DEVELOPMENT OF A CORRECTION TERM FOR THE KINETIC ENERGY DENSITY FUNCTIONAL

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A THESIS APPROVED BY THE DEPARTMENT OF THEORETICAL PHYSICS

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ABSTRACT

Density functional theory (DFT) is a useful theoretical and computational tool for electronic structure calculations, which form the basis for the classification of materials into conductors, semiconductors or insulators. DFT started with a crude approximation by Thomas and Fermi (TF theory) which calculated the kinetic energy of electrons using the so-called local density approximation (LDA). Although TF is computationally inexpensive, it provides a poor numerical result due to a lack of understanding of the density dependence of the kinetic energy. Another approximation to the kinetic energy is the von-Weizsacker (vW) term, which greatly improves the TF theory, yet the full functional form of the kinetic energy remains unknown. We seek to develop a supplemental term to the kinetic energy density functional and compute corrections to the Thomas-Fermi-von-Weizsacker kinetic energy of closed shell atoms in order to improve its accuracy.

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A work of this kind can never be the sole effort of an individual; some people must have contributed in articulating facts in one form or the other and in establishing solutions to make the work a success.

Based on this, I channel my profound appreciation to my supervisor Dr. Akin-Ojo, Omololu who not only deems it necessary for me to have a topic in **Density Functional Theory (DFT)** thereby enhancing my opportunity of exploring, researching and digging deep into the understanding of DFT but also spends time making corrections, giving instructions and guiding me on this work. Besides, his directives, criticisms, assistance, instructions and clarifications, meekness and not forgetting his ever readiness to help even at the cruelest points of sixs and sevens, that aided the realization of this work to its present status remained in indelible memory.

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I remain loyal and humble to the only but one Nwankwo’s family, viz: Papa, Mama, siblings and relatives, I doff my cap for you all.

Dec/2014

Nwankwo, Udoka

DEDICATION

To God almighty out of whose infinite mercy and grace every soul including mine finds and receives divine favor; in whose very heart the end is known from the very beginning; the only orator who can speak the beginning of my life from the very beginning of my life.

To my god parents to whom I sincerely received true blessings, love, supports, etc from in times of needs and unseasoned demands.

Contents

CHAPTER 1

Introduction

The quantum mechanics of many-electron systems which have descriptions from time-dependent and time-independent Schrödinger and Liouville equations, is to a good approximation ostensibly a well-understood subject. The Schrödinger equations present the theoretical bases for the description of both the time evolution and pure stationary states properties of atoms and molecules. In treating some quantum mechanical systems such as biological molecules and liquids where the individuality of molecules ceases to exist, rather collective effects becomes predominant, it is immaterial to talk of pure states but paramount to consider ensemble of states describable with time-dependent and time-independent Liouville equations in lieu of Schrödinger equations.

However, in each case of pure states and ensemble of non-trivial many-electron systems, the equations involved are not without complicated and complex mathematical parameters with little or no analytical or numerical solutions. In other words, systems containing thousands of electrons and hundred of nuclei are computationally demanding and, in fact, the problem is such that even if supercomputers were to be improved by several orders of magnitude, both in speed and memory, it would still be difficult, if not impossible, to obtain sufficiently accurate solutions to these equations [13].

Although, non-relativistic Hamiltonian operators for systems interacting Coulombically can be written explicitly for these equations, understanding a priori, the subtleties of the many-body behavior that ensues from these interactions remains a challenge. Thus, this calls for the formulation of a rigorous quantum mechanical approach entirely equivalent to the Schrödinger or Liouville equations which certainly opened ways for important developments in atomic, molecular and condensed matter physics as well as in quantum chemistry, particularly, to avoid the particle-number dependency. This particle number dependence, perhaps, had made it impossible to solve the equations for extended and realistic systems. Avoiding particle-number dependence is a keystone behind the formulation of what has been generically called "density functional theory (DFT)".

1.1 What is Density Functional Theory (DFT)?

To better understand the properties of materials, and to classify materials so that they can find application(s) in different spheres of life, one needs to calculate among other properties the electronic ground state structure of the material. From an electronic structure calculations (e.g., band structure calculation), one can classify a material into a conductor, a semiconductor or an insulator.

There are variety of, but not too many variant approaches, approximations, or principles to these calculations, depending on the system. These include; starting form idealized one-electron Schrödinger problem to many-electron problems and then, to real systems; many approximations, principles and theories such as perturbation theory, variational method, the Born-Oppenheimer approximation, the Hartree-Fork method, density functional theory; not forgetting the symmetry requirements that employ Pauli's exclusion principle and the Slater determinant for non-interacting fermions, etc.

Among these approaches, Density Functional theory has been held to high esteem as a linchpin of electronic structure calculation in solid state physics[1], and has made an unparalleled impact on the applications of quantum chemistry which include understanding of electron transport in solar energy materials[2]. This, perhaps, is because analytical solutions of the Schrödinger equations hold for only few simple systems, and numerical exact solutions can be obtained for a small number of atoms and molecules. Again, the recent progress in the calculation of the electronic structure of atoms, molecules and solids has emphasized, mayhap, how far we are from the objective of being able to predict the physical properties of many-electron systems reliably and with less excessive computation which DFT presents[3]. Thus, density functional theory is somewhat a completely different but formally rigorous way of approaching any interacting problem, by mapping it exactly to a much easier-to-solve non-interacting problem that is more computationally efficient than Hartree-Fock; though it has its own problems but, in a nutshell,

Definition 1.1.1. ***DFT*** *is a formalism or a way of simplifying the many-body (particle) problem by working with the electronic charge density as fundamental variable rather than the wave function and trying to find a direct relation between this density and the energy of the system.*

1.2 Why DFT?

The reasons why, at present, density functional theory has become such an attractive theory are really quite clear.
1. It provides reformulation in terms of the one-particle density, a unique and fundamental quantity which depends only upon three spatial and one spin variables, regardless of the number of particles of the physical system which it seeks to describe.
2. The one-particle density is an observable and a three-dimensional quantity that can be measured experimentally which theorists believe will elucidate the conceptualization of the properties of materials such as the nature of the chemical bond[4].
3. There is much to be gained in terms of the simplifications that such a reformulation could bring in the numerical handling of quantum mechanical problems.
4. It furnishes interpretative tools which enable researchers to grasp the essential features of physical systems; preferable, to have a vivid picture of the behavior of the wave functions, a simple description of the essence of the factors which determine cohesion, and an understanding of the origins in the variations in the properties from metal to metal.
5. The complications and cost associated with orbital manipulations, including orbital orthonormalization and localization are avoided
6. Particle number dependence of the wave function is avoided
7. DFT has many application in Chemistry and in physics such as calculating the binding energy of molecules in chemistry the band structure of solids in physics.

1.3 Uses of DFT

1. Electronic structure calculation for band-gap, density of states (DOS), and material classification.
2. Determination of the mechanical properties of a material, e.g toughness, bulk modulus
3. In Chemistry: to predict molecular properties (molecular structure, lattice constant, etc)
4. In the search for new materials with exceptional and novel properties
5. For molecular dynamics simulation, etc.

1.4 Focus of the Work

Our target in this work is to study the existing kinetic energy density functional of Thomas-Fermi and von-Weizsäcker which has not given exact numerical or analytical solution for systems with more than two electrons. We will compute corrections for the kinetic energy of some closed shell atoms under the restricted Hartree-Fock scheme, and develop correction terms for the kinetic energy functional that depend on the electron density and its gradient. Our anticipation is that the correction will be useful for any system of$N$-electrons.

1.5 The Background: The Schrödinger Equation

DFT has been in application, historically. The idea as mentioned earlier is to regard the total particle density as the fundamental quantity from which properties of a system can be calculated (determined). So, we here capture some fundamental concepts with some theoretical framework based on Time Independent Schrödinger Equation (**TISE**). We will maintain natural units (Hartree atomic unit).

1.5.1 One Particle TISE

Our interest is to develop a correction term for the kinetic energy density functional (**KEDF**) of many electron closed shell systems. A good point to start is the TISE for a single particle in an external potential $v(\vec{r})$:

$$\hat{H}\psi(\vec{r}) = E\psi(\vec{r}) \tag{1.1}$$

where,

$$\hat{H} = -\frac{1}{2}\nabla^2 + v(\vec{r}) \tag{1.2}$$

Eq.(1.1) is an eigenvalue equation for the energy operator $\hat{H}$ and defines all possible states of a system, $\psi(\vec{r})$ and their energies (eigenvalues), E. However, when there are disturbance in the system such that the Hamiltonian differs from the ground state Hamiltonian,$\hat{H}_o$, some form of approximations (perturbation and variational theories) are employed to seek for the ground state properties of the system (Note: we are interested in the ground state properties because that is where the true properties of a system can be explored):

$$\hat{H} = \hat{H}_o + \lambda\hat{H}'$$

$\hat{H}$ is the total Hamiltonian, $\hat{H}_o$ is the Hamiltonian for the undisturbed system and $\hat{H}'$ is the Hamiltonian resulting from disturbance. λ is a non-negative fictitious small number ≤ 1[18].

Perturbation Theory is a systematic procedure of obtaining approximate solutions to the perturbed problem by building on the known solution of the unperturbed case[19] and is employed when we are able to solve exactly the TISE for the unperturbed case:

$$\hat{H}^o\psi_n^o = E_n^o\psi_n^o$$

Variational theory states that the expectation value of the energy operator determined from any trial function Ψ_{trial} obeying the same boundary condition as the correct wave function of the system cannot be lower than the exact ground state energy E_o or E_{gs} of the system[18]

$$\frac{\int \Psi^*_{trial}(\vec{r})\hat{H}\Psi_{trial}(\vec{r})d^3\vec{r}}{\int \Psi^*_{trial}(\vec{r})\Psi_{trial}(\vec{r})d^3\vec{r}} \geq E_{gs} \tag{1.3}$$

The method is employed when we are unable to solve exactly the TISE for the unperturbed case of the the system and therefore are looking for approximate solution.

1.5.2 System of Several Particles

The Hamiltonian operator for N many-particle system with zero order approximation (turn off electron-electron interaction) is:

$$\hat{H} = -\sum_{i=1}^{N} \frac{1}{2}\nabla_i^2 + V(\vec{r}_i \cdots \vec{r}_N) \tag{1.4}$$

The wave function is a very complicated function of the coordinates of the particles and is given in what is known as orbital approximation[20]. In orbital approximation, the first reasonable approximation to the exact wave functions is obtained by thinking of each particle as occupying its "own" orbital, i.e as a pure state describable by a wave function then, the wave function of the ensemble or mixed state as the product of single particle wave function:

$$\Psi(\vec{r}) = \Psi(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N) = \phi(\vec{r}_1)\phi(\vec{r}_2)\cdots\phi(\vec{r}_N) \tag{1.5}$$

If all the particles are of the same kind then $\Psi(\vec{r})$ must satisfy some special symmetry properties since the expectation value of any operator, $\hat{O}$

$$\hat{O} = \int \Psi^*(\vec{r}_1, \cdots, \vec{r}_N)\hat{O}\Psi(\vec{r}_1, \cdots, \vec{r}_N)d^3\vec{r}_1 \cdots d^3\vec{r}_N \tag{1.6}$$

of a particular observable of a system must be invariant under the interchange of any two identical particle's coordinates, $\vec{r}_j$ and $\vec{r}_k$

$$\begin{aligned} \hat{O} &= \int \Psi^*(\vec{r}_1, \cdots, \vec{r}_j, \cdots, \vec{r}_k, \cdots)\hat{O}\Psi(\vec{r}_1, \cdots, \vec{r}_j \cdots \vec{r}_k \cdots)d^3\vec{r}_1 \cdots d^3\vec{r}_j \cdots \vec{r}_k \cdots \\ &= \int \Psi^*(\vec{r}_1, \cdots, \vec{r}_k, \cdots, \vec{r}_j, \cdots)\hat{O}\Psi(\vec{r}_1, \cdots, \vec{r}_k \cdots \vec{r}_j \cdots)d^3\vec{r}_1 \cdots d^3\vec{r}_k \cdots \vec{r}_j \cdots \end{aligned} \tag{1.7}$$

This is true on the condition that the probability of finding a particle irrespective of interchange of coordinates remains the same:

$$\Psi^*(\vec{r}_j, \vec{r}_k)\Psi(\vec{r}_j, \vec{r}_k) = \Psi^*(\vec{r}_k, \vec{r}_j)\Psi(\vec{r}_k, \vec{r}_j) \Longrightarrow |\Psi(\vec{r}_j, \vec{r}_k)|^2 = |\Psi(\vec{r}_k, \vec{r}_j)|^2 \tag{1.8}$$

The necessary requirements for eqs (1.7) and (1.8) is

$$\Psi(\vec{r}_j, \vec{r}_k) = \pm\Psi(\vec{r}_k, \vec{r}_j)$$

1. $\Psi(\vec{r}_j, \vec{r}_k) = +\Psi(\vec{r}_k, \vec{r}_j) \Longrightarrow$ symmetric and this is satisfied by bosons, and
2. $\Psi(\vec{r}_j, \vec{r}_k) = -\Psi(\vec{r}_k, \vec{r}_j) \Longrightarrow$ antisymmetric and it is satisfied by fermions (e.g. electrons)

In the case of just two particles, the two particle wave function $\Psi(\vec{x}_1, \vec{x}_2)$ formed by taking product of single orbital wave function of the individual particles is:

$$\Psi_{HP}(\vec{x}_1, \vec{x}_2) = \phi_a(\vec{x}_1)\phi_b(\vec{x}_2)$$

Here, $\vec{x}$ consists of the spatial coordinate $\vec{r}$ and the spin coordinate s. So that $\phi_i(\vec{x}) = \phi_i(\vec{r}, s)$; $i = a, b$. But if the particle are electrons of the same spin, the antisymmetric requirement is not satisfied since $\Psi(\vec{x}_1, \vec{x}_2) \neq -\Psi(\vec{x}_2, \vec{x}_1)$. However, a two-electron orbital wave function that satisfies the antisymmetric condition can be formed by adding a second term that is negative of the first term with the coordinates labels interchanged[18].

$$\Psi(\vec{x}_1, \vec{x}_2) = \frac{1}{\sqrt{2}}[\phi_a(\vec{x}_1)\phi_b(\vec{x}_2) - \phi_a(\vec{x}_2)\phi_b(\vec{x}_1)] \tag{1.9}$$

