. Perdew *et al.* could show [60, 61] that the total energy changes linearly with the occupation number of an orbital, the slope corresponding to its eigenvalue.

Table 1.1: *Exact energy and KS eigenvalue of atomic one-electron systems compared to LSD and PBE. The estimates of the eigenvalue $\langle\varepsilon\rangle$ are obtained by projection of equation (1.23) using the exact orbital.*

Z	$E_{\text{exact}}, \varepsilon_{\text{exact}}$	$E(\text{LSD})$	$E(\text{PBE})$	$\langle\varepsilon\rangle$ (LSD)	$\langle\varepsilon\rangle$ (PBE)
1	-0.50	-0.48	-0.50	-0.26	-0.27
2	-2.00	-1.94	-1.99	-1.50	-1.54
3	-4.50	-4.40	-4.49	-3.74	-3.80
4	-8.00	-7.86	-7.98	-6.97	-7.07
5	-12.50	-12.32	-12.47	-11.21	-11.33
6	-18.00	-17.78	-17.97	-16.44	-16.60
7	-24.50	-24.23	-24.46	-22.68	-22.86
8	-32.00	-31.69	-31.95	-29.91	-30.13
9	-40.50	-40.15	-40.45	-38.14	-38.39
10	-50.00	-49.61	-49.94	-47.38	-47.66

For LSD and PBE, however, the eigenvalues are too small in magnitude, with PBE eigenvalues being only slightly closer to the exact value. This deviation results from violation of the energy linearity by semi-local functionals. Instead of being linear, the energy is usually a convex function of the occupation number for semi-local functionals [55, 62]. Due to this, the highest KS-eigenvalue is usually too small in magnitude when compared to the ionization energy. Likewise, the errors in the dissociation limit of X_2^+ or NaCl can be traced back to this undesirable property.

In many-electron systems, equation (1.44) cannot be used to evaluate the magnitude of the self-interaction error in the energy, as it is only defined for one-electron densities. However, the presence of a many-electron self-interaction error can be described qualitatively for these systems by the violation of the energy linearity.

Several ways have been proposed to correct for the self-interaction error in semi-local functionals [21, 63, 64]. Of these, the Perdew-Zunger self-interaction correction [21] received the most attention in the past and is explored in more detail in the following sections.

2 Perdew-Zunger Self-Interaction Correction

The exact exchange-correlation functional exactly compensates the Hartree self-energy but approximate functionals usually fail to do so. It is possible to construct self-interaction free correlation functionals at the semi-local level, e.g., LYP. However, none of the available semi-local exchange functionals can compensate the fully non-local Hartree energy for all possible one-electron densities. Perdew and Zunger [21, 65–67] proposed a correction for approximate functionals that removes this particular form of self-interaction error.

2.1 Definition

The Perdew-Zunger self-interaction correction (PZ-SIC) [21] subtracts the self-interaction errors of the orbitals, as defined in equation (1.44), from the approximate exchange-correlation functional,

$$E_{\mathrm{xc}}^{\text{PZ-SIC}}[\rho^N] = E_{\mathrm{xc}}[\rho^N] - \sum_{i=1}^{N} E_{\mathrm{SI}}[\rho_i] \ . \tag{2.1}$$

This correction can be applied to any functional and has four desirable properties [68]:

1. $E_{\mathrm{xc}}^{\text{PZ-SIC}}[\rho^1]$ exactly cancels the non-local Hartree energy of any one-electron system, regardless of the functional approximation it is based on.

2. The correction has no effect when applied to the exact functional, as it is already self-interaction free, i.e., $E_{\text{SI}}^{\text{exact}}[\rho_i] = 0$.
3. $E_{\text{xc}}^{\text{PZ-SIC}}$ is self-interaction free in the sense that applying the correction a second time has no effect, i.e., it behaves like the exact functional in this respect.
4. For an atomic ion of charge $+Q$ a single electron far from the nucleus experiences the correct $-(Q+1)/r$ potential, as $E_{\text{xc}}^{\text{PZ-SIC}}$ corrects for its Hartree self-interaction.

The numerical results presented by Perdew and Zunger [21] on atomic systems were impressive: The total energy of atoms is in much better agreement with experiment and SIC-LSD also predicts stable anions, where LSD often fails. Furthermore, the negative of the orbital eigenvalues were shown to agree better with ionization energy both from the valence and core shells. For semi-local functional approximations, the orbital eigenvalues are generally higher, resulting in an underestimation of the ionization energy.

2.2 Self-Consistent Minimization

The first application of PZ-SIC was based on several approximations that did not allow for a truly self-consistent minimization. Later a self-consistent and efficient minimization became possible. In fact, the key 'ingredients' in the self-consistent minimization technique had already been mentioned in the 1981 publication, but it took a few decades until they had been implemented and their importance and implications had been understood.

Initial Formulation

Perdew and Zunger determined the ground state orbitals and energy by solving the set of Kohn-Sham-like equations,

$$\left\{-\frac{1}{2}\hat{\triangle} + v_{\text{eff}}^{\sigma}(\boldsymbol{r}) - v_{\text{H}}[\rho_i^{\sigma}](\boldsymbol{r}) - v_{\text{xc}}^{\uparrow}[\rho_i^{\sigma},0](\boldsymbol{r})\right\}\varphi_i^{\sigma} = \varepsilon_i^{\sigma}\varphi_i^{\sigma}\ . \tag{2.2}$$

These differ from the KS equations (1.23) by the orbital specific potentials $-\hat{v}_{\text{H}}[\rho_i^{\sigma}]$ and $-\hat{v}_{\text{xc}}^{\uparrow}[\rho_i^{\sigma},0]$ that arise from the SIC terms of orbital φ_i^{σ} in the variation of the PZ-SIC energy. The Hamiltonian can be written more compactly as

$$\hat{H}_i = \hat{H}_0 + \hat{V}_i\ , \tag{2.3}$$

where the spin index has been dropped for brevity, $\hat{H}_0$ contains all orbital-independent terms of the Hamiltonian, and $\hat{V}_i$ contains the orbital dependent potentials of orbital φ_i.

It is pointed out that finding the solution to this set of equations results in slightly unorthogonal orbitals, but that an enforced orthogonalization has little effect on the numerical results.

Off-diagonal Lagrange multipliers

> *"If desired, the optimum set of orthogonal orbitals could of course be found by introducing off-diagonal Lagrange multipliers."* [21]

Perdew and Zunger did not employ the mentioned off-diagonal Lagrange multipliers, but this was done by Harrison, Heaton and Lin [69]. They derived a necessary (though not sufficient) minimum condition for the PZ-SIC energy from the functional derivative with respect to the complex conjugate of the orbitals, φ_i^*,

$$\hat{H}_i \varphi_i = \sum_{j=1}^{N} \lambda_{ji} \varphi_j \ . \tag{2.4}$$

The orbitals are coupled via the matrix $\boldsymbol{\lambda}$, whose elements, the Lagrange multipliers, were defined as

$$\lambda_{ji} = \left\langle \varphi_j \,\middle|\, \hat{H}_i \,\middle|\, \varphi_i \right\rangle \ . \tag{2.5}$$

For functionals that only depend on the total density, the variation gives a similar minimum condition, with the difference that all operators $\hat{H}_i$ are identical. In this case, the matrix of Lagrange multipliers is Hermitian. By a unitary transformation of the orbitals, which does not change the total energy, the minimum condition can be reformulated as a set of eigenvalue equations. For PZ-SIC, this is not possible in a straightforward way and the set of coupled equations (2.4) has to be solved.

