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Some Fermi-Lowdin Orbital Self-Interaction Correction Studies On Atomic Systems

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SOME FERMI-LOWDIN ORBITAL SELF-INTERACTION CORRECTION STUDIES
ON ATOMIC SYSTEMS

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SOME FERMI-LOWDIN ORBITAL SELF-INTERACTION CORRECTION STUDIES ON
ATOMIC SYSTEMS

by

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Abstract

Density Function Theory (DFT) is a popular quantum chemistry calculation method with many appeals but also deficiencies. Many modification and additions to the method have been made over the years, such as self-interaction corrections and new density functional approximations. We review here the theoretical background needed for a basic understanding of quantum chemistry calculations. In addition, we present the quantum chemistry calculation method used in this paper called Fermi-Lowdin Self-Interaction Correction (FLOSIC), including the base code it was implemented on, the Naval Research Laboratory Molecular Orbital Library (NRLMOL) Code, and the resulting modified code simply called FLOSIC. Furthermore, we explore a new method of obtaining the so-called Fermi Orbital Descriptors (FODs) by looking at the Hartree self-repulsion energy between electrons. Lastly, we test two density functional approximations called RPBE and revPBE.

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1 Introduction

Density Functional Theory (DFT) has been a popular method for quantum chemistry calculations since the advancement of computational power. Despite its shortcomings such as overestimation of dissociation energies for simple molecules and underestimate of band gaps in semiconductors [1], it has still proven successful in other areas such as handling zero-gap materials, i.e. metals, without falling to the problem of singularities and in addition showing its versatility in being useful not only in chemistry and material science but also for biological systems, astrophysics, and geological systems [2], in which the idea of taking a density as the basic variable is implemented. DFT has its appeal because it has novelties compared to other methods. One such novelty is that it is computationally simpler than say first principle methods such as Hartree-Fock when calculating the same properties of the system. This is due to DFT using the electron density of the system instead of the product of one electron wave functions, each of which has as its arguments three position coordinates and one spin coordinate. Thus, the total electron density is only a function of four variables as opposed to four times the number of electrons, which is the number of coordinates needed in Hartree-Fock and other *ab-initio* methods. DFT has proven to be more computationally cheap than many post-Hartree-Fock methods such as Coupled Cluster and MP perturbation theory due to the coupling of coordinates in these more advanced ab initio methods [2].

In DFT the total energy is a functional of electron density. Although DFT is exact in principle, practical applications rely on approximations to the exchange-correlation energy functional. The failures of density functional approximations (DFA) are well documented. Many different successful DFAs have been made since its inception. One of the DFAs' shortcoming is the self-interaction error (SIE) which arises because of incomplete cancellation of

the self-Coulomb by self-exchange. Perdew and Zunger [3] have provided an orbital by orbital correction to self-interaction error. In PZSIC the orbital by orbital correction is added to the DFA exchange correlation energy term.

The presence of self-interaction error leads to incorrect asymptotic decay of the potential an electron sees. The DFAs to exchange-correlation potential gives the potential decaying as $-\exp(-r)$ instead of the correct $-1/r$. As a result, the DFT potentials are shallow which leads to a shallow potential for the valence electrons. Furthermore, the ionization potential and electron affinities in DFT are underestimated when estimated from the energy eigenvalues of the highest occupied orbitals. We test the performance of the PZSIC with two different exchange-correlation energy functionals. The PZSIC approach is used within the Fermi-Lowdin orbital self-interaction correction scheme.

The Fermi-Lowdin orbital (FLO) self-interaction correction uses Fermi orbitals which are local orbitals. [4] The Fermi orbitals are obtained after a unitary transformation of the DFT canonical orbitals. The Fermi orbitals are uniquely described by a special position known as Fermi orbital descriptor. The calculations are started with a set of trial FODs equal to the number of electrons in the system. The self-interaction corrected DFT energy is minimized by varying the positions of the FODs. The optimization of FODs is a time and resource consuming task. In this work we also outline a scheme to obtain better trial FODs by minimizing the Coulomb interaction between the Fermi orbitals.

2 Theoretical Background

In this chapter we introduce the theoretical concepts that we will be using throughout this paper. These include concepts in quantum chemistry, including a brief review of the fundamentals of quantum mechanics, the idea of quantum chemistry calculations, and the methods used to compute such calculations; delving deeper into the density functional theory method and self-interaction corrections for density functional theory within certain orbital frameworks.

2.1 Quantum Mechanics Review

In quantum chemistry, the Schrodinger equation dictates the time evolution of the state of a system, and by system we mean any physical object of interest whether it be a single atom, a single molecule, or a collection of them. This Schrodinger equation is a partial differential equation that involves the partial derivative with respect to time of the wavefunction and the Hamiltonian operator, which in this context is the sum of the component energy operators which include the kinetic energy and any potential energies present.

$$i\hbar\partial\Psi(\mathbf{r},t)/\partial t = [-\hbar^2/(2m)\nabla^2+V(\mathbf{r},t)]\Psi(\mathbf{r},t) = H\Psi(\mathbf{r},t) \quad (1)$$

Here, the potential may be a function of the position and time. However, in many cases, including our own, the potential may be a function of only position. If so, then we can derive the time-independent Schrodinger equation:

$$H\psi(\mathbf{r}) = [-\hbar^2/(2m)\nabla^2+V(\mathbf{r})]\psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad (2)$$

In which the time-independent wavefunction depends only on the position coordinates of the system and is denoted by lowercase psi (ψ).

The solutions for the time-independent Schrodinger equation are the eigenfunctions of the Hamiltonian operator and are called stationary states [4]. The stationary states have definite

energy E . The stationary states form an infinite set of eigenfunctions $\{\varphi_i\}$ with corresponding eigenvalues $\{E_i\}$.

$$H\varphi_i = E_i\varphi_i \quad (3)$$

Each eigenfunction describes a possible stationary state for the system, and each corresponding eigenvalue is the energy of the system at that stationary state [4]. The first stationary state and the one with the lowest energy is called the ground-state and the energy the ground-state energy.

$$H\varphi_{GS} = E_{GS}\varphi_{GS} \quad (4)$$

This ground-state energy is the minimum possible energy of the system, and it is never zero. Therefore, even with zero thermal energy, that is, at absolute zero temperature, all systems have some energy associated with them.

The state of a system can not only be in just one of the stationary states, but it can in fact be in a linear combination of any number of them, that is, the system can be in a superposition of stationary states for they form a complete basis for the whole space that includes all the possible states the system can occupy [4].

$$\psi = c_1\varphi_1 + c_2\varphi_2 + \dots + c_n\varphi_n \quad (5)$$

The function that describes the state of the system is thus called the wavefunction. The wavefunction is in the span of the infinite set of eigenfunctions we obtain from the Schrodinger equation.

However, the energies that can be obtained when measuring the system can only be a member of the set of eigenvalues that correspond to the eigenfunctions. When the system is in a linear combination of stationary states, then all the eigenvalue energies associated with those stationary states can be obtained in a measurement. Each energy has a nonzero probability of

being read in a measurement of the system's energy. This means that the system has a probability associated with each eigenstate of collapsing into that stationary state when a measurement is made. This probability is determined by the coefficient c_i accompanying the corresponding eigenfunction φ_i . The probability is simply the norm squared of the coefficient:

$$p(\text{system in state } i) = c_i^* \cdot c_i = |c_i|^2 \quad (6)$$

Furthermore, the norm squared of the wavefunction $|\psi(\mathbf{r})|^2$ is the so-called probability density and $|\psi(\mathbf{r})|^2 d^3r$ is the probability of the system (if it were a single particle) of being in the interval $(\mathbf{r}, \mathbf{r}+d\mathbf{r})$ [4]. Integrating over a range yields the probability of the particle being in the range $(\mathbf{r}_1, \mathbf{r}_2)$ as such:

$$p(\mathbf{r} \in (\mathbf{r}_1, \mathbf{r}_2)) = \int |\psi(\mathbf{r})|^2 d^3r \text{ from } \mathbf{r}=\mathbf{r}_1 \text{ to } \mathbf{r}=\mathbf{r}_2 \quad (7)$$

When a measurement is made of any other property of the system, the probability of that measurement being in a certain range can be obtained by transforming the time-independent wavefunction ψ into the space of the physical property we measured and following similarly as for position in the previous example.

2.2 Quantum Chemistry Calculation Methods

Quantum chemistry calculations seek to find physical properties of chemical systems. These chemical systems include single atoms, complex molecules, or a collection of molecules such as crystal structures.

Practical and useful quantum chemistry calculations in modern times can only be done numerically and computationally. That is, the wavefunction of almost all real systems cannot be found analytically, and thus is approximated with numerical methods. Furthermore, the numerical methods developed are extremely demanding for the number of computations

performed, and thus manual computation is impossible. For this reason, quantum chemistry and solid-state physics programs were developed.

In this context, when doing quantum chemistry calculations, there are two things that one must specify: the method and the basis set used [5]. The basis is a limited set of functions that are used to express the approximated wavefunction, or any function that can describe the system, and any functions that the method uses to arrive at a satisfactory approximated wavefunction, those being for example the so-called orbitals. These basis sets are chosen with care because they are limited and therefore are not complete. Depending on the method and the system, one tries to make sure the wavefunctions and orbitals of the system fall reasonably near the span of the basis set. The choice of method and basis set help determine the accuracy of the results and the computational cost [5].

Many molecular properties calculation methods have been developed since the early 20th century, but they can be classified by most into four categories: ab initio methods, semiempirical methods, the density functional theory methods, and the molecular mechanics methods [7]. Semiempirical methods use a simplified Hamiltonian and adjustable parameters, while molecular mechanical methods are not quantum mechanical in nature but instead treat atoms as classical particles [7]. These methods are not relevant to this paper and are only mentioned for completeness.

On the other hand, ab initio methods use an extremely accurate Hamiltonian and seek to find the wavefunction of the system, while density functional methods seek to find the electron probability density instead of the molecular wave function [7]. These types of methods are more relevant to this paper, and will be explored in later sections, especially density functional theory methods.