The factor $\frac{1}{\sqrt{2}}$ is to ensure normalization. We observe that $\Psi(\vec{x}_1, \vec{x}_2) = -\Psi(\vec{x}_2, \vec{x}_1)$ and if the spin orbitals $\phi_a(\vec{x}_1)$ and $\phi_b(\vec{x}_2)$ are the same, that is, if $a = b$ then, $\Psi(\vec{x}_1, \vec{x}_2) = 0 \;\; \forall \; \vec{x}_1, \vec{x}_2$. In this way, the Pauli exclusion principle (PEP) that no two electrons can occupy the same spin-orbital is obeyed. A general way of forming an antisymmetric wave function from N non-interacting system of electrons is given by Slater determinant:

$$\Psi(\vec{x}_1, \vec{x}_2, \cdots, \vec{x}_N) \approx \Phi_{SD} = \frac{1}{\sqrt{N!}} \begin{Vmatrix} \phi_1(\vec{x}_1) & \phi_2(\vec{x}_1) & \cdots \phi_N(\vec{x}_1) \\ \phi_1(\vec{x}_2) & \phi_2(x_2) & \cdots \phi_N(\vec{x}_2) \\ \vdots & \vdots & \vdots \\ \phi_1(\vec{x}_N) & \phi_2(\vec{x}_N) & \cdots \phi_N(\vec{x}_N) \end{Vmatrix} \tag{1.10}$$

1.5.3 A Real System and The Born-Oppenheimer Approximation

In the many-electrons system considered, we neglected the repulsive interactions between the electrons. However, this is an idealization because, it is not true for most practical real systems. In real systems with very few exceptions, the particles interact. So, the Hamiltonian has more terms in it than in the idealized case, and the wave function is more complicated than what we have seen in a system of non-interacting electrons. The wave function of the k-th state of a real system which depends on $3N$ spatial coordinates $\{\vec{r}_k\}$, and N spin coordinates $\{s_k\}$ of the electrons; denoted by $\{\vec{x}_k\}$ and the $3M$ spatial coordinates $\{\vec{R}_k\}$ of the nuclei is:

$$\Psi_k(\vec{x}, \vec{R}) = \Psi_k(\vec{x}_1, \vec{x}_2, \cdots, \vec{x}_N, \vec{R}_1, \vec{R}_2, \cdots, \vec{R}_M) \tag{1.11}$$

Then, the TISE for the system is:

$$\hat{H}(\vec{r}, \vec{R})\Psi_k(\vec{x}, \vec{R}) = E_k\Psi_k(\vec{x}, \vec{R}) \tag{1.12}$$

$\hat{H}(\vec{r},\vec{R})$ is the Hamiltonian operator for a real system consisting of M nuclei and N electrons and it represents the total energy of the system[16]:

$$\hat{H}(\vec{r},\vec{R}) = \underbrace{\sum_{i=1}^{N} -\frac{1}{2}\nabla_i^2}_{\hat{T}_{ele}(\vec{r})} \underbrace{-\sum_{A=1}^{M} \frac{1}{2M_A}\nabla_A^2}_{\hat{T}_{nuc}(\vec{R})} \underbrace{-\sum_{i,A=1}^{N,M} \frac{Z_A}{r_{iA}}}_{\hat{V}_{ele,nuc}(\vec{r},\vec{R})} + \underbrace{\sum_{i=1,j>i}^{N} \frac{1}{r_{ij}}}_{\hat{V}_{ele,ele}(\vec{r})} + \underbrace{\sum_{A=1,B>A}^{M} \frac{Z_A Z_B}{R_{AB}}}_{\hat{V}_{nuc,nuc}(\vec{R})} \tag{1.13}$$

i and j run over the N electrons, whereas A and B run over the M nuclei. $\hat{T}_{elec}$ and $\hat{T}_{nuc}$ are the kinetic energy operators of the electrons and the nuclei respectively. M_A is the mass of nucleus A. $V_{ele,ele}$, $V_{ele,nuc}$ and $V_{nuc,nuc}$ are the electron-electron repulsive, electron-nuclear electrostatic attractive and nuclear-nuclear repulsive interaction potential operators respectively. $r_{ij} = |\vec{r}_i - \vec{r}_j|$ is the distance between electrons i and j; $R_{AB} = |\vec{R}_A - \vec{R}_B|$ is the distance between nuclei A and B, and $r_{iA} = |\vec{r}_i - \vec{R}_A|$ is the distance between electron i and nucleus A.

In an exact quantum mechanical treatment of a real system, TISE has to be solved for M-nuclei and N-electrons, but this is practically not feasible. However, the problem is assuaged by the adoption of a number of approximations. The first approximation to solving the problem is the Born-Oppenheimer approximation (B-OA) also called *Clamped-Nuclei approximation.*

Born and Oppenheimer assumed that since the nuclei are much more massive than the electrons, the motion of the electrons are rapid compared with the motion of the nuclei. Thus, the nuclei can be assumed to be clamped at fixed inter-nuclear distances R_{AB}. Hence, the electrons are in motion in the field of the nuclei whereas the nuclei are in motion in the electronic potential surfaced as E_{tot}[18, 20].
With the B-OA, the kinetic energy of the nuclei is zero and the nuclear-nuclear repulsive potential energy can be treated as constant for a fixed configuration of the nuclei. This is because any constant added to an operator only adds to the operators eigenvalue and has no effect on the operator eigenfunction. Thus, eq.(1.13) reduces to just the electronic Hamiltonian:

$$\hat{H}(\vec{r},\vec{R}) = \underbrace{\sum_{i=1}^{N} -\frac{1}{2}\nabla_i^2}_{\hat{T}_{ele}(\vec{r})} \underbrace{-\sum_{i,A=1}^{N,M} \frac{Z_A}{r_{iA}}}_{\hat{V}_{ele,nuc}(\vec{r},\vec{R})} + \underbrace{\sum_{i=1,j>i}^{N} \frac{1}{r_{ij}}}_{\hat{V}_{ele,ele}(\vec{r})} \tag{1.14}$$

The TISE for the electronic motions is now given by:

$$\hat{H}_{ele}\Psi_{ele}(\vec{r},\vec{R}) = E_{ele}\Psi_{ele}(\vec{r},\vec{R}) \tag{1.15}$$

$\Psi_{ele}(\vec{r},\vec{R})$ describes the motion of the electrons and depends explicitly on the electronic coordinates $\{\vec{r}_i\}$ and parametrically on the nuclear coordinates $\{\vec{R}_A\}$[17]. Parametric de-

pendence means that for different arrangement of the nuclei, Ψ_{ele} is a different function of the electronic coordinate. Although, we did not mention spin which implies we have been dealing on only spatial coordinate, the Ψ_{ele} depends on the spin-orbital coordinate. To fully describe the wave function, we will employ the choice of Slater determinant discussed earlier.
The energy from the potential of the nuclear-nuclear interaction of clamped nuclei is:

$$E_{nuc} = \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_A Z_B}{|R_A - R_B|} \tag{1.16}$$

Thus, the approximated total energy of a real system of electrons is:

$$E_{tot} = E_{elec} + E_{nuc} \tag{1.17}$$

Through B-OA, the electronic Hamiltonian is successfully separated from the nuclear Hamiltonian and the wave function is also separated for every fixed value of R as:

$$\Psi(\vec{r}, \vec{R}) = \Phi(\vec{r})\Psi(\vec{R})$$

The quantity of interest is contained in the electronic Hamiltonian therefore, we will focus on eq.(1.15) and detach the subscript “ele”.

Although, it appears very simple the resulting equation is not a soft nut to chew.

$$\hat{H}\Phi(\vec{r}) = E\Phi(\vec{r}) \tag{1.18}$$

Its exact solution even for the simplest molecules with two nuclei and an electron remains to the present day a major challenge. So, the quoted words of Paul-Dirac, 1929 as contained in Von[21] remains the same

> *The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.*

Its difficulties lie in the electron-electron interaction term $\frac{1}{r_{ij}}$ which leads to particle (electron) number dependence of the wave function and difficulty in writing the wave function of the ensemble and $3N$ or $4N$ degrees of freedom of the electrons. As a result, these have called for many approximate methods and theories of solutions

1.6 The Hartree-Fock Approximation

It is hopeless to anticipate an analytical or numerical solution of eq.(1.18) whose Hamiltonian is eq.(1.14) with such a complicated potential energy terms, however, if an effective potential $V_{eff}(\vec{r})$ can be found for such potential energy term such that a single particle wave function $\Phi_i(\vec{x})$ that satisfies one particle-like TISE:

$$\left[-\frac{1}{2}\nabla^2 + V_{eff}(\vec{r})\right]\Phi_i(\vec{x}) = \epsilon_i\Phi_i(\vec{x}) \tag{1.19}$$

is obtained then, computational techniques can be applied to give detailed and reliable numerical result. This is the essence of the Hartree-Fock (HF) approximation. It replaces the complicated many-electron problem by a one-electron problem[17]. This is achieved by reducing the many-electron Hamiltonian to a single-electron Hamiltonian with an effective potential:

$$V_{eff}(\vec{r})\phi_i(\vec{r}) = \underbrace{\int \frac{n(\vec{r}')\phi_i(\vec{r})}{|\vec{r}-\vec{r}'|}d^3\vec{r}'}_{Coulomb\ repulsion} \underbrace{-\int \frac{n(\vec{r},\vec{r}')\phi_i(\vec{r}')}{|\vec{r}-\vec{r}'|}d^3\vec{r}'}_{exchange} \underbrace{-\sum_{A=1}^{M}\frac{Z_A\phi_i(\vec{r})}{|\vec{r}-\vec{R}_A|}}_{external\ term} \tag{1.20}$$

The Coulomb repulsion is the electrostatic interaction between two electrons at points $\vec{r}$ and $\vec{r}'$, which manifests in the effective potential through $\frac{1}{|\vec{r}-\vec{r}'|}$ and prevents the two electrons from coming too close to each other. The exchange has no classical analogue. It is in no way connected to the charge of the electrons, but it is a direct consequence of Pauli's exclusion principle[16] which the Slater determinant that defined the Hartree-Fock product of single particle wave function is satisfies.

Recall that if there are no electron-electron interaction (zero order approximation) in the system, eq.(1.20) reduces to a single particle problem with

$$V_{eff}(\vec{r}) = V_{ext}(\vec{r}) = \sum_{A=1}^{M}\frac{-Z_A}{|\vec{r}-\vec{R}_A|} \tag{1.21}$$

To obtain a one-particle wave function that satisfy eq.(1.19), D. R. Hartree made an approximation for the wave function by taking the product of N one-electron orbital wave functions

$$\Phi(\vec{r}_1,\vec{r}_2,\cdots,\vec{r}_N) \longrightarrow \phi_1(\vec{r}_N)\cdots\phi_N(\vec{r}_N)$$

while V. Fock modified the product by introducing the anti-symmetrization property. The antisymmetric product is the HF approximation and it is given by the Slater determinant of eq.(1.10). The choice of Slater determinant guaranteed that Pauli's Exclusion Principle (PEP) is obeyed. Eq.(1.19) is the HF equation. So, the HF approximation consists of approximating the N-electron orbitals by an antisymmetric product of N one-electron wave function $\Phi_i(\vec{x})$ composed of the spin coordinate functions[1] $\sigma(s)$ and the spatial coordinate functions $\phi_i(\vec{r})$ The optimal trial wave function is the one that minimizes the Hartree-Fock energy according to the variational method

$$E^{HF} = min_{\{\Phi_i\}_{i=1}^N} \frac{\langle \Phi_{trial}(\vec{x})|[-\frac{1}{2}\nabla^2 + V_{eff}(\vec{r})]|\Phi_{trial}(\vec{x})\rangle}{\langle \Phi_{trial}(\vec{x})|\Phi_{trial}(\vec{x})\rangle} \geq E_{GS} \tag{1.22}$$

$\{\Phi_i\}_{i=1}^N$ is a set of single particle orbitals. Full minimization of the functional E^{HF} with respect to all allowed N-electrons wave functions will give the true ground state Φ_0 and energy $E^{HF}(\Phi_0) = E_{GS}$. E_{GS} is the true ground state energy.

It necessary to note that the single-determinant description from the Slater determinant for orbits of many-electron is an approximation and can never give the exact energy for the many-electrons system. For higher accuracy in the energy calculations, the exact wave function for a system of many interacting electrons is never a single-determinant or a simple combination of a few determinants. Owing to variational principle, E_{HF} is necessarily always larger than the exact ground state energy E_{GS}. The difference between these two energies is called correlation energy E_c^{HF}:

$$E_c^{HF} = E_{GS} - E_{HF} \geq 0 \tag{1.23}$$

E_c^{HF} is a negative quantity since $E_{GS} < 0$ and $E_{HF} < 0$, therefore, $|E_{GS}| > |E_{HF}|$. Thus, E_c^{HF} is a measure for the error introduced through the HF scheme. Electron correlation is actively caused by instantaneous repulsion of the electrons, which is not covered by the effective HF potential.

The HF method is also called the **self consistent field (scf)** method. It involves solving the HF equation by assuming a trial wave function then, the new solution obtained (wave function) becomes the new trial wave function, and the iteration is continued that way until the subsequent iterations produce consistent result with the previous ones.

Expansion of eq.(1.19) for some basis functions, gives the HF energy terms as:

$$\textbf{Kinetic energy term} \equiv \int \phi_p^*(\vec{r}) \frac{-1}{2} \nabla^2 \phi_q(\vec{r}) d\vec{r} \tag{1.24}$$

$$\textbf{Electron-Nuclear attraction term} \equiv \int \phi_p^*(\vec{r}_1) \frac{1}{r_{1A}} \phi_q(\vec{r}_1) d\vec{r}_1 \tag{1.25}$$

$$e^- - e^- \textbf{repulsive energy term} \equiv \int\int \phi_p^*(\vec{r}_1)\phi_q(\vec{r}_1) \frac{1}{r_{12}} \phi_a(\vec{r}_2)\phi_b^*(\vec{r}_2) d\vec{r}_1 d\vec{r}_2 \tag{1.26}$$

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[1] The spin function denoted by $\sigma(s)$ is either $\alpha(s)$ or $\beta(s)$

The Hartree-Fock energy $E_{HF} \neq E_{GS}$. Its calculation is computer intensive. Density Functional Theory (DFT) is a computational technique employed for solving these equations in order to determine the electronic properties of any system and E_{GS} an the expense of Hartree-Fock. There are two theorems which establishes DFT.