The algorithms that had been developed for DFT could not be used to minimize the PZ-SIC energy, as they usually relied on expressing the minimization as an eigenvalue problem based on a Hermitian operator.

Unified Hamiltonian

Harrison, Heaton and Lin defined a Hermitian "unified Hamiltonian" [69],

$$\hat{H}_\mathrm{u} = \sum_{i=1}^{N} \hat{P}_i \hat{H}_i \hat{P}_i + \hat{O} \hat{H}_i \hat{P}_i + \hat{P}_i \hat{H}_i \hat{O} \, , \tag{2.6}$$

built up from the orbital specific SIC-Hamiltonians, $\hat{H}_i$, and the projection operators

$$\hat{P}_i = |\varphi_i\rangle \langle\varphi_i| \quad \text{and} \quad \hat{O} = 1 - \sum_{i=1}^{N} \hat{P}_i \, . \tag{2.7}$$

Finding a diagonal representation of this unified Hamiltonian was shown to be equivalent to fulfilling the necessary minimum condition (2.4). Thus, the proposed minimization problem could be solved by using the Hermitian unified Hamiltonian with the well established iterative diagonalization algorithms.

Localization condition

> *"The self-interaction correction depends on the choice of orbital representation. [...] Since the orbital densities [...] change under the [unitary] transformation, the SIC total energies are* not *invariant. [...] The right unitary transformation might be the one which minimizes the SIC energy expression."* [21]

The dependence of the PZ-SIC energy on the choice of the unitary transformation among the occupied orbitals was not accounted for in the unified Hamilton approach. As equation (2.4) does not take the unitary transformations into account, it is only a necessary, but not a sufficient condition for a minimum of the energy.

Pederson, Heaton and Lin analyzed the dependence of the PZ-SIC energy on unitary transformations among the occupied orbitals and derived a minimum condition for the variation in this subspace [70]. The "localization condition",

$$\left\langle \varphi_i \,\middle|\, \hat{H}_i - \hat{H}_j \,\middle|\, \varphi_i \right\rangle = \left\langle \varphi_i \,\middle|\, \hat{V}_i - \hat{V}_j \,\middle|\, \varphi_i \right\rangle = 0 \, , \tag{2.8}$$

holds for all pairs of orbitals if the energy is in a stationary state with respect to a unitary transformation amongst them. It can easily be shown that the matrix of Lagrange multipliers, as defined by equation (2.5), is Hermitian if the localization condition is fulfilled. Equations (2.4) and (2.8) together are the sufficient conditions for a stationary state of the PZ-SIC energy.

Pederson *et al.* used the unified Hamiltonian to find the ground-state energy, but included an additional step before each diagonalization, in which the orbitals were transformed to fulfill the localization condition and minimize the SIC terms. With this method, the molecules N_2 [70] and Li_2 [71] as well as atomic systems [72] were studied. The energy minimizing orbitals of the atomic systems appeared as hybrid orbitals of each shell's s and p type functions.

Analytical energy gradient

The diagonalization of the unified Hamiltonian after enforcing the localization condition can result in convergence problems in cases of (nearly) degenerate orbitals [71]. Such problems can be avoided by a direct minimization of the energy based on energy gradients. Goedecker and Umrigar derived the energy gradient with respect to variation of the orbitals as the residual [73]

$$G_i(\boldsymbol{r}) = \hat{H}_i \varphi_i(\boldsymbol{r}) - \sum_{j=1} \tilde{\lambda}_{ji} \varphi_j(\boldsymbol{r}) \ , \tag{2.9}$$

in which the Lagrange multipliers are defined from the Hermitian part of the matrix $\boldsymbol{\lambda}$,

$$\tilde{\lambda}_{ij} = \frac{1}{2}(\lambda_{ij} + \lambda_{ji}^*) = \frac{1}{2} \left\langle \varphi_i \,\middle|\, \hat{H}_i + \hat{H}_j \,\middle|\, \varphi_j \right\rangle \ . \tag{2.10}$$

With this energy gradient, the minimum of the PZ-SIC energy can be found reliably in a direct minimization using well established gradient based minimization algorithms.

Double Basis Set

It was shown by Pederson *et al.* [71] that the matrix of Lagrange multipliers becomes Hermitian and can be diagonalized to produce a set of canonical orbitals and eigenvalues. Messud *et al.* used this property in an application of PZ-SIC in time-dependent DFT [74–76]. The canonical set of orbitals, ψ^N, is connected to the energy optimizing orbitals, φ^N, by the unitary transformation, $\boldsymbol{W}$, which diagonalizes the matrix $\boldsymbol{\lambda}$,

$$\psi_i(\boldsymbol{r}) = \sum_{k=1}^{N} W_{ik}^* \varphi_k(\boldsymbol{r}) \ , \quad \lambda_{ji} = \sum_{k=1}^{N} W_{kj}^* \varepsilon_k W_{ki} \ . \tag{2.11}$$

This makes it possible to reformulate the minimum condition (2.4) in terms of the canonical orbitals as the set of eigenvalue equations,

$$\hat{H}_0\psi_k + \sum_{i,j=1}^{N} W_{ki}^* \hat{V}_i W_{ji} \psi_j = \left\{\hat{H}_0 + \hat{V}_k^c\right\} \psi_k = \varepsilon_k \psi_k \; , \tag{2.12}$$

with the canonical orbital specific operator, $\hat{V}_k^c$, defined as [77]

$$\hat{V}_k^c = \sum_{i=1}^{N} W_{ki}^* \hat{V}_i \left|\varphi_i\right\rangle \left\langle\psi_k\right| \; . \tag{2.13}$$

The formulation of the optimization problem in terms of an eigenvalue problem, which is possible by enforcing the localization condition, not only helps when PZ-SIC is used in time-dependent applications but also makes it possible to implement stationary PZ-SIC in a more efficient way [74, 75, 77].

2.3 Previous Assessment

Several studies of PZ-SIC applied to atomic and molecular systems have been published. The following list is far from complete, but gives an idea about the range of systems and observables that have been studied and the conclusions that have been drawn from those studies.

Johnson *et al.* studied the $H_2 + H$ exchange reaction and found that PZ-SIC resulted in shorter bonds and higher energy barrier [78]. This was confirmed by a later study of Csonka and Johnson [79]. Goedecker and Umrigar showed that LSD+SIC gives an improvement over LSD in the total energy of atoms. On the other hand, LSD+SIC predicted too short equilibrium bond lengths in molecules and increased the error in one calculated reaction energy [73]. Patchkovskii and Ziegler studied several reactions with respect to the reaction energy and barrier height [80]. The results indicated that SIC had a minor effect on reaction energy, while the energy of saddle point structures was increased, resulting in a correction in the predicted barrier heights. Gräfenstein *et al.* studied the dissociation of radical ions and found that SIC predicted an incorrect, non-planar ground state geometry of the CH_3 radical [81], which was also found for the isoelectronic NH_3^+ radical cation [82]. A qualitative improvement in the description of the dissociation of radical cations was obtained, but the results on equilibrium properties were generally poor.

