

# **Studies in Excited-State Density-Functional Theory**

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by  
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to the  
**DEPARTMENT OF PHYSICS**  
**INDIAN INSTITUTE OF TECHNOLOGY KANPUR**  
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September, 2006

*Dedicated to*

.....

.....

*My family*

.....

.....

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# **STATEMENT**

I hereby declare that the matter embodied in this thesis entitled “**Studies in Excited-State Density-Functional Theory**” is the result of research carried out by me in the Department of Physics, Indian Institute of Technology, Kanpur, India under the supervision of Prof. Manoj K. Harbola. In keeping with general practice of reporting scientific observations, due acknowledgments has been made wherever the work described is based on the findings of other investigators.

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**CERTIFICATE**

It is to certify that the work embodied in the thesis entitled “**Studies in Excited-State Density-Functional Theory**” by **Prasanjit Samal**, has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

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# Abstract

Studying excited-states and various properties related to it by employing density functional theory (DFT) has gained a lot of attraction during the last two decades and still continues. We have critically examined some of the fundamental aspects of time-independent excited-state DFT and time-dependent DFT.

After the introductory chapter on excited-state DFT, in the second chapter we have described the density-to-potential mapping for excited-states within time-independent density-functional formalism. This embodies a completely new approach which uniquely identifies the system for a given excited-state density. Based on the stationary state formulation due to Görling and variational approach of Levy-Nagy for the excited-states in time-independent DFT we have established the excited-state counterpart of the Hohenberg-Kohn-Sham density functional formalism.

In the third chapter we have discussed one way of developing exchange-correlation functionals for excited-states. Three such exchange-only functionals has been constructed within the local-density approximation (LDA) for three different classes of excited-states. Unlike the ground-state here, the exchange-correlation functionals are non-universal and state-dependent which are the key points for their construction. The excitation energies obtained by employing the constructed functionals leads to results comparable to TDDFT and even better than that.

In chapter four, we have analyzed the Floquet formulation of TDDFT in light of the recent criticism to density-to-potential mapping for quasienergy eigenstates. Our analysis shows that steady-state DFT is a complete theory and its earlier criticism has overlooked the basic difference between Floquet and Runge-Gross formalism of TDDFT. Based on our analysis, we conclude that it is actually the steady-state rather the Runge-Gross formalism being used in calculating the excitation and oscillator strengths.

# Synopsis

Density functional theory (DFT) as a quantum-many body technique is quite extensively used for studying electronic structure of atoms, molecules and solids in the last four decades. This is a tool which not only simplifies the many-body problem but also consumes much less time in calculating various properties of complex systems compared to other quantum chemical wavefunctional methods like configuration interactions (CI), Moller Plesset (MP) and coupled-cluster (CC) etc. . DFT was initially developed to deal with only ground-state properties and gain better insight of processes occurring in various physical/chemical environment. Later the same has been extended to study excited-states and several phenomena associated with it. However, excited-states are notoriously difficult to tackle within the framework of DFT unlike the ground-states in many counts.

There are two ways of calculating properties of excited-states employing DFT : one is within the framework of time-independent DFT and the other is the time-dependent density-functional theory (TDDFT). In any case, the calculations of excited-states are not so simple although it is possible in principle. The present thesis reports our attempt to develop excited-state DFT and is devoted to providing strong foundation to it. Here we have answered issues associated with excitations in particular to the fundamental aspects of time-independent excited-state DFT and TDDFT.

Motivation behind this work stems from the fact that the existence of a large amount of experimental spectroscopic data and also from the fact that they contain information on the electronic dynamics. Traditional DFT within the local density (LDA) and gradient corrected (GGA, meta-GGA) approximations is not a reliable approach for studying excited-states although at times they lead to better results. This is because these functionals are constructed for the ground-state. Extension of DFT to excited-states is not straightforward as it involves a number of fundamental issues to be answered. These issues are related to the formal foundation of excited-states within DFT. The first question to be answered is whether there exists a Hohenberg-Kohn like theorem for excited-states (*i.e.* uniqueness in density-to-potential mapping for excited-states) ? Secondly the construction of LDA or beyond LDA (GGA, GGA, meta-GGA) like exchange-correlation functionals for excited-states which will pave the way for its success like the ground-states in modern DFT ? Both these issues have been addressed by us: **(i)** we have established the uniqueness in density-to-potential mapping

and constructed the appropriate KS systems for the excited-states, **(ii)** we have also developed exchange-only functionals for three different classes of excited-states within the LDA which is the first ever attempt towards the construction of exchange-correlation functionals for excited-states. Based on our proposed theory and construction, we have performed several atomic excited-state calculations with great success. As is already mentioned earlier, another way to study excited-states is using the TDDFT approach. In TDDFT the excitations are obtained as the poles of the dynamic polarizabilities in the time-dependent response theory. The idea of calculating excitations in TDDFT arises from the Floquet formalism of TDDFT. Recently this formalism has also been questioned. However, in the work reported in this thesis, we have shown that the criticism regarding the foundations of Floquet formalism is invalid and Floquet theory is a well founded theory.

A few years ago Görling and Levy and Nagy tried to develop the time-independent excited-state theory based on the constrained-search formalism. Görling has developed stationary state theory for excited-states whereas Levy and Nagy variationally determined the excited-state density and energy which is analogous to the ground state theory. In the stationary-state formulation there happens to be several external potentials  $v_{ext}$  and the corresponding KS potentials for each  $\rho$ -stationary state. The question arises which potential has to be selected for a given excited-state density so that excited-state energy and other physical observables will be the functional of the density of that corresponding excited-state? This is a must if one has to perform excited-state calculations in DFT. In the same year Levy and Nagy come up with the idea that out of the many KS potentials one should select that whose ground-state density resembles the original one most closely in least square sense. So they defined an universal bi-density functional for excited-states similar to the HK functional instead it is now the functional of both ground as well as excited-state density. One important point to note at this stage is that for uniqueness of density-to-potential mapping for the excited-states, the information about the ground-state is a must.

In this thesis we have studied the density-to-potential mapping in detail. For this we first quantified the Levy-Nagy criterion of comparing the ground-state densities and then investigated this criterion quite extensively for several atomic excited-states. We found for most of the cases the criterion is satisfactory but in some cases surprisingly is not. Then we tried to find the reasons for that. We found it is because of the fact that the ground-state densities that one is comparing are not the self-consistently determined ones rather one

should be comparing self-consistently determined quantities. So we have proposed a new theory for excited-states where we have compared the original and KS kinetic energies in order to select a particular potential or KS system for a given excited-state density. We have extensively described it in the second chapter of this thesis how the newly developed time-independent excited-state theory by us uniquely establishes the density-to-potential mapping and selects the appropriate KS systems for the excited-states which answered the first issue of time-independent excited-state DFT as is mentioned above.

