Studies of Self-interaction Corrections in Density Functional Theory

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Abstract

The self-interaction error (SIE) in density functional theory (DFT) appears from the fact that the residual self-interaction in the Coulomb part and that in the exchange part do not cancel each other exactly. This error is responsible for the unphysical orbital energies of DFT and the failure to reproduce the potential energy curves of several physical processes. The present thesis addresses several methods to solve the problem of SIE in DFT.

A new algorithm is presented which is based on the Perdew-Zunger (PZ) energy correction and which includes the self-interaction correction (SIC) self-consistently (SC SIC PZ). When applied to the study of hydrogen abstraction reactions, for which conventional DFT can not describe the processes properly, SC PZ SIC DFT produces reasonable potential energy curves along the reaction coordinate and reasonable transition barriers.

A semi-empirical SIC method is designed to correct the orbital energies. It is found that a potential coupling term is generally nonzero for all available approximate functionals. This coupling term also contributes to the self-interaction error. In this scheme, the potential coupling term is multiplied by an empirical parameter α, introduced to indicate the strength of the potential coupling, and used to correct the PZ SIC DFT. Through a fitting scheme, we find that a unique α can be used for C,N,O core orbitals in different molecules. Therefore this method is now used to correct the core orbital energies and relevant properties. This method is both efficient and accurate in predicting core ionization energies.

A new approach has been designed to solve the problem of SIE. A functional is constructed based on electron-electron interactions, Coulomb and exchange-correlation parts, which are free of SIE. A post-SCF procedure for this method has been implemented. The orbital energies thus obtained are of higher quality than in conventional DFT. For a molecular system, the orbital energy of the highest occupied molecular orbital (HOMO) is comparable to the experimental first ionization potential energy.

Preface

The work presented in this thesis has been carried out at the Department of Theoretical Chemistry, Royal Institute of Technology, Stockholm, Sweden.

List of papers included in the thesis

Paper I Core ionization potentials from self-interaction corrected Kohn-Sham Orbital energies, Guangde Tu, Vincenzo Carravetta,Olav Vahtras,Hans Ågren, J.Chem. Phys. **127**, 174110 (2007).

Paper II Self-interaction-corrected time-dependent density-functional-theory calculations of x-ray-absorption spectra, Guangde Tu, Ulf Ekström, Patrick Norman, Vincezo Carravetta, Zilvinas Rinkevicius, Olav Vahtras, Hans Ågren, Phys. Rev. A 76, 022506 (2007)

Paper III Perdew-Zunger self-interaction corrections in density functional calculations of transition barriers of hydrogen abstraction reactions, Guangde Tu, Zilvinas Rinkevicius, Olav Vahtras, Hans Ågren, in manuscript

Paper IV Core electron chemical shifts of hydrogen bonded networks using self interaction corrected DFT, Guangde Tu, Yaoquan Tu, Zilvinas Rinkevicius, Olav Vahtras, Hans Ågren, submitted.

Paper V An alternative approach to the solution of the self-interaction error in density functional theory with applications to ionization potentials, Guangde Tu, Zilvinas Rinkevicius, Olav Vahtras, Hans Ågren, in manuscript

Comments on my contribution to the papers included

- I implemented the code for the self-interaction correction that was used in **all papers**.

- I performed the calculations of the self-interaction part in **all papers**

- I participated in the preparations of the manuscripts for **all papers**

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Chapter 1

Introduction

The problems of chemistry and biology can be greatly helped if our ability to see what we are doing, and to do things on an atomic level, is ultimately developed—a development which I think cannot be avoided.

Richard Feynman

Scientific activities are classified as experimental and theoretical research. The experiment is a direct way to establish relationships in nature. Two elements of the experiment are equipment and operation, which impose some restrictions on the activities. Experimental equipment may exhaust a lot monetary resources, and operation needs human beings to face expensive or potentially dangerous materials. This leads to the fact that some hypotheses can not be tested directly experimentally. In such cases computational simulations can be an inexpensive and safe replacement. With relevant theoretical models, one can get results from computational simulations which are comparable to the experiment. Computational simulations make a valuable complement to experiment and push the development of science.

In the last century, along with the development of computers, many computational methods were developed for various fields of science. In computational chemistry, one of these methods is based on Newtonian mechanics: molecular dynamics which is applied to the study of very large molecules like proteins. Other methods are based on quantum mechanics which are applied to the study of the electronic structure of molecular systems and to the research of various electric and magnetic properties of molecules. In this thesis, we focus on density functional theory which is currently the most popular method of quantum chemistry.

Density functional theory (DFT)[1–3] is one of the most successful quantum chemistry tools. Compared to other quantum chemistry methods, DFT combines low

computational cost and accurate results. DFT is the most competitive quantum chemistry method to achieve linear scaling (of computational effort vs system size) and to study large molecular systems. In the last few decades, DFT has established itself a dominant tool to simulate chemical reactions[4], to study electric, magnetic and optical properties of molecules, to design bio-molecular devices and to study nano-materials. Despite its great success in these many fields, and despite that DFT has a rigorous foundation in quantum mechanics, it remains a semi-empirical approximate method since the exact exchange correlation functional is not known. At this stage DFT faces problems in some applications. One problem is caused by the incorrect asymptotic behavior [3, 5] of the approximate exchange correlation functional. Another problem is caused by the electron self-interaction[6–8] introduced by approximate density functionals. This problem leads to wrong potential energy curves when DFT is applied to the study of some open-shell systems. The potential energy curves of these cases are related to the motion of a particular unpaired electron, for instance, in chemical reactions involving charge transfer[9, 10], dissociation processes concerning the problem about which residue an unpaired electron belongs to[11, 12].

The self-interaction error (SIE) is by definition the residual interaction of an electron with itself. This error comes from the fact that the self-interaction in the Coulomb part and that in the exchange part can not cancel each other exactly, as they do in Hartree-Fock. Many efforts are devoted to solve the problem of SIE.[6, 13–18] However, currently this error can not be eliminated completely but can be reduced to a great deal through some self-interaction correction (SIC) procedures.

The basic idea of SIC was introduced by Perdew and Zunger[6] in 1972. They suggested a simple scheme based on one electron SIE. A term

$$E^{SIE} = \sum_{i\sigma} [J[\rho_{i\sigma}] + E_{xc}[\rho_{i\sigma}]] \tag{1.1}$$

is subtracted from the Kohn-Sham energy functional, where $\rho_{i\sigma}$ is the spin orbital density, J is the classical Coulomb term, and E_{xc} is the exchange-correlation term. The method was initially developed to improve the performance of the LDA functional. PZ SIC DFT is not easy to implement self-consistently since the total energy is not invariant with respect to a unitary transformation among the occupied orbitals. Previously, the SIE term has mostly been treated as a first order correction. In this work, we have introduced a computational scheme for self-consistent PZ SIC DFT based on a quasi-Newton optimization method[19]. This can be applied to the study of chemical reactions involving transition barriers as well as dissociation processes. Besides PZ SIC, there are some other popular SIC method

based on various approximations, for instance, averaged density SIC[13, 14] which uses an averaged density $\frac{\rho}{N}$ to replace the orbital density $\rho_{i\sigma}$, and Lundin-Eriksson SIC[15]. We have developed two new SIC methods in order to improve the performance of conventional DFT. The first is a semi-empirical SIC DFT method which is used to correct the orbital energies. This method has been applied to the study of the core ionization potential energies of first-row elements in different molecules and shown to be successful. The second is the a new SIC approach, where we have a class of functionals for which PZ is a special case. Currently, only a post-SCF procedure has been implemented and the method is applied to the study of the orbital energies of atomic systems and the HOMO energies of molecular systems.

Chapter 2

Ground State Theory

In this chapter, we introduce two corner stones of quantum chemistry: Hartree-Fock theory and density functional theory. We will present the basics of the two methods, their advantages and disadvantages, their differences and similarities.

2.1 Hartree-Fock Theory

In the Hartree-Fock method (HF), we use a wave-function composed of a finite set of one-electron wave functions to approximate the true ground state. This function should be antisymmetric with respect to particle permutations. This can be always satisfied by a Slater determinant

$$\psi_0 \approx \phi_{SD} = \frac{1}{\sqrt{N!}} det|\chi_1(x_1)\chi_2(x_2)...\chi_N(x_N)|, \tag{2.1}$$

where $\chi_i(x_i)$ is the molecular spin orbital, consisting of a spatial orbital and spin function.

$$\chi(x) = \varphi(r)\sigma(s), (\sigma = \alpha, \beta). \tag{2.2}$$

The spatial part $\varphi(r)$ can be constructed as a linear combination of basis functions:

$$\varphi_i(r) = \sum_\mu c_{\mu i}\gamma_\mu(r). \tag{2.3}$$

$\gamma_1, \gamma_2, ..., \gamma_\mu, ...$ by definition form a complete basis set and $c_{\mu i}$ is the molecular orbital coefficient. According to the variational principle, the Slater determinant which minimizes the total electronic energy is the best approximate wave function of this form to the true ground state.

For an arbitrary state expressed as a Slater determinant, the total electronic energy of the system can be expressed as

$$
\begin{aligned}
E &= \sum_i^{N^{tot}} <i| -\frac{1}{2}\nabla_1^2 - \sum_A^M \frac{Z_A}{r_{1A}}|i> \\
&+ \frac{1}{2}\sum_i^{N^{tot}}\sum_j^{N^{tot}}(ii|jj) - \frac{1}{2}\sum_\sigma^{N^\sigma}\sum_i^{N^\sigma}\sum_j^{N^\sigma}(ij|ji),
\end{aligned}
\tag{2.4}
$$

where N^σ represents the number of the electrons with spin σ, N^{tot} is total number of electrons, and

$$
(pq|rs) = \int \frac{\varphi_p^*(r_1)\varphi_q(r_1)\varphi_r^*(r_2)\varphi_s(r_2)}{r_{12}}dr_1dr_2
\tag{2.5}
$$

is the two electron integral of molecular orbitals.

