

Mapping Interacting Excited States onto Kohn-Sham System: Analytic Two Particle Systems

Essraa Taha Mirghani Ahmed (essraa@aims.ac.za)

إسراء طه ميرغني أحمد

African Institute for Mathematical Sciences (AIMS)

Supervised by: Prof. Daniel Joubert
University of the Witwatersrand, South Africa

22 May 2014

Submitted in partial fulfillment of a structured masters degree at AIMS South Africa



Abstract

Density functional theory is a technique used to solve the many-body problem by introducing the electronic density as a main variable rather than using the wave function. In this work we develop an understanding of the concepts of the ground state density functional theory (DFT). We then introduce two methods by which the first excited state of an analytically solvable model known as the Hooke atom, can be mapped onto a Kohn-Sham system.

In the first method we use the density of the first excited state of the Hooke atom to map the system onto the ground state of a Kohn-Sham system. Whereas in the second method we use the calculated density to map the system onto the first excited state of the corresponding Kohn-Sham system. We then confirm that the two methods produce the same results and conclude that the mapping onto the Kohn-Sham system is not unique.

Declaration

I, the undersigned, hereby declare that the work contained in this research project is my original work, and that any work done by others or by myself previously has been acknowledged and referenced accordingly.

Essraa

Essraa Taha Mirghani Ahmed, 22 May 2014

Contents

Abstract	i
1 Introduction	1
2 Basics of Density Functional Theory	2
2.1 Many Particle Systems:	2
2.2 The Hartree-Fock Approach	3
2.3 Thomas-Fermi Model	4
2.4 Hohenberg-Kohn Theorems	5
2.5 The Constrained Search Formulation of DFT	7
2.6 The Kohn-Sham Density Functional Theory	8
3 Hooke's Atom: An Analytically Solvable Two-Electrons Model	11
3.1 The ground state of Hooke's atom	11
3.2 The first excited state of Hooke's atom	15
4 Conclusion	20
References	21

1. Introduction

The chemical and physical properties of a material are mainly determined by the behaviour of the electrons in that material. Therefore any attempt to study the electronic configurations and interactions, receives a great deal of attention not only from scientists but also from industrialists nowadays.

One attempt to understand the electronic structure of materials was made by **Hohenberg and Kohn (1964)** and **Kohn and Sham (1965)** in the theory known as the density functional theory (DFT). They proved that the properties of an electronic system depend on the space distribution of the electrons in that system (the electronic density).

According to this theory, the Schrodinger equation that describes an electronic system considering all the interactions between the electrons, can be replaced by a set of non-interacting single-electron equations assuming that the electrons are moving in an effective external field.

In this work we tried to develop an understanding of the basic concepts of DFT for the ground state. We will give a summary of these concepts in Chapter 2. We also investigated the possibility of using Kohn-Sham DFT for excited states. We will demonstrate the results of our investigation in Chapter 3 and conclude the work as a whole in Chapter 4.

2. Basics of Density Functional Theory

Density Functional Theory (DFT) is a computational quantum mechanical tool used to study the behaviour of a many-particle system (Wikipedia). In this chapter we briefly discuss the basic concepts of DFT.

2.1 Many Particle Systems:

A physical system that involves a large number of particles is referred to as a many-particle or a many-body system (Zettili, 2009). Neglecting the spin of the particles involved, the state of such a system is described quantum mechanically by a wave function $\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N, t)$ that evolves in time according to the following time-dependent Schrodinger equation (Zettili, 2009):

$$i\hbar \frac{\partial}{\partial t} \Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N, t) = \hat{H} \Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N, t), \quad (2.1.1)$$

where N is the number of particles in the system, the \vec{r}_i 's ($i = 1, \dots, N$) are the spatial coordinates of the particles and the Hamiltonian \hat{H} accounts for the kinetic energy of the particles and the potential due to the interactions within the system and the interactions between the particles and the external world:

$$\hat{H} = - \sum_{i=1}^N \frac{\hbar^2}{2m_i} \nabla_i^2 + \hat{V}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N, t). \quad (2.1.2)$$

When the potential \hat{V} is time independent, the dynamics of the many-particle system is described by a time-independent Schrodinger equation:

$$\hat{H} \Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = E \Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N), \quad (2.1.3)$$

where E is the total energy of the system and the wave function $\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$ is the solution of the time-independent Schrodinger equation.

A well-defined collection of atoms with n nuclei and N electrons is an example of a many body system that can be described by (2.1.3). The Hamiltonian \hat{H} in this case is given by (Engel and Dreizler, 2011):

$$\begin{aligned} \hat{H} &= - \sum_{\alpha=1}^n \frac{\hbar^2}{2M_\alpha} \nabla_{\vec{R}_\alpha}^2 + \sum_{\alpha, \beta=1; \alpha < \beta}^n \frac{Z_\alpha Z_\beta e^2}{|\vec{R}_\alpha - \vec{R}_\beta|} - \sum_{i=1}^N \frac{\hbar^2}{2m} \nabla_{\vec{r}_i}^2 + \sum_{i, j=1; i < j}^N \frac{e^2}{|\vec{r}_i - \vec{r}_j|^2} - \sum_{\alpha=1}^n \sum_{i=1}^N \frac{Z_\alpha e^2}{|\vec{R}_\alpha - \vec{r}_i|} \\ &= \hat{T}_n + \hat{V}_{nn} + \hat{T}_e + \hat{V}_{ee} + \hat{V}_{en}, \end{aligned} \quad (2.1.4)$$

where the Hamiltonian \hat{H} accounts for the kinetic energies (\hat{T}_n) of the nuclei with \vec{R}_α and M_α denoting the position coordinate and mass of nucleus α , the Coulomb repulsion (\hat{V}_{nn}) between the nuclei, the kinetic energies (\hat{T}_e) of the electrons with \vec{r}_i denoting the position of the electron i , the potential resulting from the electron-electron interaction (\hat{V}_{ee}) between the electrons and the electron-nucleus interactions (\hat{V}_{en}) respectively.

The degrees of freedom of all the particles are coupled due to their continuous interactions. This is the reason why Equation (2.1.3) is difficult to solve for a system with a large number of particles.

The first attempt to simplify equation (2.1.3) is the Born-Oppenheimer approximation. In this approach the different time scales of the motion of the nuclei and the motion of the electrons were used to split the total wave function of the system into a nuclear wave function and an electron wave function (Engel and Dreizler, 2011):

$$\Psi(\vec{R}_1, \dots, \vec{R}_n; \vec{r}_1 \vec{\sigma}_1, \dots, \vec{r}_N \vec{\sigma}_N) = \psi_e(\vec{R}_1, \dots, \vec{R}_n; \vec{r}_1 \vec{\sigma}_1, \dots, \vec{r}_N \vec{\sigma}_N) \psi_n(\vec{R}_1, \dots, \vec{R}_n), \quad (2.1.5)$$

where $\vec{\sigma}_i$ is the spin-orientation of the electron i . Hence, the electron's wave function is described by the following time independent Schrodinger equation:

$$\begin{aligned} \hat{H}_e \psi_e(\vec{R}_1, \dots, \vec{R}_n; \vec{r}_1 \vec{\sigma}_1, \dots, \vec{r}_N \vec{\sigma}_N) &= (\hat{T}_e + \hat{V}_{ee} + \hat{V}_{en}) \psi_e(\vec{R}_1, \dots, \vec{R}_n; \vec{r}_1 \vec{\sigma}_1, \dots, \vec{r}_N \vec{\sigma}_N) \\ &= E_e \psi_e(\vec{R}_1, \dots, \vec{R}_n; \vec{r}_1 \vec{\sigma}_1, \dots, \vec{r}_N \vec{\sigma}_N). \end{aligned} \quad (2.1.6)$$

Even though this approximation simplified the many-body problem by considering the nuclei as stationary sources of an external potential in which electrons are moving, solving Equation (2.1.6) is still a challenge due to the large number of electrons involved and their continuous interactions.