2.3 Atomic Units

All equations presented in this text will be expressed in atomic units. The benefit of using this system of units is the simplification of all equations without the need of physical constants, for many physical constants or combinations of them are used as the base units of measurement. For completeness, the atomic units for each physical quantity are as follows:

Table 2.1: Atomic Units Base Units

Physical Quantity	Base Units
Mass	m_e (mass of an electron)
Charge	e (charge of a proton)
Angular Momentum	$\hbar/(2\pi)$ (where h is Planck's constant)
Energy	$m_e e^4 / (\hbar/(2\pi))^2$ (one Hartree)

The first three units alone suffice to derive all other quantities such as energy and length [8].

2.4 Born-Oppenheimer Approximation

The Hamiltonian operator for a molecule has the following form [9]:

$$H_{\text{op}} = T_{\text{op},N}(\mathbf{R}) + T_{\text{op},e}(\mathbf{r}) + V_{\text{op},eN}(\mathbf{r},\mathbf{R}) + V_{\text{op},NN}(\mathbf{R}) + U_{\text{op},ee}(\mathbf{r}) \quad (8)$$

Where from left to right of the right-hand-side of the equation, each term represent respectively the operators of: the nuclei kinetic energy, the electrons kinetic energy, the electron-nuclei interaction potential, the nuclei-nuclei interaction potential, and the electron-electron interaction potential. In addition, the vector \mathbf{R} represents the collective position vectors of the nuclei and \mathbf{r} the collective position vectors of the electrons.

One of the approximations density functional theory and first principle methods make to simplify this equation is the Born-Oppenheimer approximation. This approximation states that

the motion of electrons and nuclei in a system can be separated in the sense that the motion of nuclei do not change appreciably during a complete cycle of motion of electrons. The reasoning behind this is that nuclei are several thousand times heavier than electrons, and thus their larger inertia makes them seem extremely slow compared to the motion of electrons. Therefore, nuclei are nearly fixed with respect to electron motion and thus their kinetic energy term is neglected [9]:

$$H_{\text{op,el}} = T_{\text{op,e}}(\mathbf{r}) + V_{\text{op,eN}}(\mathbf{r};\mathbf{R}) + V_{\text{op,NN}}(\mathbf{R}) + U_{\text{op,ee}}(\mathbf{r}) \quad (9)$$

This results for the operation on the wavefunction to yield:

$$H_{\text{op,el}}\Psi(\mathbf{r},\mathbf{R}) = E_{\text{el}}\Psi(\mathbf{r},\mathbf{R}) \quad (10)$$

Where $H_{\text{op,el}}$ is now the electronic Hamiltonian, E_{el} the electronic energy, and now $\Psi(\mathbf{r},\mathbf{R})$ is referred to as the electronic wavefunction. Furthermore, despite the term $V_{\text{op,eN}}(\mathbf{r};\mathbf{R})$ being large and not being neglectable, the \mathbf{R} doesn't change appreciably, and thus $V_{\text{op,eN}}$ depends on them parametrically, allowing for the wavefunction related to $H_{\text{op,el}}$ to be written in terms of the electronic wavefunction $\psi(\mathbf{r},\mathbf{R})$ and a nuclei wavefunction $\chi(\mathbf{R})$ [9]:

$$\Psi(\mathbf{r},\mathbf{R}) = \psi(\mathbf{r},\mathbf{R})\chi(\mathbf{R}) \quad (11)$$

The nuclei wavefunction can be obtained by trying different sets of nuclei position vectors \mathbf{R} and determining a potential energy curve affecting the nuclei [9]. However, because the most interesting properties of a system involve only its electrons, especially during chemical reactions, and because the Born-Oppenheimer approximation allows us to investigate the electronic system separately from the nuclei without introducing significant error, this paper concerns itself only with the electronic part of a system, that is, its electronic Hamiltonian, energy, wavefunction, and associated electron density.

2.5 Density Functional Theory Method

Density functional theory was first alluded in a paper by Kohn and Hohenberg in 1964 [10] and the next year (1965) published as a full-fledged theory by Kohn and Sham [11]. The main premise of density functional theory is to replace the electronic wavefunction of a system by the electron density of the system to calculate properties of the system. The electron density of the system is determined by the wavefunction in the following way

$$n(\mathbf{r}) = N \int d^3 r_2 \int d^3 r_3 \dots \int d^3 r_N \psi^*(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N) \psi(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N) \quad (12)$$

This shows that the electron density is a functional of the electronic wavefunction. However, the Hohenberg-Kohn theorem states that for a system composed of an arbitrary number of electrons, that the external potential v , due to the nuclei, of the system is a unique function of the electron density and n_{GS} and vice versa [10]:

$$v = v[n_{GS}] \text{ and } n_{GS} = n_{GS}[v] \quad (13)$$

This implies that the electron density is uniquely determined by the coulomb potential of the nuclei outside the electronic system. Hohenberg and Kohn showed that the ground state energy is a functional of ground state electron density and can be used as the basic variable instead of the electron wave function also note that the wavefunction is a functional of the electron density:

$$E_{GS} = E[n_{GS}] \quad (14)$$

Thus, this shows how the ground-state electron density can replace the ground-state wavefunction to determine the properties of the system since for quantum systems we only have information about the probability distribution of measuring outcomes of observables and the expectation value is the average of those measurements on the observable [12]. However, it must be noted that DFT is, on its own, restricted to finding the electron density of the ground state. The reason for this will be apparent shortly.

The following mathematical framework for DFT is derived with the help of a section in Ira N. Levine's book *Quantum Chemistry* [13]. We start laying the framework of DFT with the electronic Hamiltonian operator of an n-electron system under some external potential due to the positive nuclei:

$$H_{\text{op}} = V_{\text{op}}(\mathbf{r};\mathbf{R}) + T_{\text{op}}(\mathbf{r}) + U_{\text{op}}(\mathbf{r}) = \sum_{i=1}^n v(\mathbf{r}_i) + -1/2\sum_{i=1}^n \nabla_i^2 + 1/2\sum_{i=1}^n \sum_{j=1}^n 1/|\mathbf{r}_i - \mathbf{r}_j| \quad (15)$$

Where V_{op} refers to the electron-nuclear interaction potential, T_{op} the electrons kinetic energy, U_{op} the electron-electron interaction potential, and the nuclear-nuclear repulsion $V_{\text{op,NN}}(\mathbf{R})$ is neglected due to \mathbf{R} being parameters and thus $V_{\text{op,NN}}(\mathbf{R})$ being a constant that just shifts the eigenvalue energies by a constant amount [9].

The difficulty of obtaining the electronic wavefunction is the electron-electron interactions that are not only intrinsically present in the Coulomb repulsion operator $U_{\text{op}}(\mathbf{r})$ but are also present in the kinetic energy operator $T_{\text{op}}(\mathbf{r})$. For this reason, we develop a new reference system called S in which there are no interelectronic interactions. For this new system with non-interacting electrons to be useful, we impose an external potential v_s such that this potential produces an electron density n_s for the reference system S that is equal to the ground state electron density n_{GS} of the real system:

$$n_s = n_{\text{GS}} \quad (16)$$

The similarity between the real system and system S is that their electron densities are equal, but their differences can be formally stated in this equation for the general Hamiltonian dependent on the parameter λ [14]:

$$H_\lambda = \sum_i (-1/2\nabla_i^2 + v_\lambda)_i + \lambda 1/2\sum_{j \neq i} \sum_i 1/|\mathbf{r}_j - \mathbf{r}_i| \quad (17)$$

Where $\lambda=1$ for the real system and $\lambda=0$ for system S, but the corresponding external potential v_λ is determined such that n_λ is constant regardless of the value of λ , namely $n_\lambda=n_{GS}$.

As such, the non-interacting electrons of system S only have kinetic energy and potential energy due to the potential $v_0 = v_S$. This makes the Hamiltonian of system S be

$$H_{op,S} = T_{op,S} + V_{op,S} = \sum_{i=1}^n [-1/2 \nabla_{i,S}^2 + v_S(\mathbf{r}_i)] \quad (18)$$

This operator would consider the kinetic energy and potential energy of each i th electron. Now, because the electrons in system S are noninteracting, its wavefunction will simply be a Slater determinant of Kohn-Sham orbitals, that is, an antisymmetric product of Kohn-Sham orbitals u_i^{KS} as such:

$$\Psi_S = 1/\sqrt{N!} \cdot |u_1^{KS} u_2^{KS} \dots u_n^{KS}| \quad (19)$$

It is worth noting that it is harder to extract quantitative information from Kohn-Sham orbitals, but their number, symmetry, and shape are as expected from orbitals obtained in wavefunction-based methods such as Hartree-Fock [15].

The reasoning behind the wavefunction being a Slater determinant is that when applying the separation of variables method, the total Hamiltonian is formed as a sum of one-particle dependent operators. Each operator affects only one electron's coordinates, leading to the total wavefunction of a system of n non-interacting particles being composed of a product of n independent single-electron wavefunctions, each wavefunction dependent only on the position coordinates of one electron as shown below [16]:

$$\psi(q_1, q_2, \dots, q_n) = G_1(q_1) G_2(q_2) \dots G_N(q_n) \quad (20)$$

$$H_{op} = H_{op,1} + H_{op,2} + \dots + H_{op,N} \quad (21)$$

With the energy following similarly due to applying the total Hamiltonian operator on the total wavefunction:

$$E = E_1 + E_2 + \dots + E_N \quad (23)$$

with

$$H_i G_i = E_i G_i, \quad i=1,2,\dots,n \quad (22)$$

The Slater determinant ensures the Pauli exclusion principle is fulfilled.