By minimizing the total electronic energy with respect to the orbital φ_i, we obtain a set of HF equations hold for the ground state

$$
\begin{aligned}
[&- \frac{1}{2}\nabla_1^2 - \sum_A^M \frac{Z_A}{r_{1A}} + \sum_j^{N_{tot}}\int \varphi_j^*(r_2)\varphi_j(r_2)\frac{1}{r_{12}}dr_2 \\
&- \sum_j^{N_\sigma}\int \varphi_j^*(r_2)\varphi_i(r_2)\frac{1}{r_{12}}dr_2\frac{\varphi_j(r_1)}{\varphi_i(r_1)}]\varphi_i(r_1) = \epsilon_i^\sigma \varphi_i(r_1).
\end{aligned}
\tag{2.6}
$$

If we define a Fock operator $\hat{f}$,

$$
\begin{aligned}
\hat{f}^\sigma &= -\frac{1}{2}\nabla_1^2 - \sum_A^M \frac{Z_A}{r_{1A}} + \sum_j^{N_{tot}}\int \varphi_j^*(r_2)\varphi_j(r_2)\frac{1}{r_{12}}dr_2 \\
&- \sum_j^{N_\sigma}\int \varphi_j^*(r_2)\varphi_i(r_2)\frac{1}{r_{12}}dr_2\frac{\varphi_j(r_1)}{\varphi_i(r_1)}
\end{aligned}
$$

the HF equation for spin σ can be expressed as

$$
\hat{f}^\sigma \varphi_i(r_1) = \epsilon_i^\sigma \varphi_i(r_1).
\tag{2.7}
$$

Computationally, the matrix form of this equation is favorable,

$$
F^\sigma C^\sigma = SC^\sigma \epsilon^\sigma,
\tag{2.8}
$$

where F^σ is the Fock matrix for spin σ

$$
F_{\mu\nu}^\sigma = \int \gamma_\mu \hat{f}^\sigma \gamma_\nu dx
\tag{2.9}
$$
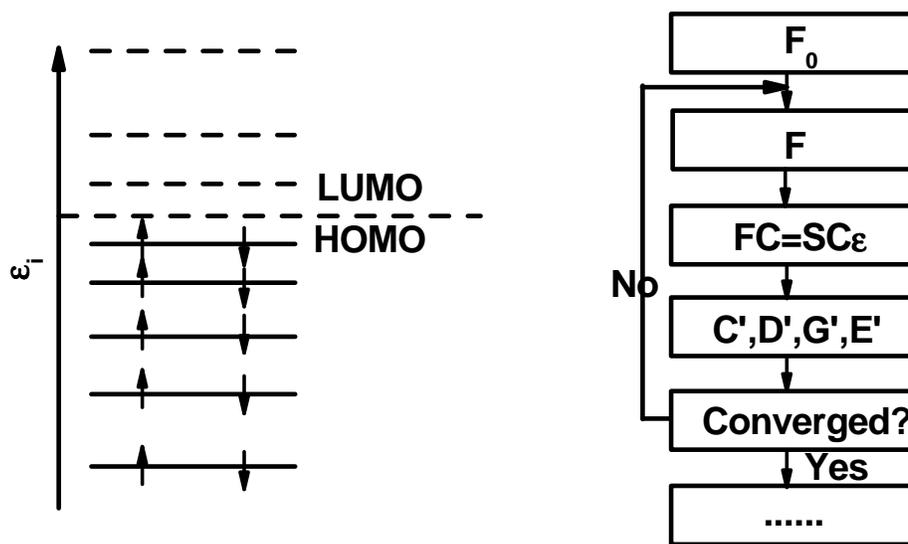
Figure 2.1: Hartree-Fock Computational Scheme. C is the molecular coefficient matrix, D the density matrix, G the gradient, and E the energy.

C^σ is the coefficient matrix of molecular orbitals for spin σ and S is the overlap of the basis functions

$$S_{\mu\nu} = \int \gamma_\mu \gamma_\nu dx. \tag{2.10}$$

ϵ^σ represents orbital energies. According to the Pauli exclusion principle and variational principle, the occupied orbitals are those N eigenstates with lowest eigenvalues of the Fock equation. Given C, F can be constructed through Eq. (2.9), and in turn, given F, C can be solved through Eq. (2.8). Hence, the HF equations must be solved iteratively, and the solution is a so called self-consistent field (SCF) solution.

For the occupied orbital energies of the HF calculation, we have the Koopman's theorem

$$\epsilon_i = E_N - E_{N-1}^i \tag{2.11}$$

which means that the orbital energies of the HF solutions are approximately the negative ionization energies.

2.2   Electron Correlation

Compared to the exact solution to the Schrödinger equation, the total Hartree-Fock energy lacks a minor, but extremely important part of energy contribution.

This contribution, namely the deviation between the exact energy and the HF energy, is called the electron correlation energy and is defined as

$$E_C^{HF} = E_0 - E_{HF}. \tag{2.12}$$

There are two components of electron correlation. One is the static correlation, which is the correlation associated with the existence of several semi-degenerate configurations. Static correlation exists when the ground state of a system can not be represented by a single Slater determinant. This problem is addressed by including more configurations such as in the multi-configurational self-consistent field (MCSCF) method. The other type of correlation is the dynamic correlation, caused by the Coulomb interaction between different electrons, which is not treated either in the HF approximation, where the electrons move in the mean field of all the other electrons.

Let $\rho(r)$ be the total electron density of finding a single electron at r. If the combined density to find simultaneous one electron at position r_1 and another electron at r_2 is $\rho(r_1, r_2)$, since there are interactions between electrons, this density should be different from the product of the corresponding one-electron densities. The difference can be used to define a correlation factor, $f(r_1, r_2)$,

$$\rho(r_1, r_2) = \rho(r_1)\rho(r_2)(1 + f(r_1, r_2)), \tag{2.13}$$

Given the one- and two-electron densities the total energy of a system can be expressed as

$$E^{total} = -\sum_i^N <\phi_i|\frac{1}{2}\nabla^2|\phi_i> - \int \sum_A^M \frac{Z_A}{r_{1A}}\rho(r_1)dr_1$$
$$+ \frac{1}{2}\int\int \frac{\rho(r_1, r_2)}{r_{12}}dr_1dr_2. \tag{2.14}$$

Introducing an exchange correlation functional of the form

$$h_{xc}(r_1, r_2) = \frac{\rho(r_1, r_2)}{\rho(r_1)} - \rho(r_2) = \rho(r_2)f(r_1, r_2), \tag{2.15}$$

the total electronic energy can be expressed as

$$E^{total} = -\sum_i^N <\phi_i|\frac{1}{2}\nabla^2|\phi_i> - \int \sum_A^M \frac{Z_A}{r_{1A}}\rho(r_1)dr_1$$
$$+ \frac{1}{2}\int\int \frac{\rho(r_1)\rho(r_2)}{r_{12}}dr_1dr_2$$
$$+ \frac{1}{2}\int\int \frac{\rho(r_1)h_{xc}(r_1, r_2)}{r_{12}}dr_1dr_2. \tag{2.16}$$

The exact form of the last term, the exchange correlation functional is unknown. However, to a good approximation, a single determinant theory can be applied which includes correlation in an approximate way. This is the basis for the most popular electronic structure theory today, density functional theory.

2.3   Density Functional Theory

The conceptual root of density functional theory (DFT) is in the Thomas-Fermi model[20, 21], developed by Thomas and Fermi in 1927, who used a statistical model to approximate the distribution of electrons in an atom. This Thomas-Fermi model is inaccurate for most applications. With the Hohenberg-Kohn theorems[1], DFT was put on a firm theoretical footing. With The Kohn-Sham computational scheme[2], using approximate functionals, it was possible to study molecular systems of chemistry successfully. Now DFT has established itself as one of the most popular quantum chemistry tools due to a rapid development after 1990.

2.3.1   The Hohenberg-Kohn Theorems

The two Hohenberg-Kohn theorems [1] are the fundamentals of density functional theory.

The first theorem states that "the external potential $V_{ext}(r)$ is (to within a constant) a unique functional of $\rho(r)$; since, in turn $V_{ext}(r)$ fixes $\hat{H}$. We see that the full many-particle ground state is a unique functional of $\rho(r)$.". According to this theorem, the ground state electronic energy is expressed as

$$E_0[\rho_0] = T[\rho_0] + E_{ee}[\rho_0] + E_{Ne}[\rho_0]. \tag{2.17}$$

This theorem formulates a one-to-one relationship between a non-degenerate ground state density and the external potential.

In Hohenberg-Kohn's second theorem it is proved that the variational principle holds for electronic ground states: "the functional that delivers the ground state energy of the system, delivers the lowest energy if and only if the input density is the true ground state density, $\rho_0(r)$". According to this theorem, for an N-electron system, we have

$$E_0 \leq E[\rho] = T[\rho] + E_{Ne}[\rho] + E_{ee}[\rho], \tag{2.18}$$

where ρ is any trial density. This theorem states that DFT is a ground state theory. However, DFT is currently also widely applied to the study of the properties of the excited state.

2.3.2 Basic Idea of the Kohn-Sham Density Functional Theory

The two Hohenberg-Kohn theorems form a theoretical foundation for DFT. However, there are still some problems left unsolved. First, only the density functional of $E_{Ne}[\rho_0]$ is exactly known but we have no exact expressions for the density functionals of the kinetic part and the electron-electron interaction part. Second, we still lack a way to construct the density which can reflect the property of a fermion system. These two problems are properly solved in the Kohn-Sham DFT (KSDFT) scheme[2].

In the Kohn-Sham DFT scheme, the density of a fictitious system with non-interacting electrons is considered to be able to represent the ground state density of a real system. The ground state wave function of such a non-interacting system can be represented by a Slater determinant. Thus, the electronic kinetic energy of such a non-interacting system is similar to that in the HF. When using this kinetic energy functional in the real system, we need to add a correction term. This means

$$T[\rho] = T_S[\rho] + T_c[\rho], \tag{2.19}$$

where $T_S[\rho]$ is the kinetic energy of the non-interacting system and $T_c[\rho]$ is the kinetic energy correction due to the electron-electron interaction. Compared to $T_S[\rho]$, $T_c[\rho]$ is assumed to be a small contribution.