1.7 Hohenberg-Kohn Theorems

Theorem 1.7.1 (The first Hohenberg-Kohn theorem). *The external potential $\nu(\vec{r})$ is (to within a constant) a unique functional of the ground state electron density $n(\vec{r})$; since, in turn, $\nu(\vec{r})$ fixes $\hat{H}$ we see that the complete many-body ground state is a unique functional of the density $n(\vec{r})$[22]*

The theorem is just saying that for an isolated many-electron system, its ground-state one-electron density $n(\vec{r})$ uniquely determines the external potential, and in turn, the density is a functional of the external potential. Thus, the external potential and the density are in a one-to-one relation[13, 14, 15, 16]: $n(\vec{r}) \Longleftrightarrow \nu(\vec{r})$

To prove this theorem, we consider two systems each of N-electrons at the ground state[2]. Suppose there were two external potentials $\nu(\vec{r})$ and $\nu'(\vec{r})$ not restricted to Coulomb potentials, and that differ not only by a constant. From the two external potential, there are two Hamiltonians $\hat{H} = T + V_{ee} + V_{en}$ and $\hat{H}' = T + V_{ee} + V'_{en}$ corresponding to two different ground state eigenfunctions Ψ with energy E and Ψ' with energy E'[15, 16, 22]. Hohenberg-Kohn assumed that the different potentials will give different Hamiltonians with different ground state properties but the same ground state electron density, i.e, $n(\vec{r}) = n'(\vec{r})$. This proof uses variational principle therefore, if we take Ψ to be a trial wave function for $\hat{H}'$ then,

$$E' < \left\langle \Psi|\hat{H}'|\Psi \right\rangle = \left\langle \Psi|\hat{H} + \hat{H}' - \hat{H}|\Psi \right\rangle = E + \langle \Psi|\nu'(\vec{r}) - \nu(\vec{r})|\Psi\rangle$$

$$\implies \quad E' = E + \int n(\vec{r})[\nu'(\vec{r}) - \nu(\vec{r})]d^3\vec{r} \tag{1.27}$$

also taking Ψ' as a trial wave function for $\hat{H}$, we obtain

$$E < \left\langle \Psi'|\hat{H}|\Psi' \right\rangle = \left\langle \Psi'|\hat{H}' + \hat{H} - \hat{H}'|\Psi \right\rangle = E' + \langle \Psi|\nu(\vec{r} - \nu'(\vec{r}))|\Psi\rangle$$

$$\implies \quad E = E' - \int n(\vec{r})[\nu'(\vec{r}) - \nu(\vec{r})]d^3\vec{r} \tag{1.28}$$

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[2] So that their kinetic energy T and electron-electron potential $V_{ee}(\vec{r})$ are equal

By adding eqs (1.27) and (1.28) we have:

$$E' + E < E + E' \quad \text{or} \quad 0 < 0$$

which is a contradiction. This implies that *there are no two different external potential that can give the same ground state electron density.*

Theorem 1.7.2 (The second Hohenberg-Kohn theorem)**.** *The energy $E_\nu[n]$ of any* v-representable *trial density $n(\vec{r})$ places an upper bound to the ground state energy $E_\nu[n_o]$, i.e,*

$$E_\nu[n] \geq E_\nu[n_o] \tag{1.29}$$

The theorem uses variational principle under the constraints that for some external potential, the trial density satisfy these conditions

- $n(\vec{r}) \geq 0$
- $\int n(\vec{r}) d^3\vec{r} = N$
- $\int |\nabla n^{\frac{1}{2}}(\vec{r})|^2 d^3\vec{r} < \infty$

Therefore, the theorem is put as: for any trial density $n(\vec{r})$ which satisfies the conditions that $n(\vec{r}) \geq 0$, $\int n(\vec{r}) d^3\vec{r} = N$ and is associated with some external potential $\nu_{ext}(\vec{r})$, the energy obtained from the functional $E[n] = F_{HK}[n] + V_{en}[n]$ places an upper bound to the ground state energy E_{GS}, but equals E_{GS} if the true ground state density is the trial[14, 16]. Where $F_{HK}[n] = T[n] + V_{ee}[n]$ is the Hohenberg-Kohn universal energy functional.

1.7.1 Represent-ability of Density

Represent-ability of density is the restriction for density to be eligible in variational principle

Definition 1.7.3. *V-represent-ability: an electron density is v-representable if it stems from an antisymmetric ground-state wave function and its Hamiltonian is associated with some external potential $\nu(\vec{r})$ other than the electron-nuclear potential.*

Definition 1.7.4. *N-represent-ability: an electron density is N-representable if it is the density obtained from some antisymmetric wave function.*

Thus, for a given density to be able to determine all the ground state properties of a system, it must be v-representable. Therefore, since the wave function determines the density and vice versa, it implies that the density and the wave function are in a one-to-one relationship. Hence, the first theorem can be restated as:

Theorem 1.7.5. *First Hohenberg-Kohn theorem: There is a one-to-one mapping between ground-state wave functions and v-representable electron densities. It is through this unique mapping that a v-representable density determines the properties of its associated ground-state.*

A direct consequence of the former theorem is that if all ground-state properties are functionals of the electron density, then these functionals are defined only for v-representable densities. Unfortunately, the conditions for a density to be v- representable are not yet completely known, since there are densities in single particle systems that do not come from the ground state wave function of any $V_{ext}(\vec{r})$[6, 23]

Fortunately, Density Functional Theory can be formulated in a way that only requires the density both in functionals and in variational principle to satisfy the N-represent-ability condition [3]. It was shown by Gilbert[24] that any reasonable electron density satisfying the three conditions given under theorem (1.7.2) is N-representable

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[3] The N-represent-ability condition is weaker condition

CHAPTER 2

Basic Tools

2.1 Density Approximations

2.1.1 Uniform Electron Gas (UEG) Model

Definition 2.1.1. *Uniform electron gas (UEG) or Homogeneous electron gas (HEG) is a system in which electrons are smeared out like a jelly (rather than being point charge) on a positive background charges distributed such that the whole ensemble is electrically neutral. The number of electrons* N *and the volume* V *containing them are considered to tend to infinity while the density* $n(\vec{r}) = \frac{N}{V}$ *remains finite and constant.*

The model is a good physical model for simple metals such as Sodium consisting of a perfect crystal of valence electrons and positive cores where the cores is smeared out to arrive at a uniform positive background charges. On the other hand, the model is far from reality for atoms and molecules which are usually characterized by rapid varying densities[12].

2.1.2 Local Density Approximation (LDA)

Definition 2.1.2. *LDA is an approximation on the electron density at each point in space, in which the electron density is treated locally as uniform. It implies ignoring the inhomogeneity of the electron density.*

Local density approximation employs the kinetic energy density calculated for a homogeneous electron gas of non-interacting electrons as a functional dependence of the electron density[25]. This over simplified model is justified for systems whose density changes slowly with $\vec{r}$. Despite its simplicity LDA can give good results for a great number of systems.

2.1.3 Gradient Expansion Approximation (GEA)

Definition 2.1.3. *Gradient expansions is a systematic corrections to LDA for electron densities that vary slowly over space.*

The von-Weizsäcker functional plus the Thomas-Fermi functional (vide infra) or simply the second-oder gradient expansion approximation (GEA2) has been in application for estimating the total kinetic energy of atom and molecules with densities obtainable from accurate methods like the Hartree-Fock method[26]. GEA is thus, the simplest improvement that can be done to LDA in order to account for the inhomogeneities of atomic and molecular electron densities by adding to the LDA potential corrections that depend on the local gradient of the electron density.

2.2 Thomas-Fermi Theory

The Thomas-Fermi model uses the electron density as the only physical quantity in treating semi-classically a system of many-particles by assuming a plane wave function of a one-particle non-interacting homogeneous electron gas for the many-particle system.

$$\phi_k(\vec{r}) = (2\pi)^{-\frac{3}{2}} e^{i\vec{k}.\vec{r}} \tag{2.1}$$

To obtain the Thomas-Fermi kinetic energy, a particle in a box model is considered in which we have cubes of sides l and volume $\Delta V = l^3$ each containing some fixed number of electrons ΔN and with the assumption that the electrons in each cell behave like independent fermions at the temperature $0K$, with the cells independent of one another[6]. From quantum mechanics,the energy levels of a particle in a 3-dimensional infinite well are given by:

$$\epsilon(n_x, n_y, n_z) = \frac{h^2}{8ml^2} R^2 \text{ where } R^2 = n_x^2 + n_y^2 + n_z^2 \text{ defined a radius of a sphere}$$

$$R = \Big(\frac{8ml^2\epsilon}{h^2}\Big)^{\frac{1}{2}} \tag{2.2}$$

Since R must be positive therefore, $\frac{1}{8}$ of the volume of the sphere in the whole space defined the number of distinct energy levels $\Phi(\epsilon)$ with energy smaller than ϵ, thus

$$\Phi(\epsilon) = \frac{1}{8}\Big(\frac{4\pi R^3}{3}\Big)$$

Putting eq (2.2), we have:

$$\Phi(\epsilon) = \frac{\pi}{6}\Big(\frac{8ml^2\epsilon}{h^2}\Big)^{\frac{3}{2}} \tag{2.3}$$

The number of energy levels between ϵ and $\epsilon + d\epsilon$ is given by

$$g(\epsilon)d\epsilon = \Phi(\epsilon + d\epsilon) - \Phi(\epsilon)$$

Where $g(\epsilon)$ is the density of states at energy ϵ. By Taylor expansion about ϵ we obtain with error of order $O((d\epsilon)^2)$:

$$g(\epsilon)d\epsilon = \dot{\Phi}(\epsilon)d\epsilon = \frac{\pi}{4}\Big(\frac{8ml^2}{h^2}\Big)^{\frac{3}{2}}\epsilon^{\frac{1}{2}}d\epsilon \tag{2.4}$$

The probability of an electron with energy ϵ occupying a quantum state is given by the Fermi-Dirac:

$$f(\epsilon) = \frac{1}{1 + e^{\beta(\epsilon-\epsilon_f)}} = \begin{cases}1, & \epsilon<\epsilon_f \\ 0, & \epsilon>\epsilon_f\end{cases} \quad T = 0K \text{ and } \epsilon_f\text{=Fermi energy} \tag{2.5}$$

The total energy ΔE in each volume ΔV of doubly occupied state of energy $\epsilon < \epsilon_f$ is:

$$\Delta E = 2\int \epsilon f(\epsilon)g(\epsilon)d\epsilon = \frac{\pi}{2}\int_0^{\epsilon_f}\Big(\frac{8ml^2}{h^2}\Big)^{\frac{3}{2}}\epsilon^{\frac{3}{2}}d\epsilon = \frac{\pi}{5}\Big(\frac{8ml^2}{h^2}\Big)^{\frac{3}{2}}\epsilon_f^{\frac{5}{2}} \tag{2.6}$$

The number of electrons ΔN doubly occupying a state in a volume ΔV is:

$$\Delta N = 2\int f(\epsilon)g(\epsilon)d\epsilon = \frac{\pi}{2}\int_0^{\epsilon_f}\Big(\frac{8ml^2}{h^2}\Big)^{\frac{3}{2}}\epsilon^{\frac{1}{2}}d\epsilon = \frac{\pi}{3}\Big(\frac{8ml^2}{h^2}\Big)^{\frac{3}{2}}\epsilon_f^{\frac{3}{2}} \tag{2.7}$$

Evaluating eq.(2.7) for ϵ_f we obtain

$$\epsilon_f = \Big(\frac{3\Delta N}{\pi l^3}\Big)^{\frac{2}{3}}\frac{h^2}{8m} \tag{2.8}$$

Substituting eq.(2.8) into eq.(2.6) and noting that the electron density $n(\vec{r}) = \frac{\Delta N}{\Delta V}$, we obtain the expression for energy in each cell in term of density as:

$$\Delta E = \frac{3h^2}{10m}\Big(\frac{3}{8\pi}\Big)^{\frac{2}{3}}n^{\frac{5}{3}}(\vec{r})\Delta V \tag{2.9}$$

We recall here that

$$\hbar = \frac{h}{2\pi} \longrightarrow h^2 = (2\pi)\hbar^2$$

Therefore,

$$\Delta E = \frac{3\hbar^2}{10m}(3\pi^2)^{\frac{2}{3}}n^{\frac{5}{3}}(\vec{r})\Delta V = \frac{3}{10}(3\pi^2)^{\frac{2}{3}}n^{\frac{5}{3}}(\vec{r})\Delta V \qquad \text{in atomic unit} \tag{2.10}$$

Hence, the Thomas-Ferm kinetic total energy of the electrons in the entire system in terms of density functional is obtained by integrating eq.(2.10) over the whole ensemble:

$$T_{TF}[n] = C_0 \int n^{\frac{5}{3}}(\vec{r}) d^3\vec{r} = \int t[n(\vec{r})] d^3\vec{r} \tag{2.11}$$

$$\text{Where} \quad t[n(\vec{r})] = C_0 n^{\frac{5}{3}}(\vec{r}) \qquad C_0 = \frac{3}{10}(3\pi^2)^{\frac{2}{3}} \tag{2.12}$$

$t[n(\vec{r})]$ is the kinetic energy density of a non-interacting homogeneous gas. The total number of electons in the space (n_x, n_y, n_z) is obtained by integrating $\Delta N = n(\vec{r})\Delta V$:

$$N[n(\vec{r})] = \int n(\vec{r}) d^3\vec{r} \tag{2.13}$$

2.3 The von Weizs$\ddot{a}$cker Functional (vW)

In the search for improved TF kinetic energy functional, von Weizs$\ddot{a}$cker modified the plane wave function used by Thomas-Fermi to the from;

$$(1 + \vec{a}.\vec{r})e^{i\vec{k}.\vec{r}} \tag{2.14}$$

where $\vec{a}$ is a constant vector and $\vec{k}$ is a local wave vector[4]. The result was the von Weizs$\ddot{a}$cker correction to the TF kinetic energy [6]. Although the von Weizs$\ddot{a}$cker functional can be written in different form, the most common in literature is[11, 9]:

$$T_{vW}[n(\vec{r})] = \frac{1}{8} \int \frac{|\nabla n(\vec{r})|^2}{n(\vec{r})} d^3\vec{r} \tag{2.15}$$

A way of improving the Thomas-Fermi functional is to introduce terms that depend on the local gradient of the density and few other higher derivatives of the density in series expansion. The new von Weizs$\ddot{a}$cker functional has a factor λ. The total kinetic energy functional is then given as:

$$T_{TF_\lambda vW}[n(\vec{r})] = T_{TF}[n(\vec{r})] + \lambda T_{vW}[n(\vec{r})] \tag{2.16}$$

The parameter λ is 1 in the original work of Weizs$\ddot{a}$cker, but was later shown to be $\frac{1}{9}$ from the gradient expansion approach[6]. The factor was introduced to make the correction consistent with the limit of small moments in the linear response function of the free electron gas[26].