Vydrov *et al.* studied the effect of SIC on the formation enthalpy of several molecules and found that for LSD, SIC reduced the errors, but the application to GGA functionals led to worse results [83]. In an extensive study they later analyzed the total energy of atoms, atomization energy and equilibrium bond length of molecules, reaction barrier heights as well as ionization energy and electron affinity calculated from energy differences. The results indicated that SIC improved energetics for LSD but often gave less accurate values for the PBE functional [84, 85].

2.4 Scaled Self-Interaction Correction

It was found that PZ-SIC often results in an overcorrection of errors in calculated observables. To improve the accuracy, scaled down versions of SIC have been proposed and tested. These modified functionals take the form

$$E^{\mathrm{SIC}}[\rho^{\uparrow},\rho^{\downarrow}] = E^{\mathrm{KS}}[\rho^{\uparrow},\rho^{\downarrow}] - \sum_{i=1}^{N} \alpha_i E^{\mathrm{SIE}}[\rho_i] \,, \tag{2.14}$$

where α_i can take any values between zero (no SIC) and one (PZ-SIC).

The simplest way to scale the SIC terms is by using a constant factor for all orbitals [86]. This global scaling could be shown to improve calculated observables, but the optimal factor differs for different observables and functionals [87, 88]. Furthermore, by using a factor other than unity, the functional will not give the correct energy for one-electron systems and will not produce the correct long range behavior of the potential.

Vydrov *et al.* proposed more flexible ways of scaling. The factor for each orbital is determined from its kinetic-energy density [85] or, in a simpler approach, based on its orbital density [89], while in both cases depending on one additional, adjustable parameter. In both schemes, the functional reduces to PZ-SIC for any one-electron density. Numerical tests showed that this way of scaling can improve the accuracy over both semi-local functionals and PZ-SIC. The optimal parameter, however, differs for different functionals and depends on which observable is studied. Also here, the correct long range behavior of the potential is lost if the factors do not equal unity.

3

Implementation of Perdew-Zunger Self-Interaction Correction

Self-consistent calculations using orbital-density dependent self-interaction correction require a reliable minimization algorithm. Furthermore, common and usually valid approximations used in applications of KS-DFT have to be reviewed, as they might be inappropriate due to the fundamentally different structure of the PZ-SIC functional. The restriction to real orbitals is one of the approximations that can be shown not to be applicable for PZ-SIC functionals.

3.1 Complex Orbitals

Orbitals in conventional, stationary DFT are commonly taken to be real valued functions. Even though wavefunctions are in general complex, the restriction to real orbitals usually does not affect the ground state properties predicted by semi-local functionals.

For example, the *p*-orbitals of hydrogen-like atoms can be described by various equivalent sets of three functions. In the familiar Cartesian representation the set consists of the 'dumbbell' shaped p_x, p_y, and p_z orbitals. However, the spherical harmonic representation of p_{-1}, p_0, and p_{+1} can also be used. As shown in figure 3.1, the complex p_0 equals the real p_z, while the density of the other two complex orbitals is different and corresponds to a ring rather than a dumbbell. The total density of three occupied p orbitals is, however, the same in both representations, so that either one of the two

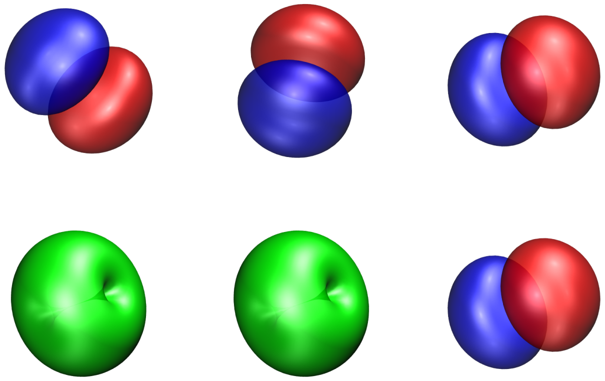

Figure 3.1: *Orbital density isosurfaces of a set of real (top) and complex (bottom) p-orbitals. For real valued orbitals, red and blue color of the isosurface indicates the sign of the wavefunction. The real orbitals are spatially degenerate. Of the complex orbitals (bottom row), the* p_0 *orbital is equivalent to* p_z*, while* p_+ *and* p_- *differ in shape and both produce the same density.*

sets of functions will give the same energy in semi-local DFT. In PZ-SIC, on the other hand, the functional depends on the individual orbital densities, so that the real and complex representation will in general not give the same energy. Harrison found the SIC energy of the complex set of orbitals to be lower than that of the real one [90]. Later, however, Pederson *et al.* could show that the energy can be lowered even further, if the s and p orbitals are allowed to hybridize to form the real sp^3 hybrid orbitals that fulfill the localization condition [72]. It is clear that the SIC energy of real and complex orbitals can differ, but the published results of previous studies did not indicate that complex orbitals give a lower ground state energy, so that they were often not even considered in the self-consistent minimization.

In a few studies, however, the SIC energy could be shown to be lowered when the orbitals are allowed to be complex. Unfortunately, these results remained unpublished [91], had been disregarded as being unphysical [92] or did not attract wide attention [93]. Systematic studies using complex orbitals with PZ-SIC functionals have been published just recently [94, 95]. The study focusing on the total energy of atoms (see appended article I) confirms the early, unpublished results by Pederson [91], which showed that a lower energy could be obtained for the neon atom if complex lin-

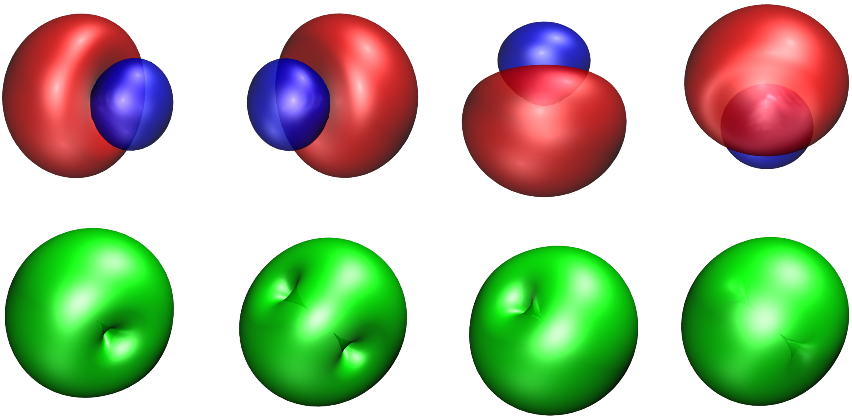

Figure 3.2: *Orbital density isosurfaces of a set of real (top) and complex (bottom)* sp^3*-orbitals. Both the real and complex orbitals are spatially degenerate.*

ear combination coefficients were allowed in the construction of the hybrid orbitals.

In figure 3.2 the set of (idealized) energy minimizing complex sp^3 orbitals of neon is compared to the set of the corresponding real orbitals. Both sets consist of four spatially degenerate hybrid orbitals, however their form and orientation to each other is very different. While the real orbitals have nodal surfaces, i.e. a two-dimensional surface of zero density, the complex orbitals are more diffuse and have only a ‘nodal line’, i.e., a vanishing density along a one-dimensional path.