The exact density functional of the classical Coulomb part of the two-electron interaction is

$$J[\rho] = \frac{1}{2} \int \int \frac{\rho(x_1)\rho(x_2)}{r_{12}} dx_1 dx_2. \tag{2.20}$$

but we lack the complete knowledge of the remaining interactions. In the Kohn-Sham DFT scheme, all unknown terms, the two-electron exchange and correlation effects as well as the correction term for the kinetic energy functional, are dropped into the approximate exchange-correlation functional,

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho] + T_c[\rho]. \tag{2.21}$$

Thus, the total electronic energy is expressed as

$$E_{elec}[\rho] = T_s[\rho] + \int V_{Ne}\rho(r)dr + J[\rho] + E_{xc}[\rho]. \tag{2.22}$$

2.3.3 KS DFT Computational Scheme

The KS DFT computational scheme is nearly the same as the HF scheme. However, there are two major differences between them; the exchange term in HF is replaced

by a exchange-correlation term in DFT, and the Fock matrix F is replaced by the Kohn-Sham matrix F^{KS}.

The total energy of the Kohn-Sham DFT can be expressed as

$$E^{KS} = T_s[\rho] + \int V_{Ne}\rho d\tau + J[\rho] + \theta K[\rho] + E'_{xc} \qquad (2.23)$$

where θ is an empirical parameter which determines the extent of the exact HF exchange in a hybrid functional and

$$E'_{xc} = \int F[\rho(r), \nabla\rho(r)]dr. \qquad (2.24)$$

Therefore, the Kohn-Sham Fock operator, which is approximately the one electron Hamiltonian, can be expressed as

$$\begin{aligned} \hat{f}^{KS} &= -\frac{1}{2}\nabla^2 + V_{Ne} + \hat{J} + \theta\hat{K} + V'_{xc}, \\ &= \hat{f}^{HF} + (\theta - 1)\hat{K} + V'_{xc}, \end{aligned} \qquad (2.25)$$

where

$$V'_{xc} = \frac{\delta E'_{xc}}{\delta\rho}. \qquad (2.26)$$

The DFT Kohn-Sham matrix F^{KS} can thus be constructed

$$F^{KS}_{\mu\nu} = F^{HF}_{\mu\nu} + \int [(\theta - 1)\hat{K} + V'_{xc}]\chi_\mu(r)\chi_\nu(r)dr. \qquad (2.27)$$

From a computational point of view, a KS-DFT calculation is similar to a HF calculation. The SCF procedure can be used in the same way as in a HF calculation.

2.3.4 The Property of the Exact Exchange-Correlation Functional.

Since the exact exchange-correlation functional (E_{xc}) is not known, we have to use approximations. Hence, how to develop better exchange-correlation functionals has been an important topic throughout the history of DFT. In order to develop a better exchange-correlation functional we need to know the characteristics of the studied systems. Some characteristics which are shared for all systems may provide us with some clues in how to proceed.

In a molecular system, if one electron is located far away from the center of the molecule, the interaction between this electron and the nuclei is considered to be shielded by the other electrons. Therefore, the net charge this electron feels is

$(Z - (N - 1))$ (Z is the total nuclear charge and N is the number of the electrons). Therefore, this electron is considered moving in a potential

$$V_i(r) = -\frac{Z - (N - 1)}{r}. \tag{2.28}$$

Analyzing the Coulomb interaction between electrons and that between electrons and nuclei, we find that in the asymptotic limit $r \longrightarrow \infty$, the exchange potential of an electron is $-\frac{1}{r}$[22]. The HF exchange functional exactly shows the correct $-\frac{1}{r}$ decay for large distances (r) while most approximate functionals in DFT fail. The corresponding potentials of most functionals used decrease exponentially rather than as $-\frac{1}{r}$.

Another phenomenon is known as the derivative discontinuity in DFT: the exchange-correlation potential actually jumps by a constant as the number of electrons passes through an integer. (This phenomenon reflects the chemical potential to exchange particles between two systems.) Again the exchange part of HF models this behavior while none of the currently available approximate functionals, which are all characterized by a continuous potential with respect to variations in the number of electrons, is able to do this.

A solution to develop approximate functionals which can model these two behaviors properly is the hybrid functional methods which incorporates some extent of exact HF exchange in the approximate exchange-correlation functional. The most popular functional B3LYP[23–27] in use today is an example of a hybrid functional.

2.3.5   Development of Approximate Functionals

The simplest functional in use nowadays is developed based on the local density approximation (LDA). In this approximation, the electron density is that of a homogeneous electron gas. According to solid state physics, the lowest exchange-correlation energy should be expressed as

$$E_{xc}^{LDA}[\rho] = \alpha \int \rho^{\frac{4}{3}} d\tau, \tag{2.29}$$

where α is a constant. Some molecular properties are successfully calculated with this functional, for example, equilibrium structures, harmonic frequencies or charge moments. However, this functional fails to reproduce those properties concerning the local density of a particular atom in a molecular system. This is because of the fact that the real electron density is not exactly homogeneous over all the molecular system. In trying to solve this problem, the generalized gradient approximation (GGA) is introduced to count for the non-homogeneity, $\Delta\rho(r)$.

$$E_{xc}^{GGA}[\rho_\alpha, \rho_\beta] = \int f(\rho_\alpha, \rho_\beta, \Delta\rho_\alpha, \Delta\rho_\beta) d\tau. \tag{2.30}$$

GGA achieves great success in predicting most molecular properties. The most successful functional in practice is of the hybrid level where an fraction of the exact exchange in the HF picture is imposed

$$E_{xc} = \alpha E_x^{HF} + (1 - \alpha) E_x^{DFT} + E_c, \tag{2.31}$$

where α is empirically determined. Further improvement is achieved when α scales along with interaction distance r. This is implemented in the newly developed CAMB3LYP[28] which aims to correct the asymptotic behavior.

2.3.6 Some Problems in DFT

DFT is by itself an exact theory without any approximations, if the exact exchange-correlation functional is available. However, the exact functional is not available, and most likely will never be in the form of a closed expression. There are some well-known problems caused by approximate functionals in DFT.

Due to the wrong asymptotic behavior of the approximate functional, the orbital energies of DFT are somewhat useless. This means that the orbital energies are not able to reflect any real physical quantities, e.g., ionization energies. Due to the residual interaction of an electron with itself (self-interaction) introduced by approximate functionals, DFT gives wrong results when applied to e.g. open shell systems. In fact, those approximate exchange-correlation functionals contain more or less amounts of the self-interaction error (SIE). Adding self-interaction corrections to a functional which is parameterized against a database of experimental data may therefore worsen the accuracy of the functional. Self-interaction corrections in energy difference calculations (dissociation, transition states) may be substantial because it may be the case that the different states of the system contains different amounts of SIE.

2.4 Comparison between HF and DFT

We have discussed two primary methods, HF and DFT, in the previous two chapters. The calculation schemes of these two methods are almost the same, which share common elements−the variational principle and the concept of single Slater determinant. However, there are some important differences between these two methods.

2.4.1   Dynamic Correlation

The dynamic correlation, caused by the electron-electron Coulomb interaction, is of great importance to the quality of a computational scheme. A very important difference recognized is that DFT handles this term properly while HF doesn't. Despite the fact that the exact exchange-correlation functional is not available, DFT generally performs better than HF when applied to the study of the electronic structure of a ground state.

2.4.2   Molecular Orbitals vs Total Density

The molecular orbitals from the HF calculation are related to the ground state of a real system. All the molecular properties can be calculated from these molecular orbitals. The molecular orbitals of Kohn-Sham DFT are those of the reference non-interacting system. The function of these orbitals is to provide a correct total density. In DFT, all the molecular properties are closely related to the total density.

This difference leads to the fact that HF performs better than DFT when applied to the study of some physical process that are closely related to the motion of an unpaired electron. For example, orbital energies vs experimental ionization potential, dissociation process associated with a singly occupied orbital, chemical reactions involving the charge transfer of an unpaired electron. These cases are generally recognized as the problems of SIE in DFT.

Chapter 3

Self-Interaction Correction Methods

3.1   Self-Interaction Error in DFT

The construction of most approximate exchange-correlation functionals leads to basic flaws. One such flaw is the self-interaction error, which comes from the residual interaction of an electron with itself. The error appears because the self-interaction of the approximate E_{xc} functional and that of the Coulomb functional do not cancel completely in the density functional scheme, as they do in Hartree-Fock. In most applications, SIE is also important for the accuracy of the DFT functionals due to the error cancellation. Systems where the effect of SIE is known to cause problems are two-center three-electron systems, charge transfer complexes, and some transition barriers.

3.1.1   Self-Interaction Error in Energy Difference

The study of any one-electron system, where Hartree-Fock provides the exact solution within a given basis set, can shed light on the effects of SIE for different chemical properties, e.g. the dissociation of the molecular ion H_2^+.

For a many-electron system, the SIE-analysis is non-trivial, but there is a number of situations where the shortcomings of DFT are believed to be main caused by the self-interaction error. With available functionals, conventional DFT gives in general very good ground state properties pertaining to equilibrium electronic structures and magnetic properties. However, when applied to the study of those properties related to energy differences, e.g., the molecular dissociation curves, the barriers of chemical reactions, and the energy curves of charge transfer processes in

molecules, SIE can be very different for the different states involved. This makes the properties related to energy differences very sensitive to SIE effects.

3.1.2   Self-Interaction Error in the Orbital Energy

Besides the energy difference, we believe that the orbital energy of DFT is also contaminated by SIE. In DFT, the orbital energy is the eigenvalue of the Fock operator,

$$\hat{f}^{KS} = -\frac{1}{2}\nabla^2 + V_{Ne} + \int \frac{\rho(r_2)}{r_{12}}dr_2 + V_{xc}(\rho) \tag{3.1}$$

This Fock operator is the same for all the orbitals. Given a particular orbital, the Coulomb potential interacting with the electron in this orbital comes from the other electrons. Thus, it is obvious that a self-interaction term is involved implicitly in the Coulomb potential. This Fock operator is free from SIE if the self-interaction in $V_{xc}(\rho)$ cancels the self-interaction in the Coulomb potential exactly. As a result, the Fock operator gives poor orbital energies.