Many approaches have been used to find an approximate solution to Equation (2.1.6). In the next two sections a couple of those approximations are discussed briefly.

2.2 The Hartree-Fock Approach

This approximation explains that Equation (2.1.6) can be simplified to a set of single particle equations by considering that the orbitals ψ_i are related to the total wave function of the system Ψ_i by the formula (Parr and Yang, 1989):

$$\Psi_{HF}(\vec{r}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\vec{r}_1) & \psi_2(\vec{r}_1) & \cdots & \psi_N(\vec{r}_1) \\ \psi_1(\vec{r}_2) & \psi_2(\vec{r}_2) & \cdots & \psi_N(\vec{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(\vec{r}_N) & \psi_2(\vec{r}_N) & \cdots & \psi_N(\vec{r}_N) \end{vmatrix}, \quad (2.2.1)$$

where \vec{r}_i accounts for both the spin and the spatial coordinates. The wave function determined by this Slater determinant predicts an energy expectation value of the form:

$$E_{HF} = \langle \Psi_{HF} | \hat{H} | \Psi_{HF} \rangle, \quad (2.2.2)$$

where

$$\hat{H} = \sum_{i=1}^N H_i + \frac{1}{2} \sum_{i,j=1}^N (J_{ij} - K_{ij}). \quad (2.2.3)$$

This Hamiltonian is separated into two parts: one that involves only one electron index and the other involving the indices of two electrons. In atomic units ($e = \hbar = m = 1$) the first part is given by:

$$H_i = -\frac{1}{2} \nabla_i^2 + \sum_{k=1}^N \frac{Z_k}{|\vec{R}_k - \vec{r}_i|}, \quad (2.2.4)$$

where the first term refers to the kinetic energy of the electron and the second to the average potential exerted by the nuclei on the electron. The second part of the Hamiltonian defined in (2.2.3) includes the Coulomb repulsion J_{ij} and the exchange potential K_{ij} .

Hence, the Hartree-Fock equation for each of the orbitals ψ_i is given by:

$$[H_i + J_{ij} - K_{ij}] \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}). \quad (2.2.5)$$

We will not discuss this method further since it is of little relevance to the subject of this work. However we must note that the idea of mapping the interacting system of electrons into a non-interacting system of electrons moving in an effective potential was first introduced in this model.

2.3 Thomas-Fermi Model

The Thomas-Fermi model is a statistical model used to approximate the total energy of the electrons in an atom. The theory behind the model postulates that electrons are uniformly distributed in phase space such that each volume element of size h^3 is occupied by two electrons. It also assumes that the electrons are moving in a potential that is determined by the nuclear charge and the electron distribution.

We can first assume that the volume in the atom is divided into many cells each of length l and volume $\Delta V = l^3$. Then we assume that the electrons in each cell behave like fermions at $0K$ and that their number inside each cell is fixed.

The energy levels of the electron inside a given cell are given by:

$$\begin{aligned} \epsilon(n_x, n_y, n_z) &= \frac{h^2}{8ml^2} (n_x^2 + n_y^2 + n_z^2) \\ &= \frac{h^2}{8ml^2} R^2, \end{aligned} \quad (2.3.1)$$

where $n_x, n_y, n_z = 1, 2, 3, \dots$. For a large R , the number of energy levels with energies between ϵ and $\epsilon + \delta\epsilon$ is given by:

$$\begin{aligned} g(\epsilon)\Delta\epsilon &= \Phi(\epsilon + \delta\epsilon) - \Phi(\epsilon) \\ &= \frac{\pi}{4} \left(\frac{8ml^2}{h^2} \right)^{3/2} \epsilon^{1/2} \delta\epsilon + O((\delta\epsilon)^2), \end{aligned} \quad (2.3.2)$$

where $\Phi(\epsilon) = \frac{1}{8} \left(\frac{4\pi R^3}{3} \right) = \frac{\pi}{6} \left(\frac{8ml^2\epsilon}{h^2} \right)^{3/2}$ is the number of energy levels with energy smaller than ϵ . At $0K$ the probability that a given state with energy ϵ is occupied is given by:

$$f(\epsilon) = \begin{cases} 1 & \epsilon < \epsilon_F \\ 0 & \epsilon > \epsilon_F \end{cases}$$

where ϵ_F is the Fermi-energy. We can use this occupation probability together with the energy of the occupied states and the density of each state to determine the total energy contribution of each state:

$$\begin{aligned} \Delta E &= 2 \int \epsilon f(\epsilon) g(\epsilon) d\epsilon \\ &= 4\pi \left(\frac{2m}{h^2} \right)^{3/2} l^3 \int_0^{\epsilon_F} \epsilon^{3/2} d\epsilon \\ &= \frac{8\pi}{5} \left(\frac{2m}{h^2} \right)^{3/2} l^3 \epsilon_F^{5/2}. \end{aligned} \quad (2.3.3)$$

Knowing that the number of electrons in the cell is related to the Fermi energy by:

$$\begin{aligned}\Delta N &= 2 \int f(\epsilon)g(\epsilon)d\epsilon \\ &= \frac{8\pi}{3} \left(\frac{2m}{\hbar^2}\right)^{3/2} l^3 \epsilon_F^{3/2},\end{aligned}\quad (2.3.4)$$

we can write the total energy of a given cell as:

$$\begin{aligned}\Delta E &= \frac{3}{5} \Delta N \epsilon_F \\ &= \frac{3\hbar^2}{10m} \left(\frac{3}{8\pi}\right)^{2/3} l^3 \left(\frac{\Delta N}{l^3}\right)^{5/3}.\end{aligned}\quad (2.3.5)$$

This equation relates the total kinetic energy of each cell directly to the electron density $\rho = \Delta N/l^3$. Hence summing over all space and taking the limit $\Delta V \rightarrow 0$, we can write the total kinetic energy of the atom as:

$$T_{TF}[n] = C_F \int \rho^{5/3}(\vec{r})d\vec{r},\quad (2.3.6)$$

where $C_F = \frac{3}{10}(3\pi^2)^{2/3} = 2.871$. Adding the classical definitions of the electron-electron repulsion and the electron-nucleus attraction (which both can be represented in terms of the electron density) the total energy in the atom as a functional of the electron density is given by (Parr and Yang, 1989):

$$E_{TF}[\rho(\vec{r})] = C_F \int \rho^{5/3}(\vec{r})d\vec{r} - Z \int \frac{\rho(\vec{r})}{r}d\vec{r} + \frac{1}{2} \int \int \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}d\vec{r}_1d\vec{r}_2.\quad (2.3.7)$$

Up to this point we have only introduced two of the approaches used to solve the many-body problem. In the next three sections we will discuss the basic theorems that were used in constructing DFT which is the approach used in this work to approximate a solution for a many-body system.