3.2 Unitary Optimization Algorithm

The direct minimization of the SIC energy using the gradients of equation (2.9) makes it possible to find the ground state energy self-consistently. However, the computational effort of this approach is usually much higher than for conventional DFT and furthermore converges at a lower rate. The convergence can be improved by using conjugate gradient methods instead of a simple steepest descent minimization, but it still cannot reach the performance obtained for conventional DFT.

The performance of the minimization algorithm can be greatly improved by using a two step scheme, where first the energy minimizing unitary transformation of the occupied orbitals is found, and these optimal orbitals then are altered according to the total energy gradient [75, 77]. The general structure of this two step scheme is described in article II included in this thesis.

The intermediate unitary optimization can give a similar convergence rate, in terms of number of iterations, as for semi-local functionals. However, for each iteration the computational effort is significantly higher than for semi-local functionals, as the additional SIC terms in the energy functional and gradients have to be evaluated, and the optimal unitary transformation has to be found. The unitary optimization is often the bottleneck of a self-consistent SIC calculation, so it is important to use an efficient algorithm to find the optimal transformation.

Many commonly used algorithms for the direct minimization of the total energy propagate the orbitals by a linear variation based on a 'direction' derived from the residual (2.9). The altered orbitals are then not orthonormal and have to be orthonormalized after each step. The breaking of orthogonality can be avoided by a careful choice of the search direction [96], in which case the use of conjugate gradients can greatly increase the convergence rate. The linear correction scheme can also be applied for the unitary optimization, but in this case orthogonality will *always* be broken.

Using the double basis set approach, the energy can be expressed as a function of the transformation matrix $\boldsymbol{W}$ that connects the canonical orbitals ψ^N to the optimized ones. The energy gradient with respect to variation of the matrix elements can be expressed as

$$\boldsymbol{G}^{UO} = \boldsymbol{W}\boldsymbol{\kappa} \; , \tag{3.1}$$

where $\boldsymbol{\kappa} = (\boldsymbol{\lambda} - \boldsymbol{\lambda}^\dagger)/2$ is the anti-Hermitian part of $\boldsymbol{\lambda}$. The steepest descent direction is defined as $\tilde{\boldsymbol{D}} = -\boldsymbol{G}^{UO}$. In the linear correction scheme, a new transformation $\boldsymbol{W}'$ of lower energy is found as

$$\boldsymbol{W}' = \hat{O}\left(\boldsymbol{W} + \delta\tilde{\boldsymbol{D}}\right) \; . \tag{3.2}$$

The orthonormalization operation $\hat{O}$ restores unitarity of $\boldsymbol{W}'$, which is broken for a finite step length δ. The energy minimizing step length can be determined by a line search or, in many cases more efficiently, by locating the minimum of a quadratic extrapolation of the energy as a function of δ. This is, however, not trivial as the effective, orthonormality conserving direction of propagation changes with the step length, due to the explicit orthogonalization.

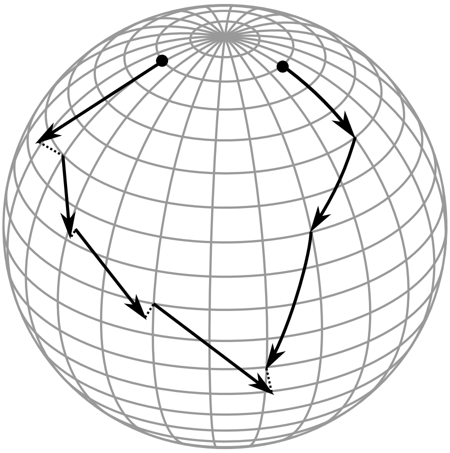

Figure 3.3: *Illustration of the linear (left) and geodesic propagation (right) of orthonormal orbitals, represented by a sphere. The linear propagation breaks orthonormality, which has to be enforced after each step (dotted lines). The geodesic propagation always maintains orthonormality.*

The constrained minimization can be converted into an unconstrained minimization by changing the domain of the energy function. The Stiefel manifold incorporates the imposed constraint of unitarity and minimization algorithms of functions on this manifold are available [97, 98]. Here, the matrix is propagated along a geodesic, i.e., a curved path on the orthonormality hypersurface, parametrized by the matrix exponential of a search direction given by $\boldsymbol{D} = \boldsymbol{W}^{\dagger}\tilde{\boldsymbol{D}}$,

$$\boldsymbol{W}' = \boldsymbol{W} \exp\left(\delta \boldsymbol{D}\right) \ . \tag{3.3}$$

In figure 3.3 the linear and geodesic schemes are illustrated on a sphere, representing the (in general high-dimensional) orthonormality hypersurface.

In the geodesic parametrization, the search direction is independent of the step length. The minimum of a quadratic extrapolation, using the initial gradient, $\boldsymbol{\kappa}_0$, and the gradient $\boldsymbol{\kappa}_{\delta_0}$ evaluated after a trial step of δ_0, is given by

$$\delta_{\min} = \delta_0 \frac{\operatorname{tr}\left(\boldsymbol{D}^{\dagger}\boldsymbol{\kappa}_0\right)}{\operatorname{tr}\left(\boldsymbol{D}^{\dagger}\boldsymbol{\kappa}_0\right) - \operatorname{tr}\left(\boldsymbol{D}^{\dagger}\boldsymbol{\kappa}_{\delta_0}\right)} \ . \tag{3.4}$$

The minimization on the Stiefel manifold furthermore can make efficient use of the nonlinear conjugate gradient method [99]. The difficulty in using this method with the orthogonality breaking scheme is the necessity to 'transport' the gradient along the propagated path, to evaluate the new search direction for the next step. On the Stiefel manifold, the search direction of iteration $(i+1)$ is given by [97, 98]

$$\boldsymbol{D}_{(i+1)} = -\boldsymbol{\kappa}_{(i+1)} + \gamma_{(i+1)} \boldsymbol{D}_{(i)} \ . \tag{3.5}$$

The factor $\gamma_{(i+1)}$ can be determined sufficiently well by the approximate Polak-Ribière formula [98, 100],

$$\gamma_{(i+1)} = \frac{\operatorname{tr}\left(\boldsymbol{\kappa}^{\dagger}_{(i+1)} \boldsymbol{\kappa}_{(i+1)}\right) - \operatorname{tr}\left(\boldsymbol{\kappa}^{\dagger}_{(i+1)} \boldsymbol{\kappa}_{(i)}\right)}{\operatorname{tr}\left(\boldsymbol{\kappa}^{\dagger}_{(i+1)} \boldsymbol{\kappa}_{(i+1)}\right)} \ . \tag{3.6}$$

With the algorithm described here, an accurate and efficient unitary optimization is possible. The formulation as a minimization problem on the Stiefel manifold makes it possible to use the method of conjugate gradients, which can reliably find the minimum in fewer iterations than the steepest descent method. This, however, requires repeated minimization of the energy along a geodesic. Expensive full line searches can be replaced by a gradient based quadratic extrapolation. This can locate the minima with sufficient accuracy for the nonlinear conjugate gradient method to work properly, as was also found for a conjugate gradient based approach to finding first order saddle points [101, 102].