3.2   History of Self-Interaction Correction

Approaches to reduce the self-interaction error in density functional calculations are known as self-interaction correction methods. The basic idea of SIC was introduced by Perdew and Zunger (PZ)[6]. They suggested a simple scheme based on the SIC for an electron. The sum of the Coulomb and exchange-correlation functionals of a one-electron density defines the self-interaction error

$$E^{SIE} = J[\rho] + E_{xc}[\rho]. \tag{3.2}$$

The self-interaction error is zero in the Hartree-Fock scheme (Coulomb and exchange integrals cancel exactly) and it maybe zero in DFT scheme when the exact exchange-correlation functional is available. However, this error is obviously nonzero with use of approximate functionals. In trying to reduce the SIE, Perdew and Zunger proposed that for a many-electron system, a term

$$E^{SIE} = \sum_{i\sigma}(J[\rho_{i\sigma}] + E_{xc}[\rho_{i\sigma}]), \tag{3.3}$$

where the summation is over all occupied spin orbitals, be subtracted from the Kohn-Sham energy functional

$$E^{SIC-DFT} = E^{KS-DFT} - E^{SIE}. \tag{3.4}$$

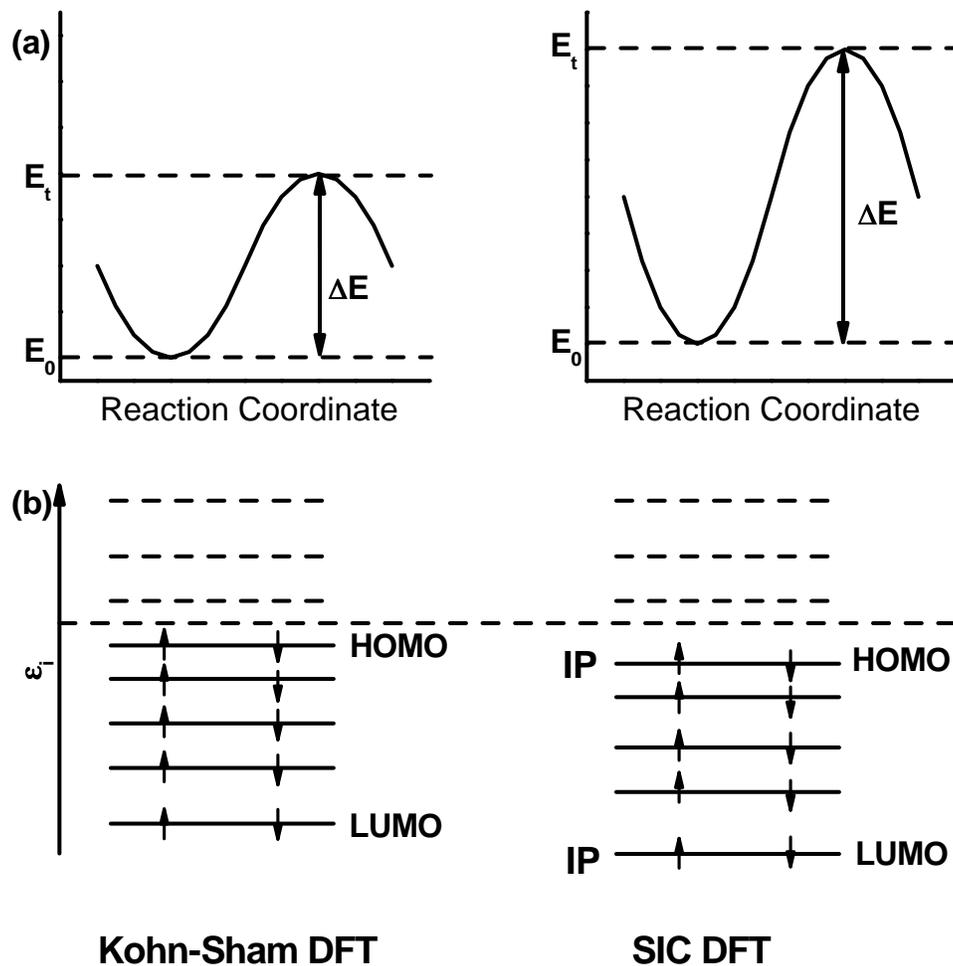Figure 3.1: The problems of SIE and expectations after SIC procedure. (a) SIC for energy differences. Some reaction barriers are underestimated in conventional DFT. SIC DFT improves the barriers. (b) SIC for orbital energies. The orbital energies of conventional DFT are considered to be useless. The SIC procedure gives better orbital energies (in particular for highest occupied molecular orbitals and core orbitals).

The SIC term $(-E^{SIE})$ introduces several difficulties, one of which is that we have a different effective one-electron Hamiltonian for different orbitals, and thus, the total energy is not invariant with respect to a unitary transformations among the occupied orbitals. This rules out that conventional Fock-matrix diagonalization approaches (Roothan-Hall[29, 30], DIIS[31]) the energy minimization in PZ SIC DFT becomes rather difficult. Another consequence is that the orbitals which do minimize the energy become non-orthogonal.

Some alternative methods have been developed, where the simplest one is the post-SCF SIC DFT method, which use the SIC term of PZ-SIC DFT as the first order correction after a conventional self-consistent field (SCF) iteration. The value of this correction term depends strongly on the internal state of the occupied orbitals. It is known that the orbitals that minimize the SIC energy tend to be more localized than the canonical KS orbitals. Therefore it is a common practice to localize the KS orbitals before applying the correction. When the Boys localization scheme[32, 33] is used we obtain in addition an origin dependent energy, since the localization is based on dipole moment integrals. This simplified approach has been applied to the study of core ionization energies. (Papers I, II, and V)

In most cases it is necessary to implement an energy minimization which includes SIC. The simplest self-consistent SIC DFT method is the averaged density (AD) SIC DFT[13, 14]. Following the idea of Fermi and Amaldi, this method uses an averaged density $\frac{\rho}{N}$ to replace the orbital density ρ_i in the SIC term of PZ SIC DFT. Hence, a common Hamiltonian is shared for all the occupied orbitals. We thus can apply the traditional SCF tools to AD SIC DFT. Due to the averaged density, this method performs quite well for large molecules and delocalized states, while it results in large deviations for atomic systems and localized states. A very successful SIC DFT method is the optimized effective potential method[16, 17] which corrects the electron potential in every iteration step to produce the correct asymptotic behavior. Thus, proper orbital energies and total energies are obtained. Following the idea of O.A.Vydrov and G.E.Scuseria[18], we have applied a quasi-Newton method[19] to implement a self-consistent PZ SIC DFT in this thesis. Our method is based on unitary transformations where there is a constraint that initially orthonormal orbitals remain orthonormal. We have applied this method to the study of a few chemical reactions barriers (Paper III).

3.3   Self-Consistent PZ SIC DFT

3.3.1   Quasi-Newton Method

Quasi-Newton methods are widely-used algorithms for finding local maxima or minima of functions in optimization. They are based on Newton's method to find the stationary point of a function. A assumption is that the function can be locally approximated as a quadratic in the region around the optimum. Thus, the second order approximation is used to find the stationary point of a function $f(x)$. The Taylor series of $f(x)$ is

$$f(x_0 + \Delta x) = f(x_0) + \nabla f(x_0)^T \Delta x + \frac{1}{2} \Delta x^T H \Delta x. \tag{3.5}$$

where ∇f is the gradient and H is the Hessian matrix. The gradient of the Taylor series is

$$\nabla f(x_0 + \Delta x) = \nabla f(x_0) + H \Delta x. \tag{3.6}$$

Solving for $\nabla f(x_0 + \Delta x) = 0$ provides the Newton step

$$\Delta x = -H^{-1} \nabla f(x_0). \tag{3.7}$$

In quasi-Newton methods the Hessian matrices do not need to be computed. It is updated by analyzing successive gradient vectors. BFGS method is one of the most common quasi-Newton algorithms, which was suggested by Broyden[34], Fletcher[35], Goldfarb[36] and Shannon[37] in 1970. In the method, the inverse Hessian is updated

$$H_{k+1}^{-1} = (I - \frac{y_k \Delta x_k^T}{y_k^T \Delta x_k})^T H_k^{-1} (I - \frac{y_k \Delta x_k^T}{y_k^T \Delta x_k}) + \frac{\Delta x_k \Delta x_k^T}{y_k^T \Delta x_k}, \tag{3.8}$$

where y_k is the gradient difference with

$$y_k = \nabla f(x_k + 1) - \nabla f(x_k) \tag{3.9}$$

and

$$\Delta x_k = \alpha_k H_k^{-1} \nabla f(x_k). \tag{3.10}$$

3.3.2   Implementation of Self-Consistent PZ SIC DFT

Since the Hamiltonian is not the same for different occupied orbitals in PZ SIC DFT, the traditional self-consistent field (SCF) method is not fit for the energy
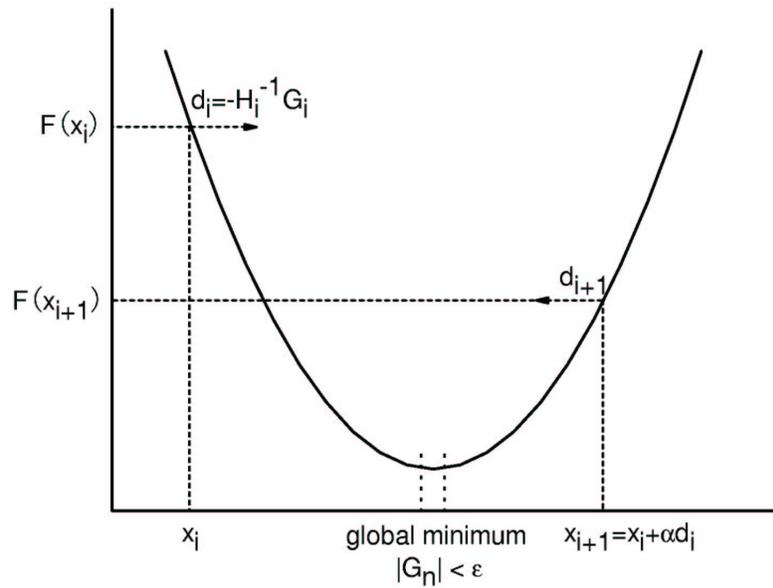
Figure 3.2: Newton iteration process. (a) The potential energy curve is supposed to be quadratic in the region close to the global minimum. (b) d_i points to the global minimum. (c) α is determined when $F(x_{i+1}) \leq F(x_i)$. (d) The global minimum is supposed to be found when the gradient $|G_n| < \varepsilon$.

minimization. One has to resort to the more classical energy minimization methods, such as the Newton method, when both gradients and Hessians are available, or quasi-Newton methods which rely on approximate Hessians.