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[4] The dot product $\vec{a}.\vec{r}$ is suppose to takes care of the slowly varying electron densities over space

2.4 Conceptualization of Density Matrices

2.4.1 Electron Density

Simply put, the electron density is the number of electrons per unit volume in a given state. In terms of wave function $\Psi(\vec{x}) = \phi(\vec{r})\alpha(s)$, for a single one-electron system, the electron density, $n(\vec{x})$ is determined by the probability density function:

$$\hat{n}(\vec{x}) = |\Psi(\vec{x})|^2 \tag{2.17}$$

Thus, the electron probability density is given by

$$\hat{n}(\vec{x})d\vec{x} = |\Psi(\vec{x})|^2 d\vec{x} = |\phi(\vec{r})|^2|\alpha(s)|^2 d\vec{r}ds \tag{2.18}$$

That is, the electron density is the probability of finding an electron in an elemental spin-orbital volume $d\vec{x} = d\vec{r}ds$. It suffices to say here that the electron density is dependent only on the spatial coordinate $\vec{r}$. To obtain the electron probability in an orbital volume element $d\vec{x}$ without spin[14], we integrate over all the spins $\alpha(s)$, which integrates to unity, and obtain:

$$n(\vec{r})d\vec{r} = d\vec{r}\int |\phi(\vec{r})|^2|\alpha(s)|^2 ds = |\phi(\vec{r})|^2 d\vec{r} \quad\Longrightarrow\quad n(\vec{r}) = |\phi(\vec{r})|^2 \tag{2.19}$$

For an $N-$electron system in a state corresponding to the wave function, $\Psi(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N)$, the electron probability density is obtained by integrating over all the spin coordinates of all electrons and over all the spatial coordinates of all the electrons except one. However, since electrons are indistinguishable, the probability of finding any electron at a position $d\vec{r}_1$ is just N times the probability of finding one particular electron at that point[6].

$$n(\vec{r}_1) = N\int ... \int |\Psi(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N)|^2 ds_1 d\vec{x}_2 ... d\vec{x}_N \tag{2.20}$$

or in general,

$$n(\vec{r}_1) = N\int ... \int \Psi^*(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N)\Psi(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N) ds_1 d\vec{x}_2 ... d\vec{x}_N \tag{2.21}$$

The electron density discussed above is a one-particle probability density with the property of being a non-negative function of only three (not $3N$) variables x, y, z; which vanishes at infinity and integrates to the total number of electrons in the system.

$$i)\ \ n(\vec{r}) \geq 0 \qquad ii)\ \int n(\vec{r})d^3\vec{r} = N \tag{2.22}$$

In a nutshell, $n(\vec{r})$ determines the probability of finding any of the N electrons within the volume element $d\vec{r}$ but with arbitrary spin while the other $(N-1)$ electrons have arbitrary positions and spin in the state represented by $\Psi(\vec{x}_1, ..., \vec{x}_N)$ [16]

2.4.2 Pair Density: $n_2(1,2)$

One may ask, "is it possible to find the probabilities for different configurations or "clusters" of any number of particles?". This question is addressed as quoted below[16]:

> *The concept of electron density, which provides an answer to the question 'how likely is it to find one electron of arbitrary spin within a particular volume element while all other electrons may be anywhere, can now be extended to the probability of finding not one but a pair of electrons with spins $\alpha(s_1)$ and $\alpha(s_2)$ simultaneously within two volume elements $d\vec{r}_1$ and $d\vec{r}_2$ while the remaining electrons have arbitrary positions and spins.The quantity which contains this information is the pair density $\rho_2(\vec{x}_1,\vec{x}_2)$, which is defined as*
>
> $$\rho_2(\vec{x}_1,\vec{x}_2) = N(N-1)\int ... \int |\Psi(\vec{x}_1,\vec{x}_2,...,\vec{x}_N)|^2\, d\vec{x}_3 d\vec{x}_N.$$

More generally

$$\hat{n}_2(\vec{x}_1,\vec{x}_2) = N(N-1)\int ... \int \Psi^*(\vec{x}_1,\vec{x}_2,...,\vec{x}_N)\Psi(\vec{x}_1,\vec{x}_2,...,\vec{x}_N)d\vec{x}_3...d\vec{x}_N \tag{2.23}$$

determines the probability of any two electrons being found simultaneously at spin-orbital "points" $\vec{x}_1, \vec{x}_2$, while

$$n_2(\vec{r}_1,\vec{r}_2) = N(N-1)\int ... \int \Psi^*(\vec{x}_1,\vec{x}_2,...,\vec{x}_N)\Psi(\vec{x}_1,\vec{x}_2,...,\vec{x}_N)ds_1 ds_2 d\vec{x}_3...d\vec{x}_N \tag{2.24}$$

is the probability of finding them at orbital "points" $\vec{r}_1$ and $\vec{r}_2$ with any combination of spins (one up, one down; both up, both down)[14]. The pair (two electron) density has similar properties as the one electron density

$$i)\ n_2(\vec{r}_1,\vec{r}_2) \geq 0 \quad ii)\ n_2(\vec{r}_1,\vec{r}_2) = n_2(\vec{r}_2,\vec{r}_1) \quad iii)\ \int\int n_2(\vec{r}_1,\vec{r}_2)d^3\vec{r}_1 d^3\vec{r}_2 = N(N-1) \tag{2.25}$$

Since electrons are viewed as idealized mass points with no extended volume, there are possibilities that both electrons are simultaneously found in both volume element [12]. In such case, the pair density would reduce to the product of the individual probabilities of indistinguishable particles:

$$n_2(\vec{r}_1,\vec{r}_2) = \frac{N-1}{N} n(\vec{r}_1)n(\vec{r}_2) \tag{2.26}$$

$n(\vec{r}_1)$ is the probability that any of the $N-$electrons is at $\vec{r}_1$ while $\frac{N-1}{N}n(\vec{r}_2)$ is the probability that another electron is simultaneously at $\vec{r}_2$ since the particles are identical. Therefore, the probability is reduced by the factor $\frac{N-1}{N}$ because of Pauli exclusion principle. The two-particle function (pair density) tell us how the motions of two different electrons are "correlated" as a result of their interactions. Because electrons interact only in pairs, there is no need to consider distribution functions higher than the pair function $n_2(\vec{r}_1,\vec{r}_2)$ for orbital wave functions or, $\hat{n}_2(\vec{r}_1,\vec{r}_2)$ if spin-orbital properties are considered.

2.4.3 Reduced Density Matrix (RDM)

We learned from quantum mechanics that all information about a system is contained in, and can be extracted from its wave function. Equivalently, a system of N particles can be described by its N -body density matrix or density operator generally defined as[17];

$$\gamma_N(\vec{x}'_i, \cdots, \vec{x}'_N; \vec{x}_i, \cdots, \vec{x}_N) = \Psi^*_N(\vec{x}'_i, \cdots, \vec{x}'_N)\Psi_N(\vec{x}_i, \cdots, \vec{x}_N) \tag{2.27}$$

The primed factors are sets of independent quantities that can give a numerical value. If $\vec{x}_i = \vec{x}'_i \ \forall \ i$, we obtain a diagonal element of the matrix. Because nature provides us with systems constituting of fermions that can be described with two-particle interactions only, we will only use the first and the second order of eq.(2.27)

Beside that electrons are fermions and have antisymmetric wave function, they are charged particles and interact via Coulomb repulsion; they try to stay away from each other as much as possible. These properties influence the pair density and reduce it to what is in general known as Reduced Density Matrix (*RDM*).

The *Nth* order density matrix for a pure state of an N-electron system is given by the probability function; and can be defined in terms of the reduced density matrix of order p by the expression[15, 14, 13]:

$$\begin{aligned}&\gamma_p(\vec{x}'_1, ..., \vec{x}'_p; \vec{x}_1, ..., \vec{x}_P)\\ &\quad= \begin{pmatrix} N \\ p \end{pmatrix} \int ... \int \gamma_N(\vec{x}'_1, ..., \vec{x}'_p, \vec{x}_{p+1}, ..., \vec{x}_N; \vec{x}_1, ..., \vec{x}_p, ..., \vec{x}_N) d\vec{x}_{p+1}, ..., d\vec{x}_N\end{aligned} \tag{2.28}$$

$\begin{pmatrix} N \\ p \end{pmatrix}$ is a binomial coefficient. In addition to electrons interacting in pairs, the electronic Hamiltonian operators consist of one electron and two electron terms, i.e, operators that involve the coordinate of one and two electrons only. Therefore, to compute the energy, the knowledge of two-particle probability density is sufficient. In particular, we have for the first and second order reduced matrices as:

$$\gamma_1(\vec{x}'_1; \vec{x}_1) = N \int ... \int \Psi^*(\vec{x}'_1 \vec{x}_2 ... \vec{x}_N)\Psi(\vec{x}_1 \vec{x}_2 ... \vec{x}_N) d\vec{x}_2 ... d\vec{x}_N \tag{2.29}$$

$$\gamma_2(\vec{x}'_1 \vec{x}'_2; \vec{x}_1 \vec{x}_2) = \frac{N(N-1)}{2} \int ... \int \Psi^*(\vec{x}'_1 \vec{x}'_2 \vec{x}_3 ... \vec{x}_N)\Psi(\vec{x}_1 \vec{x}_2 \vec{x}_3 ... \vec{x}_N) d\vec{x}_3 ... d\vec{x}_N \tag{2.30}$$

The *RDM* has the property of its trace normalizing to the number of electrons pair(s). So eqs (2.29) and (2.30) yield:

$$\mathbf{Tr}\ \gamma_1(\vec{x}'_1; \vec{x}_1) = \int \gamma_1(\vec{x}_1, \vec{x}_1) d\vec{x}_1 = N \tag{2.31}$$

$$\mathbf{Tr}\ \gamma_2(\vec{x}'_1, \vec{x}'_2; \vec{x}_1 \vec{x}_2) = \int\int \gamma_2(\vec{x}_1, \vec{x}_2; \vec{x}_1 \vec{x}_2) d\vec{x}_1 d\vec{x}_2 = \frac{N(N-1)}{2} \tag{2.32}$$

CHAPTER 3

Calculation of Corrections for KEDF of closed shell systems

3.1 Kinetic Energy Expectation Value

The Hamiltonian operator contains one- and two-particle terms. The former (one-particle term) consists of the kinetic energy and the electron-nuclear interaction energy, while the latter is the electron-electron Coulomb interaction. We consider the expectation value $T[\Psi]$ of the kinetic energy operator

$$\hat{T} = -\frac{1}{2}\sum_{i=1}^{N} {\nabla_i}^2 \tag{3.1}$$

with respect to the wave function ϕ which is a set of normalized antisymmetric N-particle wave function given by the Slater determinant

$$\Psi(\vec{x}) = (N!)^{-\frac{1}{2}} det\Big[\phi_1(\vec{x}_1)\phi_2(\vec{x}_2)...\phi_N(\vec{x}_N)\Big].$$

The kinetic energy expectation value is

$$T = \langle\Psi(\vec{x})|\hat{T}|\Psi(\vec{x})\rangle = \int \Psi^*(\vec{x})\hat{T}(\vec{x})\Psi(\vec{x})d\vec{x} = \int \Big[\hat{T}(\vec{x})\Psi^*(\vec{x}')\Psi(\vec{x})\Big]_{\vec{x}'=\vec{x}} d\vec{x} \tag{3.2}$$

We see that $\hat{T}$ works on the functions of $\vec{x}$ only, and we change the name of the variables in $\Psi^*(\vec{x})$ from $\vec{x}$ to $\vec{x}'$ to protect them from the effect of $\hat{T}$[14]. It implies that the primed coordinates are changed to unprimed ones after the $\hat{T}$ operates on $\Psi(\vec{x})$, then follows the integration. Now, let us compute

$$\Psi^*(\vec{x}')\Psi(\vec{x}) = \frac{1}{N!} det\Big[\phi_1^*(\vec{x}_1')\phi_2^*(\vec{x}_2')...\phi_N^*(\vec{x}_N')\Big] det\Big[\phi_1(\vec{x}_1)\phi_2(\vec{x}_2)...\phi_N(\vec{x}_N)\Big] =$$

$$\frac{1}{N!}\left|\{\phi_1^*(\vec{x}'_1)\phi_2^*(\vec{x}'_2)...\phi_N^*(\vec{x}'_N)\}\{\phi_1(\vec{x}_1)\phi_2(\vec{x}_2)...\phi_N(\vec{x}_N)\}\right| = \gamma_N(\vec{x}'_1,\cdots,\vec{x}'_N;\vec{x}_1,\cdots,\vec{x}_N) =$$

$$\frac{1}{N!}\left\|\begin{matrix} \phi_1^*(\vec{x}'_1)\phi_1(\vec{x}_1)+\cdots+\phi_N^*(\vec{x}'_1)\phi_1(\vec{x}_N) & \phi_1^*(\vec{x}'_1)\phi_2(\vec{x}_1)+\cdots+\phi_N^*(\vec{x}'_1)\phi_2(\vec{x}_N) & \phi_1^*(\vec{x}'_1)\phi_N(\vec{x}_1)+\cdots+\phi_N^*(\vec{x}'_1)\phi_N(\vec{x}_N) \\ \phi_1^*(\vec{x}'_2)\phi_1(\vec{x}_1)+\cdots+\phi_N^*(\vec{x}'_2)\phi_1(\vec{x}_N) & \phi_1^*(\vec{x}'_2)\phi_2(\vec{x}_1)+\cdots+\phi_N^*(\vec{x}'_2)\phi_2(\vec{x}_N) & \phi_1^*(\vec{x}'_2)\phi_N(\vec{x}_1)+\cdots+\phi_N^*(\vec{x}'_2)\phi_N(\vec{x}_N) \\ \vdots & \vdots & \vdots \\ \phi_1^*(\vec{x}'_N)\phi_1(\vec{x}_1)+\cdots+\phi_N^*(\vec{x}'_N)\phi_1(\vec{x}_N) & \phi_1^*(\vec{x}'_N)\phi_2(\vec{x}_1)+\cdots+\phi_N^*(\vec{x}'_N)\phi_2(\vec{x}_N) & \phi_1^*(\vec{x}'_N)\phi_N(\vec{x}_1)+\cdots+\phi_N^*(\vec{x}'_N)\phi_N(\vec{x}_N) \end{matrix}\right\| \tag{3.3}$$

Taken that besides being normalized the set of one electron wave functions in eq.(3.3) is orthogonal, i.e orthonormalized, we observe that for $N = 1, 2, \cdots$, the determinant equals the corresponding order of the reduced density matrix each determined by the the first order reduced density function $\gamma_1(\vec{x};\vec{x}')$. Expressing the two or many electrons density in terms of one electron density is peculiar to the single Slater determinant approximation[14], For example,N=2,

$$\gamma_2(\vec{x}_1,\vec{x}_2;\vec{x}'_1,\vec{x}'_2) = \frac{1}{2}\begin{vmatrix} \gamma_1(\vec{x}_1;\vec{x}'_1) & \gamma_1(\vec{x}_1;\vec{x}'_2) \\ \gamma_1(\vec{x}_2;\vec{x}'_1) & \gamma_1(\vec{x}_2;\vec{x}'_2) \end{vmatrix} \tag{3.4}$$

implies that every thing in the determinant is determined through $\gamma_1(\vec{x},\vec{x}')$ often called the Fock-Dirac density matrix given by[13, 14, 15, 17]:

$$\gamma_1(\vec{x};\vec{x}') = \sum_{i=1}^{Noccupied} \phi_i(\vec{x})\phi_i^*(\vec{x}') \tag{3.5}$$