2.4 Hohenberg-Kohn Theorems

The two theorems stated by Hohenberg and Kohn (1964) used the same idea introduced in the Thomas-Fermi model of reformulating the many-body problem in terms of the electron density instead of the complicated wave function.

The first theorem suggested the replacement of the wave function by the corresponding electronic density. The argument was that the kinetic energy T_e and the Coulomb repulsion V_{ee} depend by definition on the electron density, hence, the only term left to prove the dependency of the system's Hamiltonian on the density, is the external potential $V_{ext}(\vec{r})$.

2.4.1 Theorem. (Hohenberg and Kohn, 1964) *The external potential $V_{ext}(\vec{r})$ is a unique functional of the electronic density $\rho(\vec{r})$, to within a trivial additive constant.*

Proof. Assume that there are two wave functions Ψ and Ψ' producing the same electronic density, but corresponding to two different external potential V_{ext} and V'_{ext} . These two wave functions satisfy different Schrodinger equations (unless the external potentials differ by a constant) hence we can write their Hamiltonians as H, H' and ground state energies as E, E' .

Considering that the ground state has by definition the minimum energy, we can choose the wave function Ψ to be the ground state and another wave function Ψ' to be a trial wave function. Then we can write:

$$\begin{aligned}
\langle \Psi | H | \Psi \rangle &< \langle \Psi' | H | \Psi' \rangle \\
&< \langle \Psi' | T_{ee} + V_{ee} + V_{ext} | \Psi' \rangle \\
&< \langle \Psi' | T + V_{ee} + V'_{ext} + V_{ext} - V'_{ext} | \Psi' \rangle \\
&< \langle \Psi' | T + V_{ee} + V'_{ext} | \Psi' \rangle + \langle \Psi' | V_{ext} - V'_{ext} | \Psi' \rangle \\
&< \langle \Psi' | H' | \Psi' \rangle + \langle \Psi' | V_{ext} - V'_{ext} | \Psi' \rangle,
\end{aligned} \tag{2.4.1}$$

consequently;

$$E < E' + \int \rho(\vec{r})(V_{ext} - V'_{ext})d\vec{r}. \tag{2.4.2}$$

Similarly, we can consider Ψ to be the trial wave function and obtain:

$$\begin{aligned}
\langle \Psi' | H' | \Psi' \rangle &< \langle \Psi | H' | \Psi \rangle \\
&< \langle \Psi | T_{ee} + V_{ee} + V'_{ext} | \Psi \rangle \\
&< \langle \Psi | T + V_{ee} + V_{ext} + V'_{ext} - V_{ext} | \Psi \rangle \\
&< \langle \Psi | T + V_{ee} + V_{ext} | \Psi \rangle + \langle \Psi | V'_{ext} - V_{ext} | \Psi \rangle \\
&< \langle \Psi | H | \Psi \rangle + \langle \Psi | V'_{ext} - V_{ext} | \Psi \rangle,
\end{aligned} \tag{2.4.3}$$

hence

$$E' < E + \int \rho(\vec{r})(V'_{ext} - V_{ext})d\vec{r}. \tag{2.4.4}$$

Adding Equations (2.4.2) and (2.4.4) we end with the contradiction:

$$E + E' < E' + E. \tag{2.4.5}$$

This contradiction shows that our assumption of the existence of another external potential that can give rise to the same electron density is wrong. Hence the external potential is a unique functional of the electron density. \square

The universal functional $F[\rho(\vec{r})]$ was introduced in the paper by [Hohenberg and Kohn \(1964\)](#) as:

$$F[\rho(\vec{r})] = \langle \psi | T + V_{ee} | \psi \rangle. \tag{2.4.6}$$

The Coulomb repulsion term can be factored out of this functional because of the "long range of the Coulomb interactions". Hence, we can now write the functional as:

$$F[\rho(\vec{r})] = \frac{1}{2} \int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}d\vec{r}' + G[\rho(\vec{r})], \tag{2.4.7}$$

where $G[\rho(\vec{r})]$ is also a universal functional, i.e. does not depend on the external potential.

Using the functional $F[\rho(\vec{r})]$, we can write the energy functional of a system with an external potential $V_{ext}(\vec{r})$ as:

$$\begin{aligned}
E[\rho(\vec{r})] &= \int V_{ext}\rho(\vec{r})d\vec{r} + F[\rho(\vec{r})] \\
&= \int V_{ext}\rho(\vec{r})d\vec{r} + \frac{1}{2} \int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}d\vec{r}' + G[\rho(\vec{r})].
\end{aligned} \tag{2.4.8}$$

The second theorem illustrates how the true ground state density can be found given a set of electronic densities.

2.4.2 Theorem. (*Hohenberg and Kohn, 1964*): "The energy functional $E[\rho(\vec{r})]$ assumes its minimum value for the correct density $\rho(\vec{r})$, if the admissible functions are restricted by the condition

$$N[\rho] \equiv \int \rho(\vec{r}) d\vec{r} = N, \quad (2.4.9)$$

where N is the number of particles in the system".

Proof. We know from the variational principle that any guessed wave function ψ' will be an overestimation of the ground state wave function ψ unless it is the correct ground state (*Parr and Yang, 1989*), hence if we considered the universal functional of that function $F[\rho']$ and the associated density we can write:

$$\begin{aligned} \langle \psi' | H | \psi' \rangle &= F[\rho'] + \int \rho' d\vec{r} \\ &= E[\rho'] \end{aligned} \quad (2.4.10)$$

$$> E[\rho]. \quad (2.4.11)$$

□

These theorems proved a one-to-one correspondence between the electron density $\rho(\vec{r})$ and the external potential V_{ext} . The two theorems also illustrated the mechanism by which the ground state electron density can be determined given a set of densities. However, these theorems can not distinguish between different energy states which produces the same density (*Sahni, 2004*).

2.5 The Constrained Search Formulation of DFT

As stated previously in Section 2.4, the two Hohenberg-Kohn theorems assumed the non-degeneracy of the ground state wave functions (*Hohenberg and Kohn, 1964*). In the case where the states are degenerate the Hohenberg-Kohn theorems do not provide a method by which the ground state can be determined. Such a method was introduced by *Levy and Perdew (1985)* in what is known as the Levy-constrained search formulation of DFT. They suggested that the correct ground state wave function ψ is the one that produces the exact ground state density ρ and at the same time minimizes the energy expectation value. In other words, we must find a "universal variational functional" let us say $Q[\rho]$ that scans a given set of wave functions corresponding to the same density such that:

$$Q[\rho] = \text{Min} \langle \psi | T + V_{ee} | \psi \rangle. \quad (2.5.1)$$

Considering any trial wave function ψ' that yields the same ground state density ρ as the wave function ψ without being a ground state wave function, we can write:

$$\begin{aligned} \langle \psi' | H | \psi' \rangle &\geq \langle \psi | H | \psi \rangle \\ \langle \psi' | T + V_{ee} + V_{ext} | \psi' \rangle &\geq \langle \psi | T + V_{ee} + V_{ext} | \psi \rangle \\ \langle \psi' | T + V_{ee} | \psi' \rangle + \int \rho(r) V_{ext}(r) dr &\geq \langle \psi | T + V_{ee} | \psi \rangle + \int \rho(r) V_{ext}(r) dr \\ \langle \psi' | T + V_{ee} | \psi' \rangle &\geq \langle \psi | T + V_{ee} | \psi \rangle \\ &\geq Q[\rho]. \end{aligned} \quad (2.5.2)$$

Equation (2.5.2) proves that the wave function ψ' can produce the universal variational functional $Q[\rho]$ if and only if it is the ground state wave function.