Now we introduce Kohn and Sham's formulation of the ground state electronic energy by introducing the quantities for the difference between the kinetic energy of the real system and the kinetic energy of system S and the difference between the real system inter-electronic energy and the classical electrostatic energy of a continuous charge distribution (U_{class}):

$$\Delta T_{\text{avg}} = T_{\text{avg}} - T_{\text{avg,S}} \quad (23)$$

$$\begin{aligned} \Delta U_{\text{avg}} &= U_{\text{avg}} - U_{\text{class}} \\ &= U_{\text{avg}} - 1/2 \iint n(\mathbf{r})n(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'| d^3\mathbf{r}d^3\mathbf{r}' \end{aligned} \quad (24)$$

Where the average values are the expectation values of the corresponding operators and calculated as such:

$$T_{\text{avg}} = \langle \Psi_{\text{GS}} | T_{\text{op}} | \Psi_{\text{GS}} \rangle \quad (25)$$

$$T_{\text{avg,S}} = \langle \Psi_{\text{GS}} | T_{\text{op,S}} | \Psi_{\text{GS}} \rangle \quad (26)$$

$$U_{\text{avg}} = \langle \Psi_{\text{GS}} | U_{\text{op}} | \Psi_{\text{GS}} \rangle \quad (27)$$

With these definitions, we can write the ground-state electronic energy of the system as such:

$$E_{\text{GS}} = V_{\text{avg}} + U_{\text{class}} + T_{\text{avg,S}} + \Delta T_{\text{avg}} + \Delta U_{\text{avg}} \quad (28)$$

This can further be expanded upon if we consider V_{op} as the potential by the nuclei imposed upon a continuous distribution of charge, namely the electron density. Therefore, the ground-state energy can be written as:

$$E_0 = \int n_0(\mathbf{r})v(\mathbf{r})d^3\mathbf{r} + 1/2 \iint n_0(\mathbf{r})n_0(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'| d^3\mathbf{r}d^3\mathbf{r}' + T_{\text{avg,S}} + \Delta T_{\text{avg}} + \Delta U_{\text{avg}} \quad (29)$$

With

$$V_{\text{avg}} = \int n_0(\mathbf{r})v(\mathbf{r})d^3r \quad (30)$$

Two of the terms in the energy are functionals of the electron density and thus can easily be determined if we had such function. Now, we can use the fact that the ground state wavefunction of system S is determined by the determinant of Kohn-Sham spin orbitals as shown in equation (20).

Each Kohn-Sham orbital is equivalent to the product of a spatial-orbital θ^{KS}_i and a spin-orbital σ_i as such:

$$u^{\text{KS}}_i = \theta^{\text{KS}}_i \sigma_i \quad (31)$$

As a result, the ground state electron density of system S, which is assumed to be equivalent to that of the real system, is this:

$$n_S = n_0 = \sum_{i=1}^n |\theta^{\text{KS}}_i|^2 \quad (32)$$

The kinetic energy operators of $T_{\text{op},S}$ act individually and only on the spatial part of the Kohn-Sham orbitals because the electrons are not interacting with each other in system S, and thus the kinetic energy of system S is

$$T_{\text{avg},S} = -1/2 \sum_{i=1}^n \langle \theta_i(\mathbf{r}) | \nabla^2 | \theta_i(\mathbf{r}) \rangle \quad (33)$$

As a result, we can now write the ground-state energy in a more explicit fashion as such:

$$E_0 = \int n_0(\mathbf{r})v(\mathbf{r})d^3r + 1/2 \iint n_0(\mathbf{r})n_0(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|d^3r d^3r' \\ - 1/2 \sum_{i=1}^n \langle \theta_i(\mathbf{r}) | \nabla^2 | \theta_i(\mathbf{r}) \rangle + \Delta T_{\text{avg}} + \Delta U_{\text{avg}} \quad (34)$$

Now, because the ground-state electron density is determined by the spatial-components of the Kohn-Sham spin orbitals, as was shown above, $T_{\text{avg},S}$ has the same dependency as n_{GS} , that

is, they are both determined by the correct set of spatial Kohn-Sham orbitals $\{\theta_i^{\text{KS}}\}$. Therefore, again, if we can determine this set, we can calculate all three quantities V_{avg} , U_{class} , and $T_{\text{avg,S}}$ relatively easily. The only quantities we need to determine are ΔT_{avg} and ΔU_{avg} . In reality, these quantities cannot be determined exactly, but must be redefined jointly and approximated, but to do this we must first explore why U_{class} and $T_{\text{avg,S}}$ fail to adequately describe the true interelectronic repulsion energy of the electrons and their true kinetic energy respectively.

As is well known in quantum mechanics, electrons interact with each other in two ways: Coulombic repulsion and Pauli repulsion. Because electrons all have the same negative charge, they feel a repulsive force from each other and thus tend to move away from each other. This effect has a correlation with their motion and a so-called Coulomb hole forming around each electron with respect to all other electrons [17]. This indicates that the set of Kohn-Sham spatial orbitals $\{\theta_i^{\text{KS}}\}$ with the kinetic operator $T_{\text{op,S}}$, which are determined for non-interacting electrons, cannot adequately describe the kinetic energy of the actual electrons. The energy determined by $T_{\text{op,S}}$, that is $T_{\text{avg,S}}$, must thus be an underestimation of the true kinetic energy T_{avg} because interacting electrons repel each other and thus increase their kinetic energy.

Furthermore, although U_{class} accounts for most of the repulsion energy between electrons, it is still derived from a potential that is an average effect from all other electrons:

$$V_{\text{class}}(\mathbf{r}) = 1/2 \int n_0(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'| d^3 \mathbf{r}' \quad (35)$$

where

$$U_{\text{class}}[n] = \int V_{\text{class}}(\mathbf{r}) n(\mathbf{r}) d^3 \mathbf{r} \quad (36)$$

Since V_{class} is an average potential, it does not account for the effect of other electrons on the potential of a single electron. This neglects the so-called exchange and correlation effects.

In addition, because all electrons have the same fractional spin quantum number, namely one half, all electrons are fermions. Thus, as is shown, because the interchange of two electrons with the same position and spin lead to the wavefunction being multiplied by negative one, the probability of two electrons with the same spin quantum number being in the same place is zero.

$$\begin{aligned} \Psi(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_j, \dots, \mathbf{r}_N; \sigma_1, \dots, \sigma_i, \dots, \sigma_j, \dots, \sigma_N) = \\ -\Psi(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_j, \dots, \mathbf{r}_N; \sigma_1, \dots, \sigma_i, \dots, \sigma_j, \dots, \sigma_N) = 0 \text{ for } \mathbf{r}_i = \mathbf{r}_j \text{ and } \sigma_i = \sigma_j \end{aligned} \quad (37)$$

This implies that the integral involved in calculating the probability of an electron being near the vicinity of an electron with the same spin, either 1/2 or -1/2, will be smaller. This is interpreted as a repelling force, and thus leads to another source of repulsion between electrons and a so-called Fermi-hole forming around each electron with respect to another electron of equal spin [17]. On the other hand, if the two electrons of differing spin are near each, they do not experience this unfavorable probability, and thus feel no spin repulsion, although they still experience Coulomb repulsion. These nuances in the interaction between electrons are not addressed by U_{class} and $T_{\text{avg,S}}$.

The Coulomb and Fermi holes lead to electrons having regions around them where the probability of finding another electron is lower. These two types of interactions between electrons make it more difficult to account for the extra energy terms ΔT_{avg} and ΔU_{avg} .

Therefore, as was done by Kohn and Sham in their 1965 paper [11], these corrective energy terms ΔT_{avg} and ΔU_{avg} are redefined as a single term called the exchange-correlation energy

$$E_{\text{XC}} = \Delta T_{\text{avg}} + \Delta U_{\text{avg}} \quad (38)$$

The reason for the definition is that the errors in energy ΔT_{avg} and ΔU_{avg} are due to the correlation between the motion of all electrons and the anti-symmetry effect present when electrons' coordinates are exchanged. This exchange correlation energy E_{XC} can only be approximated but it must be a functional of the electron density since total energy is a functional of density:

$$E_{\text{XC}}=E_{\text{XC}}[n] \quad (39)$$

Many types of exchange correlation functionals exist. Some deal with the exchange and correlation parts separately, others deal with them together. These functionals fall into categories that include Local Density Approximation (LDA), Local Spin Density Approximation (LSDA), Generalized Gradient Approximation (GGA), meta-GGA, and so on. However, for the purposes of this paper, the exchange-correlation functional used will be indicated but the mechanics behind it will not be delved into.

Having defined the exchange-correlation energy, we can now write the electronic ground-state energy of the n-electron system as such

$$E_0 = \int n_0(\mathbf{r})v(\mathbf{r})d^3r + 1/2 \iint n_0(\mathbf{r})n_0(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|d^3rd^3r' - 1/2 \sum_{i=1}^n \langle \theta_i(\mathbf{r}) | \nabla^2 | \theta_i(\mathbf{r}) \rangle + E_{\text{XC}}[n] \quad (40)$$

With an approximated exchange-correlation functional, we now have an expression for all the energy terms, but the problem remains on finding the set of Kohn-Sham orbitals $\{\theta^{\text{KS}}_i\}$. The correct set of Kohn-Sham orbitals will minimize the above expression (41) for the ground state energy, and in addition will yield a ground-state electron density $n_0(\mathbf{r})$ such that when integrated over all space should yield the total number of electrons in the system N. Thus, through the method of Lagrange multipliers and other constraints, including the requirement that the orbitals be orthogonal to each other, we derive this self-consistent equation [18]:

$$[-1/2\nabla^2 - \sum_a Z_a/|\mathbf{R}_a - \mathbf{r}| + \int n(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'| d^3r' + v_{xc}(\mathbf{r})] \theta_i^{KS} = \epsilon_i^{KS} \theta_i^{KS}, \quad (41)$$

Where the term $v_{xc}(\mathbf{r})$ is the functional derivative of the exchange-correlation energy functional:

$$v_{xc}(\mathbf{r}) = \partial E_{XC}[n(\mathbf{r})] / \partial n(\mathbf{r}) \quad (42)$$

Equation (42) constitutes a self-consistent field (SCF) calculation in the sense that the initial Kohn-Sham orbitals that are used on the left-hand side of the equation produce new orbitals on the right-hand side of the equation (hence the primed orbitals) that are closer to the correct set of KS orbitals. As a result, the orbitals that correctly optimize the ground-state energy are derived through an iterative method. This method starts with an initial guess, and in practice the method concludes when the forces on the electrons are small. If this is achieved, then the method is said to have converged.