We have been writing $\phi_i(\vec{x}_i)$ to mean the spin-orbital, that is, $\phi_i(\vec{x}_i) = \phi_i(\vec{r}_i, s_i)$ and similarly $\gamma_i(\vec{x}_i;\vec{x}'_i) = \gamma_i(\vec{r}_i, s_i;\vec{r}'_i, s'_i)$. Since the kinetic energy operator $\hat{T}$ is spin independent and integral over all spin is unity, we can now write, dropping the subscripts

$$\gamma(\vec{x},\vec{x}') \equiv \gamma(\vec{r};\vec{r}') = \sum_{i=1}^{Noccupied} \phi_i(\vec{r})\phi_i^*(\vec{r}') \tag{3.6}$$

Eq(3.6) has a symmetric property, i.e $\gamma(\vec{r};\vec{r}') = \gamma(\vec{r}';\vec{r})$ and is positive. Now, we can evaluate the determinant directly in terms of reduced density matrix defined by eq (2.27). The kinetic energy operates is one-electron operator therefore the determinant is approximated to the first order reduced density matrix of the orbital coordinate[13]:

$$\Psi(\vec{r}')\Psi(\vec{r}) = \frac{1}{N!}\left|\{\phi_1^*(\vec{x}'_1)\phi_2^*(\vec{x}'_2)...\phi_N^*(\vec{x}'_N)\}\{\phi_1(\vec{x}_1)\phi_2(\vec{x}_2)...\phi_N(\vec{x}_N)\}\right| \approxeq \gamma(\vec{r}'_1;\vec{r}_1) \tag{3.7}$$

Therefore, eq.(3.2) becomes[5]:

$$T = \int d^3\vec{r}\hat{T}\gamma(\vec{r};\vec{r}')\Big|_{\vec{r}=\vec{r}'} = \int -\frac{1}{2}\nabla^2_{\vec{r}}\gamma(\vec{r};\vec{r}')\Big|_{\vec{r}=\vec{r}'} d^3\vec{r} = \int t_o[\gamma(\vec{r},\vec{r}')]d^3\vec{r} \tag{3.8}$$

---

[5] $\vec{r} = \vec{r}'$ is applied after the operator operates on $\gamma(\vec{r};\vec{r}')$ with respect to $\vec{r}$,

$$t_o[\gamma(\vec{r},\vec{r}')] = -\frac{1}{2}\nabla^2_{\vec{r}}\gamma(\vec{r};\vec{r}')|_{\vec{r}=\vec{r}'} \tag{3.9}$$

Also, T can be expressed in a different form as follows:

$$T = \sum_{i=1}^{Noccupied} \int -\frac{1}{2}\phi_i^*(\vec{r}')\nabla^2\phi_i(\vec{r})d^3\vec{r} = \sum_{i=1}^{Noccupied} \int -\frac{1}{2}\Big[\nabla\cdot\Big(\phi_i^*(\vec{r}')\nabla\phi_i(\vec{r})\Big) - \nabla\phi_i^*(\vec{r}')\nabla\phi_i(\vec{r})\Big]d^3\vec{r}$$

$$= \underbrace{\sum_{i=1}^{Noccupied} -\frac{1}{2}\int \nabla\cdot\Big(\phi_i^*(\vec{r}')\nabla\phi_i(\vec{r})\Big)d^3\vec{r}}_{=0,\ \forall\ \vec{r}\ \in\ \Re^3\ \longrightarrow\infty\ \text{by Gauss' theorem}} + \sum_{i=1}^{Noccupied} \int \frac{1}{2}\nabla\phi_i^*(\vec{r}')\nabla\phi_i(\vec{r})d^3\vec{r}$$

$$= \sum_{i=1}^{Noccupied} \int \frac{1}{2}\nabla_{\vec{r}}\nabla_{\vec{r}'}\phi_i^*(\vec{r}')\phi_i(\vec{r})d^3\vec{r} = \int \frac{1}{2}\nabla_{\vec{r}}\nabla_{\vec{r}'}\gamma(\vec{r};\vec{r}')|_{\vec{r}'=\vec{r}}d^3\vec{r} = \int t[\gamma(\vec{r};\vec{r}')]d^3\vec{r} \tag{3.10}$$

where,

$$t[\gamma(\vec{r};\vec{r}')] = \frac{1}{2}\nabla_{\vec{r}}\nabla_{\vec{r}'}\gamma(\vec{r};\vec{r}')|_{\vec{r}'=\vec{r}} \tag{3.11}$$

3.2 Expression for First Order RDM

The motion of a pair of electrons in an N-electron system is not independent. They are correlated through an antisymmetric wave function that must be chosen so that Pauli exclusion principle is satisfied, and through the $\frac{1}{r_{12}}$ term controlling the electron-electron repulsion in the Hamiltonian[12]. The correlation is not a real physical quantity as it reflects a given level of approximation chosen for quantum mechanical description of a system. The approximation is based on the choice of reference state where by definition, all correlation is absent.

Definition 3.2.1. *The reference state or level of description of a system of interacting particles is basically defined as that where particles are independent in a statistical sense. [13].*

In such a case, for example, correlation could be measured as the difference between the exact pair density $n_2(\vec{r}_1,\vec{r}_2)$, the diagonal part of the reduced two-particle density operator, and the product of the exact one-electron densities for particles 1 and 2, i.e., $n(\vec{r}_1)n(\vec{r}_2)$ the product of the reduced one-particle densities at points $\vec{r}_1$ and $\vec{r}_2$[14, 27, 28].

From eq.(3.4), the two-particle (second order) reduced density matrix for spin-less orbitals is:

$$2\gamma_2(\vec{r}_1,\vec{r}_2;\vec{r}_1',\vec{r}_2') = \gamma_1(\vec{r}_1,\vec{r}_1')\gamma_1(\vec{r}_2,\vec{r}_2') - \gamma_1(\vec{r}_1,\vec{r}_2')\gamma_1(\vec{r}_2,\vec{r}_1') \tag{3.12}$$

By comparison of eqs.(2.22iii and 2.31) and eqs.(2.25iii and 2.32) assuming spin-less orbitals, we obtain, respectively:

$$\gamma_1(\vec{r}_i, \vec{r}_i) = n(\vec{r}_i) \text{ and } 2\gamma_2(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2) = n_2(\vec{r}_1, \vec{r}_2) \tag{3.13}$$

With the symmetric property of $\gamma(\vec{r}, \vec{r}')$, we substitute eq(3.13) appropriately into (3.12) and obtain[6]:

$$n(\vec{r}, \vec{r}') = n(\vec{r})n(\vec{r}') - \gamma(\vec{r}, \vec{r}')^2 \tag{3.14}$$

For systems with definite spins, the electron density and the pair density may be written in their spin coordinates as[13, 14]

$$n(\vec{r}) = n_\uparrow(\vec{r}) + n_\downarrow(\vec{r}) \tag{3.15}$$

$$n(\vec{r}, \vec{r}') = n_{\uparrow\uparrow}(\vec{r}, \vec{r}') + n_{\uparrow\downarrow}(\vec{r}, \vec{r}') + n_{\downarrow\uparrow}(\vec{r}, \vec{r}') + n_{\downarrow\downarrow}(\vec{r}, \vec{r}') \tag{3.16}$$

That is, for instance, $n_{\uparrow\uparrow}(\vec{r}, \vec{r}')$ gives the probability of finding electrons with spins-up at points $\vec{r}$ and $\vec{r}'$ simultaneously. For a correlated electronic motion, the pair density is defined in terms of the electron density and the correlation factor $g(\vec{r}, \vec{r}')$ between parallel spin electrons, e.g spin-ups ($g_{\uparrow\uparrow}(\vec{r}, \vec{r}')$) and anti-parallel spin electrons ($g_{\uparrow\downarrow}(\vec{r}, \vec{r}')$)[6, 13, 14, 29, 30]:

$$n_{\uparrow\uparrow}(\vec{r}, \vec{r}') = n_\uparrow(\vec{r})n_\uparrow(\vec{r}')\Big(1 + g_{\uparrow\uparrow}(\vec{r}, \vec{r}')\Big) \tag{3.17}$$

$$n_{\uparrow\downarrow}(\vec{r}, \vec{r}') = n_\uparrow(\vec{r})n_\downarrow(\vec{r}')\Big(1 + g_{\uparrow\downarrow}(\vec{r}, \vec{r}')\Big) \tag{3.18}$$

We note that the correlation between electrons of different spins is zero in the Hartree-Fock level where it is assumed that

$$g_{\uparrow\downarrow}(\vec{r}, \vec{r}') = g_{\downarrow\uparrow}(\vec{r}, \vec{r}') = 0 \tag{3.19}$$

With eqs.(3.17),(3.18) and (3.19), eq.(3.14) becomes:

$$n(\vec{r}, \vec{r}') = n_\uparrow(\vec{r})n_\uparrow(\vec{r}') + n_\downarrow(\vec{r})n_\downarrow(\vec{r}') + n_\uparrow(\vec{r})n_\uparrow(\vec{r}')g_{\uparrow\uparrow}(\vec{r}, \vec{r}') + n_\downarrow(\vec{r})n_\downarrow(\vec{r}')g_{\downarrow\downarrow}(\vec{r}, \vec{r}')$$

$$= n(\vec{r})n(\vec{r}') + n(\vec{r})n(\vec{r}')g(\vec{r}, \vec{r}') = n(\vec{r})n(\vec{r}')\Big(1 + g(\vec{r}, \vec{r}')\Big) \tag{3.20}$$

Comparison of eqs.(3.14) and (3.20) yields:

$$\gamma(\vec{r}, \vec{r}') = \sqrt{n(\vec{r})n(\vec{r}')}\sqrt{-g(\vec{r}, \vec{r}')} = \sqrt{n(\vec{r})n(\vec{r}')}\Gamma(\vec{r}, \vec{r}') \tag{3.21}$$

---

[6] We will drop all subscripts and use unprimed and primed $\vec{r}$ to mean positions 1 and 2 respectively, and also keep in mind that $n(\vec{r}, \vec{r}')$ is pair density. $i = 1, 2$

$$\Gamma(\vec{r},\vec{r}') = \sqrt{-g(\vec{r},\vec{r}')} \tag{3.22}$$

We can show that $\Gamma(\vec{r},\vec{r}')|_{\vec{r}=\vec{r}'}$ is positive and equals one. It is defined as the statistical correlation term. Recall that the pair density is the probability of simultaneously finding two electrons at points $\vec{r}$ and $\vec{r}'$; and by Pauli exclusion principle, $n(\vec{r},\vec{r}')|_{\vec{r}=\vec{r}'} = 0$; therefore from eq.(3.20) we have[7]:

$$g(\vec{r},\vec{r}')|_{\vec{r}=\vec{r}'} = -1 \implies \text{from eq(3.22) that: } \Gamma(\vec{r},\vec{r}')|_{\vec{r}=\vec{r}'} = 1 \tag{3.23}$$

3.3 The Kinetic Energy Density

Equations (3.9), and (3.11) are the kinetic energy density functionals. They are related by or differ by:

$$t[n(\vec{r})] - t_o[n(\vec{r})] = \frac{1}{4}\nabla^2 n(\vec{r}) \tag{3.24}$$

$t_{div}[n(\vec{r})] = \frac{1}{4}\nabla^2 n(\vec{r})$ is a divergence term whose contribution to the total kinetic energy varnishes upon integration over all space. While the two kinetic energy densities integrate to the same correct total kinetic energy with the difference existing between them, $t[n]$ is a better well behaved function than $t_o[n]$, in that: it is finite, non-negative, continuous and varies smoothly for all points $\vec{r} \in \Re^3$, except for internuclear region for molecules[31, 30]. Therefore, substituting eq.(3.21) into eq.(3.11), and applying eq.(3.23) after performing the operations, one obtains:

$$t[n(\vec{r})] = \frac{|\nabla n(\vec{r})|^2}{8n(\vec{r})} + \frac{n(\vec{r})}{2}\nabla_{\vec{r}}\cdot\nabla_{\vec{r}'}\Gamma(\vec{r},\vec{r}')\Big|_{\vec{r}=\vec{r}'} + \frac{\nabla n(\vec{r})}{4}\underbrace{\left[\nabla_{\vec{r}}\Gamma(\vec{r},\vec{r}')\Big|_{\vec{r}=\vec{r}'} + \nabla_{\vec{r}'}\Gamma(\vec{r},\vec{r}')\Big|_{\vec{r}'=\vec{r}}\right]}_{=0} \tag{3.25}$$

To show that the last term in eq.(3.25) is zero, consider eqs (3.21) and (3.6). This implies that:

$$\nabla_{\vec{r}}\gamma(\vec{r},\vec{r}')\Big|_{\vec{r}=\vec{r}'} = \frac{\nabla n(\vec{r})}{2} + n(\vec{r})\nabla_{\vec{r}}\Gamma(\vec{r},\vec{r}')\Big|_{\vec{r}=\vec{r}'} = \sum_{i=1}^{Nocc.}\phi_i^*(\vec{r})\nabla_{\vec{r}}\phi_i(\vec{r}) \tag{3.26}$$

Similarly,

$$\nabla_{\vec{r}'}\gamma(\vec{r},\vec{r}')\Big|_{\vec{r}'=\vec{r}} = \frac{\nabla n(\vec{r})}{2} + n(\vec{r})\nabla_{\vec{r}'}\Gamma(\vec{r},\vec{r}')\Big|_{\vec{r}'=\vec{r}} = \sum_{i=1}^{Nocc.}\phi_i(\vec{r})\nabla_{\vec{r}}\phi_i^*(\vec{r}) \tag{3.27}$$

Addition of eqs.(3.26) and (3.27) results in:

$$\nabla n(\vec{r}) + \left[\nabla_{\vec{r}}\Gamma(\vec{r},\vec{r}')\Big|_{\vec{r}=\vec{r}'} + \nabla_{\vec{r}'}\Gamma(\vec{r},\vec{r}')\Big|_{\vec{r}'=\vec{r}}\right] = \sum_{i=1}^{Nocc.}\phi_i^*(\vec{r})\nabla_{\vec{r}}\phi_i(\vec{r}) + \sum_{i=1}^{Nocc.}\phi_i(\vec{r})\nabla_{\vec{r}}\phi_i^*(\vec{r}) \tag{3.28}$$

---

[7] Any further consideration takes us into discussing correlation holes

We note that

$$n(\vec{r}) = \gamma(\vec{r}, \vec{r'})\Big|_{\vec{r}=\vec{r'}} = \sum_{i=1}^{Nocc.} \phi_i(\vec{r})\phi_i^*(\vec{r})$$

$$\implies \quad \nabla n(\vec{r}) = \sum_{i=1}^{Nocc.} \phi_i^*(\vec{r})\nabla_{\vec{r}}\phi_i(\vec{r}) + \sum_{i=1}^{Nocc.} \phi_i(\vec{r})\nabla_{\vec{r}}\phi_i^*(\vec{r}) \tag{3.29}$$

Therefore putting eq.(3.29) into eq.(3.28) we have that:

$$\left[\nabla_{\vec{r}}\Gamma(\vec{r}, \vec{r'})\Big|_{\vec{r}=\vec{r'}} + \nabla_{\vec{r'}}\Gamma(\vec{r}, \vec{r'})\Big|_{\vec{r'}=\vec{r}}\right] = 0 \tag{3.30}$$

Hence, eq.(3.25) becomes:

$$t[n(\vec{r})] = \frac{|\nabla n(\vec{r})|^2}{8n(\vec{r})} + \frac{n(\vec{r})}{2}\nabla_{\vec{r}} \cdot \nabla_{\vec{r'}}\Gamma(\vec{r}, \vec{r'})\Big|_{\vec{r}=\vec{r'}} \tag{3.31}$$

Putting eq.(3.24) into eq.(3.31) gives:

$$t_0[n(\vec{r})] = \frac{|\nabla n(\vec{r})|^2}{8n(\vec{r})} - \frac{1}{4}\nabla^2 n(\vec{r}) + \frac{n(\vec{r})}{2}B(r) \tag{3.32}$$

$$B(r) = \nabla_{\vec{r}} \cdot \nabla_{\vec{r'}}\Gamma(\vec{r}, \vec{r'})\Big|_{\vec{r}=\vec{r'}} \tag{3.33}$$

At this juncture, we revert to computing the various terms in eq.(3.32) and then determine the correction for the kinetic energy density of various closed shell systems.