Any real unitary operator can be written as

$$U = exp(-K), \tag{3.11}$$

where K is a real anti-symmetric matrix,

$$K_{i,j} = -K_{j,i}. \tag{3.12}$$

In density functional theory the Kohn-Sham determinant is a representation of the density, i.e., if the initial state is transformed

$$|\Phi_f> = U|\Phi_0>, \tag{3.13}$$

the modified density can be expressed as

$$\rho_f = <\Phi_f|\hat{\rho}|\Phi_f> . \tag{3.14}$$

Since the energy is a functional of the density we can carry out a Taylor expansion of E_f in terms of the angular variables, the matrix elements of K. When the initial state is near the global minimum, if a small orbital rotation is imposed, which means that the molecular orbital varies little, the higher order terms quadratic in the expansion are assumed to be small enough and can be neglected. ρ_f can thus be expressed as

$$\begin{aligned} \rho_f &= \rho_0 + <\Phi_0|[K,\hat{\rho}]|\Phi_0> + \frac{1}{2!}<\Phi_0|[K,[K,\hat{\rho}]]|\Phi_0> \\ &= \rho_0 + \rho_1 + \rho_2, \end{aligned} \tag{3.15}$$

which are then used in the expansion of the energy

$$E_f \approx E_0 + \int dV \frac{\delta E}{\delta \rho} \rho_1 + \int dV \frac{\delta E}{\delta \rho} \rho_2 + \frac{1}{2} \int dV dV' \frac{\delta^2 E}{\delta \rho \delta \rho'} \rho_1 \rho_1'. \tag{3.16}$$

The gradient can be exactly evaluated with modest computational cost, while it is computationally time-consuming to evaluate the exact Hessian. Instead of Newton-Raphson, there is a number of quasi-Newton methods, where the exact Hessian is not required.

The purpose of all minimization methods is to find an efficient way to the global minimum on the energy surface. In a the quasi-Newton method, the direction (d) is determined by forming

$$d_i = -H_i^{-1}G_i. \tag{3.17}$$

where H^{-1} is an approximation to the Hessian inverse and G is the gradient. H_i is updated in each iteration. In this family of the methods, one of the most commonly used is the BFGS update[19]. Traditionally the initial guess used for the Hessian inverse is a unit matrix. When applied to quantum chemistry in general and to the SIC methods in particular, it has been observed[18] that a better starting point is the diagonal matrix with inverse orbital energy differences

$$H^{-1}_{mn,mn} = -\frac{1}{2(\epsilon_m - \epsilon_n)}. \tag{3.18}$$

3.4 Semi-Empirical SIC DFT

3.4.1 Some Aspects of PZ SIC DFT

The PZ SIC DFT can be applied to most cases when DFT faces the problem of SIE. However, the fact that PZ SIC DFT reduces the SIE in DFT, does not mean that SIE is eliminated completely. For a one-electron system, the electron-electron interaction which remains in a DFT procedure is exactly the SIE. This means

$$E^{SIE} = J[\rho] + E_{xc}[\rho]. \tag{3.19}$$

This final expression can be reached by PZ SIC DFT and many other SIC DFT methods as well. For example, the newly developed Lundin-Eriksson SIC DFT [15] provides

$$
\begin{aligned}
E^{SIE} &= \frac{1}{2} \int \int \frac{\rho(r_1)(\rho(r_2) - (\rho(r_2) - \rho(r_2)))}{r_{12}} dr_1 dr_2 \\
&+ \int \rho(r)(\epsilon_{xc}(\rho(r)) - \epsilon_{xc}(\rho(r) - \rho(r))) dr \\
&= J[\rho] + E_{xc}[\rho].
\end{aligned}
$$

Thus, considering an SIC term of a many-electron system as the sum of a single orbital SIC, the correction

$$E^{SIC} = -\sum_{i\sigma}(J[\rho_{i\sigma}] + E_{xc}[\rho_{i\sigma}]) \tag{3.20}$$

is only one of those many approximations. The many-electron self-interaction can not be exactly eliminated.[38]

Given two occupied orbitals having the same orbital form, where one orbital is of a one-electron system, and the other is of a many-electron system, in the DFT

scheme, the electron in the one-electron system generates a one-electron potential

$$V_1 = \int \frac{\rho_1(r_2)}{r_{12}} dr_2 + V_{xc}[\rho_1], \tag{3.21}$$

and thus the self-interaction is expressed as

$$\int \rho_1 V_1 d\tau = \int \int \frac{\rho_1(r_2)\rho_1(r_1)}{r_{12}} dr_1 dr_2 + \int V_{xc}[\rho_1(r)]\rho_1(r)dr. \tag{3.22}$$

For the many-electron system, due to the approximate functionals used in DFT,

$$
\begin{aligned}
V[\rho] &= \int \frac{\rho(r_2)}{r_{12}} dr_2 + V_{xc}[\rho] \\
&\neq V[\rho - \rho_i] + V[\rho_i] \\
&= \int \frac{\rho(r_2) - \rho_i(r_2)}{r_{12}} dr_2 + V_{xc}[\rho - \rho_i] + \int \frac{\rho_i(r_2)}{r_{12}} dr_2 + V_{xc}[\rho_i].
\end{aligned}
$$

Therefore, in the Kohn-Sham DFT scheme, if approximate functionals are used, there is a non-zero coupling term for a many-electron system,

$$V_{xc}[\rho] - (V_{xc}[\rho - \rho_i] + V_{xc}[\rho_i]) \neq 0. \tag{3.23}$$

This coupling term affects not only the potential generated by (N-1) electrons but also that of the remaining one electron as well. Hence, for a many-electron system, the coupling term also contributes to the self-interaction of an electron with itself.

3.4.2   Semi-Empirical SIC DFT Method

Given some of the problems of PZ SIC DFT we would like to find ways for improvement. With the one-electron system as the simplest examples, all the SIC DFT methods developed should totally eliminate the SIE for this kind of systems. Meanwhile, for many-electron systems, we should consider the contribution of electron potential coupling caused by the approximate functionals.

In this thesis, we have proposed an approximate method which corrects the PZ SIC DFT by adding a part of the coupling term of the electron potential. In this SIC DFT method, the potential interacting on a particular electron in orbital i is corrected by a SIC term

$$
\begin{aligned}
V_i^{SIC} &= -(\int \frac{\rho_i(r_2)}{r_{12}} dr_2 + V_{xc}[\rho_i] \\
&+ \alpha(V_{xc}[\rho - \rho_i] + V_{xc}[\rho_i] - V_{xc}[\rho])). \tag{3.24}
\end{aligned}
$$

It is obvious that this term exactly eliminates the potential, the electron-electron interaction part, of one-electron system in DFT scheme,

$$V_i = \int \frac{\rho_i(r_2)}{r_{12}} dr_2 + V_{xc}[\rho_i]. \tag{3.25}$$

This method is used as the first order correction for the conventional DFT and is applied to the study of core binding energies. We have calculated the core binding energies for some molecules for elements C,N,O using SIC B3LYP with $\alpha = 0.72$. The results are quite good compared to the experimental values. The deviation is below 1.5 eV. (The core orbital energies of conventional DFT are all about more than 10 eV above the experimental value and the orbital energy difference between different elements are not correctly described.) Our method can not reach the accuracy of the $\Delta Kohn - Sham$ method. The advantage is that this SIC DFT method, when applied to large molecular system, can provide all the core ionization potentials in a single ground state calculation. In those molecules we have studied, there are some cases that the core 1s orbitals are unphyisically delocalized due to the symmetry. For such cases, the Boys localization procedure[33] is applied to make the core orbital localized to particular atom.

The parameter α is determined empirically. Different kinds of orbitals rarely share the same α value. For instance, we should use different α values for localized orbitals and for delocalized orbitals. We should also use different α values for core orbitals and for valence orbitals.

3.5 New SIC Approaches

The problem of SIE can be avoided if the electron-electron interactions, the Coulomb term J^c and the exchange-correlation term E_{xc}^c, which are directly constructed without SIE, are applied in the expression of the total electronic energy,

$$E^c = T_s + \int V_{Ne} \rho d\tau + J^c + E_{xc}^c. \tag{3.26}$$

The exact form of the Coulomb interaction between an electron in orbital $i\sigma$ and other electrons is easily obtained,

$$f_{i\sigma}^{co} = \int \int \frac{\rho_{i\sigma}(r_1)(\rho(r_2) - \rho_{i\sigma}(r_2))}{r_{12}} dr_1 dr_2, \tag{3.27}$$

and thus the electron-electron Coulomb interaction can be evaluated as,

$$J^c = \sum_{i\sigma} \frac{1}{2} f_{i\sigma}^{co}. \tag{3.28}$$

While the form of the exchange-correlation interaction between an electron in orbital $i\sigma$ and other electrons is not obvious. From a comparison between HF and DFT, we propose that this interaction is can be expressed as,

$$f_{i\sigma}^{xc} = 2(\int \xi_{xc}(\rho - \rho_{i\sigma})\rho_{i\sigma}d\tau + \alpha \int \xi_{xc}^{i\sigma}\rho_{i\sigma}d\tau) \tag{3.29}$$

or

$$f_{i\sigma}^{xc} = 2(\int \xi_{xc}(\rho_{i\sigma})(\rho - \rho_{i\sigma})d\tau + \beta \int \xi_{xc}^{i\sigma}(\rho - \rho_{i\sigma})d\tau), \tag{3.30}$$

where

$$\xi_{xc}^{i\sigma} = \xi_{xc}(\rho) - (\xi_{xc}(\rho - \rho_{i\sigma}) + \xi_{xc}(\rho_{i\sigma})). \tag{3.31}$$

α and β denote the extent that $\xi_{xc}^{i\sigma}$ contributes to the interaction between an electron in orbital $i\sigma$ and the others. Thus, the electron-electron exchange-correlation interaction can be evaluated,

$$E_{xc}^c = \sum_{i\sigma} \frac{1}{2}f_{i\sigma}^{xc}. \tag{3.32}$$

With the use of this $f_{i\sigma}^{co}$ and $f_{i\sigma}^{xc}$, the orbital energy, by definition, the energy to remove an electron from a particular orbital, is approximately expressed as

$$\varepsilon_{i\sigma} = <\phi_{i\sigma}| - \frac{1}{2}\nabla^2|\phi_{i\sigma}> + \int V_{Ne}\rho d\tau + f_{i\sigma}^{co} + f_{i\sigma}^{xc}. \tag{3.33}$$

It is expected that the orbital energy can properly reflect the experimental ionization potential. Some approximations are need to determine α and β. In this work, we introduce two extreme approximations.