With this formulation of DFT, degeneracy is no longer an issue. Up until this point we did not say anything about how we can determine this energy functional or how the density can be used to extract the properties of the ground state. These questions were answered one year later in a formalism of DFT that was introduced by Kohn-Sham. The next section discusses this formalism briefly.

2.6 The Kohn-Sham Density Functional Theory

In 1965 W. Kohn and L. J. Sham introduced the idea of replacing the interacting system of electrons with a fictitious non-interacting system that yields the same charge density (Kohn and Sham, 1965).

The Hamiltonian of such a non-interacting system is given by:

$$\hat{H} = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 \right) + \sum_{i=1}^N V_{ks}, \quad (2.6.1)$$

where the potential V_{ks} is an effective potential in which the electrons were assumed to be moving. Since these electrons are not interacting, the total wave function of the system $\psi(\vec{r})$ can be expressed in terms of the orbitals $\psi_i(\vec{r})$ as (Parr and Yang, 1989):

$$\psi(\vec{r}) = \frac{1}{\sqrt{N}} \det[\psi_1(\vec{r}) \psi_2(\vec{r}) \dots \psi_N(\vec{r})], \quad (2.6.2)$$

with the electronic density defined as:

$$\rho(\vec{r}) = \sum_{i=1}^N |\psi_i(\vec{r})|^2, \quad (2.6.3)$$

where these orbitals ψ_i are obtained by solving the Kohn-Sham equation:

$$\left[-\frac{1}{2} \nabla_i^2 + V_{ks} \right] \psi_i(\vec{r}) = E_i \psi_i(\vec{r}). \quad (2.6.4)$$

To solve the above equation we must find an exact formula for the external potential V_{ks} (Nguimdo, 2012). We will start by assuming that ψ is a wave function of an interacting system that yields a specific ground state density ρ . We also assume that the same ρ is produced by another wave function ψ' of a non-interacting system.

Then we define the universal functional for the non-interacting system similar to the definition of the Hohenberg-Kohn universal functional in Equation (2.4.6) to be:

$$\begin{aligned} F_{ks}[\rho] &= \langle \psi' | T + V_{ee} | \psi' \rangle \\ &= \langle \psi' | T | \psi' \rangle + \langle \psi' | V_{ee} | \psi' \rangle \\ &= T_{ks}[\rho] + \langle \psi' | V_{ee} | \psi' \rangle, \end{aligned} \quad (2.6.5)$$

where the first term T_{ks} is the kinetic energy of the Kohn-Sham system and the second term $\langle \psi | V_{ee} | \psi \rangle$ accounts for the Coulomb repulsion $U[\rho]$ and the exchange energy functionals $E_x[\rho]$:

$$\langle \psi | V_{ee} | \psi \rangle = U[\rho] + E_x[\rho]. \quad (2.6.6)$$

We have to note that the correlation energy is not included in this functional, hence we can express it as the difference between the two functionals:

$$E_c[\rho] = F[\rho] - F_{ks}[\rho]. \quad (2.6.7)$$

Rearranging Equation (2.6.7) and substituting the value of the functional $F_{ks}[\rho]$, we obtain the following expression for the universal functional of the interacting system:

$$\begin{aligned} F[\rho] &= \langle \psi' | T_{ks} + V_{ee} | \psi' \rangle + [\langle \psi | T + V_{ee} | \psi \rangle - \langle \psi' | T_{ks} + V_{ee} | \psi' \rangle] \\ &= \langle \psi' | T | \psi' \rangle + \langle \psi' | V_{ee} | \psi' \rangle + E_c[\rho] \\ &= T_{ks}[\rho] + \langle \psi' | V_{ee} | \psi' \rangle + E_c[\rho] \\ &= T_{ks} + U[\rho] + E_x[\rho] + E_c[\rho]. \end{aligned} \quad (2.6.8)$$

Here the two functionals $E_x[\rho]$ and $E_c[\rho]$ are often expressed as one term E_{xc} known as the exchange-correlation energy. In order to obtain a minimization of the energy functional $E[\rho]$, the following condition must hold (Parr and Yang, 1989)

$$\frac{\delta[E[\rho] - \mu(\int \rho(\vec{r}) d\vec{r})]}{\delta\rho} = 0, \quad (2.6.9)$$

with μ being the Lagrange multiplier. This condition leads to:

$$\begin{aligned} \frac{\delta[F[\rho] + \int V_{ext}\rho(\vec{r})d\vec{r} - \mu(\int \rho(\vec{r})d\vec{r})]}{\delta\rho} &= 0 \\ \frac{\delta T_{ks}[\rho]}{\delta\rho} + \frac{\delta U[\rho]}{\delta\rho} + \frac{\delta E_{xc}[\rho]}{\delta\rho} + V_{ext} - \mu &= 0 \\ \frac{\delta T_{ks}[\rho]}{\delta\rho} + V_{ks}[\rho] &= \mu, \end{aligned} \quad (2.6.10)$$

where

$$\begin{aligned} V_{ks} &= \frac{\delta U}{\delta\rho} + \frac{\delta E_{xc}}{\delta\rho} + V_{ext}[\rho] \\ &= V_H[\rho] + V_{xc}[\rho] + V_{ext}, \end{aligned} \quad (2.6.11)$$

and the Hartree potential is given by:

$$V_H = \int \frac{\rho(\vec{r}') d\vec{r}'}{|\vec{r} - \vec{r}'|}, \quad (2.6.12)$$

and the exchange-correlation potential given by:

$$V_{xc} = \frac{\delta E_{xc}}{\delta\rho}. \quad (2.6.13)$$

Now we can substitute the Hartree potential term defined by (2.6.12) into (2.6.11) and use the resulting expression to write the Kohn-Sham equation (2.6.4) in terms of the electronic density as:

$$\left[-\frac{1}{2}\nabla^2 + \int \frac{\rho(\vec{r}') d\vec{r}'}{|\vec{r} - \vec{r}'|} + V_{xc} + V_{ext} \right] \psi_i(\vec{r}) = E_i \psi_i(\vec{r}). \quad (2.6.14)$$

The most challenging task in finding the Kohn-Sham potential is the determination of the exchange-correlation term V_{xc} since it has no exact formula and can only be approximated (Filippi et al., 1994). Several approximations have been used in determining the exchange-correlation potential, one of which is the local density approximation (LDA).

In this approximation the density of a uniformly distributed electron gas in a box is used to approximate (within a small volume of space) the non-uniformly distributed density of the real system of electrons. Another example is an approximation that accounts for the gradient of the density as well as the density itself is known as the gradient expansion approximation (GEA) (Pielak, 2013).

So far we have explained that the main goal of DFT is to find a solution to the many-body problem using the electronic density. We also showed that the two Hohenberg-Kohn theorems were refined by the theory of Kohn-Sham theorem one year later. DFT is incapable of finding an exact solution to the many-body problem and can only provide approximations.