3.4 Kinetic Energy Corrections for some closed shell Systems

The correction for the kinetic energy is the last term of eq.(3.32) which we solved computationally for some closed shell atoms.

$$t_{correction}[n(\vec{r})] = \frac{n(\vec{r})}{2}B(r) = t_0[n(\vec{r})] - \frac{|\nabla n(\vec{r})|^2}{8n(\vec{r})} + \frac{1}{4}\nabla^2 n(\vec{r}) \tag{3.34}$$

The total energies are calculated by method of numerical integration and results are reported in table 3.1. The result obtained for the helium atom is exactly in agreement with the Hartree-Fock. The Weizsäcker term $\mathrm{T}_{vW}[n(\vec{r})]$ gives the exact kinetic energy of two electron (helium) system. This result provides a check for the correctness of the numerical code used in evaluating the kinetic energy density $T_0[n(\vec{r})]$, the von-Weizsäcker term $\mathrm{T}_{vW}[n(\vec{r})]$ and the divergent term $T_{div}[n(\vec{r})] = \frac{\nabla^2 n(\vec{r})}{4}$. The code is found valid because it gives zero for the

Atoms	Z	HF	T_0	T_{vW}	T_{div}	T_{exact}	Exp	$T_{exact} - T_{vW}$
He	2	2.860	2.860	2.860	0.000	2.860	2.904	0.000
Be	4	14.567	14.562	13.690	0.020	14.582	14.667	0.892
Ne	10	128.412	126.724	90.748	1.677	128.401	128.928	37.653
Mg	12	199.487	191.834	132.532	7.648	199.482	200.042	66.960
Ar	18	527.784	502.059	308.412	24.624	526.683	527.549	218.271
Ca	20	676.758	626.788	383.306	49.402	676.190	—	292.883

Table 3.1: Correction energy for some closed shell atoms in Hartree units.

1. The Hartree-Fock energies calculated directly from the PyQuante package are in good agreement with HF calculations by Clementi and Roetti (1974)[34]
2. The experimental values are as calculated by Veillard and Clementi (1968) and referenced in Eugene[13]

correction as expected for the two electron system.
The exact kinetic energy value is computed according to equation (3.24) or (3.31), that is:

$$T_{exact}[n(\vec{r})] = T_{vW}[n(\vec{r})] + T_{correction}[n(\vec{r})] = T_{div}[n(\vec{r})] + T_0[n(\vec{r})] \tag{3.35}$$

The total kinetic energy T_{exact} for the other closed shell atoms are closer to the Hartree-Fock energy and are comparable to the experimental results with a relative errors as shown in table 3.1. The results could be improved by employing more accurate numerical integration methods such as trapezoidal or Simpson's rules in lieu of the triangular rule employed here.

CHAPTER 4

Development of a Correction term and Discussion of Results

4.1 Development of a correction term

We record here attempts we made towards developing a correction term for the kinetic energy density. Solving eq.(3.34) one obtains the correction term as:

$$\frac{n(\vec{r})B(\vec{r})}{2} = \sum_{i,j=1}^{Nocc} D_{ij} \nabla\phi_i \cdot \nabla\phi_j - \frac{|\nabla n(\vec{r})|^2}{8n(\vec{r})} \tag{4.1}$$

Computationally eq.(4.1) can be evaluated and the statistical correlation term is determined from it numerically. However, even though this rightly gives the correction to the total energies of the trial closed shell systems, it is not yet our target because we have just represented the correction term and of-course the statistical correlation term in a "hybrid" of orbitals and density terms.

Considering eq.(3.32), for LDA, the von-Weizsäcker and the divergent terms are zero, that is the gradient of density; since density is assumed constant (the same every where) in the system; is zero. Again, following the LDA approximation, there should not be correction for the kinetic energy of a system such as Helium atom, i.e t_{corr} should be zero. But if t_{vW}, t_{div} and $\frac{nB}{2}$ are each zero then, t_0 is zero and this is a contradiction for the kinetic energy of the electronic motion. Nevertheless, a numerical result tabulated in table (3.1) as obtained from coding in Pyquante package shows for the He atom that T_{div} is to three decimal places (3 d.p.) zero; T_{corr} is much insignificant (order of 10^{-17}, therefore it is zero) and T_0 is to 3 d.p. equal to t_{vW}.

But the simplest improvement that can be done to LDA is to correct for the inhomogeneities of atomic electron density. This can be done by adding to the LDA, corrections that depend on the local gradient of the electron density. In this way, the correct treatment of the shell structure may be achieved[22, 24, 25]. Also, at a lowest limit of LDA (i.e. as we come down to UEG), the kinetic energy of the system is given by the Thomas-Fermi energy. Thus, gradient expansions, which offer systematic corrections to LDA for electron densities that vary slowly over space, is employed here. Hence we write the correction term as:

$$t_{ucorr} = \frac{nB}{2} = C_0 n^{\frac{5}{3}} \Big[1 + C_1 |\nabla n|^p n^q\Big] \tag{4.2}$$

$C_0 n^{\frac{5}{3}} = t_{TF}$ is the Thomas-Fermi kinetic energy density for a uniform electron gas, C_1 is a numerical constant which we will determine, $C_0 = 2.871234$ is given by eq. (2.12), p and q are index powers. Dimensionally, t_{corr} and t_{TF} each has a dimension of inverse length of order five, so $C_1 |\nabla n|^p n^q$ must be a dimensionless quantity. For this to be true, we have from the dimension of the product:

$$4p + 3q = 0 \Longrightarrow q = -\frac{4p}{3}$$

For first trial, we take $p = 2$ and then, $q = -\frac{8}{3}$, so that:

$$t_{ucorr} = C_0 n^{\frac{5}{3}} \Big[1 + C_1 \frac{|\nabla n|^2}{n n^{\frac{5}{3}}}\Big] = t_{TF} + C_0 C_1 \frac{|\nabla n|^2}{n} \tag{4.3}$$

Hence, we can generally written that:

$$t_0 = t_{vW} - t_{div} + t_{TF} + C_0 C_1 \frac{|\nabla n|^2}{n}$$

Integrating the equation above gives:

$$KE = T_{vW} + T_{TF} - (T_{div} \overset{?}{=} 0) + C_0 C_1 \int \frac{|\nabla n|^2}{n} d^3\vec{r} \tag{4.4}$$

T_{vW} is given by eq. (2.15) and $T_{div} = 0$ if $\vec{r}$ approaches ∞, i.e. the volume integral could be taken as surface integral and by Gauss or divergence theorem, T_{div} will be zero. Assuming $\vec{r}$ approaches infinity then, eq. (4.4) could be written as:

$$KE = T_{TF} + \left(\frac{1}{8} + C_0 C_1\right) \int \frac{|\nabla n|^2}{n} d^3\vec{r} \tag{4.5}$$

This could be compared with the gradient expansion:

$$KE = \int C_0 n^{\frac{5}{3}} d^3\vec{r} + \frac{1}{72} \int \frac{|\nabla n|^2}{n} d^3\vec{r}$$

truncated at the second term. But the accuracy when the series is truncated at zeroth- or second-order is poor by any contemporary standard[35]. More authentically, we solve for C_1 from eq. (4.4) but with $T_{div} \neq 0$ because from our computational calculations, the integral of t_{div} did not turn out to be zero. This may probably be that our largest $|\vec{r}|$ in the integration is not large enough for it to be a surface integral. Thus, we write from eq.(4.4):

$$A_0 C_1 = A_1 \Longrightarrow C_1 = \frac{A_1}{A_0} \tag{4.6}$$

$$A_1 = KE - T_{vW} - T_{TF} + T_{div} \text{ and } A_0 = C_0 \int \frac{|\nabla n|^2}{n} d^3\vec{r}$$

The result obtained computationally is recorded in Table (4.1):

Atoms	Z	A_1(Hartree)	A_0(Hartree)	C_1
He	2	0.000	0.000	0.000
Be	4	-12.211	314.451	-0.0387
Ne	10	-79.892	2084.475	-0.0383
Mg	12	-116.587	3044.253	-0.0383
Ar	18	-268.807	7084.195	-0.0379
Ca	20	-331.756	8804.497	-0.0377

Table 4.1: Values of C_1 for some closed shell atoms

Averaging C_1 over the number of contributing atoms, we write generally and hope that it works for any restricted closed shell atom:

$$C_1 \longrightarrow \langle C_1 \rangle = -0.03818 \tag{4.7}$$

We verify the correctness of eq.(4.7) using our numerical codes and obtain Table(4.2). The numerical code(s) used for these calculation is added as attachment at the last page of this document.

Atom	Z	T_{corr}(Hartree)	T_{ucorr}(Hartree)
Be	4	0.892	1.117
Ne	10	37.653	37.930
Mg	12	66.950	67.308
Ar	18	218.271	216.630
Ca	20	292.883	288.480

Table 4.2: Comparison of the correction to kinetic energy of trial systems computed using eqs. (3.34) and (4.3)

4.2 Discussion of Results

Fig.4.1 is the plot of density against position which shows that the density is a positive quantity. It also shows that the density varies slowly and decays as $\vec{r}$ increases; a behavior that is not accounted for by the LDA; but has maximum around the nucleus.

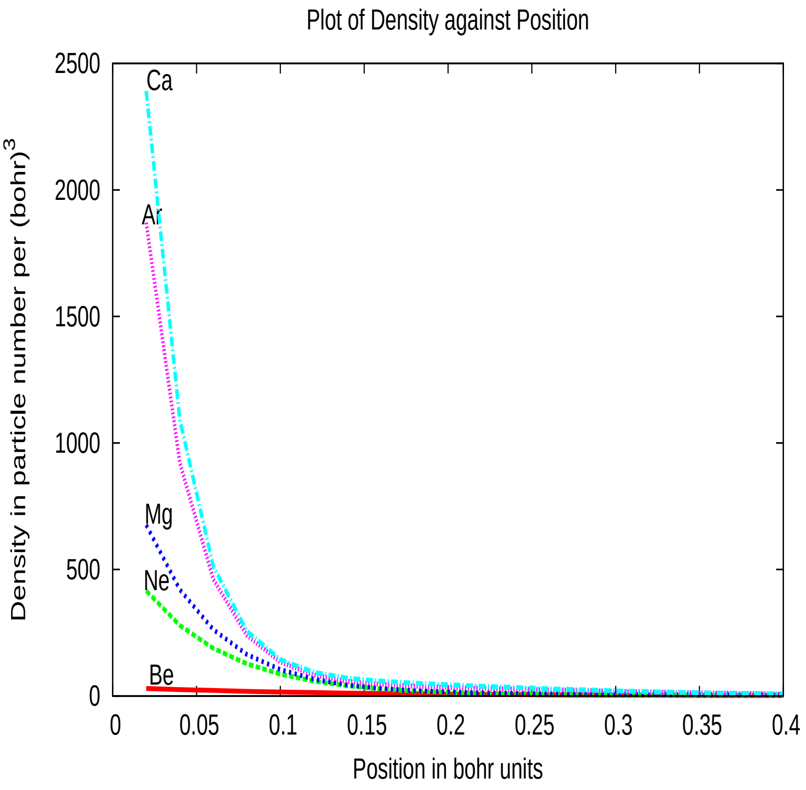

Figure 4.1: Graph of density versus position for some closed shell atoms

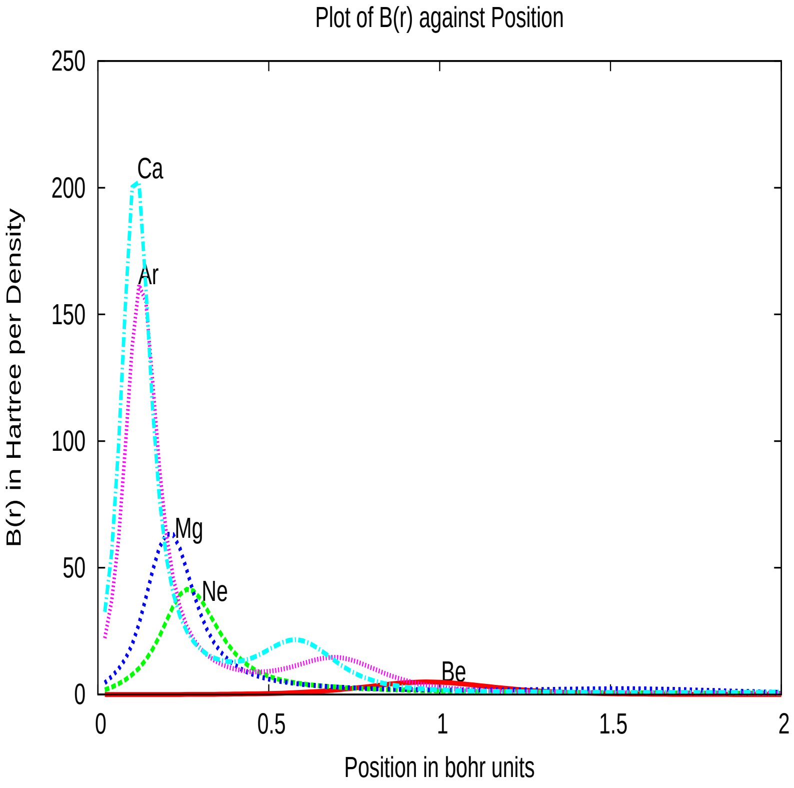

Figure 4.2: Graph of B(r) versus position for some closed shell atoms

Fig.4.2 is the plot of B(r) against position r. We noted from Fig.4.1 that the density does not die off abruptly but dies off slowly.