In the Levy-Nagy variational description of excited-states, the excited-state density functionals have implicit ground-state dependence. The ground-state dependence comes through the orthogonality constraint while defining the bi-density functional unlike the universal functional for the ground-states. Because of the constraint of orthogonality the excited-state functional becomes non-universal and state-dependent. So unlike the ground-state in excited-state DFT exchange-correlation functionals should be structurally different for various classes of excited-states. Also application of ground-state functionals to excited state will lead to erroneous results because they don't incorporate in them the state-dependence nature. Taking into account the state-dependence, we have constructed three different exchange-only functionals for excited-states within the LDA. Depending upon the orbital excitation we made similar excitation in the  $k$ -space for the homogeneous electron gas and then tried to construct these functionals. We have provided an in depth discussion on the construction of functionals in the third chapter. The results obtained for single as well as double excitations using the constructed functionals within two different approaches comes pretty close to the exact exchange only results of Hartree-Fock (HF), Harbola-Sahni (HS) approaches and Optimized Potential Method (OPM). In one case we have obtained results better than that obtained using TDDFT. In our case we have obtained results for double excitations which are not possible to get within the linear response theory of TDDFT. So far there is no reliable TDDFT approach to account for the doubly excited-states. Like in the case of ground-state DFT here too possible gradient corrections can be made to the excited-state functionals to improve the accuracy of the approximation. Although we have constructed exchange-only functionals but its also possible to construct correlation functionals for excited-states in a similar manner.

So far the mostly applied technique to obtain excitations of atoms and large molecules, is time-dependent density functional response theory. In TDDFT within the linear response regime excitations are nothing but the poles of the dynamic polarizability. The first attempt

made by Casida to obtain excitations in this manner arises from the Floquet formalism of TDDFT although later Petersilka et al. did so using the density-density response function but within the Runge-Gross formalism of TDDFT. So its clear from Casida's work that in calculating frequency dependent polarizability  $\alpha(\omega)$ , it is the steady-states of a system that is employed. Thus in calculation of  $\alpha(\omega)$ , and related quantities such as excitation energies and oscillator strengths, it is the Floquet theory of TDDFT rather than the RG theory that is being applied. However, the Floquet formalism recently has been questioned by Maitra et al. in light of its basic density functional aspect (*i.e. density-to-potential mapping*). Also, they have shown that this formalism is incomplete as it couldn't account for the initial state dependence and also showed through an example the non-uniqueness of the density-to-potential mapping in Floquet formalism. We have further analyzed the Floquet formalism of TDDFT in light of its recent criticism. Through the comparison of the Runge-Gross and Floquet formalism, we are able to show that earlier researchers have overlooked the crucial aspects of the two theories which made them to conclude that Floquet formalism is incomplete. In fact, they have made some misleading statements by taking into account an excited Floquet state, but the original Floquet formulation is quite similar to HK formulation of DFT. We have discussed in detail our analysis of Floquet theory in the fourth chapter of this thesis.

In conclusion, we have proposed possible solutions to various issues in time-independent excited-state DFT and Floquet formulation of TDDFT. We have discussed how our attempts in this direction will be helpful for further developments in excited-state DFT.

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# List of Publications

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# Chapter 1

## Introduction to Excited-States in (TD)DFT

### 1.1 INTRODUCTION

Density Functional Theory (DFT) has become a general method for calculating the ground-state properties of interacting many electron systems such as atoms, molecules or solids [1–34] and attempts have been made to extend it to obtain excited-states [35, 36]. Its most attractive feature is that it transforms the many-body system into a system of non-interacting fermions in an effective field. This makes the method of great practical use. The price one has to pay for transforming the interacting problem to an effective non-interacting one is that it requires an approximation for the effective field. This will be transparent as we move through this introduction. Since its inception DFT has become very popular among researchers in physics, chemistry and material science, due to ease of its implementation and due to the development of accurate density functionals. The theory originates from the pioneering work due to Thomas [1] and Fermi [2] in the early thirties of the twentieth century and further refinements by Hartree [3], Dirac [4, 5], Fock [6] and Slater [7]. It was given a firm foundation by Hohenberg, Kohn and Sham almost forty years after the work of Thomas and Fermi. The original scheme as proposed by Hohenberg and Kohn (HK) [8] and Kohn and Sham (KS) [9] is a ground-state theory which provides a reliable and inexpensive method for the calculation of ground-state energy of an interacting many Fermionic system. Subsequently this has been used to extract a wealth of observable quantities, such as band gaps in solids, energies of surface defects, bond angles and lengths and their dynamics in the case of molecules, electric dipole moments, electric quadrupole moments, static polarizabilities, infrared intensities,

magnetic susceptibilities, Raman intensities, etc. Although the rigorous legitimization and therefore the origin of the theory is the proof of the HK theorem and the formulation of the KS construction of an auxiliary effective non-interacting system, the ideas contained in the density functional approach to the many-body problem have been influenced by different historical developments.

Of such historical developments, one is concerned with the notion of an effective one-particle problem and the issue of self-consistency. In 1928 Hartree [3] came up with the suggestion for an approximation to the  $N$ -particle problem which was aimed at the construction of an effective single particle Hamiltonian. In this approximation every electron is assumed to move in an effective potential composed of the external potential due to the nuclei and a contribution which describes the average electrostatic interaction between the electrons. The approximated Hamiltonian is then the sum of the effective one particle Hamiltonians, and the approximate wavefunction can be written as a product of the single particle orbitals which are the solution of the corresponding single particle Schrödinger equation. This approximation had, however, the problem that it ignored the antisymmetric nature of the total wavefunction. One important point to note is that the effective one-particle potential is free from self-interaction<sup>1</sup>.

The problem of the antisymmetric nature of the many-body wavefunction was circumvented in 1930 by Fock [6] who suggested using an already antisymmetric Slater determinant as a trial function for the Rayleigh-Ritz variational principle. Assuming again, as an approximation for the  $N$ -particle Hamiltonian, a sum of effective single particle Hamiltonians leads then via the variational principle to the Hartree-Fock equations [7]. The requirement of antisymmetry leads in addition to the classical Hartree term in the effective one-particle potential to a so called non-classical exchange term. It depends on, besides the eigenstate which is considered, all other eigenstates of the effective Hamiltonian and is a fully nonlocal potential unlike the Hartree term. The corresponding one particle Schrödinger equation is a multidimensional integro-differential equation which is in addition also nonlinear like Hartree equations. For obtaining the solutions these equations have to be solved in a self-consistent manner. One starts with a guess for the effective potential, then solves the Hartree-Fock equations for the new one particle orbitals and constructs from these a new effective potential. This cycle

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<sup>1</sup>The electron whose effective potential has to be determined contributes via the total charge density already to its own effective potential therefore causing a self-interaction error.

is iterated until self-consistency is reached. The ideas of an effective one-particle Hamiltonian and a self-consistent solution originating from these historical developments were later incorporated in the KS ansatz [9] of density-functional theory.