This algorithm has been implemented in different software applications and was used for efficient unitary optimization in several studies on PZ-SIC [94, 95, 103, 104]. A modified version of this algorithm has been proposed by Park *et al.*, which uses a quadratic extrapolation based on the energy to estimate the minimum in the line search [105]. A detailed presentation of the developed algorithm and a study of the performance and comparison to other methods is given in reference [106].

3.3 Quantice

The study of electronic systems with PZ-SIC requires implementation in a quantum chemistry software application. A software application capable of PZ-SIC calculations of atoms and molecules had been developed earlier [107], but was based on using real orbitals. A search for a free,[1] all-electron quantum chemistry software application which could use complex orbitals in stationary, i.e., ground state calculations, did not reveal any candidate that could be easily extended to work with PZ-SIC functionals. Thus, development of QUANTICE [109] began, based on a code written by P. Klüpfel, which was capable of describing molecular orbitals as complex linear combinations of Gaussian type orbitals. The code was consequently extended to full functionality for PZ-SIC calculations as a part of this thesis project.

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[1] "free" as in "free speech," not as in "free beer" [108]

QUANTICE is capable of calculations using LSD, GGA, hybrid, and PZ-SIC functionals, as well as Hartree-Fock. The energy is minimized in the generalized Kohn-Sham scheme. For the unitary optimization, the algorithm described in section 3.2 is used. The total energy is minimized using the linear correction scheme with a conjugate gradient method. QUANTICE was used to obtain all numerical results presented in the following sections.

4

Numerical results

The effect of complex orbitals in self-interaction corrected functionals is studied by comparing several calculated observables to experimental or theoretical reference values. The most fundamental observable available from a calculation is the total energy. The potential energy surface (PES) can be constructed from repeated calculations at different geometry. The location of minima on this surface represent equilibrium structures of the system within the Born-Oppenheimer approximation. From energy differences of points on the PES, the atomization energy of molecules or the height of reaction barriers can be calculated. Ionization energy and electron affinity can be calculated from energy differences of neutral and charged systems.

In the following sections, several observables obtained with different functionals are analyzed. In addition to PZ-SIC, the effect of scaling the SIC terms, globally by a factor of one half, has also been studied for the molecular systems.

4.1 Atomic Systems

In appended article I, the difference between using real or complex orbitals with PZ-SIC is studied for atoms, using LSD+SIC and PBE+SIC. The results show, that the total energy is strongly affected by the restriction to real orbitals, giving generally higher energy for the larger atoms. A smaller effect is found for some other observables, such as ionization energy.

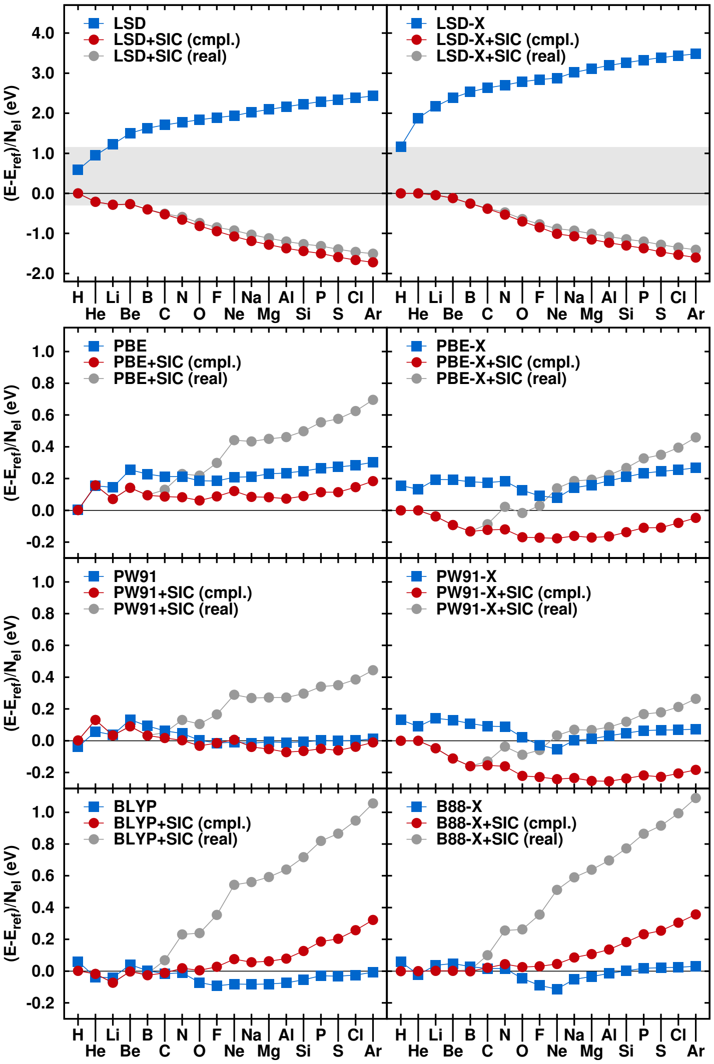

Figure 4.1: *Energy of atoms H to Ar using the uncorrected and PZ-SIC versions of LSD, PBE, PW91 and BLYP functionals and their corresponding exchange components. The total energy is compared with accurate, non-relativistic estimates [110] (left panel), the exchange only energy is compared to Hartree-Fock values (right panel). The figure shows the deviation per electron from the reference value.*

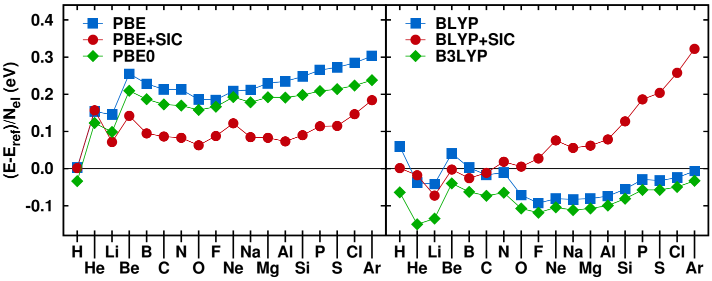

Figure 4.2: *Errors in total energy for the atoms H to Ar. PBE and BLYP are compared to the respective SIC and hybrid functionals.*

Total Energy

The total energy of atoms is overestimated in LSD, i.e., atoms are predicted to be too unstable. GGA functionals give a total energy much closer to accurate reference values [110], but, depending on the functional, the energy can be overestimated or underestimated. In the left column of figure 4.1, the error per electron in the total energy is shown for the atoms up to argon, for four different functionals without (blue squares) and with PZ-SIC (red points). PBE overestimates the total energy and the errors per electron increase slightly with system size for the larger atoms. For PW91, the energy is overestimated for the small systems, but the errors decrease in the second row of the periodic table and the elements of the third row are predicted very accurately. BLYP underestimates the energy for the intermediately sized atoms, but the errors reduce approaching argon.

The effect of applying PZ-SIC has a different effect on the accuracy of the various functionals. The application of PZ-SIC to LSD leads to strong overcorrection, but gives a slightly smaller absolute error than LSD. For PBE, application of PZ-SIC lowers the energy and gives better but still too high energy. Application of PZ-SIC to PW91 only improves the energy for the atoms of intermediate size, while it gives too low energy for the larger atoms. PZ-SIC applied to BLYP improves the energy for most atoms of the first two rows, but the errors increase strongly in the third row of the periodic table. For atoms larger than carbon or nitrogen, the total energy obtained with PZ-SIC using real orbitals (grey points) is always higher than when complex orbitals are used. For the GGA functionals, the energy difference is larger than for LSD+SIC and the errors eventually exceed those of the uncorrected functionals.