At this point it is important to emphasize that in this paper we will be looking at the ground-state electron density and the ground-state energy. The reason we limit our exploration to this state is because the basic density functional method aims to minimize the energy functional $E[n]$. Minimization with no constraints is the simplest approach to find an allowed energy of the system, and this energy happens to be the ground-state energy E_0 because, by definition, it is the lowest allowed energy.

3 Fermi-Lowdin Orbital Self-Interaction Correction (FLOSIC)

In this chapter we introduce the self-interaction error (SIE) present in DFT. We then delve into the modification made into DFT to solve for SIE called self-interaction correction (SIC). With this, the emergence of DFT SIC began and further improvements were made to the methods, including consideration of the type of orbitals used besides the standard Kohn Sham orbitals.

3.1 Self-Interaction Error

The self-interaction error (SIE) in DFT is an energy that is not physical and thus should not be present but is a by-product of the mathematical method used. This SIE energy is due to an electron interacting with itself [19]. This can be seen clearly in the hydrogen atom system. In this system, there is only one electron, and because an electron cannot physically interact with itself (e.g. it cannot repel itself), then there should be no Hartree energy or Exchange-Correlation energy. That is, the ground state energy should only have a kinetic energy term and an external potential energy term as such:

$$E_0^H = V_{\text{avg}} + T_{\text{avg},S} = \int n_0(\mathbf{r})v(\mathbf{r})d^3r - 1/2 \sum_{i=1}^n \langle \theta_i(\mathbf{r}) | \nabla^2 | \theta_i(\mathbf{r}) \rangle \quad (43)$$

Therefore, ideally, the sum of the Hartree energy and the Exchange-Correlation energy for Hydrogen should add up to zero. In particular, the Hartree energy and the exchange energy should cancel each other out and the correlation energy should equal to zero [19]:

$$E_x[n] + U[n] = 0; E_c[n] = 0 \quad (44)$$

Where

$$E_x[n] + E_c[n] = E_{xc}[n] \quad (45)$$

However, when a calculation of the ground state energy of the Hydrogen atom is made, one sees that the Hartree energy and the Exchange-Correlation energy altogether do not cancel each other out:

$$U_{\text{class}} + E_{\text{XC}} \neq 0 \quad (46)$$

3.2 Self-Interaction Correction

A self-interaction correction (SIC) for SIE was introduced in a paper by Perdew and Zunger in 1981 [3]. This modification gets inspiration from one-electron systems such as Hydrogen. For Hydrogen, this SIC modifies the Exchange-Correlation terms such that it is as such:

$$E_{\text{XC}}^{\text{PZSIC}}[n] = E_{\text{XC}}[n] - E_{\text{XC}}[n] - U_{\text{class}}[n] \quad (47)$$

Therefore, the total ground state energy would be correct, that is, being the sum of kinetic and external potential energy terms only. In Perdew and Zunger's SIC-DFT (PZSIC-DFT), this modification is taken in an orbital by orbital basis, looking at each Hartree energy and Exchange-Correlation functional as being composed of a sum of single-orbital-density dependent functionals, like one-electron systems, and subtracting the error (in an orbital-by-orbital basis). This leads to the reformulation of the Exchange-Correlation energy for any system as such [20]:

$$E_{\text{XC}}^{\text{PZSIC}} = E_{\text{XC}}[n] - \sum_i U_{\text{class}}[n_i] + E_{\text{XC}}[n_i] \quad (48)$$

Where n_i is the electron density due to only the i th orbital as such:

$$n_i = |\theta^{\text{KS}}_i|^2 \quad (49)$$

And n is the sum of such one-orbital densities:

$$n = \sum_{i=1}^n |\theta^{\text{KS}}_i|^2 \quad (50)$$

With this reformulation of the Exchange-Correlation energy, we can rewrite the ground state energy as such:

$$E_0 = V_{\text{avg}} + U_{\text{class}} + T_{\text{avg,S}} + E_{\text{XC}}^{\text{PZSIC}} \quad (51)$$

With $n = n_0$ in this situation. The new method PZSIC-DFT mitigates the SIE but does not eliminate it completely. Besides this reformulation, another improvement can be made by improving the orbitals generated from the SCF equation.

3.3 Fermi Orbitals Framework in Fermi-Lowdin-Orbital Self-Interaction Correction

The Perdew-Zunger correction to DFT is better suited for small systems, such as molecules of a handful of atoms. However, for larger systems, such as crystals where an arrangement of atoms is repeated throughout space, the correction tends to diminish and vanishes completely in the limit of infinitely large periodic systems [20].

This problem shows up in any situation in which the system is extended throughout space, another example being stretched bonds. This is called the size-extensivity problem where size-extensivity refers to the property of a quantum chemistry calculation method to properly calculate properties that are size-independent or that scale linearly with the number of electrons [21].

It was discovered that for PZSIC DFT to acquire size-extensivity, the orbitals used must be localized. This means that the orbitals making up the electron density must peak at certain points in space and decay in value as the distance from these points increases. That is, these localized orbitals exist essentially only in a limited region in space as opposed to covering the whole space occupied by the whole system [22]. For the method used in this research, the procedure followed to localize the canonical orbitals, that is the Kohn-Sham orbitals, was through the FLOSIC framework. Briefly explained, with the FLOSIC method, the KS orbitals are linearly transformed into the so-called Fermi Orbitals (FOs). These FOs are localized and as a result do not need to satisfy the so-called localization equations [23], which would make the

method more computationally expensive. The linear transformation from KS orbitals to FO is as follows:

$$F_{i\sigma}(\mathbf{r}) = \sum_{\alpha} \{ \psi_{\alpha\sigma}^*(\mathbf{a}_{i\sigma}) \psi_{\alpha\sigma}(\mathbf{r}_{i\sigma}) / (\sum_{\alpha} |\psi_{\alpha\sigma}(\mathbf{a}_{i\sigma})|^2)^{1/2} \} \quad (52)$$

Where the Fermi orbitals (FOs) are denoted by $F_{i\sigma}$, in which α denotes the occupied canonical orbital index, i denotes the Fermi orbital in question, and σ denotes the spin quantum number. The Kohn-Sham Orbitals are denoted by $\psi_{\alpha\sigma}$ and the vectors $\mathbf{a}_{i\sigma}$ are the position vectors of the so-called Fermi-Orbital Descriptors (FODs) [20]. These FODs can be thought of as semi-classical electrons, and the number of FODs equals the number of electrons N_{σ} . In FLOSIC, these FOs are then orthogonalized with respect to each other, that is, their dot product, which is an integral over all space, equals zero as such:

$$\int_{\text{all space}} \varphi_{\alpha\sigma}(\mathbf{r}) \varphi_{\alpha'\sigma'}(\mathbf{r}) d^3r = 0 \text{ for} \quad (53)$$

$$\alpha \neq \alpha' \text{ and } \sigma \neq \sigma',$$

where the new Fermi-Lowdin Orbitals are denoted by $\varphi_{\alpha\sigma}$. For the purposes of this paper, the Lowdin orthogonalization scheme will not be delve into despite being implemented on the codes used for this paper.

4 Naval Research Laboratory Molecular Orbital Library Code

In this chapter, we cover the program used that implements DFT for quantum chemistry calculations. This program is called Naval Research Laboratory Orbital Library or NRLMOL. NRLMOL was initiated mainly by Dr. Mark Pederson and others [24][25][26][27][28][29][30]. We will go over the input files, the code procedure, and the output files. NRLMOL can calculate several properties of a system, but for this research, the molecular geometry and the electronic geometry optimizations were the only ones considered. Molecular geometry optimization is when the positions of the nuclei of the system yield the minimum energy of the system, while electronic geometry optimization is when the positions of the FODs yield the minimum electronic energy. These energies will be considered for a system in absolute zero and in the ground state. The code was originally used for molecular geometry optimization before the FLOSIC version of it was developed. As such, the molecular geometry optimization is discussed first.

4.1 Input Files

To start things off, NRLMOL is a program written in FORTRAN. To execute this file for a molecular geometry optimization, one needs at minimum one input file that contains the information about the system. This sole input file must be named CLUSTER. This CLUSTER file must provide these details for the program to run: the exchange-correlation parametrization, the point groups of symmetry, the number of inequivalent atoms, the coordinates of the atoms, the atomic numbers, the number of electrons for each atom, the charge of the system and the dipole moment.

The exchange-correlation parametrization refers to the exchange-correlation functional used. NRLMOL has a list of exchange-correlation functionals implemented into it. The default

functionals used are from the GGA group and for both the exchange and correlation the Perdew-Burke-Ernzerhof (PBE) and variations of it are used. The point group symmetry of the system comes from the set of atom-coordinate transformations that leave the system unchanged. The types of symmetries a molecule can have fall under line of symmetry, plane of symmetry, center of symmetry, rotation and reflection axis, and identity. All these are operators that act on the position-coordinates of the atoms. The name point groups of symmetry comes from the fact that molecules have a group of symmetry operators that leave one point in space unchanged.

The number of inequivalent atoms refers to the number of distinct atoms in the system. For example, for a water molecule, there would be only two inequivalent atoms, those being the oxygen atom and the hydrogen atom despite there being three atoms in total. Next, the positions of the atoms are specified in cartesian coordinates using Bohrs, the atomic units of length. The atomic number refers to the number of protons in the nuclei of each atom type, and the number of electrons specifies how many electrons each atom has. All this information is specified for each atom, inequivalent or not, in their own line. One thing to note is that the number of electrons is specified while the number of neutrons, that is, the possibility of isotopes of that atoms, is not specified because chemical reactions occur due only to the interaction between charged particles.