The correlation at these regions places difficulty in precisely determining how the density varies within the inter-shell region and with different electron positions; thus the LDA of von-Weizs$\ddot{a}$cker underestimates the density at these regions. Therefore, one may say that the correlation between electrons influences the electronic kinetic energy and is determined by the function $\Gamma(\vec{r}, \vec{r}')$ which essentially depends on the correlation effect between electrons.

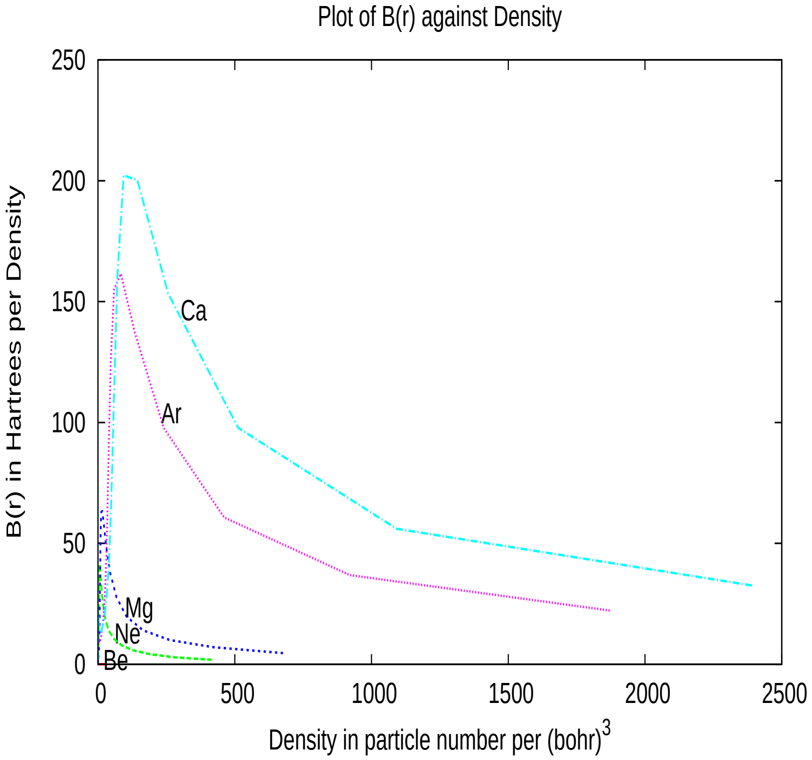

Figure 4.3: Graph of B(r) versus density for some closed shell atoms

From Fig.(4.3), we observe that the statistical correlation term B(r) does not have abrupt decay behavior with density and varies slowly in a non-linear rise and exponential decay trend. Its jointed rise and decay order perhaps depicts the correlation between the density function of two electrons.

The result shown in Table(4.2) is with a slight deviation, in agreement with the values of the correction to the kinetic energies of the closed shell atoms computed from eq.(3.34). Numerically, we will say this result is satisfactory and therefore, eq.(4.3) can be used as a functional for the correction term then when inverted gives an expression for the statistical correlation term.

4.3 Results of the Correction Terms

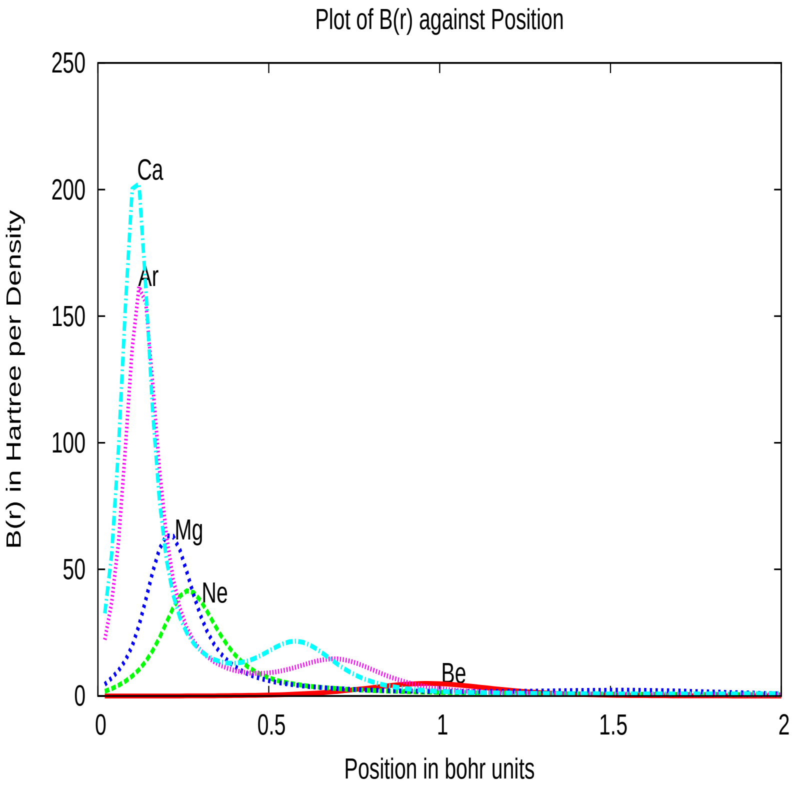

Figure 4.4: Plots of the statistical correlation functions against position for B(r) of eq.(3.34)

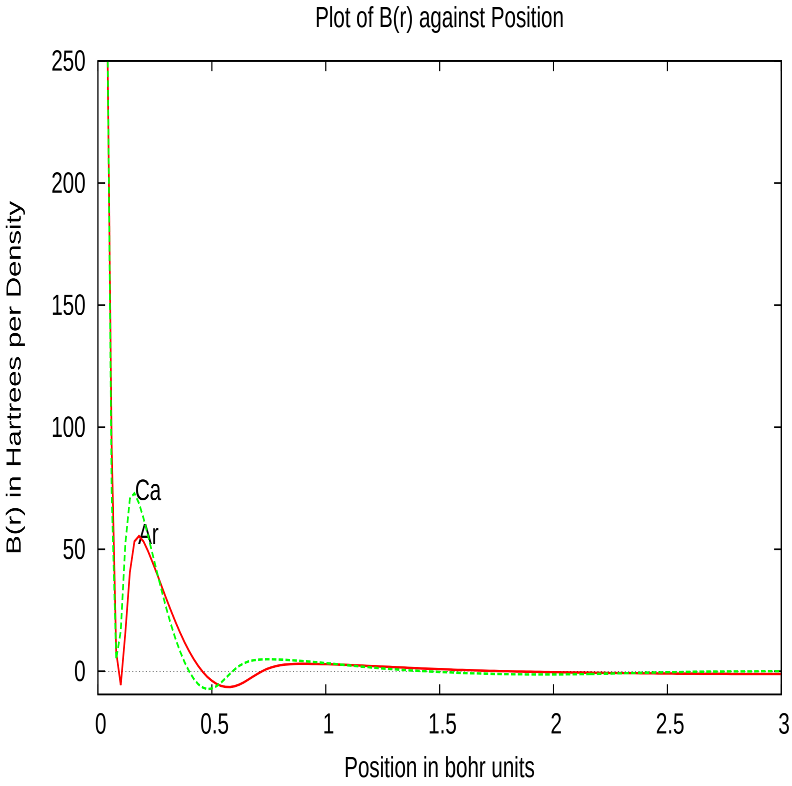

Figure 4.5: Plots of the statistical correlation functions against position for B(r) of eq.(4.3)

The graphs of Fig.(4.4) and Fig.(4.5) are comparable except that Fig.(4.5) predicts that B(r) can have negative values at some points. This contradiction is however an indication that t_{ucorr} is not completely adequate for describing the correction to the kinetic energy though it delivered almost the same result as t_{corr}.

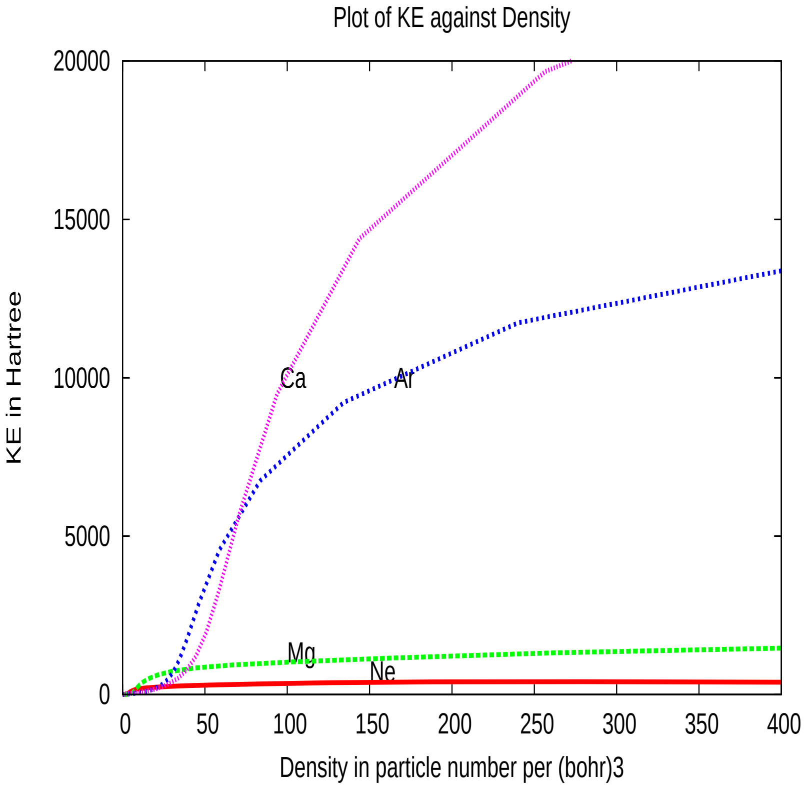

Figure 4.6: Plots of kinetic energy density terms against density for t_{corr}

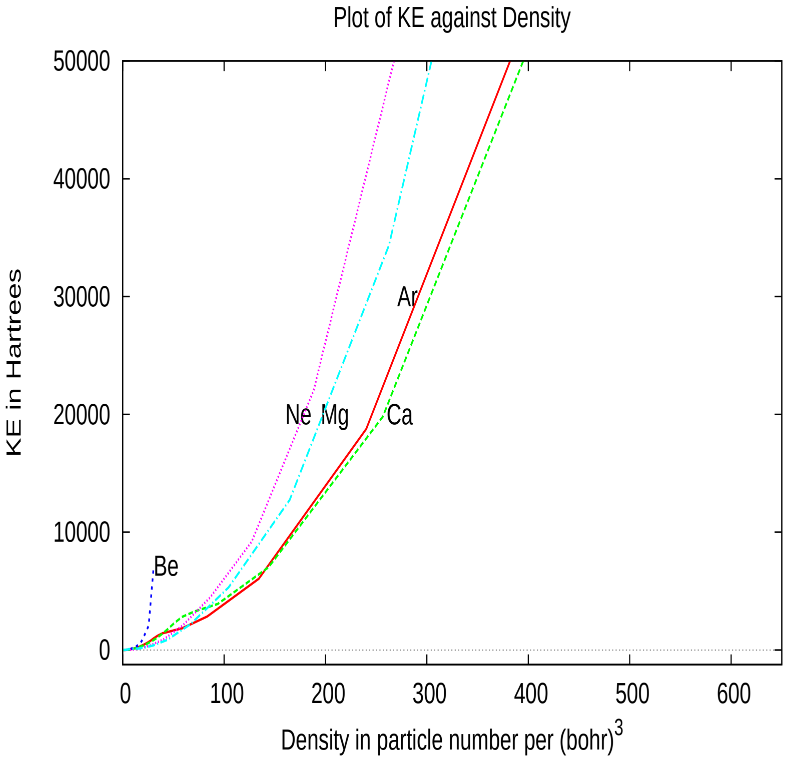

Figure 4.7: Plots of kinetic energy density terms against density for t_0

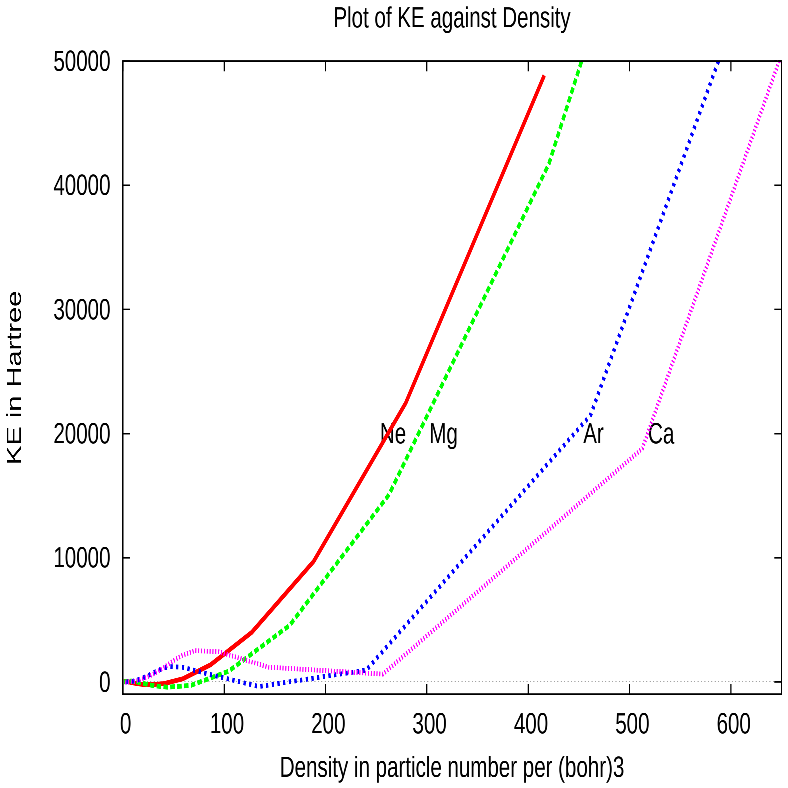

Figure 4.8: Plots of kinetic energy density terms against density for t_{ucorr}

Figures (4.6 and 4.8) are respectively, comparison of t_{corr} and t_{ucorr} with t_0 of Fig.(4.7). We observe that t_{ucorr} takes after t_0. However, this does not mean that t_{corr} is not correct, the three graphs have the same pattern when one zooms in on Fig.4.6.