When evaluating the total ground-state energy in the Hartree-Fock approximation for the homogeneous free electron gas (HEG), the exchange term in the Hartree-Fock equations causes an additional energy contribution which is called the exchange energy [4, 5]. It has the form  $\frac{E_x}{N} = -\frac{3k_f}{4\pi}$  (atomic units will be used throughout), where Fermi wave vector  $k_f = \{3\pi^2\rho_0\}^{\frac{1}{3}}$ . Later, in order to model exchange effects in interacting inhomogeneous systems Slater suggested [7] using the exchange contribution of the homogeneous electron gas but to replace the constant density  $\rho_0$  by the actual local density  $\rho(\vec{r})$  at the space point  $\vec{r}$  of the considered system. He then used for his calculations this additional potential in the form  $v_x(r) = -\alpha\frac{\{3\pi^2\rho_0\}^{\frac{1}{3}}}{\pi}$  in a one-particle Schrödinger equation similar to the Hartree equations. This is known as Slater's  $X\alpha$  theory. To improve numerical results the constant  $\alpha$  often was varied but this had the notion of a somewhat arbitrary choice for the potential and lead to the discussion whether or not it is legitimate to work in an independent particle picture and if there is a unique effective one electron potential that corresponds to the real interacting system under consideration. Because of the replacement of the constant density  $\rho_0$  by the actual local  $\rho(\vec{r})$ , Slater's  $X\alpha$  method can be viewed as a precursor to the concept of the Local Density Approximation (LDA). With time, LDA has given rise to other accurate local and semilocal functionals like GGA to meta-GGA.

The earlier attempts in formulating density based approximate methods culminated in the form of an exact framework for the density based theory which is based on the HK theorem [8]. The theorem states that the ground-state density of a system of  $N$ -interacting electrons uniquely determines (to within an additive constant) the external potential of the system. This also determines the number of particles by quadrature. Since the Hamiltonian is a functional of the external potential and the particle number, the density also determines the Hamiltonian uniquely. As a consequence of the theorem, it can be concluded that the ground-state density completely determines all properties of the system such as the wavefunction, ground-state as well as excited-state energies, response properties, etc. Because of this one-to-one mapping, all the properties then become functionals of the ground state density either explicitly or implicitly. The HK theorem gives no practical way of constructing these functionals; it only ensures their uniqueness.

The one-to-one mapping between potentials and densities can be established for any arbitrary inter particle interaction, including the vanishing interaction, i.e. for a system of non-interacting particles. This ensures the uniqueness of an effective one-particle potential which corresponds to the ground-state density of the interacting system. The proof of the theorem strongly legitimizes the use of an effective single particle potential which results in the KS method. In the KS system the introduction of an auxiliary non-interacting system [9] instead of its interacting counterpart simplifies the problem to a great extent.

The problem of calculating the ground-state properties is no doubt handled successfully through DFT. The question arises if it is possible to extend DFT to excited-states? The present work evolves in this context. According to the HK theorem, DFT can in principle, be used to calculate excitation energies. Unfortunately the route from the ground-state electron density to the excitation energies is not necessarily simple (excited-state energy then have to be expressed as a functional of the ground-states density) one and it appears that the computation of electronic spectral properties is far more complicated in DFT than in the traditional schemes of quantum chemistry. For instance in Hartree-Fock (HF) theory, it is easy to prove the Koopman's theorem: neglecting the electronic relaxation effects, electron removal energies are directly related to the eigenvalues of the HF single electron equations [37]. In DFT such a correspondence between KS eigenvalues and excitation energies is not valid as discussed, for example, by Perdew and Zunger [38].

Excited-state properties in terms of the corresponding densities are notoriously difficult to calculate within the traditional density functional framework, although DFT has been extended to incorporate low lying excited-states [39,40]. The simplest DFT scheme for the computation of excitation energies (and in particular the electron removal energies) has been the evaluation of the total energy difference between the initial and the final states. This same method is also used within HF (also called the self-consistent-field method) to compute excitation energies including relaxation effects, and for this reason it is known as  $\Delta$ SCF method. Obviously, this method can be applied when both the initial and the final state are within the reach of DFT, that is, when both states have the lowest energy for a given symmetry or a given number of electrons. This is the case for many excitation energies, like, for instance, the ionization potentials. When applicable, this method has allowed a reliable estimation of excitation energies. However, in general, excited states cannot always be identified with a DFT solution. For these reasons, the search for simple schemes providing at the same

time a reliable description of ground and excited state properties is an active subject of research. In our discussion, we shall consider only some of the excited-state density-functional approaches based on which the present work has been evolved.

Nowadays, there are several methods to treat excited-states of atoms, molecules and solids within the framework of DFT. The first rigorous generalization of the DFT for excited-states has been given by Theophilou [41] and later by Gross, Oliveira and Kohn [42]. Till date several calculations have been performed with this method [43]. However, this approach has the disadvantage that one has to calculate all the ensemble energies lying under the given ensemble to obtain the desired excitation energy. It is especially inconvenient to handle higher excited-states if required. Görling [44] has presented a density functional formalism for excited-states based on perturbation theory [45, 46]. An alternative theory is the time-dependent density functional theory (TDDFT) [29, 33, 47] in which transition energies are obtained from the poles of the dynamic linear response. The work formalism proposed by Harbola and Sahni [48] and the optimized potential method (OPM) [49–51] have also been applied in excited-state density-functional calculations [52, 53]. Görling [54] has presented a generalized density functional formalism for excited-states based on generalized adiabatic connection (GAC). The local scaling theory of Kryachko and Ludena [55] was also generalized for excited-states. Nagy has developed a non-variational theory for single excited-states based on Kato's theorem and the concept of adiabatic connection that is valid for Coulombic external potentials (*i.e.* free atoms, molecule and solid). The latest of the theories is the Levy-Nagy proposed variational density-functional theory [56] with minimum principle for self-consistent determination of individual excited-states and Sahni *et al.* quantal DFT for excited-states [35]. The work described in this thesis is the unified theory for handling excited-states and construction of exchange-correlation (*XC*) functionals for excited-states within the framework of DFT. First we will present a short review of ground-state DFT and then concentrate on excited-state calculations being done so far in DFT.