In the right column of figure 4.1, the exchange-only energy obtained from the various functionals is compared to Hartree-Fock energy. It should be noted here that comparison of the Hartree-Fock energy and that obtained using the exchange component of an approximate functional does not necessarily give an indication of the accuracy of the functional. Exchange and correlation functionals usually complement each other to give a good total energy or to fulfill known constraints of the exact functional. Functional components, thus, should not be randomly mixed, or applied by themselves. On the other hand, an orbital-density dependent functional that can reproduce the Hartree-Fock energy accurately could probably replace the exact exchange used in hybrid functionals.

PZ-SIC gives the exact HF energy for hydrogen and helium, as here all exchange energy is self-exchange. For the larger atoms, exchange-only SIC does not reproduce HF energy very well. For PBE-X+SIC and PW91-X+SIC, the energy is always lower than in HF. The average deviation of PBE-X+SIC is slightly smaller than for PBE, but for PW91-X, PZ-SIC increases the errors. As in the case of BLYP, B88+SIC improves the results for the smaller atoms, but the errors strongly increase for the larger atoms.

When real orbitals are used, the GGA+SIC energy eventually exceeds the GGA energy, as a result of a positive net contribution from the SIC terms. It has been pointed out that spherical averaging of the orbital densities before evaluation of the SIC terms reduces the magnitude of SIC for GGA functionals and by this the total energy [84, 111]. By averaging the p-orbitals, the nodal planes are removed and the region of space where the electron density is small is thereby reduced. This region is expected to have a strong effect on the SIC energy, in particular for gradient dependent SIC functionals [85]. As the complex sp^3 hybrid orbitals to large extend avoid nodal regions, they may show similar effects as density averaging, while being physically more justified and furthermore not restricted to atomic calculations.

In figure 4.2, PBE and BLYP are compared to their corresponding SIC and hybrid functionals. For PBE, the three curves are qualitative similar. The energy of the atoms from lithium is lowered by both PBE0 and PBE+SIC and for these functionals cusps at helium, beryllium and neon are more pronounced than in PBE. PBE+SIC gives the lowest energy and best agreement with the reference values, but the errors increase more rapidly towards argon than for PBE or PBE0. The curves of B3LYP and SIC+BLYP are significantly different. As for PBE0 and PBE, the curve of B3LYP is below that

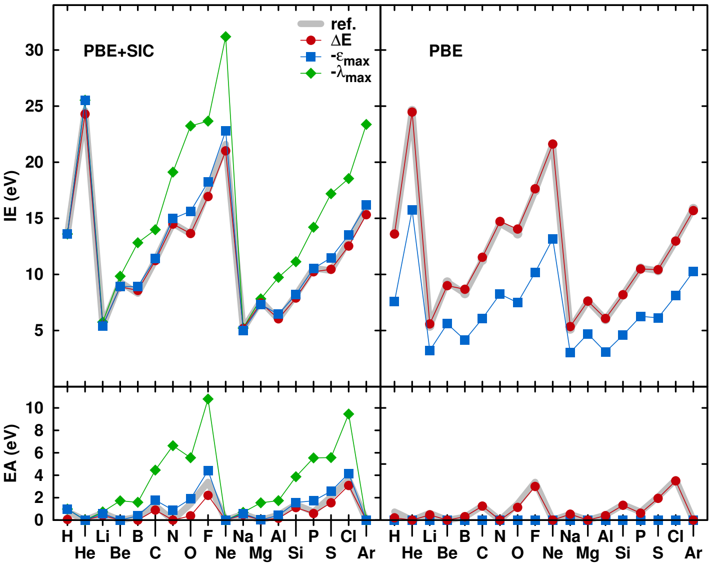

Figure 4.3: *Comparison of the ionization energy (IE, top) and electron affinity (EA, bottom) evaluated from the total energy difference of the charged and neutral ground state (ΔE), from the negative of the highest eigenvalue, $-\varepsilon_{max}$, of the neutral atom (IE) or anion (EA), and from the negative of the highest diagonal element of the matrix of Lagrange multipliers, $-\lambda_{max}$.*

of BLYP, but here it slightly increases the errors. BLYP+SIC always predicts a higher energy than the hybrid functional and a larger deviation for the heavier atoms.

Ionization Energy and Electron Affinity

The ionization energy (IE) and electron affinity (EA) obtained with PBE and PBE+SIC is shown in figure 4.3. The direct way to calculate these values is to evaluate the difference in total energy of the neutral and charged system, depicted by red points in the figure. These results agree well for PBE, while PBE+SIC underestimates the EA in particular for atoms with a partially filled *p* shell.

The highest orbital eigenvalue of exact KS-DFT equals the negative of the ionization energy [59]. For semi-local functionals, this is usually not the case, as is evident for PBE. The highest eigenvalue (blue squares) is not negative enough, resulting in a general underestimation of the IE. The EA

Table 4.1: *Mean absolute errors (in eV) of the ionization energy (IE) and electron affinity (EA) evaluated from energy differences (ΔE) and the highest eigenvalues ($-\varepsilon$) for the different functionals. The relative errors are larger for EA than IE, as can be seen by the magnitude of the mean of the reference values in the last row.*

	IE (eV)		EA (eV)	
	ΔE	$-\varepsilon$	ΔE	$-\varepsilon$
LSD	0.27	4.94	0.08	0.92
PBE	0.15	4.93	0.11	0.92
PW91	0.18	4.88	0.09	0.92
BLYP	0.19	5.06	0.17	0.92
LSD+SIC	0.30	0.87	0.12	0.53
PBE+SIC	0.24	0.53	0.31	0.31
PW91+SIC	0.23	0.55	0.30	0.32
BLYP+SIC	0.25	0.56	0.33	0.31
mean ref.	12.02		0.92	

can be evaluated in the same way from the highest eigenvalue of the anion, which is positive for PBE, resulting in an EA of zero (by definition). One reason for this large error is the incorrect long-range behavior of the Kohn-Sham potential in semi-local functionals, which is improved by the Hartree self-energy terms in PZ-SIC. Here, the highest eigenvalue of the matrix of Lagrange multipliers corresponds much better to IE and EA. However, the values are overestimated by the eigenvalues in particular for atoms with p^4, p^5, and p^6 electron configuration. It was shown in a study of PZ-SIC applied to systems with fractional occupation numbers [112] that the highest diagonal element of the matrix of Lagrange multipliers should be the correct orbital energy rather than the highest eigenvalue of the matrix. These values were shown to agree better with the energy derivative for fractional occupation, but as shown in figure 4.3 (green diamonds) they do in most cases not provide a good estimate for the energy required to remove a whole electron.

The values obtained with the other functionals reveal the same qualitative features and are summarized in table 4.1 which lists the mean absolute errors. The eigenvalues obtained by applying PZ-SIC with real and complex orbitals differ less than the total energy does, as shown in figure 2 of article I for PBE+SIC. Complex orbitals usually give less negative eigenvalues for all PZ-SIC functionals.