In the next chapter we will introduce a model that has an analytic solution and hence can be used as a test of the accuracy of the Kohn-Sham DFT approximations.

3. Hooke's Atom: An Analytically Solvable Two-Electrons Model

Hooke's atom is a model of a helium-like atom in which the potential caused by the nucleus-electrons interaction, is replaced by a simple harmonic potential while keeping the repulsive Coulomb electron-electron interaction potential unchanged.

The fact that this model can be solved analytically to produce the exact values of the exchange-correlation functional, makes it of great importance in testing the accuracy of the Kohn-Sham DFT (Kais et al., 1993).

In this chapter we discuss the properties of this model in its ground and first excited state.

3.1 The ground state of Hooke's atom

A system of two interacting electrons in a harmonic potential can be described in atomic units ($\hbar = m = e = 1$) by the Hamiltonian:

$$\hat{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) + \frac{k}{2}(r_1^2 + r_2^2) + \frac{1}{|\vec{r}_1 - \vec{r}_2|}, \quad (3.1.1)$$

where in this Hamiltonian the first term refers to the kinetic energies of the two electrons, the second refers to the electron-nucleus interaction with k being the spring constant, \vec{r}_1 and \vec{r}_2 are the position coordinates of the two electrons and the third term denotes the electron-electron interaction.

For simplification we can use the centroid coordinates: $\vec{R} = \frac{1}{2}(\vec{r}_1 + \vec{r}_2)$ and $\vec{r} = \vec{r}_1 - \vec{r}_2$ in describing the Hamiltonian of the system as follows:

$$\frac{1}{2}k(r_1^2 + r_2^2) = kR^2 + \frac{1}{4}kr^2, \quad (3.1.2)$$

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \frac{1}{r}, \quad (3.1.3)$$

and

$$\begin{aligned} \frac{d}{dr_1} &= \frac{dR}{dr_1} \frac{d}{dR} + \frac{dr}{dr_1} \frac{d}{dr} = \frac{1}{2} \frac{d}{dR} + \frac{d}{dr} \\ \Rightarrow \frac{d^2}{dr_1^2} &= \left(\frac{1}{2} \frac{d}{dR} + \frac{d}{dr} \right)^2 = \frac{1}{4} \frac{d^2}{dR^2} + \frac{d}{dR} \frac{d}{dr} + \frac{d^2}{dr^2} \\ \frac{d}{dr_2} &= \frac{dR}{dr_2} \frac{d}{dR} + \frac{dr}{dr_2} \frac{d}{dr} = \frac{1}{2} \frac{d}{dR} - \frac{d}{dr} \\ \Rightarrow \frac{d^2}{dr_2^2} &= \left(\frac{1}{2} \frac{d}{dR} - \frac{d}{dr} \right)^2 = \frac{1}{4} \frac{d^2}{dR^2} - \frac{d}{dR} \frac{d}{dr} + \frac{d^2}{dr^2} \\ \Rightarrow -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) &= -\frac{1}{4} \frac{d^2}{dR^2} - \frac{d^2}{dr^2}. \end{aligned} \quad (3.1.4)$$

Using (3.1.2), (3.1.3) and (3.1.4) the Hamiltonian of the system can be written as

$$\hat{H} = -\frac{1}{4} \frac{d^2}{dR^2} - \frac{d^2}{dr^2} + \frac{1}{4}kr^2 + kR^2 + \frac{1}{r}. \quad (3.1.5)$$

Now, we can express the wave function ψ as the product $\chi(\vec{R})\Phi(\vec{r})$ and use the Hamiltonian defined in (3.1.5) to separate the time independent Schrodinger equation;

$$\hat{H}\chi(\vec{R})\Phi(\vec{r}) = E\chi(\vec{R})\Phi(\vec{r}), \quad (3.1.6)$$

into the following set of equations

$$\left(-\frac{1}{4}\nabla_R^2 + kR^2\right)\chi(\vec{R}) = E_R\chi(\vec{R}), \quad (3.1.7)$$

$$\left(-\nabla_r^2 + \frac{1}{4}kr^2 + \frac{1}{r}\right)\Phi(\vec{r}) = E_r\Phi(\vec{r}), \quad (3.1.8)$$

where the total energy is given by $E = E_r + E_R$.

The solution of the first equation (3.1.7) is given, in atomic units ($e = m = \hbar = 1$) by (Kestner and Sinanoglu, 1962):

$$\chi(\vec{R}) = \exp(-\sqrt{k}R^2)R^l Y_{lm}(\theta, \phi)G(R^2), \quad (3.1.9)$$

where $Y_{lm}(\theta, \phi)$ are the spherical harmonics, $G(R^2)$ is a confluent hyper geometric function and the value used for k is $\frac{1}{4}$.

For an oscillator in its ground state, Y_{00} and $G(R^2)$ are constants and the ground state energy is given by:

$$E_R = \frac{3}{2}\sqrt{k} = \frac{3}{4}. \quad (3.1.10)$$

The solution of the second equation (3.1.8) was suggested by Taut (1993) to be:

$$\Phi(\vec{r}) = \frac{u(r)}{r} y_{lm}(\theta, \phi), \quad (3.1.11)$$

where $y_{lm}(\theta, \phi)$ are the spherical harmonics and the wave function $u(r)$ is obtained by solving the equation:

$$-\frac{d^2u(r)}{dr^2} + \frac{k}{4}r^2u(r) + \frac{l(l+1)}{r^2}u(r) + \frac{1}{r}u(r) - E_r u(r) = 0. \quad (3.1.12)$$

Taut (1993) proved that the wave function $u(r)$ can be expressed as the product of an infinite series and a Gaussian. When terminating the series at $n = 2$ and taking the value of the spring constant $k = \frac{1}{4}$ the following is obtained as an expression for $u(r)$:

$$u(r) = r^{l+1} \left(1 + \frac{r}{2(l+1)}\right) e^{-r^2/8(l+1)}. \quad (3.1.13)$$

By substituting Equation (3.1.13) into (3.1.11) and considering the fact that the radial part of the wave function Φ is a constant for the ground state ($l = 0$) (Kestner and Sinanoglu, 1962), we can write Equation (3.1.11) as:

$$\Phi(\vec{r}) = \left(1 + \frac{r}{2}\right) e^{-r^2/8}, \quad (3.1.14)$$

where the spring constant is $k = \frac{1}{4}$ and the corresponding energy is:

$$E_r = \frac{5}{4}. \quad (3.1.15)$$

Equations (3.1.14) and (3.1.9) defines the total wave function in terms of the electron's position coordinates \vec{r}_1, \vec{r}_2 by:

$$\psi(\vec{r}_1, \vec{r}_2) = N_0 \left(1 + \frac{r}{2}\right) e^{-(1/4)(r_1^2 + r_2^2)}, \quad (3.1.16)$$

where N_0 is the normalization constant which is constrained by the condition:

$$\int \rho(\vec{r}) d\vec{r} = 2, \quad (3.1.17)$$

and has the value:

$$N_0 = \frac{\pi^3}{(8 + 5\pi^{1/2})^2}. \quad (3.1.18)$$

The corresponding total ground state energy is

$$E = E_r + E_R = \frac{3}{4} + \frac{5}{4} = 2. \quad (3.1.19)$$

To find an exact expression for the ground state density $\rho_0(r)$ for a single electron in Hooke's atom, we can substitute the wave function obtained in (3.1.16) into the following equation (Kais et al., 1993):

$$\rho_0(r) = \int |\psi(\vec{r}_1, \vec{r}_2)|^2 d\vec{r}, \quad (3.1.20)$$

where \mathbf{r} represents the position coordinate of the electron relative to the nucleus.