## 1.2 History of Density Based Theory

### 1.2.1 Solving the Schrödinger Equation

The solution of the Schrödinger equation gives information about various processes and phenomena occurring in complex systems. The complexity of the solution increases with the increasing number of particles in the system. Consider a system of  $N$ -particles interacting with each other via Coulomb potential and subjected to an external potential  $v_{ext}(\vec{r})$ . The Schrödinger equation for it reads as

$$\left\{ -\frac{1}{2}\nabla^2 + \sum_i v_{ext}(\vec{r}_i) + \sum_{i>j} \frac{1}{r_{ij}} \right\} \Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = E\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N), \quad (1.1)$$

where the first, second and third terms in Eq. 1.1 represents the kinetic energy, interaction with the external potential and the interparticle interaction respectively. The major difficulty in solving 1.1 arises because of the electron-electron interaction. Due to this interaction, the electrons tend to avoid one another. This effect should be reflected in the wavefunctions  $\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$  along with it being antisymmetric. These are the well known Coulomb-Pauli correlations among the electrons. Since the exact solution is not possible so attempts have been made to get approximate solutions of the Schrödinger equation. So various theories have been developed starting from Hartree, HF, Thomas-Fermi-Dirac (TFD) now to the modern density-functional theory . Whereas the first two are wavefunction based approaches, the latter are density-based theories for the ground-state. Most of the theories are based on variational principle which we describe next.

### 1.2.2 Wave-function Variational Principle

The most important theoretical principle, upon which many calculations rely, is the variational principle for the energy. It tells us how to look for ground-state solutions by guessing them. For instance, the exact ground-state wave-function minimizes the expectation value of the Hamiltonian,  $\hat{H}$ :

$$E_0 = \min_{\Psi} \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \quad (1.2)$$

A guess approximate normalized wave-function will always give an upper bound to the ground-state energy unless of course the guess is exact. A systematic derivation of the variational principle is as follows. Imagine we start with a trial wavefunction  $\Psi$ , which can be expanded in the complete basis of exact solutions for a chosen Hamiltonian:

$$\Psi = \sum_i c_i \phi_i , \quad (1.3)$$

where

$$\hat{H}\phi_i = E_i\phi_i . \quad (1.4)$$

The requirement is that the trial wave-function be normalized (*i.e.*):

$$\langle \Psi | \Psi \rangle = \sum_i c_i^2 = 1 . \quad (1.5)$$

So the energy expectation value using the trial wave-function becomes,

$$E = \langle \Psi | \hat{H} | \Psi \rangle = \sum_i |c_i|^2 E_i . \quad (1.6)$$

Since  $E_0$  is the lowest-energy eigenvalue of  $\hat{H}$ , so  $E_i > E_0$ , by construction. Since  $|c_i|^2$  is non-negative so the Eq.(1.6) proves the variation theorem (*i.e.*  $E > E_0$  for any trial wavefunction). Two popular electronic structure methods, HF and configuration-interaction (CI), rely on this principle. HF theory is based on the minimization of Eq.1.2 using one anti-symmetrized product of N single-particle orbitals or a Slater determinant [7]:

$$\Psi_{HF}(x_1, x_2, \dots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(x_1) & \psi_1(x_2) & \dots & \dots & \psi_1(x_N) \\ \vdots & \vdots & & & \vdots \\ \psi_i(x_1) & \psi_i(x_2) & \dots & \dots & \psi_i(x_N) \\ \vdots & \vdots & & & \vdots \\ \psi_N(x_1) & \psi_N(x_2) & \dots & \dots & \psi_N(x_N) \end{vmatrix} \quad (1.7)$$

where  $\psi_i(x)$  is the spin orbitals defined as

$$\psi_i(x) = \phi_i(\vec{r})\chi(\zeta) . \quad (1.8)$$

Here  $x = (\vec{r}, \zeta)$ , where  $\vec{r}$  is the spatial and  $\zeta$  is the spin coordinate of the electron. Spatial orbitals appearing in the above equations are those which minimize the expectation value of the Hamiltonian. Expectation value of the Hamiltonian with respect to a Slater determinant is given as:

$$\begin{aligned} \sum_i \int \phi_i^\dagger(\vec{r}) \left( -\frac{1}{2} \nabla^2 \right) \phi_i(\vec{r}) d\vec{r} + \int \rho(\vec{r}) v_{ext}(\vec{r}) d\vec{r} + \frac{1}{2} \int \int \frac{\rho(\vec{r}) \rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' \\ - \frac{1}{2} \sum_{i,j(\sigma_i || \sigma_j)} \int \int \frac{\phi_i^\dagger(\vec{r}) \phi_j(\vec{r}) \phi_j^\dagger(\vec{r}') \phi_i(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' \end{aligned} \quad (1.9)$$

where  $\sigma_i$  refers to the spin of the electron in the  $i^{th}$  spatial orbital. The first and second term in Eq.1.9 are the kinetic energy and interaction of the electron with the external potential respectively. The third term is the classical Coulomb energy of the electrons and the last term is the exchange energy arising due to Pauli correlations. This also includes the self-interaction energy in it. Thus the self-interaction energy is properly subtracted from the classical Coulomb energy. Minimizing the expression above with respect to the orbitals leads to the canonical Hartree-Fock equation for the  $i^{th}$  orbital:

$$\left\{ -\frac{1}{2} \nabla^2 + v_{ext}(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' \right\} \phi_i(\vec{r}) - \sum_{(\sigma_j || \sigma_i)} \int \int \frac{\phi_j(\vec{r}) \phi_j^\dagger(\vec{r}') \phi_i(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' = \varepsilon_i \phi_i(\vec{r}) \quad , \quad (1.10)$$

where  $\varepsilon_i$  appears as the Lagrange multiplier to ensure the orthonormality of orbitals. The Hartree-Fock equations are solved self-consistently. The configuration interaction involves minimization over a sum of different N-particle Slater determinants. But since the number of Slater determinants can often be large, this scheme is only useful for small systems.