3.5.1 Extreme Approximation A

When $\alpha = 1$ in Eq. (3.29), where we use the approximation that $\xi_{xc}^{i\sigma}$ does not contribute to the self-interaction of an electron, the exchange-correlation interaction between an electron in orbital $i\sigma$ to the others is expressed as

$$f_{i\sigma}^{xc} = 2(\int \xi_{xc}^{i\sigma}\rho_{i\sigma}d\tau + \int \xi_{xc}(\rho - \rho_{i\sigma})\rho_{i\sigma}d\tau). \tag{3.34}$$

Thus, the total electronic energy can be evaluated

$$\begin{aligned}
E^c &= T_s + \int V_{Ne}\rho d\tau + \frac{1}{2}\sum_{i\sigma}(f_{i\sigma}^{co} + f_{i\sigma}^{xc}), \\
&= T_s + \int V_{Ne}\rho d\tau + J[\rho] + E_{xc}[\rho] \\
&\quad - \sum_{i\sigma}(J[\rho_{i\sigma}] + E_{xc}[\rho_{i\sigma}]).
\end{aligned} \tag{3.35}$$

The total electronic energy is the same as that of the PZ SIC DFT. With use of the proper interaction $f_{i\sigma}^{co}$ and $f_{i\sigma}^{xc}$, the corrected orbital energy of PZ SIC DFT is expressed as

$$
\begin{aligned}
\varepsilon_{i\sigma}^c &= <\phi_{i\sigma}| - \frac{1}{2}\nabla^2|\phi_{i\sigma}> + \int V_{Ne}\rho_{i\sigma}d\tau + \int \frac{\rho_{i\sigma}(\rho - \rho_{i\sigma})}{r_{12}}dr_1 dr_2 \\
&+ 2(\int \xi_{xc}(\rho)\rho_{i\sigma}d\tau - \int \xi_{xc}(\rho_{i\sigma})\rho_{i\sigma}d\tau).
\end{aligned} \tag{3.36}
$$

3.5.2 Extreme Approximation B

When $\beta = 1$ in Eq. (3.30), where we use the approximation that $\xi_{xc}^{i\sigma}$ does not contribute to the self and inner interaction of the (N-1) electrons, the exchange-correlation interaction between an electron in orbital $i\sigma$ and the other electrons is expressed as

$$
f_{i\sigma}^{xc} = 2(\int \xi_{xc}(\rho)(\rho - \rho_{i\sigma})d\tau - \int \xi_{xc}(\rho - \rho_{i\sigma})(\rho - \rho_{i\sigma})d\tau). \tag{3.37}
$$

Thus, the total electronic energy can be expressed as

$$
\begin{aligned}
E^c &= T_s + \int V_{Ne}\rho d\tau + J[\rho] - \sum_{i\sigma} J[\rho_{i\sigma}] \\
&+ (N-1)E_{xc}[\rho] - \sum_{i\sigma} E_{xc}[\rho - \rho_{i\sigma}],
\end{aligned} \tag{3.38}
$$

and the corrected orbital energy

$$
\begin{aligned}
\varepsilon_{i\sigma}^c &= <\phi_{i\sigma}| - \frac{1}{2}\nabla^2|\phi_{i\sigma}> + \int V_{Ne}\rho_{i\sigma}d\tau + \int \frac{\rho_{i\sigma}(\rho - \rho_{i\sigma})}{r_{12}}dr_1 dr_2 \\
&+ 2(\int \xi_{xc}(\rho)(\rho - \rho_{i\sigma})d\tau - \int \xi_{xc}(\rho - \rho_{i\sigma})(\rho - \rho_{i\sigma})d\tau).
\end{aligned} \tag{3.39}
$$

Combined with the post-SCF procedure, these two methods are applied to the study of the atomic electron removal energies as well as the molecular ionization energies. The results are quite good agreement with the experimental values.

Chapter 4

Applications

Several ideas of SIC and corresponding methods have been introduced in the previous chapter. Each method has its advantages and disadvantages when applied to the studies of electronic systems. In this chapter, some applications of these methods are displayed.

4.1 Applications of Self-Consistent PZ SIC DFT

DFT has faced some difficulties in the study of the potential energy curves of some open-shell systems, for instance, the reaction barriers of some reactions are too low[9, 10, 39–43], the dissociation curves of some molecules are totally wrong[11, 12]. Many efforts are devoted to the analysis of these problems, we know now that these problems are all caused by SIE in DFT[11, 44]. In this thesis, we applied the self-consistent PZ SIC DFT method to the study of some such cases.

The dissociation of H_2^+ illustrates the problem of SIE. The dissociation potential energy curves are displayed in figure 4.1. It is obvious that the dissociation process is not properly described in conventional DFT scheme. The curves from DFT calculations show a barrier during the dissociation, which is not physically reasonable. This barrier doesn't exist in the curves from SIC DFT calculation (which for a one-electron system is equivalent to HF).

We have also studied some hydrogen absorption reactions. For such reactions, there is a large difference between the product state and the transition state, a large SIE difference contributes to the reaction barrier in the DFT approach. SIC DFT, which reduces the SIE in both states, significantly improves the barriers. Therefore, as long as functionals free of SIE are not available, SIC DFT is the
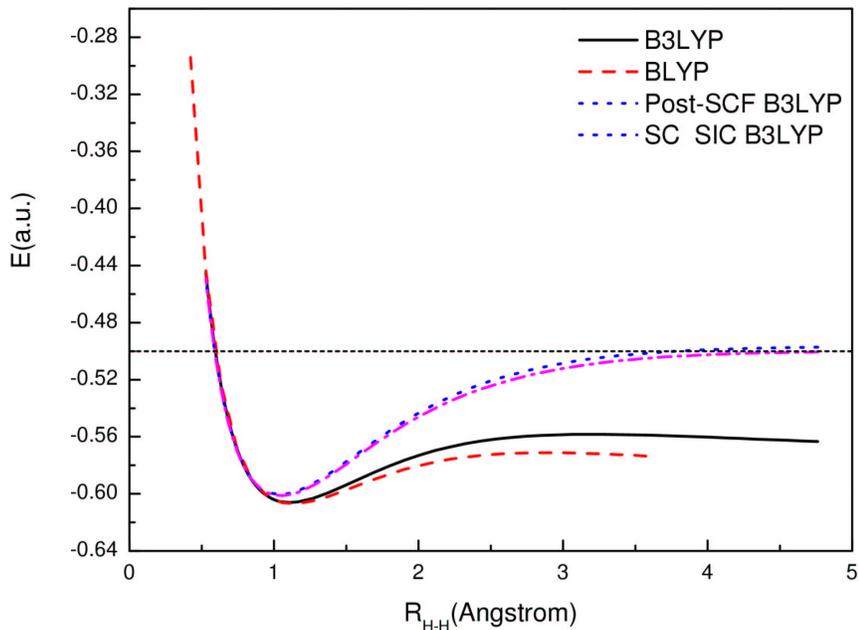
Figure 4.1: Dissociation curves of H_2^+, calculations are done with 6-311G(d,p) basis set.

only reasonable way to study this kind of chemical reactions, except for special functionals parameterized for these reactions.

4.2 Applications of Semi-Empirical SIC DFT

The semi-empirical SIC DFT method is designed to correct all the orbital energies of Kohn-Sham DFT. However, it is rather difficult to determine the parameter α. This α, which reflects the contribution of the correlation potential to the SIC term, should have different values for different orbitals. Fortunately, the core orbitals are generally rarely affected by the environment. Thus, it is possible to use the same α value for the same elements in different molecules. This may lead to some good applications. Further, through an α fitting scheme, we find that the α value is about the same for C, N, O 1s orbitals. Hence, this method is now applied to the study of the core orbital energies (and relevant properties) of C, N, O in some molecules.

4.2.1 Core Orbital Energy Correction

It is commonly held true that KS orbital energies have no physical interpretation except for the HOMO, for which it has been established that it reproduces the first ionization potential for the exact exchange-correlation potential.[45] Recent work even shows that the KS orbital energies sometimes have better quality than the corresponding Koopman's values from Hartree-Fock calculations.[46]

The straightforward method to calculate core ionization energies is the Δ DFT ($\Delta Kohn - Sham$) method[47]. However, computationally, it is still very demanding to calculate the core hole states, in particular if one is considering large systems with many centers of interest. Therefore one would like to use an orbital-based approach. However, because of the incorrect asymptotic behavior introduced by approximate functionals, the orbital energies of conventional DFT can not directly reflect the real physical quantities—ionization energies/binding energies. In this thesis, we find a simple way which uses a semi-empirical SIC DFT method to correct the core orbital energies from a single DFT calculation.

In table 4.1, we listed the core ionization energies of some molecules from B3LYP and SIC B3LYP calculation. In the table, we can find that there are large deviations between the IPs without SIC and experiment values[48]. The deviations become much smaller when SIC DFT is applied. The mean absolute error in the theoretical values for IPs is 0.43 (e.V) with SIC.