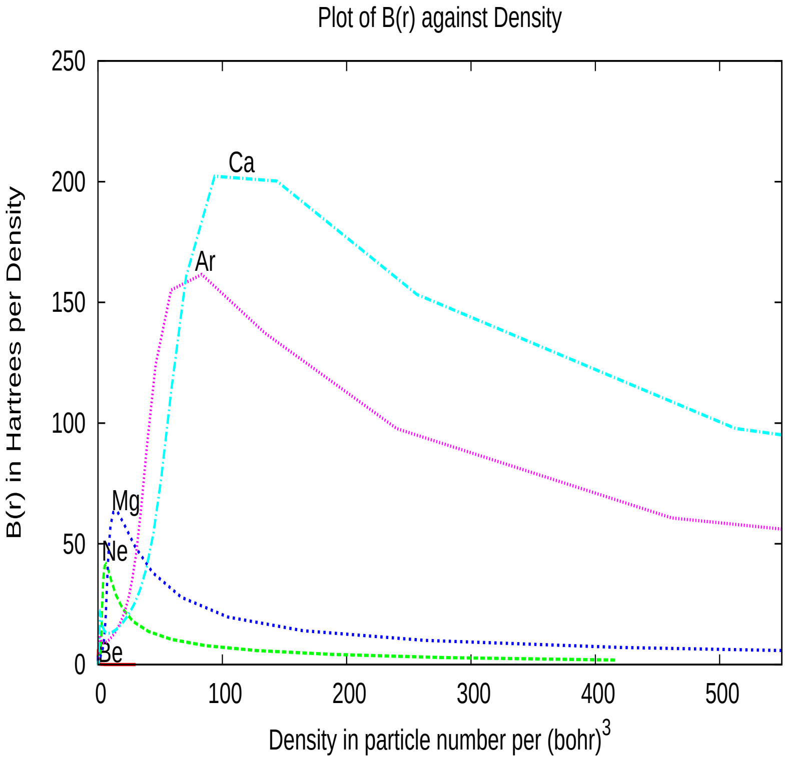

Figure 4.9: Statistical correlation function plotted against density for B(r) of eq.(3.34).

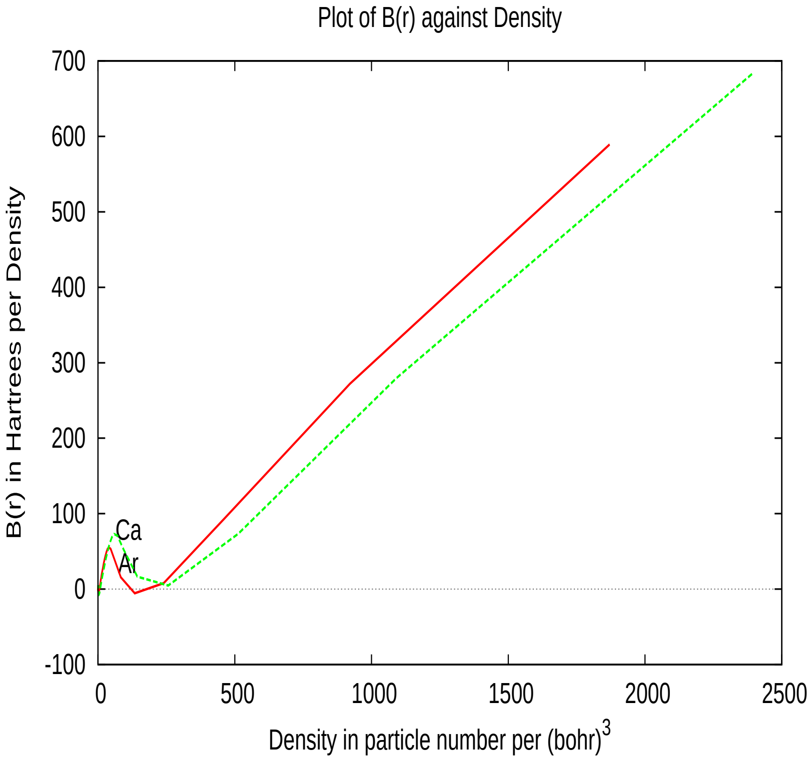

Figure 4.10: Statistical correlation function plotted against density for B(r) of eq.(4.3).

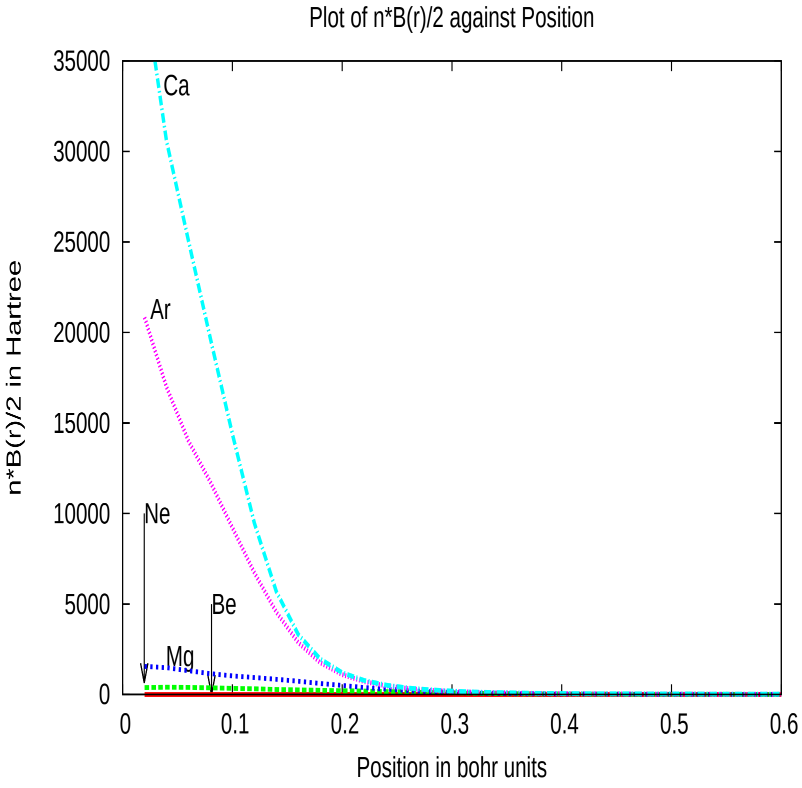

Figure 4.11: Plot of correction to kinetic energy density, t_{corr} against position.

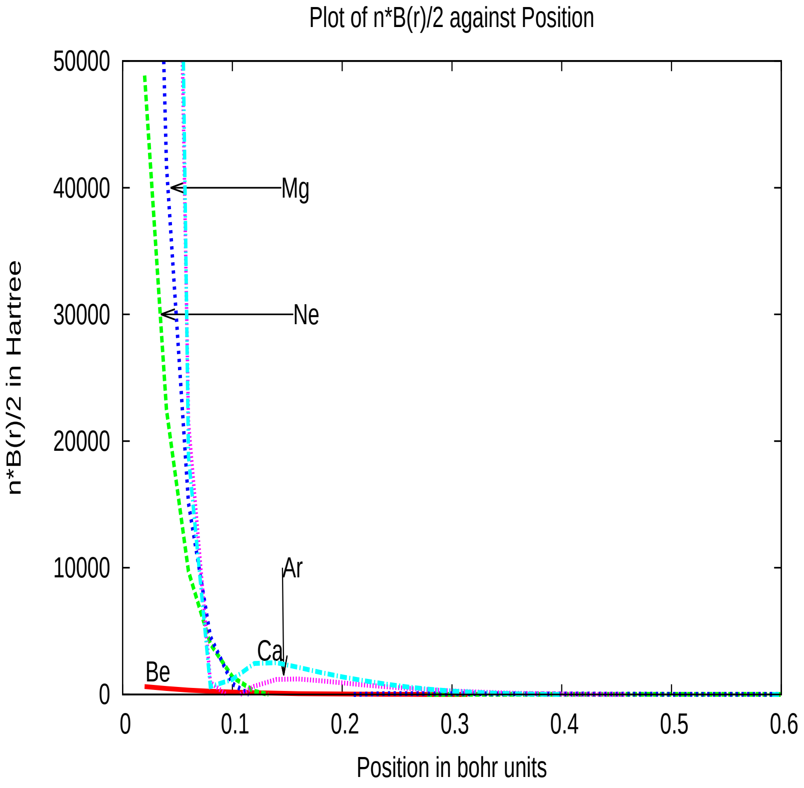

Figure 4.12: Plot of correction to kinetic energy density, t_{ucorr} against position.

4.4 Conclusion

These energy plots of t_{ucorr} could be said to arise from a more local density functional than t_{corr} or that the Thomas-Fermi term in eq.(4.3) dominates over the gradient term. This could be justified from Fig.(4.11) and Fig.(4.12) which shows that t_{ucorr} decays more rapidly than t_{corr}. On the other hand, our equation does not off set the non-locality of the electron density. Thus, this calls for reformulation of a qualitative statistical correlation functional that could depend on the position of the electrons in the system as well.

4.5 Further work

Possible things that could be tried are suggested here. Work should be done on functions such as:

1. $$B_u(r) = |\vec{r}|^3\Big(\frac{7|\nabla n|^2}{8n} + \frac{1}{2}\frac{\nabla^2 n}{4}\Big)$$

   that produces Fig.(4.13) which is a plot of $B_u(r)$ in comparison to

   $$B(r) = \frac{2}{n}\Big(t_0 - t_{vW} + t_{div}\Big)$$

   against n and the energies computed from the $B_u(r)$ is recorded in Table 4.5(a) in comparison to those computed from $B(r)$.

2. $$B_u(r) = (|\vec{r}|n^2)^{\frac{2}{3}} + 8.5|\vec{r}|^3\frac{|\nabla n|^2}{8n}$$

   plotted against n in Fig.(4.14) and compared with $B(r)$ versus n, gives the energy values given in Table 4.5(b).

Atom	$t_{ucorr}(Hartree)$	$t_{corr}(Hartree)$
Be	3.550	0.892
Ne	39.051	37.653
Mg	62.780	66.950
Ar	180.010	218.271
Ca	235.529	292.882

Table 4.5(*a*)

Atom	t_{ucorr}(Hartree)	$t_{corr}(Hartree)$
Be	2.865	0.892
Ne	34.880	37.653
Mg	58.089	66.950
Ar	177.831	218.271
Ca	236.741	292.882

Table 4.5(*b*)

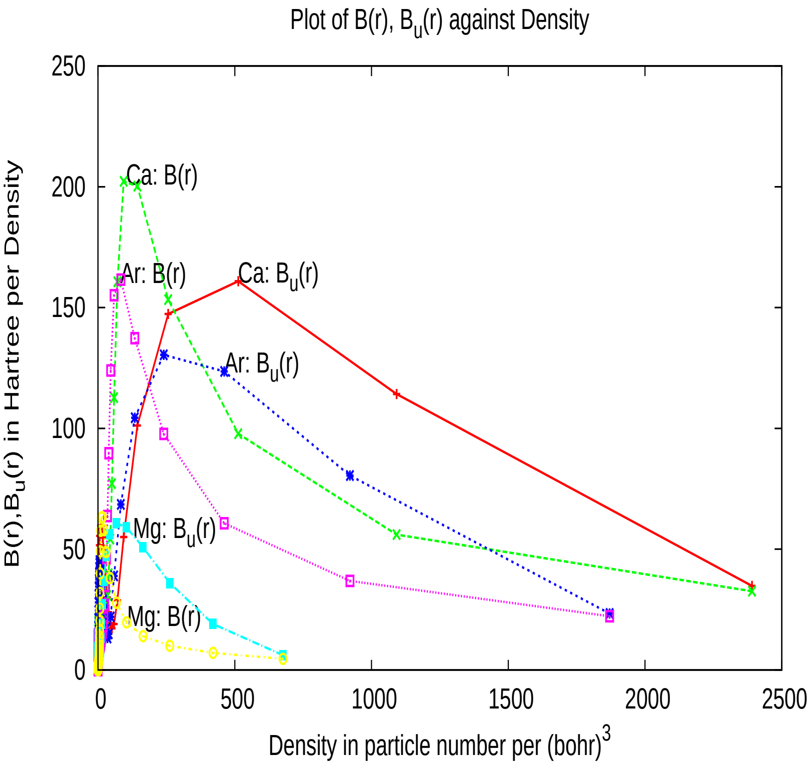

Figure 4.13: Plot of $B(r)$ and $B_u(r)$ against density

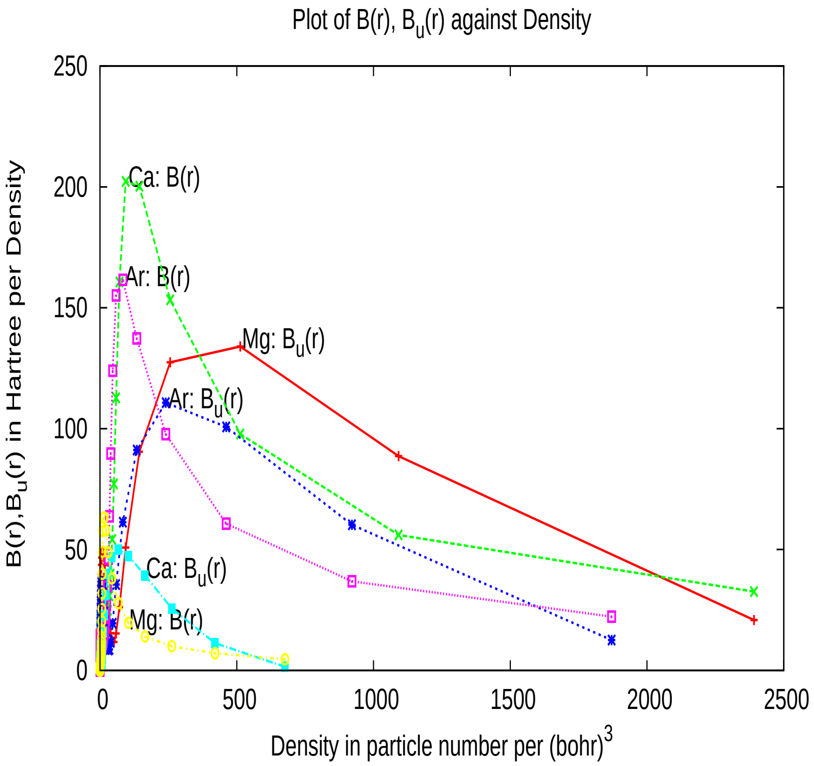

Figure 4.14: Plot of $B(r)$ and $B_u(r)$ against density

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