The variational method as presented above provides information about only the ground-state energy and wavefunction. It can also be extended for obtaining excited-states and the associated energies. In Eq.1.3 let us restrict ourselves to normalized variational functions  $\Psi$  that are orthogonal to the true ground-state wave function  $\Psi_1$ . Then we have  $c_1 = \langle \Psi_1 | \Psi \rangle = 0$  and

$$\int \Psi^\dagger \hat{H} \Psi d\tau = \sum_{i=2}^{\infty} |c_i|^2 E_i \quad ; \quad \int \Psi^\dagger \Psi d\tau = \sum_{i=2}^{\infty} |c_i|^2 = 1 \quad (1.11)$$

For  $i \geq 2$ , we have  $E_i \geq E_2$  and  $|c_i|^2 E_i \geq |c_i|^2 E_2$ . Hence

$$\sum_{i=2}^{\infty} |c_i|^2 E_i \geq \sum_{i=2}^{\infty} |c_i|^2 E_2 = E_2 \sum_{i=2}^{\infty} |c_i|^2 = E_2 \quad (1.12)$$

Combining equations 1.11,1.12, we have the desired result:

$$\int \Psi^\dagger \hat{H} \Psi d\tau \geq E_2 \quad \text{if} \quad \int \Psi_1^\dagger \Psi d\tau = 0 \quad \text{and} \quad \int \Psi^\dagger \Psi d\tau = 1 \quad (1.13)$$

The above inequality allows us to get an upper bound to the energy  $E_2$  of the first excited-state. It can also be generalized to any arbitrary excited-state say  $k^{\text{th}}$  excited-state:

$$\frac{\int \Psi^\dagger \hat{H} \Psi d\tau}{\int \Psi^\dagger \Psi d\tau} \geq E_{k+1} \quad \text{if} \quad \int \Psi_1^\dagger \Psi d\tau = \int \Psi_2^\dagger \Psi d\tau = \dots \int \Psi_k^\dagger \Psi d\tau = 0 \quad (1.14)$$

DFT relies on the variational principle, but in a different way as we will see later in this chapter.

### 1.2.3 Thomas-Fermi Theory and Extensions

Density-based theory for the ground-state is closely interlinked with the Thomas-Fermi (TF) [1, 2] theory for a many-body system. This is the first density-based theory to deal with a many-electron systems. It approximates the kinetic energy of an  $N$ -particle interacting many-fermionic system by that of a homogeneous  $N$ -independent fermions. The latter is given by the expression

$$T_{TF}[\rho] = \frac{3}{10} (3\pi^2)^{\frac{2}{3}} \int \rho(\vec{r})^{\frac{5}{3}} d^3 r, \quad (1.15)$$

where  $\rho(\vec{r})$  is the density of the electrons which is spatially uniform. In TF theory, the same expression is used for obtaining the kinetic energy of a system of electrons although they may be moving in a potential that varies in space. Their density therefore is no longer spatially uniform. Nonetheless, their kinetic energy density at a point  $\vec{r}$  is approximated by the expression of Eq. (1.15) but with the density at that point. In TF theory the total energy is determined by adding to the kinetic energy functional above, the electrostatic energy and interaction with the external potential  $v$ . Thus the energy is given as

$$E[v, \rho] \approx T_{TF}[\rho] + \frac{1}{2} \int \int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r d^3r' + \int \rho(\vec{r})v(\vec{r})d^3r . \quad (1.16)$$

The energy obtained using the above expression overestimates the total energy because the exchange and correlation energy has not been taken into account in it. As a further improvement the energy obtained above can partially corrected using the Fermi-Amaldi [57] correction. On the other hand, if the exact exchange energy could be included in the energy expression, not only will the self-interaction go away automatically but the total energy will also become more accurate. Notice that the energy expression in Eq. (1.16) is a functional of the density and is determined explicitly – albeit approximately – by it. Equation for the density can therefore be obtained by applying the variational principle for the energy with respect to it. The Thomas-Fermi equation for density is obtained by the minimization of the TF energy expression with the constraint that the density gives the proper number of particle. This leads to the equation

$$\frac{1}{2} \left[ 3\pi^2 \rho(\vec{r}) \right]^{\frac{2}{3}} + v_{ext}(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' = \mu , \quad (1.17)$$

where  $\mu$  is the Lagrange multiplier to ensure the satisfaction of the constraint  $\int \rho(\vec{r})d\vec{r} = N$ . The density is given in terms of the potential as

$$\begin{aligned} \rho(\vec{r}) &= \frac{2^{\frac{3}{2}}}{3\pi^2} [\mu - v(\vec{r})]^{\frac{3}{2}} \quad \text{for } \mu \geq v(\vec{r}) \\ &= 0 \quad \text{otherwise} , \end{aligned} \quad (1.18)$$

where

$$v(\vec{r}) = v_{ext}(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' \quad (1.19)$$

is the total potential seen by the electrons. In general, the equation has to be solved self-consistently. As noted above, the accuracy of the Thomas-Fermi energy functional will increase if the exchange energy is included in it. However, exchange energy cannot be expressed as a functional of the density in general. Only for the homogeneous electron gas the exchange energy density can be written in terms of the density as

$$\mathcal{E}_x = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{\frac{1}{3}} \rho^{\frac{4}{3}} . \quad (1.20)$$

Thus, like the kinetic energy, for inhomogeneous systems the exchange energy in terms of the density can be included in the total energy by approximating it with the above expression. This was suggested by Dirac [4,5] and the resulting formulation is known as the TFD theory with the energy expression and the corresponding equation given as follows:

$$E_{TFD}[\rho] = \frac{3}{10} (3\pi^2)^{\frac{2}{3}} \int \rho(\vec{r})^{\frac{5}{3}} d\vec{r} + \int \rho(\vec{r}) v_{ext}(\vec{r}) d\vec{r} + \frac{1}{2} \int \int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' - \frac{3}{4} \left( \frac{3}{\pi} \right)^{\frac{1}{3}} \int \rho^{\frac{4}{3}} d\vec{r} , \quad (1.21)$$

and

$$\frac{1}{2} \left[ 3\pi^2 \rho(\vec{r}) \right]^{\frac{2}{3}} + v_{ext}(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' - \left( \frac{3}{\pi} \rho(\vec{r}) \right)^{\frac{1}{3}} = \mu . \quad (1.22)$$

There are further extensions of Thomas-Fermi theory based on improved forms for the kinetic energy that incorporate corrections due to density gradients. This is known as Weizsäcker correction [21]. Also the inclusion of correlation energy was done in an approximate manner. One feature of the Thomas-Fermi density is that it does not show any signatures of the usual shell structure. Nonetheless, the theory can be used effectively to describe approximate behavior of systems ranging from atoms to various complex systems. Thomas-Fermi theory was also extended by Bloch [58] to describe dynamics of electrons in time-dependent potentials.

