

STUDY OF BARRIER HEIGHTS AND MAGNETIC PROPERTY USING
LOCALLY SCALED AND PERDEW-ZUNGER SELF-INTERACTION
METHODS

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PREVIEW

DEDICATION

I dedicate the thesis to my family and wife Sushila Baniya Chhetri.

PREVIEW

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THESIS

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ABSTRACT

Kohn-Sham density functional theory is a widely used method to estimate the ground state total energies and densities of interacting correlated electronic structures of atoms, molecules, clusters, solids, and liquids. In theory, exact solutions for these properties can be obtained by solving self-consistent one-electron Schrodinger equations based on density functionals for the energy. The practical application of KS DFT require approximation to the exchange-correlation energy functional. Many density functional approximations (DFAs) have been developed with various degree of sophistication and complexity by the satisfaction of exact constraints. Depending on the complexity, these functionals include electron density, density gradients, density Laplacian, kinetic energy densities, Hartree-Fock exchange etc. Some examples of widely used non-empirical functionals are local density approximation (LDA), Perdew-Burke-Ernzerhof (PBE) generalized-gradient approximation (GGA), and strongly constrained and appropriately normalized (SCAN) meta-GGA.

However, the remarkable success of the approximate density functional theory comes at a cost. There is an incomplete cancellation of the hartree and approximate exchange energies for one-electron densities, giving rise to a spurious interaction of an electron with itself. This is called the self-interaction error (SIE). Perdew-Zunger self-interaction correction (PZ SIC) makes an approximate density functional SIE free for all one-electron density. These DFAs can fail dramatically for cases such as systems with a stretched bond, transition state, where SIE is pronounced. Thus LDA, PBE and SCAN predict too low barrier height for a chemical reaction. We tested the Perdew and Zunger self-interaction correction (PZSIC) for the barrier heights of the representative test set BH76. The present work uses Fermi-Löwdin orbitals (FLOS) which are Fermi orbitals orthogonalized via Löwdin scheme. FLOs are localized orbitals through Fermi orbital descriptors (FODs) which are special positions to capture the electronic density of a system. The PZSIC implementation using FLOs, called FLOSIC, results in size-extensive implementation of the PZSIC. The PZSIC calculations provide more accurate results for stretched bond and anionic states but worsen properties where DFA performs well, this is known as the PZSIC paradox.

The present thesis deals with development and assessments of methods to overcome the paradoxical behavior of PZSIC. We compare PZSIC against the new local scaling SIC (LSIC)

with two different approaches. The first approach uses ratio of kinetic energy densities referred to as LSIC(z) hereafter. It showed impressive results by keeping the correct behavior PZSIC and improving it where PZSIC fails. LSIC(w), the second method that uses orbital and total densities as scaling factor. We compare the methods against orbital scaling SIC (OSIC). The comparison is done with an extensive test of reaction barrier heights of molecules and magnetic properties namely exchange coupling. Overall, the thesis presents application of new methods for self-interaction free density functional calculations for the study of barrier heights and magnetic exchange coupling.

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CHAPTER 1: DENSITY FUNCTIONAL THEORY

1.1 BASICS OF WAVEFUNCTION THEORY

A wealth of information can be extracted by solving the non-relativistic time-independent Schrodinger equations [1]:

$$\hat{H}\Psi = E\Psi \quad (1.1.1)$$

Where \hat{H} is the Hamiltonian operator for a system of M nuclei and N electrons and Ψ is the wave function of the system which depends on the spatial coordinates of electrons $\{\vec{r}_i\}, i = 1 \dots N$, spatial coordinates of nuclei $\{\vec{R}_\alpha\}, \alpha = 1 \dots M$ and spin coordinates of electrons $\{\sigma_i\}, i = 1 \dots N$. The Hamiltonian of such system interacting through Coulomb interaction in atomic units ($m_e = m_e = c = 1$)

$$\hat{H} = -\frac{1}{2} \sum_{\alpha=1}^M \frac{\nabla_{\vec{R}_\alpha}^2}{M_\alpha} - \frac{1}{2} \sum_{i=1}^N \nabla_{\vec{r}_i}^2 + \frac{1}{2} \sum_{\alpha=1}^M \frac{Z_\alpha Z_\beta}{|\vec{R}_\alpha - \vec{R}_\beta|} - \sum_{\alpha=1}^M \sum_{i=1}^N \frac{Z_\alpha}{|\vec{r}_i - \vec{R}_\alpha|} + \frac{1}{2} \sum_{i=1}^N \frac{1}{|\vec{r}_i - \vec{r}_j|} \quad (1.1.2)$$