Finally, the last line of CLUSTER specifies the total charge of the system in units of proton charge. The moment of the system is specified by the number of unpaired electrons.

The file CLUSTER is what is required to run NRLMOL for the start of the calculation. More files are produced on each SCF cycle. These files specify various information about the system and are updated after each SCF cycle until the procedure is finished.

A pair of input files can be used to replace CLUSTER to run nrlmol_exe. These files are called SYMBOL and ISYMGGEN. These files better specify the information that CLUSTER provides. Both inputs types were used for this research.

4.2 Running High-Performance Calculations with NRLMOL

NRLMOL can be run on any desktop computer or laptop for only small systems. These may include single atoms or small molecules. The code can be used for several hundreds of atoms using high-performance computing platforms where the code runs parallelly. Usually a batch job script is used to submit jobs to the queue.

The job script is a file written for the message passing interface (mpi), which is a message passing standard used to run multiple processors and manage traffic between the local computer and the cores used to perform the calculation. The job scrip has some other specifications, such as the number of cores requested for use or the allowed amount of runtime for the job. One specification of interest for this paper is if the program will run more than once. That is, the job script can specify a loop dictating how many times NRLMOL will run. This loop can stop once a condition is achieved. For the experiments performed on this paper, the program stopped once a certain condition was set (e.g. the biggest force on the collection of atoms or FODs was smaller than a set tolerance).

4.3 Output Files

Once NRLMOL finishes an SCF cycle, the code prints several output files. These output files are either updated after each SCF cycle or are used as input files for the next SCF cycle. The previously mentioned files SYMBOL and ISYMGGEN are produced after the first SCF cycle, and they then replace CLUSTER as the information needed for the code about the system of interest,

for the position coordinates of the molecules are updated for a geometry optimization calculation.

The output file GEOCNVRG indicates as true or false whether the geometry has converged or not, with the tolerance for convergence indicated as well. The file indicates the total electronic energy as well as the current largest nuclear gradient (i.e. the biggest force from the set acting on the nuclei). If this gradient is smaller than a set tolerance, then the geometry is said to have converged.

Of the output files of interest, the position coordinates of the atoms in an XMOL file is included. This file lets us see the molecule in any molecule visualization programs. The one used here is called Avogadro. The benefit of this is to keep track of the molecule's shape and qualitatively make sense of it to make sure the calculation is converging to a realistic geometry.

Another output file of interest for this research is the file named SUMMARY. This file documents the energy of the system after each SCF cycle. This cycle is useful because, as we mentioned before, DFT is a variation method, and as such, we hope the energy of the system decreases and does not either increase or oscillate for these are indications of the calculation diverging.

5 Fermi-Lowdin Orbital Self-Interaction Correction (FLOSIC) Code

As previously mentioned, despite the success of DFT, the method still suffers from SIE. Over the development of NRLMOL, new versions of the code were made that included SIC. This new code that built upon NRLMOL is named Fermi-Lowdin Orbital Self-Interaction Correction or FLOSIC for short. This new method requires either one or two additional input files in addition to NRLMOL executable and outputs new files that involve the Fermi orbital descriptors previously mentioned.

5.1 Input Files

The code used for DFT SIC calculations the input files needed for DFT calculations, the input file CLUSTER and a job script for large systems. However, FLOSIC is based upon defining new orbitals called Fermi Orbitals and later Fermi-Lowdin orbitals to improve upon the DFA. As was explained previously, Fermi Orbitals are defined according to FODs. As such, an input file specifying the FODs is required.

The additional input file specifying the FODs must be named FRMORB. This file must contain an equal number of FODs as the number of electrons in the system, and the number of up and down spin electrons must be specified, with the first set of coordinates indicating the up-spin electron FODs and the last set the down-spin electron FODs. These FODs can only be guesses for the initial input. The guess for the FODs must be reasonable for the SIC calculation to converge. There is a theoretical procedure to place the FODs in reasonable places for non-transition metal elements. However, for the purposes of this research, a program called fodMC, developed by Trepte and Schwalbe [1], was used to generate guesses for the FODs.

The program fodMC requires the position of the atoms of the system, the number of up and down electrons, and the types of bonds between the atoms (at least if there is a double or

higher order bond, these must be specified). The program then treats the FODs as classical electrons and uses the Coulomb repulsion between them to find the positions in which the electrons feel the least amount of repulsion, while still being bound to the correct subshell. This program only works for non-transition metals and thus this research only made calculations using systems composed of relatively low atomic numbers.

Although the FRMORB file suffices to start an SIC calculation, this file can be replaced by two other files called FRMIDT and FRMGRP. The file FRMGRP contains the group symmetry transformation matrix of the molecule while the file FRMIDT contains the same information as FRMORB. The program outputs the XMOL files of the FOD positions and XMOL movie files of the movement of the FODs.

5.2 Output Files

The FRMORB file is not only used as an input but also as an output file. The FODs are used to calculate the Fermi orbitals and in turn the electron density. As previously stated, the SCF equation updates the electron density by updating the FODs in FRMORB. As previously mentioned, another file that can be generated using the file FRMORB is a molecular visualizer file for the FODs. This file is extremely useful for qualitative evaluation of the calculation.

Although a methodical procedure for the initial guess of FODs is an unresolved matter, it is known that the the number and position of FODs should be the same as the number of electrons forming a bond and near the vicinity of that bond. Therefore, the molecular visualizer file of FODs lets us keep track of the position of the FODs and make sure the system is converging to FODs that are reasonable.

Another file of interest is the SUMMARY file once again. In this file, various energies and other information is listed, including: the trace of the Hamiltonian matrix, the total energy,

the total charge of the system, and the sum of the total energy and the SIC energy, each one corresponding to a SCF cycle and program iteration. However, as opposed to the DFT calculation, in SIC the column named DFT+SIC is not equivalent to the DFT energy, for the SIC calculation is performed this time. This also indicates the type of calculation performed. As the theory suggests, the energy in this column usually is smaller, i.e. more negative, than the energy in the DFT column because SIC energy is negative. This can be seen easily when considering that the SIE energy of a hydrogen atom is due to a non-existing interelectronic repulsion energy. Because it is a repulsive energy, it would increase the kinetic energy of the system as particles of the system move away from each other, and thus, it is a positive energy. Therefore, the SIC energy must be negative to cancel out this energy.

Two more important files are `fande.dat` and `fforce.dat`. The file `fande.dat` indicates four pieces of information, but for our purposes we are interested in the total energy and the magnitude of the maximum force on the FODs from the latest SCF cycle respectively. As a calculation converges, this maximum force should decrease. The file `fforce.dat` on the other hand contains the forces on each of the FODs.

As has been stated before, DFT is a variational method, and so is the SIC modification. Therefore, with this procedure, we not only expect the DFT+SIC energy to be lower than the DFT energy, but we expect the energy to be continually decrease until it converges. That is, we hope the energy from the next SCF cycle to be lower than the energy of the current SCF cycle.

6 Optimization of FODs with Hartree Self-Repulsion Energy Minimization

In this chapter, we introduce a modification that can help in fast generation of initial FOD positions. This modification attempts to optimize the Coulomb energy between the Fermi orbitals of the system, that is the energy due to the repulsion between electrons, here referred to as the Hartree energy.

Equations Derivation

We start off with the expression for the Hartree energy

$$U[\rho]=\frac{1}{2}\sum_{k,j}\iint\rho_k(\mathbf{r})\rho_j(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|d^3\mathbf{r}d^3\mathbf{r}'. \quad (54)$$

This energy is treated as the classical electrostatic energy of a continuous volume charge distribution. This energy can be thought of as adding the works in taking infinitesimal amounts of the charge distribution from infinity to the configuration in question [34]. One thing to note is that the $\frac{1}{2}$ factor in front is to avoid double counting.

This energy, along with the exchange-correlation energy described previously, make up the contributions to the interelectronic interaction energy, and, between the two, the Hartree (or Coulomb) term dominates for the computational cost as a system grows larger [32]. This functional is homogenous of degree two with respect to density scaling and is strictly local [33]. This energy in DFT comes from treating the probabilistic nature of electrons as a density. That is, the electrons are considered together and spread out throughout space.

Afterwards, because we define the electron density in terms of Fermi orbitals, which are defined according to the FODs, we can explicitly state the dependency of the Hartree energy on the FODs as shown:

$$U=U(\mathbf{a}) \quad (55)$$

The FODs are contained inside the electron densities $\rho_i(\mathbf{r})$ and $\rho_j(\mathbf{r}')$. As such, we must use the expression for the electron density of the i th electron:

$$\rho_i(\mathbf{r}) = \sum_{\sigma} |F_{i\sigma}(\mathbf{r})|^2 \quad (56)$$

In addition, we may also note that the total electron density is the sum over all the individual electrons densities as such:

$$\rho(\mathbf{r}) = \sum_i \rho_i(\mathbf{r}) = \sum_i \sum_{\sigma} |F_{i\sigma}(\mathbf{r})|^2 \quad (57)$$

Going back to the individual electron density, we look at the expression for the i th Fermi orbital with spin σ to find the dependency of the orbitals in the FODs:

$$F_{i\sigma}(\mathbf{r}) = \sum_{\alpha} \{ \psi_{\alpha\sigma}^*(\mathbf{a}_{i\sigma}) \psi_{\alpha\sigma}(\mathbf{r}_{i\sigma}) / (\sum_{\alpha} |\psi_{\alpha\sigma}(\mathbf{a}_{i\sigma})|^2)^{1/2} \} \quad (58)$$

With

$$\rho_{\sigma}(\mathbf{a}_{i\sigma}) = \sum_{\alpha} |\psi_{\alpha\sigma}(\mathbf{a}_{i\sigma})|^2 \quad (59)$$

yields this expression for $F_{i\sigma}(\mathbf{r})$ as well:

$$F_{i\sigma}(\mathbf{r}) = \sum_{\alpha} \{ \psi_{\alpha\sigma}^*(\mathbf{a}_{i\sigma}) \psi_{\alpha\sigma}(\mathbf{r}_{i\sigma}) / (\rho_{\sigma}(\mathbf{a}_{i\sigma}))^{1/2} \} \quad (60)$$

where each $\psi_{\alpha\sigma}$ is a Kohn Sham orbital for the α th electron with spin orbital σ .