### 1.2.4 Basics of DFT

In this section we will describe the DFT of the ground-state. The ground-state energy is a functional of both the potential  $v(\vec{r})$  and the number of particles  $N = \int \rho(\vec{r}) d\vec{r}$ . Thus the ground-state energy is, at first glance, a functional of both density and the external potential  $E = E[v, \rho]$ , which makes the functional a bit complicated. If somehow or the other one can establish a mapping between the two physical quantities then the energy would be a functional of only one of these quantities. This is what Hohenberg and Kohn showed [8]. According to them, "there exists an one-to-one mapping between the density and the external potential". It is rather simple to prove, that if two densities corresponding to two different

potentials are equal,  $\rho(\vec{r}, v) = \rho'(\vec{r}, v')$ , then the potentials  $v$  and  $v'$  can differ at most by an additive constant. This theorem enables us to establish a *unique correspondence* between the external potential and the ground-state density, which in turn makes the energy and other physical observables only as a functional of the ground-state density.

Hohenberg and Kohn showed this by assuming the ground-state to be *non-degenerate*, and that  $v(\vec{r}) - v'(\vec{r}) \neq c$  (*constant*). Then the two ground-state wavefunctions  $\Psi$  and  $\Psi'$ , corresponding to the two potentials, cannot be identical  $\Psi \neq \Psi'$ . Their proof follows from the principle of "*reductio ad absurdum*". One starts by assuming that also by  $v \neq v'$ , their ground-state densities are the same. The ground-state energy corresponding to  $v$  is

$$\begin{aligned} E &= \langle \Psi | \hat{H}_v | \Psi \rangle < \langle \Psi' | \hat{H}_v | \Psi' \rangle \\ &= \langle \Psi' | \hat{H}_v | \Psi' \rangle + \int \{v(\vec{r}) - v'(\vec{r})\} \rho(\vec{r}) d^3r \\ &= E' + \int \{v(\vec{r}) - v'(\vec{r})\} \rho(\vec{r}) d^3r \quad , \end{aligned} \quad (1.23)$$

where the Eq.(1.23) follows from the *variational principle* since  $\Psi$  is the ground-state wavefunction of the Hamiltonian corresponding to the external potential  $v$ . Since the same is also true for the ground-state  $E'$  of  $v'$ ,

$$\begin{aligned} E' &= \langle \Psi' | \hat{H}_{v'} | \Psi' \rangle < \langle \Psi | \hat{H}_{v'} | \Psi \rangle \\ &= \langle \Psi | \hat{H}_{v'} | \Psi \rangle + \int \{v'(\vec{r}) - v(\vec{r})\} \rho(\vec{r}) d^3r \\ &= E + \int \{v'(\vec{r}) - v(\vec{r})\} \rho(\vec{r}) d^3r \quad , \end{aligned} \quad (1.24)$$

so by adding these equations,  $E + E' < E' + E$ , which is a contradiction. Thus our assumption was false. So two potentials differing by more than an additive constant cannot have the same ground-state density. Hence it must also be possible to unambiguously invert the relation  $\rho(\vec{r}) = \rho[v(\vec{r})] \iff v(\vec{r}) = v[\rho(\vec{r})]$ , and thus the total energy may be uniquely expressed as a functional of density alone. This is the first of the two fundamental DFT theorems of Hohenberg and Kohn which guarantees the existence of the energy density functional. Then comes the second theorem which helps to obtain the equation for the density. The second theorem of DFT asserts that the total energy functional

$$E[\rho] = F[\rho] + \int v(\vec{r})\rho(\vec{r})d^3r \quad , \quad (1.25)$$

has a *minimum* equal to the ground-state energy at the ground-state density of the system. The proof follows by recasting the traditional wavefunctional variational principle in terms of the density. Consider a system of N-particles under the external potential  $v$ . The system is assumed to have non-degenerate ground-state  $\Psi$  with a corresponding density  $\rho(\vec{r})$ . Define a functional  $F[\rho]$  by

$$F[\rho] = \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle \quad , \quad (1.26)$$

which is a unique functional of density by the first theorem as  $\Psi$  is a functional of density  $\rho(\vec{r})$ . Similarly one can also define the energy functional for any other ground-state  $\rho'(\vec{r})$ ,

$$E_v[\rho'] = F[\rho'] + \int v(\vec{r})\rho'(\vec{r})d^3r \quad . \quad (1.27)$$

Suppose  $\Psi'$  be the ground-state of a different external potential  $v'$  having density  $\rho'(\vec{r})$ . The traditional Rayleigh-Ritz functional for  $\Psi'$

$$E_v[\Psi'] \equiv \langle \Psi' | \hat{H}_v | \Psi' \rangle = \langle \Psi' | \hat{T} + \hat{V}_{ee} | \Psi' \rangle + \int v(\vec{r})\rho'(\vec{r})d^3r \quad (1.28)$$

has, from variational principle, a lower value for the exact ground-state wavefunction  $\Psi$  than any other wavefunction (due to the assumption of non-degeneracy the inequality is strict)<sup>2</sup>. So by the variational principle<sup>3</sup>

$$\begin{aligned} E_v[\Psi'] &= \langle \Psi' | \hat{T} + \hat{V}_{ee} | \Psi' \rangle + \langle \Psi' | \hat{v} | \Psi' \rangle \\ &= F[\rho'] + \int v(\vec{r})\rho'(\vec{r})d^3r \\ &> E_v[\Psi] = F[\rho] + \int v(\vec{r})\rho(\vec{r})d^3r \quad . \end{aligned} \quad (1.29)$$

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<sup>2</sup>A density  $\rho$  is  $v$ -representable if it corresponds to an wavefunction which is solution of the Schrödinger equation with some external potential  $v$ .

<sup>3</sup>It has been identified that  $F[\rho'] = \langle \Psi' | \hat{T} + \hat{V}_{ee} | \Psi' \rangle$  because  $\Psi'$  is the ground-state corresponding to some density  $\rho'$ . This is where  $v$ -representability gets in.

The inequality (1.29) immediately gives the desired result

$$E_v[\rho] < E_v[\rho'] \quad . \quad (1.30)$$

Now assuming the differentiability of the energy functional we will get

$$\delta \left\{ E_v[\rho] - \mu \left[ \int \rho(\vec{r}) d\vec{r} - N \right] \right\} = 0 \quad . \quad (1.31)$$

This leads to the Euler-Lagrange equation for density

$$\mu = \frac{\delta E_v[\rho]}{\delta \rho(\vec{r})} = v(\vec{r}) + \frac{\delta F[\rho]}{\delta \rho(\vec{r})} \quad . \quad (1.32)$$

So now from the definition of functionals described earlier in this section, it is obvious that the minimum value is the ground-state energy, and that the minimizing density is the correct ground-state density associated with the external potential  $v$ . So far we have discussed only the ground-states which are non-degenerate. For degenerate ground-states the equivalence of the ground-state density and the external potential is established through the Levy's constrained search approach to be discussed next.