Where first term is the nuclear kinetic energy operator \hat{T}_n where M_α represents the mass of the α th nucleus to the mass of an electron and the Laplacian operator ∇^2 (cartesian coordinates) is

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad (1.1.3)$$

Second term \hat{T}_e is the electronic kinetic energy operator. The third term \hat{V}_{nn} represents the repulsive nucleus-nucleus interaction energy operator. The remaining terms represents nucleus-electron interactions \hat{V}_{ne} (also called external potential \hat{V}_{ext}) and \hat{V}_{ee} electron-electron interaction energy.

Equation (1.1.2) can be rewritten as,

$$\hat{H} = \hat{T}_n + \hat{T}_e + \hat{V}_{nn} + \hat{V}_{ne} + \hat{V}_{ee} \quad (1.1.4)$$

The exact solutions of Eq(1.1.1) is complicated even for a system with $M=2, N=1$ (i.e. two electrons). Based on the observation that nuclei are substantially heavier than electrons and travel much slower than electrons, the Born-Oppenheimer approximation [2] allows separation of nuclear and electronic degrees of freedom. As a result, a system's wavefunction can be divided into nuclear and electron wavefunctions. Because the nuclei do not provide much to the kinetic energy contribution in Eq (1.1.31) when compared to the electron contribution, we can exclude

the nuclei contribution of kinetic energy. The potential generated by nuclei-nuclei interactions is also frozen and can be considered constant. This allows us to write by breaking down the wave function given as in Eq (1.1.1) as

$$\Psi(\vec{R}_\alpha, \vec{r}_i, \sigma_i) = \Phi(\vec{R}_\alpha) \Psi(\vec{r}_i, \sigma_i), \quad (1.1.5)$$

Where $\Phi(\vec{R}_\alpha)$ is the nuclear wavefunction and $\Psi(\vec{r}_i, \sigma_i)$ is the electronic wave function.

Therefore, the complicated Schrodinger equation now reduces to solving the electronic wave function only.

$$H_e \Psi(\vec{r}_i, \sigma_i) = E_e \Psi(\vec{r}_i, \sigma_i) \quad (1.1.6)$$

With

$$\vec{H}_e = \hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee} \quad (1.1.7)$$

The wave function Ψ has no physical meaning by itself. The square of wavefunction gives the probability of finding the electrons in the volume element $d^3r_1 d^3r_2 \dots d^3r_N$ and in the spin states $\sigma_1, \sigma_2 \dots \sigma_N$.

$$|\Psi(\vec{r}_1 \sigma_1, \vec{r}_2 \sigma_2, \dots, \vec{r}_i \sigma_i, \dots, \vec{r}_j \sigma_j, \dots, \vec{r}_N \sigma_N)|^2 d^3r_1 d^3r_2 \dots d^3r_N \quad (1.1.8)$$

The electronic wave function Ψ must be orthonormalized and must be antisymmetric when spatial and spin coordinates of any two electrons are interchanged, i.e.

$$\Psi(\vec{r}_1 \sigma_1, \vec{r}_2 \sigma_2, \dots, \vec{r}_i \sigma_i, \dots, \vec{r}_j \sigma_j, \dots, \vec{r}_N \sigma_N) = -\Psi(\vec{r}_1 \sigma_1, \vec{r}_2 \sigma_2, \dots, \vec{r}_i \sigma_j, \dots, \vec{r}_j \sigma_i, \dots, \vec{r}_N \sigma_N) \quad (1.1.9)$$

Eq. (1.1.5) cannot be solved precisely because of the correlated motions of electrons in the many-electron systems. To decouple the coupled motion, we must use some approximation.