Evaluating this integral the following expression for the ground state density is obtained:

$$\rho_0(r) = 2N_0^2 e^{-(1/2)r^2} \left[\left(\frac{\pi}{2}\right)^{1/2} \left[\frac{7}{4} + \frac{1}{4}r^2 + \left(r + \frac{1}{r}\right) \operatorname{erf}(2^{-1/2}r) \right] + e^{-(1/2r^2)} \right], \quad (3.1.21)$$

where erf is the error function.

We plotted the density $\rho(r)$ as a function of the distance r for the Hooke's atom using the formula stated in equation (3.1.21) and the following figure was obtained:

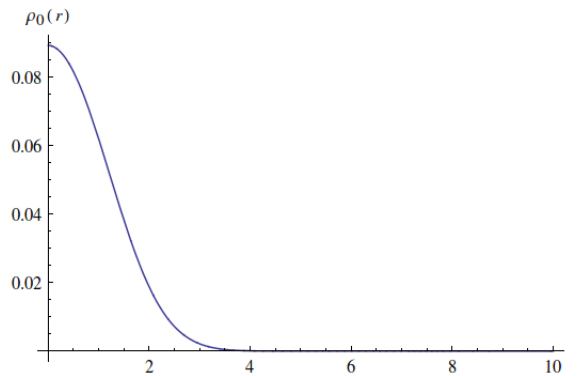


Figure 3.1: The radially symmetric ground state density ρ_0 for a single electron in Hooke's atom as a function of the radial coordinate r . The plot illustrates that the charge density and consequently the probability of finding an electron decreases as the distance from the nucleus increases and vanishes at about 5 *au*.

Equation (2.6.14) illustrated how the ground state density was used to describe the Hartree potential term in the Kohn-Sham equation. In the case of the Hooke atom, we can replace the external potential V_{ext} by the harmonic potential $\frac{1}{2}k(r_1^2)$ so that the Kohn-Sham equation reads:

$$\left[-\frac{1}{2}\nabla^2 + \int \frac{\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_2 + V_{xc} + \frac{1}{2}k(r_1^2) \right] \psi_1(\vec{r}_1) = E_1 \psi_1(\vec{r}_1). \quad (3.1.22)$$

Equation (3.1.22) can be inverted to obtain the exchange-correlation potential (Filippi et al., 1994):

$$V_{xc} = E_{ks} + \frac{1}{2} \frac{\nabla^2 \psi}{\psi} - \frac{1}{2}k(r_1^2) - \int \frac{\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_2, \quad (3.1.23)$$

where E_{ks} is equivalent to the eigenvalue E_r appearing in Equation (3.1.8) under the condition that the exchange-correlation potential tends to zero at infinity.

For a system of two electrons the exchange potential is determined by:

$$V_x = -\frac{1}{2} \int \frac{\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_2, \quad (3.1.24)$$

hence, we can determine the exact value for the correlation potential V_c by substituting (3.1.23) into the following:

$$V_c = V_{xc} - V_x. \quad (3.1.25)$$

The Kohn-Sham potential in terms of the ground state density is given by:

$$V_{ks} = \mu + \frac{1}{2\sqrt{\rho_0}} \frac{1}{r^2} \frac{d^2}{dr^2} (r^2 \sqrt{\rho_0}), \quad (3.1.26)$$

where the chemical potential μ is:

$$\mu = E - E_r = 2 - \frac{3}{4} = \frac{5}{4}. \quad (3.1.27)$$

Arranging (2.6.11) we can write:

$$V_{ks} - V_{ext} = V_H + V_{xc}, \quad (3.1.28)$$

hence, knowing that the value of the external potential is $V_{ext} = \frac{1}{8}r^2$ and using (3.1.26), we plotted the exchange- correlation plus the Hartree potential and the following figure was obtained:

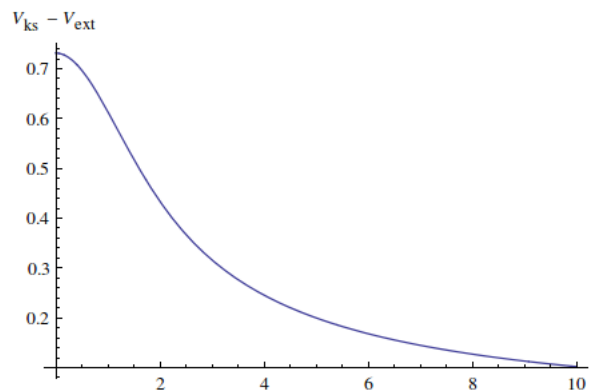


Figure 3.2: The Hartree plus the exchange-correlation potential obtained from the ground state density.

We can calculate the exchange-correlation energy E_{xc} using Equation (3.1.23) to be:

$$E_{xc} = E - 2 \int \psi \left(-\frac{1}{2} \nabla^2 \right) \psi d\vec{r}_1 - \frac{1}{2} \int \int \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 - \int \rho(\vec{r}_1) \left(\frac{1}{2} k(r_1^2) \right) d\vec{r}_1. \quad (3.1.29)$$

Using (3.1.24) we can write the exchange energy as:

$$E_x = -\frac{1}{4} \int \int \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2. \quad (3.1.30)$$

Knowing that $E_c = E_{xc} - E_x$, we can use (3.1.29) and (3.1.30) to determine the correlation energy:

$$E_c = E - 2 \int \psi \left(-\frac{1}{2} \nabla^2 \right) \psi d\vec{r}_1 + \frac{1}{2} \int \int \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 - \int \rho(\vec{r}_1) \left(\frac{1}{2} k(r_1^2) \right) d\vec{r}_1. \quad (3.1.31)$$

3.2 The first excited state of Hooke's atom

In this section we discuss how the first excited state density of the Hooke atom can be determined analytically. We then discuss two methods of mapping the Hooke atom in its excited states onto a Kohn-Sham system.

3.2.1 Analytic study of the density of the first excited state. Similar to the route we followed in describing the density of the ground state, we can use the set of equations (3.1.7) and (3.1.8) in describing the first excited state of the Hooke atom.