### 1.2.5 Constrained-Search Approach

It is possible to have a density functional analogy of the wavefunctional variational principle Eq.1.2. Instead of the original derivation of the Hohenberg-Kohn-Sham, which was based upon the principle "*reductio ad absurdum*", we will use the "*constrained search approach*" of Levy [59–61] and Lieb [62], which is in some respect simpler and more constructive. From the variational principle, the ground-state energy can be found by minimizing  $\langle \Psi | \hat{H} | \Psi \rangle$  over all normalized, antisymmetric  $N$ -particle wave functions

$$E = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle \quad . \quad (1.33)$$

This minimization process can be separated into two steps. First we consider all wavefunctions  $\Psi$  which yield a given density  $\rho$ , and then minimize over the wavefunctions:

$$\mathbf{min}_{\Psi \rightarrow \rho} \langle \Psi | \hat{H} | \Psi \rangle = \mathbf{min}_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle + \int v(\vec{r}) \rho(\vec{r}) d^3r \quad , \quad (1.34)$$

where the second term on the right hand side of Eq. (1.34) remains unchanged for a given density. This fact has been exploited for further decomposition of the energy functional. Now it's possible to define the universal functional

$$F[\rho] = \mathbf{min}_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle = \langle \Psi_{\rho}^{min} | \hat{T} + \hat{V}_{ee} | \Psi_{\rho}^{min} \rangle \quad , \quad (1.35)$$

where  $\Psi_{\rho}^{min}$  is that wavefunction which delivers the minimum for a given  $\rho$ . Finally the minimization is over all N-electron densities  $\rho(\vec{r})$ :

$$E = \mathbf{min}_{\rho} E_v[\rho] = \mathbf{min}_{\rho} \left\{ F[\rho] + \int v(\vec{r}) \rho(\vec{r}) d^3r \right\} \quad , \quad (1.36)$$

where  $v(\vec{r})$  is kept at a fixed value during the minimization. The density that minimizes is the ground-state density. The constraint of fixed number of particles can be handled formally through introduction of a Lagrange multiplier  $\mu$ :

$$\delta \left\{ F[\rho] + \int v(\vec{r}) \rho(\vec{r}) d^3r - \mu \int \rho(\vec{r}) d^3r \right\} = 0 \quad , \quad (1.37)$$

which leads to the Euler equation

$$\frac{\delta F[\rho]}{\delta \rho(\vec{r})} + v(\vec{r}) = \mu \quad . \quad (1.38)$$

The Lagrange multiplier in Eq.(1.38) is to be varied until the density gives the correct number of particles. The equation above implies that the external potential  $v(\vec{r})$  is uniquely determined by the ground-state density (or by any of them, if the ground-state is degenerate). The density variational principle described here on the basis of Levy's constrained search approach overcomes the "v-representability" problem of the original Hohenberg-Kohn-Sham theory. Whether the density is either "N-representable"<sup>4</sup> or "v-representable", the above description is equally applicable. In the degenerate cases it is the density-matrix which is used to define

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<sup>4</sup>A density  $\rho$  is N-representable if it is associated with many-body systems and integrates to the correct number of particles.

the functional  $F[\rho]$  [59–62]. It is also possible to extend this to the cases where the potential is spin-dependent. Similar and analogous principle can also be applicable for excited-states will be described latter.

### 1.2.6 Kohn-Sham Construction

Even if the HK theory implies the reformulation of the many-particle interacting systems in terms of the density, it doesn't guarantee the possibility for the exact solution of such systems. In Hohenberg-Kohn theory, both the kinetic energy (KE) and exchange-correlation energy has to be approximated. Thus with approximations the theory is like the TF theory discussed earlier. Kohn and Sham treated the kinetic energy in a much better manner. They replaced the interacting system by an auxiliary non-interacting system whose particle number density is same as the interacting system, which is the key concept for such construction. For a system of  $N$  non-interacting electrons, the Hamiltonian reduces to

$$\hat{H} = \hat{T} + \underbrace{\hat{V}_{ee} = 0} + \sum_{i=1}^N v(\vec{r}_i) = \hat{T} + \sum_{i=1}^N v(\vec{r}_i) . \quad (1.39)$$

Now for a non-interacting system, from Eq.(1.35)

$$F_{non-interacting}[\rho] = T_s[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} | \Psi \rangle = \langle \Phi_{\rho}^{min} | \hat{T} | \Phi_{\rho}^{min} \rangle . \quad (1.40)$$

Although in practice one can search over any arbitrary N-electron wavefunctions, the minimizing wavefunction  $\Phi_{\rho}^{min}$  for a given density  $\rho$  will be a non-interacting wavefunction (a single Slater determinant) for some external potential  $v_s$  such that

$$\frac{\delta T_s[\rho]}{\delta \rho(\vec{r})} + v_s(\vec{r}) = \mu_s . \quad (1.41)$$

The newly found KS potential  $v_s(\vec{r})$  is also a functional of density  $\rho(\vec{r})$ . If the effective potential in Eq.1.41 will be

$$v_s(\vec{r}) = v(\vec{r}) + \frac{\delta U[\rho]}{\delta \rho(\vec{r})} + \frac{\delta E_{xc}[\rho]}{\delta \rho(\vec{r})} , \quad (1.42)$$

then by construction  $\mu_s$  for the auxiliary system and  $\mu$  for the interacting system are the same. In the above equation the second and third terms on the right hand side represents the Coulomb and exchange-correlation potentials, the latter arising due to Pauli-Coulomb correlations. So the Euler equation for the auxiliary system becomes:

$$\frac{\delta T_s[\rho]}{\delta \rho(\vec{r})} + v_s(\vec{r}) = \mu \quad . \quad (1.43)$$

Now we define the exchange-correlation energy, for the interacting system by the equation

$$F[\rho] = T_s[\rho] + U[\rho] + E_{xc}[\rho] \quad , \quad (1.44)$$

where  $T_s[\rho]$  is the KS kinetic energy defined by Eq. (1.40) above, and can be written in terms of single particle orbitals to be:

$$T_s[\rho] = \sum_i \langle \phi_i | -\frac{1}{2} \nabla^2 | \phi_i \rangle \quad , \quad (1.45)$$