In addition, since we are making a linear transformation from the set of Kohn Sham orbitals to the set of Fermi orbitals, we can express a Fermi orbital as the linear combination of Kohn Sham orbitals like so:

$$F_{i\sigma}(\mathbf{r}) = \sum_{\alpha} F_{i\alpha}^{\sigma} \cdot \psi_{\alpha\sigma}(\mathbf{r}_{i\sigma}) \quad (61)$$

where the $F_{i\alpha}^{\sigma}$ are the elements of the transformation matrix, which is defined when given the set of FODs ($\{\mathbf{a}\}$).

Thus, we now see from where the FODs come into play in the electron density for the i th electron. The motivation to find this relationship between the Hartree energy and the FODs is to experiment whether minimizing the Hartree energy with respect to the FODs will improve the convergence of the calculation by improving the quality of the FOs. For this, we need to take the negative gradient with respect to the FODs of the Hartree energy U to find the direction of greatest descent in the immediate vicinity. Because we treat the FODs as a given degree of freedom of the system, we refer to this vector as a Hellmann-Feynman force [37] and call it \mathbf{f} :

$$\mathbf{f}_i = -\nabla_{\mathbf{a}_i} U \quad (62)$$

which can be expanded as follows:

$$\mathbf{f}_i = -\nabla_{\mathbf{a}_i} \frac{1}{2} \sum_{k,j} \iint \rho_i(\mathbf{r}) \rho_j(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'| d^3\mathbf{r} d^3\mathbf{r}' \quad (63)$$

This can be calculated with the help of the generalization of the DFT version of the Hellmann-Feynman theorem in which λ is a degree of freedom of the system [38]:

$$\partial E / \partial \lambda = \int d^3\mathbf{r} \rho(\mathbf{r}) \partial v(\mathbf{r}) / \partial \lambda \quad (64)$$

Using this vector \mathbf{f}_i in numerical methods will allow us to find a minimum of U . When taking this gradient, we note that it only acts on one of the electron densities, the i th ones, and that we can move it inside both integrals as such:

$$\mathbf{f}_i = -\frac{1}{2} \sum_j \iint \nabla_{\mathbf{a}_i} \{ \rho_i(\mathbf{r}) \rho_j(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'| \} d^3\mathbf{r} d^3\mathbf{r}' \quad (65)$$

Because the only factor dependent on the i th FODs is $\rho_i(\mathbf{r})$, we only take the gradient of the electron density of the i th electrons in ρ_i with respect to FOD \mathbf{a} of the i th electron, disregarding spin σ in calculation since we separate the spin up and spin down electrons into noninteracting sets during numerical methods:

$$\nabla_{\mathbf{a}_i} \rho_i = \sum_{x=1}^3 (\partial \rho_i / \partial a_{ix}) \mathbf{e}_x \quad (66)$$

Here the x indicates the x -component of the FOD \mathbf{a}_i , which in this case there are three, for \mathbf{a}_i is a position vector in three-dimensional real space. As such, we look only at one representative x -component for we can iterate the procedure with the rest of the components. Using the definition of ρ_i (58) that was previously stated, we arrive at

$$\partial\rho_i/\partial\mathbf{a}_{ix} = \sum_{\sigma=1}^2 2F_{i\sigma}(\mathbf{r})\partial F_{i\sigma}/\partial\mathbf{a}_{ix} \quad (67)$$

Noting that because the Fermi orbitals are real functions, the absolute value in the expression for the electron density of the i th electron ρ_i is inconsequential. However, we now need to calculate the partial derivative of the i th Fermi orbital F_i with respect to the x -component of the i th FOD \mathbf{a}_i . This is accomplished by using the expression of the Fermi orbitals as functions of the FODs as shown below:

$$\partial F_{i\sigma}/\partial\mathbf{a}_{ix} = \partial \left\{ \sum_{\alpha} \psi_{\alpha\sigma}^*(\mathbf{a}_{i\sigma}) \psi_{\alpha\sigma}(\mathbf{r}_{i\sigma}) / (\sum_{\alpha} |\psi_{\alpha\sigma}(\mathbf{a}_{i\sigma})|^2)^{1/2} \right\} / \partial\mathbf{a}_{ix} \quad (68)$$

And now using the product rule to distribute the derivative over each of the factors in the expression that contain the variable \mathbf{a}_{ix} : $\psi_{\alpha\sigma}^*(\mathbf{a}_{i\sigma})$ in the numerator and the terms in $(\sum_{\alpha} |\psi_{\alpha\sigma}(\mathbf{a}_{i\sigma})|^2)^{1/2}$ in the denominator we get:

$$\begin{aligned} \partial F_{i\sigma}/\partial\mathbf{a}_{ix} = & \sum_{\alpha} \left\{ \partial(\psi_{\alpha\sigma}^*(\mathbf{a}_{i\sigma})) / \partial\mathbf{a}_{ix} \cdot \psi_{\alpha\sigma}(\mathbf{r}_{i\sigma}) / (\rho_{\sigma}(\mathbf{a}_{i\sigma}))^{1/2} - \right. \\ & \left. (1/2) \left\{ \psi_{\alpha\sigma}^*(\mathbf{a}_{i\sigma}) \psi_{\alpha\sigma}(\mathbf{r}_{i\sigma}) / (\rho_{\sigma}(\mathbf{a}_{i\sigma}))^{3/2} \right\} \cdot \partial\rho_{\sigma}(\mathbf{a}_{i\sigma}) / \partial\mathbf{a}_{ix} \right\} \end{aligned} \quad (69)$$

This can be furthered simplified if we use the expression for an element in the transformation matrix from Kohn Sham orbitals to Fermi orbitals:

$$F_{i\sigma}^{\alpha} = \psi_{\alpha\sigma}^*(\mathbf{a}_{i\sigma}) / (\sum_{\alpha} |\psi_{\alpha\sigma}(\mathbf{a}_{i\sigma})|^2)^{1/2} = \psi_{\alpha\sigma}^*(\mathbf{a}_{i\sigma}) / \rho_{\sigma}(\mathbf{a}_{i\sigma})^{1/2} \quad (70)$$

With these coefficients, we can factor out common terms from the two summands as the following series of derivations demonstrate:

$$\begin{aligned} \partial F_i / \partial\mathbf{a}_{ix} = & \sum_{\alpha} \left\{ (\partial\psi_{\alpha\sigma}^*(\mathbf{a}_{i\sigma}) / \partial\mathbf{a}_{ix}) \psi_{\alpha\sigma}(\mathbf{r}_{i\sigma}) / (\rho_{\sigma}(\mathbf{a}_{i\sigma}))^{1/2} \cdot \psi_{\alpha\sigma}^*(\mathbf{a}_{i\sigma}) / \psi_{\alpha\sigma}^*(\mathbf{a}_{i\sigma}) - \right. \\ & \left. (1/2) \left\{ \psi_{\alpha\sigma}^*(\mathbf{a}_{i\sigma}) \psi_{\alpha\sigma}(\mathbf{r}_{i\sigma}) / (\rho_{\sigma}(\mathbf{a}_{i\sigma}))^{1/2} \right\} \cdot (\partial\rho_{\sigma}(\mathbf{a}_{i\sigma}) / \partial\mathbf{a}_{ix}) / \rho_{\sigma}(\mathbf{a}_{i\sigma}) \right\} \end{aligned} \quad (71)$$

$$\begin{aligned} \partial F_i / \partial \mathbf{a}_{ix} = & \sum_{\alpha} \{ \psi_{\alpha\sigma}^*(\mathbf{a}_{i\sigma}) / (\rho_{\sigma}(\mathbf{a}_{i\sigma}))^{1/2} \} \cdot \psi_{\alpha\sigma}(\mathbf{r}_{i\sigma}) \cdot (\partial \psi_{\alpha\sigma}^*(\mathbf{a}_{i\sigma}) / \partial \mathbf{a}_{ix}) / \psi_{\alpha\sigma}^*(\mathbf{a}_{i\sigma}) - \\ & (1/2) \{ \psi_{\alpha\sigma}^*(\mathbf{a}_{i\sigma}) / (\rho_{\sigma}(\mathbf{a}_{i\sigma}))^{1/2} \} \cdot \psi_{\alpha\sigma}(\mathbf{r}_{i\sigma}) \cdot \partial \rho_{\sigma}(\mathbf{a}_{i\sigma}) / \partial \mathbf{a}_{ix} / \rho_{\sigma}(\mathbf{a}_{i\sigma}) \} \end{aligned} \quad (72)$$

Where the first factor in each summand is the element from the transformation matrix

$F_{i\alpha}^{\sigma}$. We further simplify:

$$\begin{aligned} \partial F_i / \partial \mathbf{a}_{ix} = & \sum_{\alpha} \{ F_{i\alpha}^{\sigma} \cdot \psi_{\alpha\sigma}(\mathbf{r}_{i\sigma}) \cdot (\partial \psi_{\alpha\sigma}^*(\mathbf{a}_{i\sigma}) / \partial \mathbf{a}_{ix}) / \psi_{\alpha\sigma}^*(\mathbf{a}_{i\sigma}) - \\ & F_{i\alpha}^{\sigma} \cdot \psi_{\alpha\sigma}(\mathbf{r}_{i\sigma}) \cdot \partial \rho_{\sigma}(\mathbf{a}_{i\sigma}) / \partial \mathbf{a}_{ix} / (2\rho_{\sigma}(\mathbf{a}_{i\sigma})) \} \end{aligned} \quad (73)$$