4.2.2 Core Ionization Energy and Hydrogen Bond Structure

Hydrogen bonding[49, 50], which combines directionality and strength, is a type of interactions that is abundant in chemical and biological systems. There are three main, independent, ingredients in hydrogen bonded system: covalence, electrostatics and van der Waals character. Thus, hydrogen bond structure is difficult to study theoretically. In this work, we examine the possibility to study the hydrogen bond structures through core ionization energies. The semi-empirical SIC DFT method is applied to the study of the core ionization energies for all chemically shifted elements. In some cases, the $\Delta Kohn - Sham$ approach is also applied. A direct dependency between the hydrogen atom to acceptor atom length and the chemical shift of core ionization energy is found, something that has ramifications on the possibility of effective predictions of hydrogen bond lengths in hydrogen bonded system.

The idea of this work comes from the study of a water-dimer system, where the O 1s ionization potential of the acceptor is very sensitive to the bond length $R(H \cdots O)$.

Table 4.1: Core ionization energies compared to the negative 1s orbital energies from conventional DFT and SIC DFT calculations. B3LYP calculation with 6-311G(d,p) basis set; $\alpha = 0.72$, all energies in eV.

molecule	atom	$-\epsilon^{DFT}$	SIC	$-\epsilon^{SIC}$	Exp.	Δ IP
CO	O	523.14	18.25	541.39	542.10	-0.71
	C	279.82	14.64	294.16	295.90	-1.44
CH_4	C	276.15	14.83	290.98	290.83	0.15
CH_3CN	N	389.24	16.53	405.77	405.60	0.17
	$C*H_3$	278.14	14.84	292.98	292.98	0.00
	C*N	277.76	14.54	292.30	292.44	-0.14
CH_3COOH	COO*H	521.47	18.38	539.85	540.09	-0.24
	CO*OH	519.84	18.35	538.19	538.36	-0.17
	C*OOH	280.38	14.85	295.23	295.38	-0.15
	$C*H_3$	277.07	14.83	291.90	291.55	0.45
Glycine	COO*H	521.60	18.39	539.99	540.20	-0.21
	CO*OH	520.08	18.35	538.43	538.40	0.03
	N	388.76	16.73	405.49	405.40	0.09
	C*OOH	280.43	14.84	295.27	295.20	0.07
	C*H	277.85	14.88	292.73	292.30	0.43
MBO	O	522.62	18.40	541.02	540.58	0.44
	N	391.62	16.69	408.31	407.01	1.30
	C*S	280.83	14.91	295.74	295.71	0.03
	C*O	279.06	14.69	294.75	293.19	1.56
	C*N	278.75	14.67	293.42	293.01	0.41
	C*CN	277.65	14.57	292.22	291.45	0.77
	C*CO	277.56	14.41	291.97	291.67	0.30
C_2H_2	C	276.76	14.63	291.39	291.20	0.19
C_2H_4	C	276.60	14.76	291.36	290.70	0.66
C_2H_6	C	276.30	14.86	291.16	290.60	0.56

A linear dependence between the core IP and the bond length is achieved through the calculation. We then performed a lot of calculations for a series of molecules to study the core electron chemical shifts of hydrogen bonded networks. Some of the results are displayed in Fig. (4.3). An obvious linear dependency between the chemical shift and the $H \cdots O$ length is displayed.
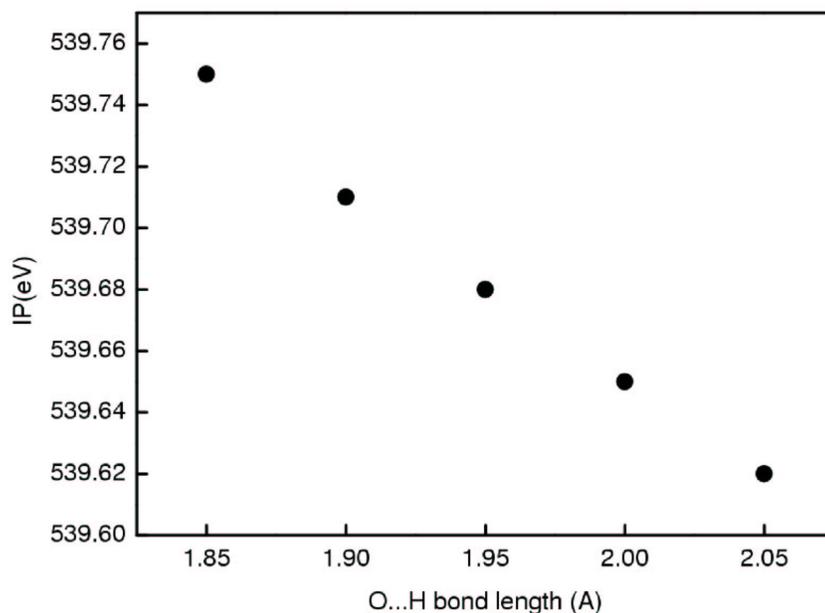
Figure 4.2: Relationship between the O1s IP of the acceptor and the $H \cdots O$ length. The hydrogen bond system is composed by two water molecule.

4.2.3 Near-edge X-ray Absorption Fine Structure Spectrum

X-ray spectrum is closely related to the nature of elementary excitations of molecules and condensed species. Since the spectrum connect to the core electron excitation, the core orbital energy is a very important element to the property of the spectrum. In this work, we outline an approach which rests on the resonant convergent first-order complex polarization propagator (CPP) approach and self-interaction correction of the core orbital energy. The CPP approach makes it possible to directly calculate the photoabsorption cross section at a particular frequency without explicitly addressing the excited state spectrum. The self-interaction correction accounts for an energy shift of the spectrum. Thus, fully correlated absolute-scale X-ray spectra are obtained based on the optimization of the electronic ground state.

This approach has been applied to the study of the Near-edge X-ray absorption fine structure (NEXAFS) spectrum. In figure 4.4 and 4.5 we display the K-edge NEXAFS spectrum of formamide, formic acid, (c)methanol, and (d)methyl format. These spectra are directly calculated using the ground state complex polarization propagator (CPP) approach[51, 52] and then uniformly shifted by the core orbital
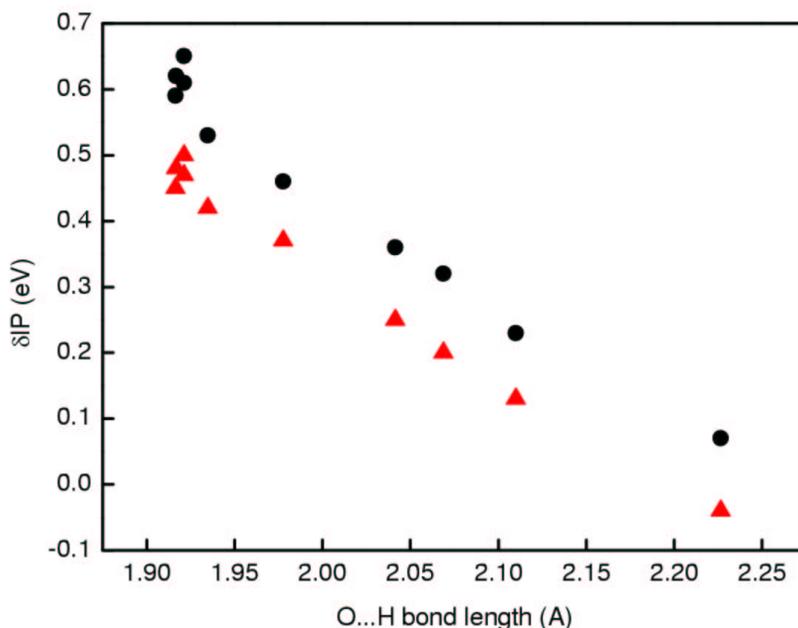
Figure 4.3: Relationship between the O1s IP of the acceptor and the $H\cdots O$ length in a hydrogen bond system. Dots are from SIC DFT calculations while triangular from ΔKohn-Sham calculations.

SIC correction. The deviations between the main peaks of theoretical calculation and those of experiment are all less than 2.0 (e.V).

4.3 Applications of the New SIC Approach

The new SIC approach is developed based on the interaction between an electron and the others. The total electronic energy is counted without SIE. Meanwhile, the orbital energy, which in this approach is defined as the energy to remove an electron from the orbital, is also properly constructed. However, as many SIC approaches do, an orbital dependent Hamiltonian is also introduced in this approach. Therefore, it is rather difficult to implement the minimization process. We restricted ourselves to a post-SCF procedure.

This post-SCF SIC approach has been applied to the study of some atomic systems as well as some molecular systems. The HOMO energies of molecular systems studied are greatly improved by this approach, the negative values of HOMO energies can be compared to the experimental ionization potentials. For atomic
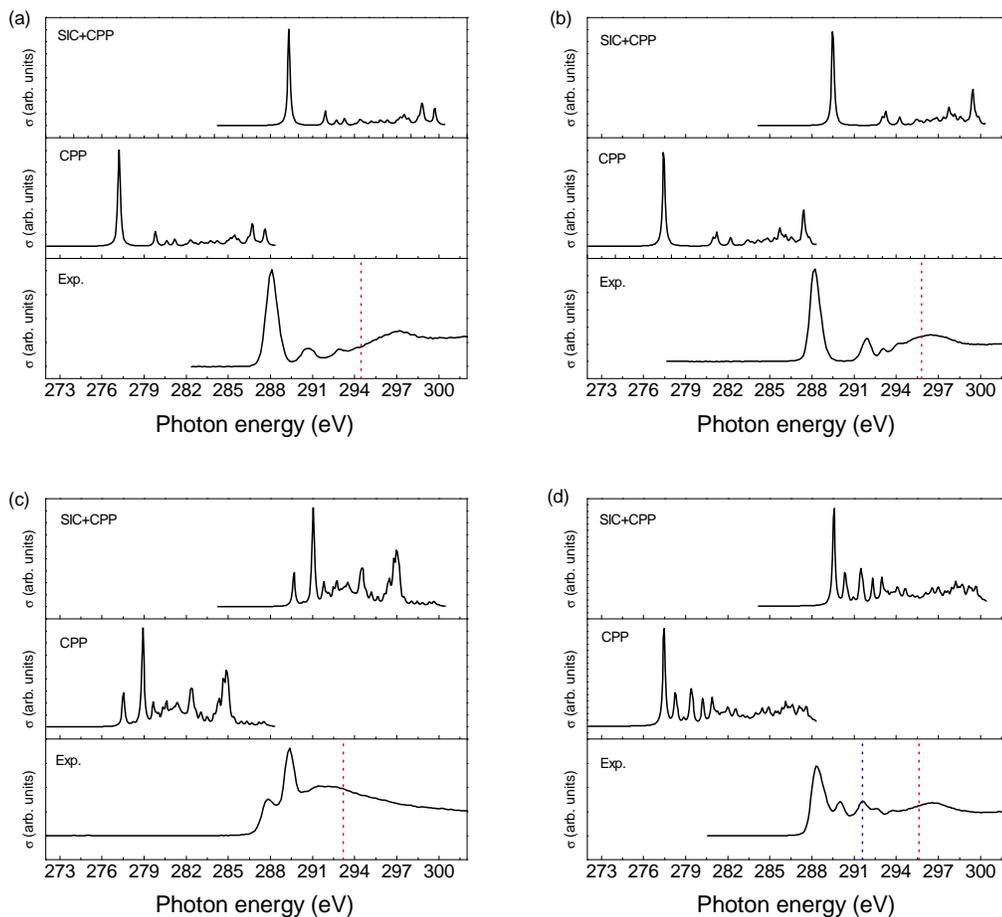
Figure 4.4: Experimental and theoretical NEXAFS spectra at the C K-edge.(a) formamide, (b) formic acid, (c)methanol, and (d)methyl format