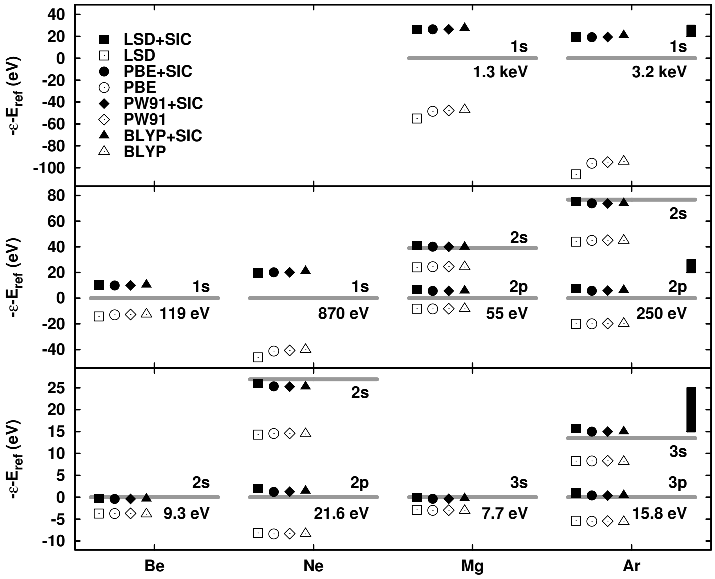

Figure 4.4: *Comparison of ionization energy from photoelectron spectroscopy [113] to lower eigenvalues of the closed shell atoms. The classical electron shells are depicted separately with the outermost shell in the bottom. Grey lines indicate experimental data. Values are plotted relative to the first excitation energy, which is denoted for the respective shells and atoms. The black bar (10 eV) indicates the different energy scales of the shells.*

It was found already in the first calculations using PZ-SIC [21], that not only the highest orbital eigenvalue agreed with the first ionization energy, but that also the lower eigenvalues are in better agreement with ionization from deeper levels. In figure 4.4 the energy levels obtained from photo-electron spectroscopy of closed shell atoms [113] are compared to the eigenvalues obtained from semi-local and PZ-SIC functionals. As for the first ionization energy, all eigenvalues of the uncorrected functionals underestimate the energy. A better agreement, but a general overestimation, is found for the SIC eigenvalues. The largest deviation of the eigenvalues is found for the innermost shell, which might be affected by limitations of the basis sets that were used. The PZ-SIC eigenvalues differ only slightly between the four functionals.

4.2 Molecular Systems

In appended article III, molecular systems are studied with focus on atomization energy, equilibrium structure and the energy barrier of some reactions. The effect of scaling the SIC terms by a factor of one half was also explored and is denoted as SIC/2 in the following results.

Atomization Energy

From earlier studies it was shown that atomization energy of molecules is in many cases overestimated by semi-local functionals, but that PZ-SIC only gave an improvement when applied to LSD. Application to PBE resulted in a large overcorrection [83, 85]. The overcorrection is reduced when complex orbitals are used, but still persists for the GGA+SIC functionals that were studied. Scaling the SIC by one half greatly reduces the mean deviation in PBE+SIC/2, but significant unsystematic errors remain.

By comparing the errors in the total energy of the molecules to those of their atoms, it can be seen why no systematic improvement is obtained with SIC. The errors in some cases decrease but increase in other cases and the magnitude of the changes is often different for the molecules and the atoms. This results in many cases in an unbalanced cancellation of errors when observables are evaluated as energy differences.

Equilibrium Geometry

Equilibrium bond lengths are often slightly too long for semi-local functionals. PZ-SIC overcorrects this in most cases both when using real [73] and complex orbitals. Also here, SIC/2 gives better agreement on average, but affects bond lengths in an unsystematic way. The F_2 molecule is a special case within the test set, as here GGA+SIC/2 shortens the bond, but for full SIC it increases again. In BLYP+SIC, the molecule is predicted to be unstable towards dissociation, corresponding to an infinite 'bond length'.

For bond angles, the difference between real and complex orbitals is more significant than for most bond lengths. Calculations using complex orbitals predict angles much larger than when real orbitals are used and are in worse agreement with experiment for NH_3 and H_2O.

The geometry of organic radicals can be a problematic case for semi-local functionals. The ethynyl radical, C_2H, is predicted to have an incorrect bent structure when PBE is used [57]. This can be corrected by admixture of

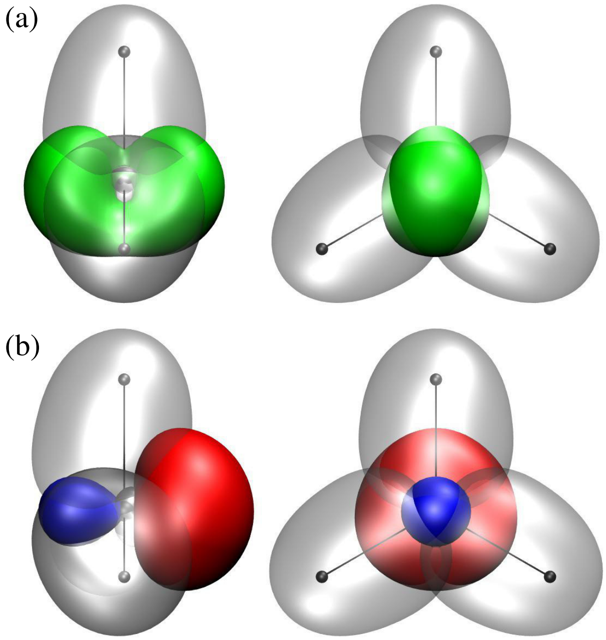

Figure 4.5: *Isosurfaces of the complex (a) and real (b) PBE+SIC optimized valence orbitals of the planar CH_3 radical. The 'unpaired' orbital is emphasized by color.*

exact exchange using the PBE0 functional, but also by using PBE+SIC or PBE+SIC/2. On the other hand, the methyl radical, CH_3, is correctly predicted to be planar by semi-local functionals, but was reported to have a non-planar structure when calculated with SIC functionals [81]. This could be shown to be an artifact of restricting the variational space to real orbital. The optimized valence orbitals of the planar structure of CH_3 are visualized in figure 4.5. The real orbitals corresponding to C-H bonds are forced into the shape of unfavored 'banana bonds' by the sp^3 hybridization of the unpaired orbital. The 'stress' can be released by moving the hydrogen atoms out of the plane into a geometry more in favor of this hybridization. The complex orbitals show a qualitatively different hybridization of the unpaired orbital by which the banana bonds are avoided and the equilibrium structure is correctly predicted to be planar.

Table 4.2: *Reactants, saddle point, products, and saddle point symmetry of the four studied reactions.*

reactants		saddle point		products	symmetry
$H_2 + H$	$\longrightarrow$	H_3	$\longrightarrow$	$H + H_2$	$D_{\infty h}$
$H_2 + H_2$	$\longrightarrow$	H_4	$\longrightarrow$	$H_2 + H_2$	D_{4h}
$HF + H$	$\longrightarrow$	HFH	$\longrightarrow$	$H + HF$	$D_{\infty h}$
HNH_2	$\longrightarrow$	NH_3	$\longrightarrow$	H_2NH	D_{3h}

Energy Barriers

The energy barriers of the four reactions listed in table 4.2 have been studied. The ammonia inversion (fourth reaction) is different from the others in that no bond breaking occurs. For this reaction, SIC decreases the energy barrier, while it is increased for the other three.