We note that the first two products inside the summation over α for each summand is the i th Fermi orbital and thus:

$$\partial F_i / \partial \mathbf{a}_{ix} = F_{i\sigma} \cdot \{ (\partial \psi_{\alpha\sigma}^*(\mathbf{a}_{i\sigma}) / \partial \mathbf{a}_{ix}) / \psi_{\alpha\sigma}^*(\mathbf{a}_{i\sigma}) - \partial \rho_{\sigma}(\mathbf{a}_{i\sigma}) / \partial \mathbf{a}_{ix} / (2\rho_{\sigma}(\mathbf{a}_{i\sigma})) \} \quad (74)$$

Looking back at the definition of the electron density but as a function of the FODs instead of the electron positions we can write:

$$\rho(\mathbf{a}) = \sum_i \rho_i(\mathbf{a}) \quad (75)$$

Taking the derivative and replacing i by β as the dummy variable yields:

$$\partial \rho_{\sigma}(\mathbf{a}_{i\sigma}) / \partial \mathbf{a}_{ix} = \partial \sum_{\beta} |\psi_{\beta}(\mathbf{a}_i)|^2 / \partial \mathbf{a}_{ix} \quad (76)$$

$$\partial \rho_{\sigma}(\mathbf{a}_{i\sigma}) / \partial \mathbf{a}_{ix} = \sum_{\beta} 2\psi_{\beta}(\mathbf{a}_i) \cdot \partial \psi_{\beta}(\mathbf{a}_i) / \partial \mathbf{a}_{ix} \quad (77)$$

Plugging this into the expression for $\partial F_i / \partial \mathbf{a}_{ix}$ yields:

$$\partial F_i / \partial \mathbf{a}_{ix} = F_{i\sigma} \cdot \{ (\partial \psi_{\alpha\sigma}^*(\mathbf{a}_{i\sigma}) / \partial \mathbf{a}_{ix}) / \psi_{\alpha\sigma}^*(\mathbf{a}_{i\sigma}) - \sum_{\beta} 2\psi_{\beta}(\mathbf{a}_i) \cdot \partial \psi_{\beta}(\mathbf{a}_i) / \partial \mathbf{a}_{ix} / (2\rho_{\sigma}(\mathbf{a}_{i\sigma})) \} \quad (78)$$

Which readily simplifies to

$$\partial F_i / \partial \mathbf{a}_{ix} = F_{i\sigma} \cdot \{ (\partial \psi_{\alpha\sigma}^*(\mathbf{a}_{i\sigma}) / \partial \mathbf{a}_{ix}) / \psi_{\alpha\sigma}^*(\mathbf{a}_{i\sigma}) - \sum_{\beta} \{ \psi_{\beta}(\mathbf{a}_i) \cdot \partial \psi_{\beta}(\mathbf{a}_i) / \partial \mathbf{a}_{ix} \} / \rho_{\sigma}(\mathbf{a}_{i\sigma}) \} \quad (79)$$

Now we can plug this back into the derivative of the i th electron density which in turn is plugged back into the component derivative of the self-repulsion energy, noting that it is

sufficient to look at just one of the components (x) of the Hellmann Feynman force \mathbf{f}_i for the i th electron:

$$f_{ix} = -\frac{1}{2} \sum_j \iint \partial \{ \rho_i(\mathbf{r}) \rho_j(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'| \} / \partial a_{ix} d^3 \mathbf{r} d^3 \mathbf{r}' \quad (80)$$

$$f_{ix} = -\frac{1}{2} \sum_j \iint \{ \partial \rho_i(\mathbf{r}) / \partial a_{ix} \} \rho_j(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'| d^3 \mathbf{r} d^3 \mathbf{r}' \quad (81)$$

Plugging in for $\partial \rho_i(\mathbf{r}) / \partial a_{ix}$ we get:

$$f_{ix} = -\frac{1}{2} \sum_j \iint \partial \{ 2F_i(\mathbf{r}) \partial F_i / \partial a_{ix} \} \rho_j(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'| d^3 \mathbf{r} d^3 \mathbf{r}' \quad (82)$$

$$f_{ix} = -\sum_j \iint F_i(\mathbf{r}) \{ \partial F_i / \partial a_{ix} \} \rho_j(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'| d^3 \mathbf{r} d^3 \mathbf{r}' \quad (83)$$

From this, we see that the coulomb potential v_c is present, that is

$$v_c = -\sum_j \int \rho_j(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'| d^3 \mathbf{r}' \quad (84)$$

As a result, we replace this into the expression for f_{ix}

$$f_{ix} = \int F_i(\mathbf{r}) \{ \partial F_i / \partial a_{ix} \} v_c d^3 \mathbf{r} \quad (85)$$

Now, for purposes of the code implementation, we want to express the i th Fermi orbital as a linear combination of the Kohn Sham orbitals as so:

$$F_{i\sigma}(\mathbf{r}) = \sum_{\alpha} F_{i\alpha}^{\sigma} \cdot \psi_{\alpha\sigma}(\mathbf{r}_{i\sigma}) \quad (86)$$

But, as was previously stated, we want to disregard the spin components because the spin up and the spin down electrons can be separated into two sets. Therefore, we can write for the i th Fermi orbital just

$$F_i(\mathbf{r}) = \sum_{\alpha} F_{i\alpha} \cdot \psi_{\alpha\sigma}(\mathbf{r}_{i\sigma}) \quad (87)$$

We thus insert this expression for the x-component of the force in the i th FOD:

$$f_{ix} = \sum_{\alpha} \int F_{i\alpha} \cdot \psi_{\alpha\sigma}(\mathbf{r}_{i\sigma}) \{ \partial F_i / \partial a_{ix} \} v_c d^3 \mathbf{r} \quad (88)$$

In bra-ket notation this becomes

$$f_{ix} = \sum_{\beta} \sum_{\alpha} \partial F_i / \partial a_{ix} \langle \psi_{\beta} | v_c | \psi_{\alpha} \rangle \quad (89)$$

Afterward, we want to do the same for the Fermi orbitals inside the bra, with a β as the dummy variable over the sum

$$F_i = \sum_{\beta} F_{i\beta} \psi_{\beta} \quad (90)$$

This gives that

$$f_{ix} = \sum_i \sum_{\alpha} \sum_{\beta} \partial F_i / \partial a_{ix} \langle \psi_{\beta} | v_c | \psi_{\alpha} \rangle \quad (91)$$

This is the expression we can use to determine the forces on each FOD, extending to all three components and for all the FODs. These equations can be implemented in code in future studies.

7 The revPBE and RPBE Exchange Functionals Testing

In this chapter, we go over the GGA-RPBE and GGA-REVPBE exchange functionals. The revPBE and RPBE functionals are functionals based on the PBE (Perdew-Burke-Ernzerhof) functional. The PBE functional itself was based on a numerical GGA in which the exchange correlation hole satisfied exact constraints [31]. The revPBE functional was constructed by optimizing one parameter of the PBE functional against the exchange energy of noble gas elements from He to Ar [35]. The RPBE functional on the other hand gives nearly the same results as the revPBE functional but without the fitting of parameters [35].

These functionals were tested with a set of neutral atoms, anions, and cations. For a good calculation, the first ionization energies and electron affinities had to be in good agreement with experimental results from literature [36]. The all energies were calculated using FLOSIC.

7.1 The revPBE First Ionization Energy

This table (Table 7.1) gives the first ionization energy of the atoms using the revPBE functional. The first ionization energy represents the energy required to free the outermost-bound electron from a neutral atom. The energy is calculated by subtracting the ground state energy of the neutral atom from that of the cation. The conversion is made to electron volts (1 Hartree = 27.2114 eV).

Table 7.1 Ionization Energy from revPBE Functional Comparison with Accepted Values

Element	Ref. 1st Ionization Energy (Ev)	revPBE 1st Ionization Energy (Ev)	Percent Error revPBE
2	24.29282145	24.29314022	0.001312

3	5.460959863	5.413495358	0.86916
4	8.901934572	8.841234483	0.681875
5	8.558937093	8.42316688	1.586298
6	10.97391934	10.7691723	1.86576
7	13.79089864	13.54331424	1.795274
8	13.69189937	13.47553072	1.580268
9	16.61187791	16.30645304	1.838593
10	20.10685222	19.75708078	1.739563
11	5.194961818	5.090926749	2.002615
12	7.477945038	7.372522253	1.409783
13	5.980956041	5.91387894	1.121511
14	7.828942458	7.706353516	1.565843
15	9.933926987	9.757505798	1.775946
16	10.29392434	9.740897278	5.372364
17	12.49090819	11.94816965	4.345069
18	14.99888976	14.78822666	1.404525
20	5.891956695	5.776443433	1.960525
26	8.17293993	8.267721509	1.1597
27	7.77294287	7.593415576	2.309644
30	9.024933668	8.812480981	2.354064
32	7.452945222	7.307749023	1.948172
33	9.371931118	9.221050586	1.609919
34	9.533929927	9.380492383	1.609384

36

13.49090084

13.29345981

1.463513

7.2 RPBE First Ionization Energy

This table (Table 7.2) is derived from the same procedure as in the last section except the RPBE functional was used this time. The values for the IP's are expressed in electro-volts as well.

Table 7.2 Ionization Energy from RPBE Functional Comparison with Accepted Values

Element	Ref. 1st Ionization Energy (Ev)	RPBE 1st Ionization Energy (Ev)	Percent Error RPBE
2	24.29282145	24.29314022	0.001312
3	5.460959863	5.45569138	0.096475
4	8.901934572	8.900635894	0.014589
5	8.558937093	8.42825324	1.52687
6	10.97391934	10.76969132	1.861031
7	13.79089864	13.53916211	1.825382
8	13.69189937	13.48549583	1.507486
9	16.61187791	16.30852911	1.826096
10	20.10685222	19.75002216	1.774669
11	5.194961818	5.137015393	1.115435
12	7.477945038	7.425669519	0.699063
13	5.980956041	5.929241821	0.864648
14	7.828942458	7.721301184	1.374915
15	9.933926987	9.790722839	1.441566

16	10.29392434	10.17437966	1.161313
17	12.49090819	12.31106583	1.439786
18	14.99888976	14.79653092	1.349159
20	5.891956695	5.826268994	1.114871
26	8.17293993	8.35740752	2.257053
27	7.77294287	7.639919434	1.711365
30	9.024933668	8.81912439	2.280452
32	7.452945222	7.327679248	1.680758
33	9.371931118	9.214407178	1.680806
34	9.533929927	9.413709424	1.260975
36	13.49090084	13.30010322	1.414269

7.3 The revPBE First Electron Affinity

This table (Table 7.3) gives the first electron affinities of the atoms using the revPBE functional. The electron affinity represents the energy needed to remove the outermost electron from an anion to bring the element back to neutral. The electron affinity is calculated by subtracting the ground state energy of the anion from that of the neutral element.