systems, the corrected orbital energies can properly reflect the atomic electron removal energies. Some of the results are listed in table (4.2) and table (4.3).
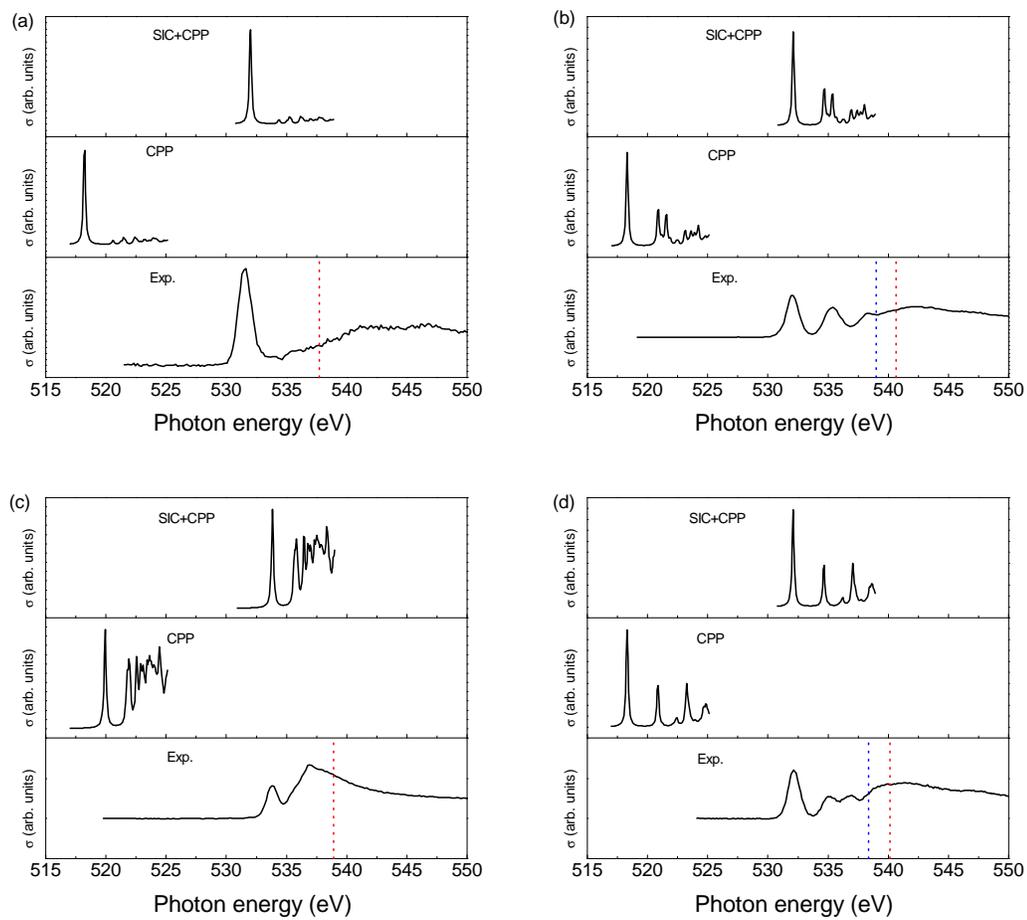
41

Figure 4.5: Experimental and theoretical NEXAFS spectra at the O K-edge.(a) formamide, (b) formic acid, (c)methanol, and (d)methyl format

Table 4.2: Electron removal energies compared to the negative orbital energies for Ar. Calculations are done with a 6-311G(d,p) basis set. All energies are in eV.

Molecule	Exp	A B3LYP	B B3LYP
1s	118.100	118.510	118.705
2s	12.100	12.056	11.690
2p	9.250	9.527	9.383
3s	1.080	1.248	1.097
3p	0.580	0.618	0.540

Table 4.3: Ionization potentials compare to the negative HOMO energies. Calculations are done with a 6-311G(d,p) basis set. All energies are in eV.

Molecule	Exp	A B3LYP	A BLYP
C2H2	11.40	12.00	11.75
C2(CH3)2	9.58	10.32	9.95
HC2CH3	10.36	11.07	10.75
C2H4	10.51	11.33	11.11
H2C2HCN	10.91	10.73	10.14
H2C2O	9.62	9.99	9.40
H2C2HF	10.36	10.85	10.26
H2C2HCl	9.99	10.23	9.65
C2F4	10.14	10.51	9.55
C2Cl4	9.33	9.93	9.21
H2C2(CH3)2	9.22	10.14	9.79
C3H6	9.73	10.54	10.22
C2H6	11.52	12.37	11.65
OHC2HO	10.20	10.08	8.96
NCCN	13.37	13.01	12.28
CF3CN	13.93	14.94	14.15
C2H5SH	9.31	10.14	9.75
C3H8	10.94	11.65	10.87
CH2HC2CH2H	9.07	8.90	8.39
C4H10	10.53	11.75	11.02

Chapter 5

Final Remarks

The present thesis consists of a collection of methods to solve the problem of self-interaction error in density functional theory.

1. A self-consistent PZ SIC DFT computational scheme is implemented by the use of Quasi-Newton optimization method. This approach helps to improve the performance of DFT in predicting the potential energy curves of some chemical reactions involving transition barriers.

2. A semi-empirical SIC DFT method is devised to correct the orbital energy. It is now applied to the study of the core orbital energies and relevant properties.

3. A new SIC approach, where the electron-electron interactions are counted without SIE, is developed. A post-SCF procedure is now available. The orbital energies are proved to be improved compared to that from the conventional DFT calculations.

5.1   Comments on Included Papers

In **paper I**, we have introduced a new self-interaction correction (SIC) method. This method was applied to the study of the core ionization energies. Compared to the traditional Δ Kohn-Sham method, this semi-empirical SIC combines proper accuracy with much lower computational cost in the study of core IPs.

In **paper II**, we proposed a procedure, which combines the new self-interaction correction method with the complex polarization propagator (CPP) approach, to the study of the K-edge near-edge X-ray absorption fine structure (NEXAFS) spectrum. The CPP approach makes it possible to directly calculate the X-ray absorption cross section at a particular frequency without explicitly addressing

the excited state spectrum. However, an error common to all functionals, that becomes very visible for X-ray spectra, is in the orbital energy of core orbitals. As this error is inherited by the ground state CPP approach, we propose to apply a correction−a self-interaction correction− to a core orbital and use this for a uniform shift of the full NEXAFS spectra. In doing so we obtain a direct, absolute scale approach to computationally assign X-ray spectra.

In **paper III**, we implemented a new algorithm for minimizing the density functional energy with the Perdew Zunger self-interaction correction (SIC) self-consistently. The optimization is based on angular variables so that orthogonality between molecular orbitals is preserved, using a quasi-second-order optimization. This SIC DFT is applied to the study of a set of chemical reactions including their transition barriers. In these reactions, the self-interaction error (SIE) is very different in the product/reactant states and in the transition states, which makes the barrier heights very sensitive to SIE. Thus, SIC DFT may produce better barriers than conventional DFT does. It is shown that the Perdew-Zunger formulation can overestimate SIE in system with many electrons.

In addition to SIC DFT approaches, in **paper IV**, we have introduced a new approach to solve the problem of SIE. This approach is to construct the electron-electron interactions J^c and E_{xc}^c, without SIE, with use of the proper interaction between an electron in a particular orbital and the other electrons. We can thus obtain the corrected total energy and the corrected orbital energies as well. The orbital energy that obtained, is greatly improved compared to that of DFT. The HOMO energy is comparable to the experimental ionization energy.

In **paper V**, we have studied the hydrogen bond structures against the core ionization energies. Hydrogen bond system is difficult to study theoretically. We have studied many hydrogen bond systems and found a linear dependence between the core ionization energy of residue A and the bond distance $(R(H \cdots A))$ in a hydrogen bond structure $(O - H \cdots A)$.

5.2   Future Outlook

Today, many ideas of SIC are carried out. Most of which introduce an orbital dependent one electron Hamiltonian. Thus, the traditional self-consistent field approach is not applicable. Currently, most SIC methods are implemented as a post-SCF scheme, and the convergence becomes a big problem for those of a few self-consistent SIC DFT methods. This limits the application of SIC DFT methods.

In the absence of new fast optimization method, the most practical way (personal point of view) is to divide the SIC term into orbital dependent part and orbital independent part. The orbital dependent part should be small enough so that it can be treated as a perturbation, and the independent part accompany with the energy functional of conventional DFT can be optimized by a SCF procedure. Thus, the ultimate result is of a state close to that of a energy-minimized SIC DFT and the computational effort is comparable to that of conventional DFT.

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