In this case the Hamiltonian of equation (3.1.7) is of a harmonic oscillator with energy $\epsilon_{nlm} = \sqrt{k} (2n + l + \frac{3}{2})$ and a wave function given by:

$$\Psi_{nlm}(r, \phi, \theta) = N_{kl} r^l e^{-\sqrt{k}r^2} L_k^{l+\frac{1}{2}}(2\sqrt{k}r^2) Y_{lm}(\phi, \theta), \quad (3.2.1)$$

where $L_k^{l+\frac{1}{2}}$ is the Laguerre polynomial $Y_{lm}(\phi, \theta)$ is the spherical harmonics and r denotes either of the position coordinates r_1 or r_2 . Integrating the wave function given by (3.2.1), we obtained the following value for the charge density:

$$\rho(r) = \frac{\left(e^{-r^2} \left(8(r + r^3) + e^{\frac{r^2}{2}} \sqrt{2\pi} \left(r(27 + 6r^2 + r^4) + 4(7 + 2r^2 + r^4) \operatorname{erf}\left(\frac{r}{\sqrt{2}}\right) \right) \right) \right)}{\left(24 \left(5 + \frac{8}{\sqrt{\pi}} \right) \pi^2 r \right)} \quad (3.2.2)$$

We plotted this value of the charge density of the first excited state together with the density of the ground state for comparison and we obtained the following plot:

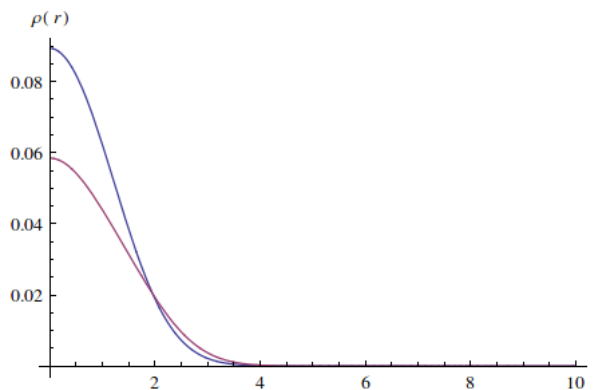


Figure 3.3: The ground and the first excited states of Hooke's atom at the value of the spring constant $k = \frac{1}{4}$. The figure demonstrates that despite the fact that the ground state has a higher population near the nucleus, it vanishes at shorter distances compared to the first excited state.

3.2.2 Mapping the first excited state. Considering the density of the first excited state obtained theoretically, we used (3.1.26) to find the the Kohn-Sham potential V_{ks} . Then we used that value and the relation (3.1.28) with $V_{ext} = \frac{1}{8}r^2$, to plot the Hartree plus the exchange-correlation potential.

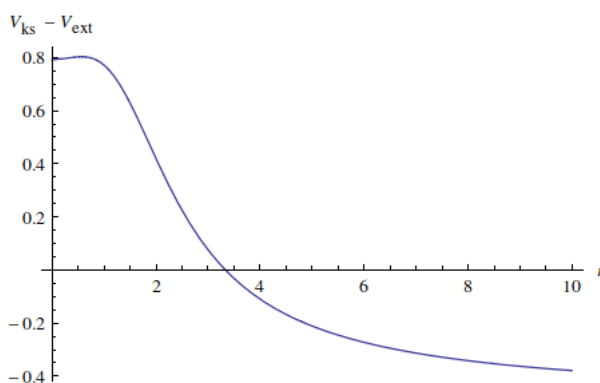


Figure 3.4: The Hartree plus the exchange-correlation potential obtained when using the density of the first excited state in determining the Kohn-Sham potential.

We substituted the value of the Kohn-Sham potential obtained using the first excited state density, into the equation:

$$\frac{1}{2}y''(r) + y(r)(\lambda - V_{ks}) = 0, \quad (3.2.3)$$

where $y(r)$ is the radial part of the wave function multiplied by r . In order to numerically find the orbitals ψ_i corresponding to values of the parameter λ ranging from 0.2 to 2.5, we imposed the boundary condition that the wave function vanishes as r goes to ∞ and then we searched for solutions where $y(0) = 0$.

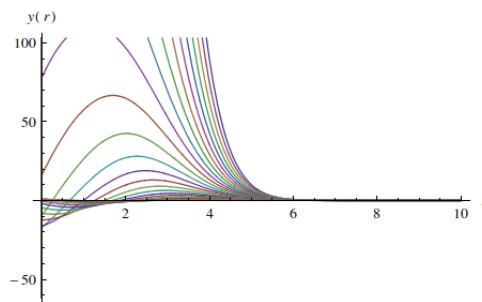


Figure 3.5: The numerical solutions of the Kohn-Sham equation.

To determine which of the orbitals obtained corresponds to the ground state, we first plotted the solutions at $r = 0.0001$ ($r = 0$ was avoided for numerical stability) as a function of the values of the parameter λ .

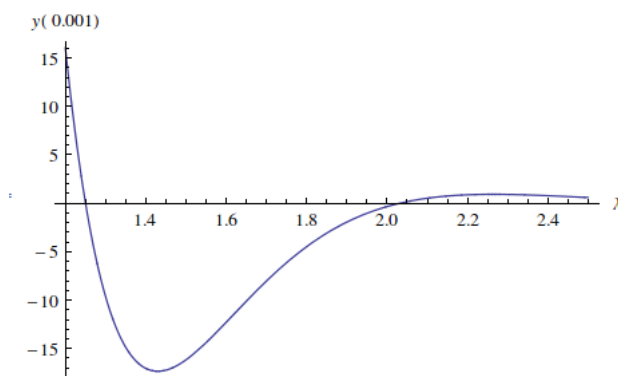


Figure 3.6: The values of the solutions $y(r)$ plotted at the point $r = 0.0001$ for a range of values of the parameter λ . The lowest value obtained i.e the ground state energy is 1.25003. The energy of the first excited state was found to be 2.1615.

We used the value obtained for the ground state energy to identify the ground state wave function. The next plot confirms that the resulting wave function is the correct first excited state and compare it to the first excited state wave function.

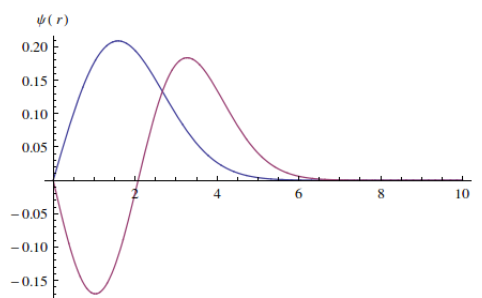


Figure 3.7: The ground state (the blue curve) and the trial wave function obtained from the numerical solutions of the Kohn-Sham equation. The ground state wave function has only one node, while the the other wave function has two nodes indicating that it is the correct first excited state.

The following plot compares the density of the Kohn-Sham system to the density of the first excited state of Hooke's atom:

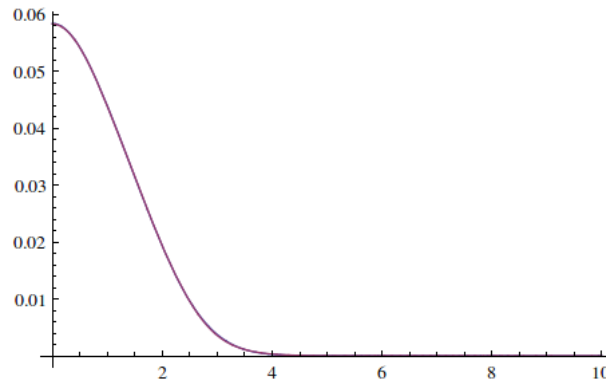


Figure 3.8: The density corresponding to the first excited state of Hooke's atom coinciding with the density of the ground state of the Kohn-Sham system proving the possibility of mapping the first system onto the other.

Figure 3.8 proves that we can map the excited state density of a two electrons system onto the ground state of the Kohn-Sham system.