Table 7.3 Electron Affinities from revPBE Functional Comparison with Accepted Values

Element	Ref. 1st Electron Affinity (Ev)	revPBE 1st Electron Affinity (Ev)	Percent Error revPBE
1	0.754189457	0.329229859	56.34653128
3	0.431996825	0.428227346	0.872571072

5	-0.124999081	-0.239474105	91.58069212
6	0.562995862	0.403483245	28.33282227
8	0.347997442	0.128300821	63.13167704
11	0.478996479	0.460471231	3.867512428
14	0.966992893	0.869456049	10.08661438
15	0.568995818	0.514864136	9.513546584
16	1.575988417	1.861815149	18.13634727
17	2.892978737	3.079219702	6.437688697
33	0.913993282	0.498255615	45.48585589

7.4 RPBE First Electron Affinity

The table below (Table 7.4) is derived from the same procedure as the last table except the RPBE functional is used this time around. The values for the EA's are expressed in electro-volts as well.

Table 7.4 Electron Affinities from RPBE Functional Comparison with Accepted Values

Element	Ref. 1st Electron Affinity (Ev)	RPBE 1st Electron Affinity (Ev)	Percent Error RPBE
1	0.754189457	0.329229859	56.34653128
3	0.431996825	0.455826035	5.516061514
5	-0.124999081	-0.232726894	86.18288329
6	0.562995862	0.404417474	28.16688334
8	0.347997442	0.13432141	61.4016101
11	0.478996479	0.506144662	5.667720786
14	0.966992893	0.873608179	9.657228581
15	0.568995818	0.497425189	12.57841033
16	1.575988417	1.442450006	8.473311681
17	2.892978737	2.732101624	5.560950428
33	0.913993282	0.498255615	45.48585586

8 Conclusion

In this chapter, we explore the results of the exchange-correlation functionals we tested on chapter 7.

8.1 Exchange-Correlation Functionals Evaluation

The performance of one functional over the other for the IP and EA values of each atom is evaluated relatively to all other results.

Analyzing the results for the first ionization potentials of the systems tested, from tables 7.1 and 7.2, we can plot the data as shown below (Figure 8.1):

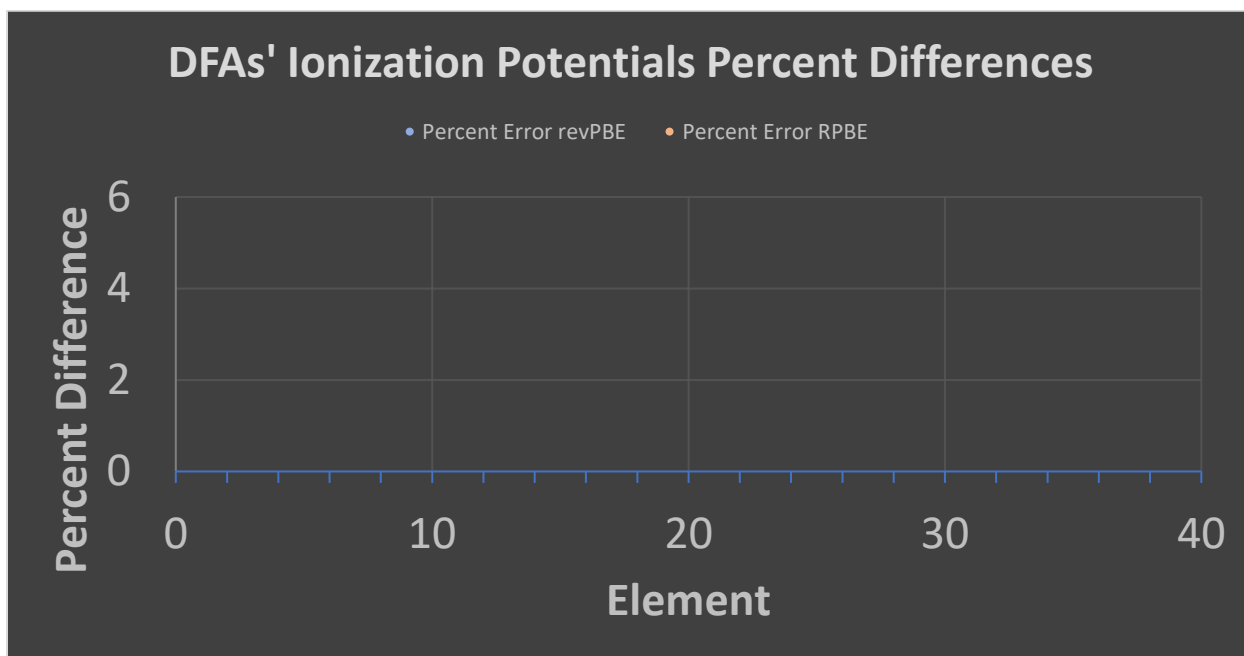


Figure 8.1 DFAs' Ionization Potentials Percent Differences from Accepted Values

The data visualization indicates that for elements atomic numbers 3, 4, 8, 11 to 18, 20, 27, 32, and 34 the RPBE functional yields better results. On the other hand, only for elements of atomic number 26 and 33 did the revPBE functional work better. For the rest of the elements atomic numbers there was no significant performance difference between the DFA's.

In the case of the electron affinities, we look at the data from tables 7.3 and 7.4 and plot it against the base element as shown below:

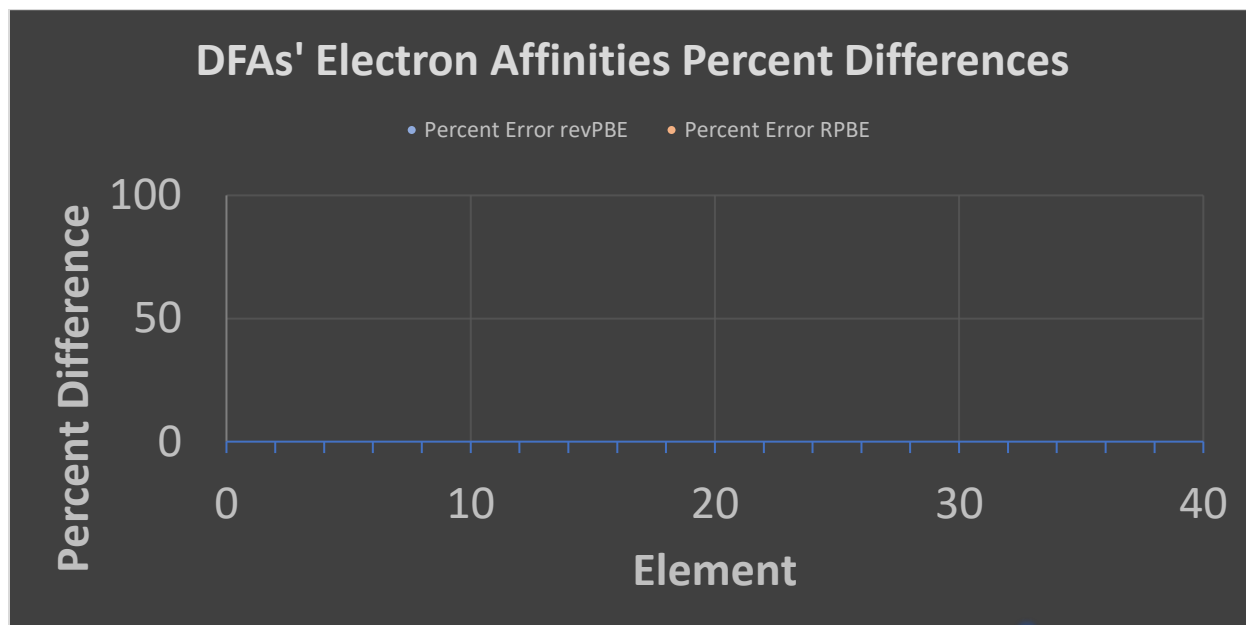


Figure 8.2 DFAs' Electron Affinities Percent Differences from Accepted Values

For the electron affinities, we do not see significant difference between the performance of revPBE and RPBE as can be seen from the above plot.

Overall, the FLOSIC-revPBE and FLOSIC-RPBE functionals did yielded better results for the ionization potentials than with the electron affinities as can be easily seen in figures 8.1 and 8.2, where the percent differences for the ionization potentials tend to fall in the range of 0 to 6% while that of the electron affinities spread out more into the range of 0 to 100%. However, in comparison to each other, the data for IP's strongly suggests that the RPBE functional performs better than the revPBE functional. In addition, the mean average error (MAE) from the reference values for the revPBE functional IP was 0.19 eV while that for the RPBE functional IP was 0.14 eV. This gives a more quantitative indication that the RPBE function did better. On the other hand, at first glance, the EA data does not seem to strongly indicate that either functional performs better. However, a quantitative analysis indicates that the MAE for revPBE functional's EA from the

reference values evaluates to 0.18 eV while that of the RPBE functional's EA is 0.17 eV. As such, the RPBE functional again performs better than the revPBE functional since for this data as well it has the lower MAE. This shows that the MAE for both IP and EA are of similar order although the percent error is large. We point out that the IP of the systems are much larger than the typical electron affinity which leads the larger percent errors for EA compared to IP although the absolute errors are of similar order. The small errors (<0.2 eV) shows that FLOSIC with both revPBE and RPBE can be used to determine the IP and EA of atomic systems.

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Vita

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