1.2 THE HARTREE APPROXIMATION

Hartree [3] introduced a simplest approximation to deal with many-electron wave functions by assuming that an electron moves in the field of nuclei and the average of N-1 electrons. In this approximation many-electron wave functions

$$\Psi(\vec{x}_1, \vec{x}_2 \dots \vec{x}_N) \approx \psi(\vec{x}_1) \psi(\vec{x}_2) \dots \psi(\vec{x}_N) \quad (1.2.1)$$

This method doesn't take account the antisymmetric properties of electrons. Later Fock modified it to incorporate the antisymmetry property of the many electron wavefunctions. So in the Hartree-Fock approximation a single Slater determinant of the spin-orbitals represents the many-electron wavefunction. This approximation misses the correlation effects.

1.2.1 HARTREE-FOCK APPROXIMATION

The Hartree-Fock approximation [4] assumes that the wavefunction can be approximated by a single Slater determinant, and that this approximation is done using the variational principle (undetermined multipliers to enforce orthonormality of the orbitals), minimizing the Hartree-Fock energy by tweaking the orbitals ψ .

$$\Psi_{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\vec{x}_1) & \psi_2(\vec{x}_1) & \dots & \psi_N(\vec{x}_1) \\ \psi_1(\vec{x}_2) & \psi_2(\vec{x}_2) & \dots & \psi_N(\vec{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(\vec{x}_N) & \psi_2(\vec{x}_N) & \dots & \psi_N(\vec{x}_N) \end{vmatrix} \quad (1.2.3)$$

The Slater determinant [5] is used to find the expectation value of energy.

$$E_{HF} = \langle \Psi_{HF} | \hat{H} | \Psi_{HF} \rangle \quad (1.2.4)$$

The total energy minimization is constrained here by the requirement that the spin-orbitals $\{\psi_i\}$ satisfy the orthonormality criterion given in Eq. 1.1-11, which introduces the Lagrangian multipliers ε_i in the resultant Hartree-Fock equations. These equations determine the set of spin-orbitals which has the lowest EHF and are given as,

$$\hat{F}\psi_i(\vec{x}) = \sum_{j=1}^N \varepsilon_{ij} \psi_j(\vec{x}) \quad (1.2.5)$$

Where \hat{F} is the Fock operator,

$$\hat{F} = -\frac{1}{2} \nabla^2 + \hat{V}_{ext}(i) + \hat{V}_{HF}(i) \quad (1.2.6)$$

1.3 DENSITY FUNCTIONAL THEORY

Density functional theory (DFT) [5] [6] is an alternative approach of solving the many-electron Schrodinger equation, in which the complicated wavefunction is replaced by the electron density.

The electronic spin density of a system of N electrons can be written as

$$n_{\sigma}(\vec{r}) = N \sum_{\sigma_2 \dots \sigma_N} \int d^3r_2 \int d^3r_3 \dots \int d^3r_N |\Psi(\vec{r}\sigma, \vec{r}_2\sigma_2, \dots, \vec{r}_N\sigma_N)|^2 \quad (1.3.1)$$

The primary distinction between Hartree-Fock and DFT is that Hartree-Fock calculates the entire N-electron wave function, whereas DFT only attempts to calculate total electronic energy and the overall electronic density distribution. The primary ideal in DFT is that there is a distinct relationship between the total electronic potential and the total electronic potential energy, as well as the overall electronic density. Despite the fact that this is not a completely novel concept; the similar model proposed in the late 1920s [2]. However, the real breakthrough is made by Hohenberg and Kohn demonstrated in 1964 [5] that the ground-state energy and other. The electron density was used to define observables in a molecular system.

1.3.1 THOMAS-FERMI MODEL

The Thomas-Fermi [7] model takes electron density as its basic variable instead of a wavefunction. The kinetic energy is based on the uniform electron gas model given as

$$T_{TF}[n] = A_F \int n^{\frac{5}{3}}(\vec{r}) d^3r, \quad A_F = \frac{3}{10} (3\pi^2)^{\frac{2}{3}} \quad (1.3.2)$$

The nucleus-electron and nucleus-nucleus interaction are treated classically. Hence, the total energy of an atom using the Thomas-Fermi model can be expressed as

$$E_{TF}[n] = A_F \int n^{\frac{5}{3}}(\vec{r}) d^3r + \int n(\vec{r}) v(\vec{r}) d^3r + \frac{1}{2} \iint \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r d^3r' \quad (1.3.3)$$

where the second term on the right represents the interaction with the external potential, $V_{ext}[n]$ and the last term represents the classical Coulomb interaction $U_{ee}[n]$ between two electron density distributions.