In this work we also investigated another method to map the first excited state of the Hooke atom. Rather than mapping onto the ground state, this method suggests mapping onto excited states of the corresponding Kohn-Sham system. The first excited state of the Kohn-Sham system is defined as:

$$\rho_1 = \phi_0^2 + \phi_1^2, \quad (3.2.4)$$

where ϕ_0 and ϕ_1 are the wave functions of the ground state and the first excited state of the Kohn-Sham system.

The Kohn-Sham potential for a system of two electrons is given by:

$$V_{ks} = V_{ext} + \frac{1}{2}V_H + V_c, \quad (3.2.5)$$

where for such a system the exchange potential is equivalent to $-\frac{1}{2}V_H$. Hence, the only difficulty now is to determine the correlation potential V_c .

We used a simple "self-consistent" approach in determining V_c . We started by setting the value of V_c to zero and then we calculated the density ρ_1 and compared it to the density of the first excited state of Hooke's atom. In the next cycle we changed V_c by adding a term proportional to the difference between ρ_1 and the density of the first excited state. To achieve numerical stability, we used a linear combination of the density of the current cycle and the one before. The linear combination is controlled by some parameter $\beta = 0.6$. We kept repeating those cycles until the correct value of the density was found for a specific value of V_c .

The figure below shows the ground state and the first excited state of the Kohn-Sham system obtained using this method:

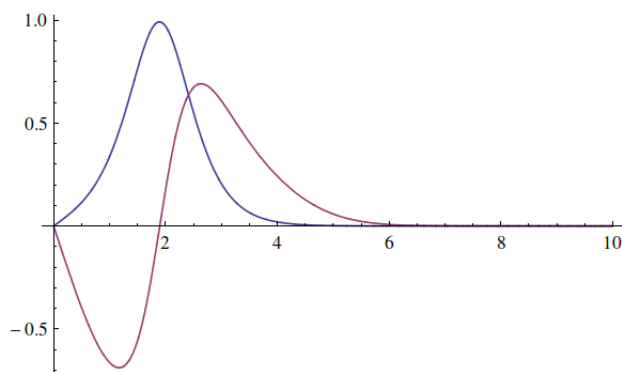


Figure 3.9: The ground state and the first excited state of the Kohn-Sham system obtained using the self-consistent method.

The exchange-correlation potential is plotted in the figure below:

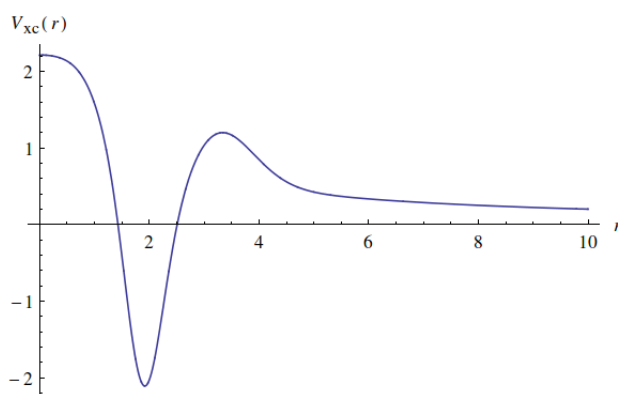


Figure 3.10: The exchange-correlation potential of the Kohn-Sham density.

Plotting the density of the first excited state obtained by this method and the density of the first excited state of Hooke atom, we found that the two densities are identical.

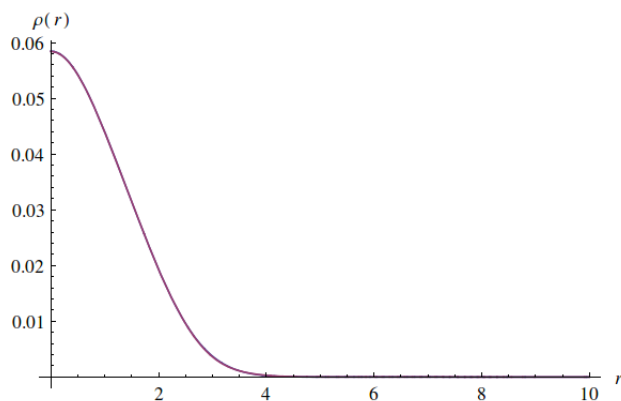


Figure 3.11: The overlap of the density of first excited state of the Hooke atom and the density of the first excited state of the Kohn-Sham system.

4. Conclusion

The aim of this project was to investigate the possibility of mapping excited states of an interacting system onto excited states of a Kohn-Sham system. As a model we used the analytically solvable, two-electron system known as the Hooke atom.

In work done earlier by ASHEBIR (2013), the possibility of mapping the first excited state of Hooke atom onto the ground state of a Kohn-Sham system was investigated. The result was that this map is not possible "within the general adiabatic connection".

In this work we replicated the mapping of the first excited state of Hooke atom onto the Kohn-Sham system and proved its possibility by comparing the resulting densities of the two systems. Then we proved numerically that the first excited state of a Hooke atom can be mapped onto any of the excited states of the corresponding Kohn-Sham system.

Accordingly we conclude that the mapping of an excited state of an interacting system to a Kohn-Sham system is not unique. Any formalism of the theory developed in the future, must take that into account.

References

- S. E. ASHEBIR. Density Functional Theory: Excited States of Two Particle Systems . Master's thesis, African Institute for Mathematical Sciences, South Africa, 2013.
- E. Engel and R. M. Dreizler. *Density Functional Theory: An Advanced Course*. Springer, 2011.
- C. Filippi, C. Umrigar, and M. Taut. Comparison of exact and approximate density functionals for an exactly soluble model. *The Journal of chemical physics*, 100(2):1290–1296, 1994.
- P. Hohenberg and W. Kohn. Inhomogeneous electron gas. *Physical review*, 136(3B):B864, 1964.
- S. Kais, D. Herschbach, N. Handy, C. Murray, and G. Laming. Density functionals and dimensional renormalization for an exactly solvable model. *The Journal of chemical physics*, 99(1):417–425, 1993.
- N. R. Kestner and O. Sinanoglu. Study of electron correlation in helium-like systems using an exactly soluble model. *Physical Review*, 128(6):2687, 1962.
- W. Kohn and L. J. Sham. Self-consistent equations including exchange and correlation effects. *Physical Review*, 140(4A):A1133, 1965.
- M. Levy and J. P. Perdew. The constrained search formulation of density functional theory. In *Density Functional Methods in Physics*, pages 11–30. Springer, 1985.
- G. M. D. Nguimdo. Functional derivative discontinuity in ensemble density functional theory. Submitted in partial fulfillment of a postgraduate diploma at AIMS, 2012.
- R. G. Parr and W. Yang. *Density Functional Theory of Atoms and Molecules*, volume 16. Oxford University Press, 1989.
- L. Piela. *Ideas of quantum chemistry*. Elsevier, 2013.
- V. Sahni. *Quantal density functional theory*. Springer, 2004.
- M. Taut. Two electrons in an external oscillator potential: Particular analytic solutions of a coulomb correlation problem. *Physical Review A*, 48(5):3561–3566, 1993.
- Wikipedia. Density functional theory. Wikipedia, the Free Encyclopedia, http://en.wikipedia.org/wiki/Density_functional_theory, Accessed April 2014.
- N. Zettili. *Quantum mechanics: concepts and applications*. John Wiley & Sons, 2009.