The restriction to real orbitals has a different effect on the HFH and NH_3 barrier. In NH_3, the molecular geometry at the saddle point is qualitatively similar to the planar CH_3 structure. The same 'unfavorable' hybridization is found for both the spin up and spin down electrons when real orbitals are used. This increases the total energy and by this the barrier height. For HFH, on the other hand, real orbitals slightly decrease the energy barrier.

The effects of SIC on the reaction barriers can be understood in more detail by comparison of the errors in the total energy. The energy of the H_4 system is in very good agreement with the reference energy for SIC+PBE, while it is too low for PBE. PZ-SIC thereby increases the energy barrier but it is still severely underestimated, as the errors in the reactants are hardly affected by SIC. For H_3, SIC increases the errors in the total energy, but a very good barrier height is obtained, as the errors are very close to those of the reactants. In HFH, on the other hand, the introduced errors exceed those of the reactants, so the cancellation of errors is better for the scaled SIC.

5

Summary and Outlook

The scope of this thesis is the implementation and reassessment of the Perdew-Zunger self-interaction correction, with emphasis on the implications of using complex orbitals rather than restricting the orbitals to be real functions.

Implementation of a self-consistent treatment of SIC functionals in QUANTICE made it possible to carry out a reliable minimization of the energy, using the unitary optimization algorithm developed in our group. Several atomic and molecular systems have been studied with different functionals.

The total energy is most affected by extending the variational space from real to complex orbitals, as illustrated by the atomic calculations. In contrast to previous results based on real orbitals, PZ-SIC can improve the total energy when it is applied to GGA functionals. However, not all functionals are suited for the application of SIC. Energy differences are not affected in a systematic way, but are in some cases improved by a more balanced cancellation of errors. Errors can increase when the energy of one of the two systems that are compared becomes more accurate than the energy of the other one.

Molecular geometry can be affected strongly by SIC. The incorrect prediction of a bent ground state geometry for the C_2H radical is corrected when PZ-SIC is applied to the PBE functional. The correct planar structure of the CH_3 radical, however, is only obtained when PZ-SIC is applied to a GGA functional and complex orbitals are used. The geometry predicted by LDA+SIC is still incorrect. Bond lengths are usually predicted to be too short by PZ-SIC, while bond angles increase substantially and show large deviations.

This study extends earlier assessments of the PZ-SIC by lifting the restriction of the variational space to real orbitals. While promising features of this correction could be confirmed and some shortcomings cured, new problems were revealed, such as the hardly bound F_2 molecule and the poor accuracy of predicted equilibrium bond angles.

From this point, the development of improved functionals based on or related to PZ-SIC can take different directions. These paths might eventually merge again, in the form of a functional that exceeds the accuracy of semilocal approximations for all, or at least most quantities of interest. The results presented here for atoms and molecules show that in any case the orbitals should be complex functions and the functional should go beyond the local spin density approximation.

The functional form has a strong effect on the performance of SIC. Application to BLYP revealed unacceptable effects and while PBE+SIC can give better performance than LSD+SIC, it still has severe problems. A more detailed study with focus on different GGA functional forms will give a deeper insight into the proper form for an exchange-correlation functional that will work well for application of PZ-SIC.

The global scaling of the SIC terms can provide some, but not systematic improvement over PZ-SIC. The more sophisticated approaches to adaptively scale the SIC terms may yield a more systematic improvement. Without a further study of their performance using complex orbitals, this is not clear. A possible alternative scaling approach, in which not only the SIC energy of each orbital is scaled individually, but also the separate contributions of Hartree, exchange and correlation self-energy, would provide more flexibility and may give a further improvement. Such a functional form is also able to retain more of the desirable features of PZ-SIC, some of which are lost in the currently used scaling schemes.

The quality of a functional can only be judged by comparison to reference data. Most approaches compare calculated observables to a test set of experimental and/or theoretical values. This will reveal the accuracy of a functional to predict *these* observables, but does not test the *general* accuracy of a functional. Taking into account the total energy as well, a more detailed analysis is possible, by which the origin of errors might be identified. The analysis of the reaction barriers revealed that the errors in both the H_2 atomization energy and the H_4 barrier height stem from an inaccurate description of the H_2 molecule when applying PZ-SIC to PBE.

A functional used in studies of chemical reactions does not have to reproduce the total energy accurately, but for many applications merely give good energy differences. Not aiming at a perfect total energy, an 'improved' version of the PBE functional would actually have to describe the hydrogen atom *worse*, to result in a better cancellation of errors. Such an approach might produce good estimates of reaction energy, but does not bring the functional as such closer to the exact functional.

All one-electron systems are described perfectly with PZ-SIC. The natural next step would be to develop a functional that can accurately describe two-electron systems, such as helium or H_2. In these systems, the exchange energy is described correctly with PZ-SIC, but errors are made in the correlation energy. A functional form beyond the Perdew-Zunger self-interaction correction might be able to describe correlation in these systems more accurately, while still being exact for all one-electron systems. Such a functional might give an improved accuracy for many-electron systems as well, but most probably will not be perfect, or even give worse results. By adding one electron at a time to the test set, one might be able to approach, step by step, a functional that can accurately describe systems of both few and many electrons.

List of Figures

1.1 The enhancement factor for exchange, $F(s)$, as a function of the reduced density gradient, s, for B88, PW91 and PBE. LSD corresponds to a constant factor of one. 12

3.1 Orbital density isosurfaces of a set of real and complex p-orbitals. 28
3.2 Orbital density isosurfaces of a set of real and complex sp^3-orbitals. 29
3.3 Illustration of the linear and geodesic propagation of orthonormal orbitals, represented by a sphere. 31

4.1 Energy of atoms H to Ar using the uncorrected and PZ-SIC versions of LSD, PBE, PW91 and BLYP functionals and their corresponding exchange components. The total energy is compared with accurate, non-relativistic estimates, the exchange only energy is compared to Hartree-Fock values. 36
4.2 Errors in total energy for the atoms H to Ar. PBE and BLYP are compared to the respective SIC and hybrid functionals. 37
4.3 Comparison of the ionization energy (IE) and electron affinity (EA) evaluated from the total energy difference of the charged and neutral ground state, from the negative of the highest eigenvalue of the neutral atom (IE) or anion (EA), and from the negative of the highest diagonal element of the matrix of Lagrange multipliers. 39
4.4 Comparison of ionization energy from photoelectron spectroscopy to lower eigenvalues of the closed shell atoms. 41
4.5 Isosurfaces of the complex and real PBE+SIC optimized valence orbitals of the planar CH_3 radical. 43

List of Tables

1.1 Exact energy and KS eigenvalue of atomic one-electron systems compared to LSD and PBE. 17

4.1 Mean absolute errors of the ionization energy and electron affinity evaluated from energy differences and the highest eigenvalues for the different functionals. 40
4.2 Reactants, saddle point, products, and saddle point symmetry of the four studied reactions. 44

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Included Publications

I

Article 1

Importance of complex orbitals in calculating the self-interaction-corrected ground state of atoms

Simon Klüpfel, Peter Klüpfel, and Hannes Jónsson

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II

Article 2

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III

Article 3

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