The total energy can be minimized with respect to the density under the constraint

$$\delta N = \delta \int d^3r n(\vec{r}) = 0 \quad (1.3.4)$$

$$\delta \left(E_{TF} - \mu \int d^3r n(\vec{r}) \right) = 0 \quad (1.3.5)$$

where Lagrange multiplier is the chemical potential. Solving this equation yields,

$$\mu = \frac{5}{3} C_F n^{\frac{2}{3}}(\vec{r}) + v(\vec{r}) + \int d^3r' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} \quad (1.3.6)$$

This model makes the molecules unbound, as the model completely neglects the exchange-correlation energy. The kinetic energy density is solely determined by the density at a point whereas the Laplacian is not a local object. The exchange energy, correlation energy, and gradient adjustment for the kinetic energy have all been tried to improve the TF model, but this does not make it a good theory. It has, nevertheless, played a significant role in the development of current density functional theory, as it suggests a one-to-one mapping between electron density and external potential.

1.3.2 HOHENBERG-KOHN THEOREM

The total energy is expressed as a function of the electron density in the TF model using approximations. Hohenberg and Kohn [5] formalized the existence of such an exact energy functional in 1964 by demonstrating the one-to-one mapping between the external potential and the ground state electron density, as well as proposing the variational principle for the energy functional and density. Hohenberg and Kohn (HK) [5] developed two theorems that are considered the cornerstone of contemporary density functional theory (DFT). Apart from a trivial additive constant, the first theorem states that the external potential v_{ext} is a unique functional of $n(\vec{r})$. Using reductio ad absurdum, Hohenberg and Kohn proved the theorem. Consider two Hamiltonians \hat{H} and \hat{H}' , both of which have external potentials that differ by more than a trivial additive constant but correspond to the same electronic ground state $n(\vec{r})$. Let their respective ground state wavefunctions be Ψ and Ψ' and the ground state energies be E and E' . Using the variational principle we get

$$E' < \langle \Psi' | \hat{H} | \Psi' \rangle = \langle \Psi' | \hat{H}' | \Psi' \rangle + \langle \Psi' | \hat{H} - \hat{H}' | \Psi' \rangle \quad (1.3.7)$$

$$E < E' + \int d^3r n(\vec{r})(v(\vec{r}) - v'(\vec{r})) \quad (1.3.8)$$

Similarly, by interchanging the prime and unprimed quantities we obtain

$$E' < E - \int d^3r n(\vec{r})(v(\vec{r}) - v'(\vec{r})) \quad (1.3.9)$$

Add Eq (1.3.8) and Eq(1.3.9) we get

$$E + E' < E + E' \quad (1.3.10)$$

This contradicts our assumption concluding that external potentials corresponding to same ground state density cannot differ by more than the additive constant. Thus, ground state density uniquely determines the external potential. The only information that depends on an actual system is the number of electrons N in the system and V_{ext} , which determine the Hamiltonian of the system. This leads to the fact that the total energy of a many-electron ground state system is a unique functional of $n(\vec{r})$ and we could find all other properties of the system using $n(\vec{r})$ as a basic variable. This theorem enables us to write the energy as a functional of the density

$$E[n] = T[n] + V_{ee}[n] + \int d^3r n(\vec{r})(v(\vec{r})) \quad (1.3.11)$$

Where $T[n] + V_{ee}[n]$ remains the same for N -electron system and is defined as universal functional that is true for all electron systems as

$$QHKn = T[n] + V_{ee}[n] \quad (1.3.12)$$

Whereas the $\int d^3r n(\vec{r})(v(\vec{r}))$ is system dependent.

The second HK theorem [8] states that for any non-negative trial density $n'(\vec{r})$ with

$$\int d^3r n(\vec{r}) = N, \quad (1.3.13)$$

$$E_o \leq E[n'(\vec{r})], \quad (1.3.14)$$

Where E_o is the ground state energy of the system.