$U[\rho]$  the Coulomb energy and the rest constitutes the exchange-correlation energy  $E_{xc}[\rho]$ . The procedure is considered to be the better one because for several reasons: (i)  $T_s[\rho]$  forms typically a very large part of the total kinetic energy. (ii)  $T_s[\rho]$  is largely responsible for density oscillations of the shell structure, which are accurately described by the KS method. (iii)  $E_{xc}[\rho]$  is better suited for local and semilocal approximations than  $T_s[\rho]$ . The exchange-correlation energy  $E_{xc}[\rho]$  is the sum of independent exchange and correlation terms:

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho] \quad , \quad (1.46)$$

where [21]

$$E_x[\rho] = \langle \Phi_\rho^{min} | \hat{V}_{ee} | \Phi_\rho^{min} \rangle - U[\rho] \quad . \quad (1.47)$$

When  $\Phi_\rho^{min}$  is a single Slater determinant defined by Eq. (1.40), the equation above is the Fock integral applied to the KS orbitals. Also one can notice that

$$\langle \Phi_{\rho}^{min} | \hat{T} + \hat{V}_{ee} | \Phi_{\rho}^{min} \rangle = T_s[\rho] + U[\rho] + E_x[\rho] \quad , \quad (1.48)$$

and in the one electron ( $\hat{V}_{ee} = 0$ ) limit  $E_x[\rho] = -U[\rho]$ . The correlation energy is

$$\begin{aligned} E_c[\rho] &= \langle \Psi_{\rho}^{min} | \hat{T} + \hat{V}_{ee} | \Psi_{\rho}^{min} \rangle - \langle \Phi_{\rho}^{min} | \hat{T} + \hat{V}_{ee} | \Phi_{\rho}^{min} \rangle \\ &= F[\rho] - \{T_s[\rho] + U[\rho] + E_x[\rho]\} \quad . \end{aligned} \quad (1.49)$$

As expected correlation is always negative, since  $\Psi_{\rho}^{min}$  is the wavefunction which yield density  $\rho$  and minimizes the  $\langle \hat{T} + \hat{V}_{ee} \rangle$ , whereas  $\Phi_{\rho}^{min}$  is that wavefunction which also yields the same density  $\rho$  but minimizes  $\langle \hat{T} \rangle$  only. Thus  $\langle \Psi_{\rho}^{min} | \hat{T} + \hat{V}_{ee} | \Psi_{\rho}^{min} \rangle < \langle \Phi_{\rho}^{min} | \hat{T} + \hat{V}_{ee} | \Phi_{\rho}^{min} \rangle$ . For making DFT practicable the approximation for the exchange-correlation energy functional is a must. The various local and semilocal approximations like LDA, GGA or meta-GGA starts from the pioneering work of Kohn and Sham in 1965 [9]. To date there are number of accurate functionals that have been developed and tested for electronic structure calculations of atoms, molecules and solids.

### 1.3 Local-Density Approximation (LDA) and Beyond

For making DFT practically implementable the most important type of approximation for the exchange-correlation density functional is the local-density approximation (LDA), we will describe briefly several local and semilocal approximations being made in DFT here. This will help us for understanding the construction of XC functionals for excited-states to be described in the third chapter. For understanding the concept of LDA recall first how the noninteracting kinetic energy  $T_s[\rho]$  is treated in the Thomas-Fermi approximation<sup>5</sup>: In a homogeneous system one knows that, per volume<sup>6</sup>

$$\tau_s^{hom}(\rho) = \frac{3}{10}(3\pi^2)^{2/3}\rho^{5/3} \quad (1.50)$$

where the density remains constant over the space ( $\rho = const.$ ). In an inhomogeneous system, with  $\rho = \rho(\vec{r})$ , one approximates locally

<sup>5</sup>This is the first ever LDA made in the history of density-functional formalism.

<sup>6</sup>We will use capital  $T$  to  $\tau$  just to represent the same quantities per unit volume.

$$\tau_s(\vec{r}) \approx \tau_s^{hom}(\rho(\vec{r})) = \frac{3}{10}(3\pi^2)^{2/3} \rho(\vec{r})^{5/3} \quad (1.51)$$

which lead to the full kinetic energy by integration over the space co-ordinates

$$T_s^{LDA}[\rho] = \int d^3r \tau_s^{hom}(\rho(\vec{r})) = \frac{3}{10}(3\pi^2)^{2/3} \int \rho(\vec{r})^{5/3} d^3r. \quad (1.52)$$

Gradient correction to the Thomas-Fermi kinetic energy functional has also been done by Weizsäcker. Although one understands that the approximation  $T_s[\rho] \approx T_s^{LDA}[\rho]$  is much inferior to the exact treatment of  $T_s$  in terms of orbitals, as is done by the KS equations, the LDA concept turns out to be highly useful for another component of the total energy, the exchange-correlation energy  $E_{xc}[\rho]$ . For the exchange energy  $E_x[\rho]$  the procedure is very simple, as its already discussed in detail by Parr *et al.* [21] and Gross *et al.* [24]

$$\mathcal{E}_x^{hom}(\rho) = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \rho^{4/3}, \quad (1.53)$$

so that

$$E_x^{LDA}[\rho] = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \int \rho(\vec{r})^{4/3} d^3r. \quad (1.54)$$

This is the LDA for the exchange energy density functional  $E_x$ .<sup>7</sup>

For the correlation energy  $E_c[\rho]$  the situation is more complicated since  $\mathcal{E}_c^{hom}[\rho]$  is not known exactly: the determination of the correlation energy of a homogeneous interacting electron system (an electron liquid) is already a difficult many-body problem on its own. Earlier approximate expressions for  $\mathcal{E}_c^{hom}[\rho]$  were based on applying perturbation theory, for example the *random-phase approximation* (RPA) to this problem [63, 64]. These approximations became outdated with the advent of highly precise *Quantum Monte Carlo* (QMC) calculations for the electron liquid, by Ceperley and Alder [65]. Modern expressions for  $\mathcal{E}_c^{hom}[\rho]$  [38, 66, 67] are parameterizations of these data. These expressions are implemented in most standard quantum many-body packages and in typical applications give almost identical results.

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<sup>7</sup>If one adds this term to the LDA for kinetic energy in the Thomas-Fermi approximation which gives the so-called Thomas-Fermi-Dirac approximation to  $E[\rho]$ . By multiplying it with an adjustable parameter  $\alpha$  one obtains the so-called  $X\alpha$  approximation to  $E_{xc}[\rho]$ . Which are now a days not much of use in DFT as very efficient functionals has already been developed.

Independently of the parametrization, the LDA for  $E_{xc}[\rho]$  formally consists of <sup>8</sup>

$$E_{xc}[\rho] \approx E_{xc}^{LDA}[\rho] = \int \left\{ \mathcal{E}_x^{hom}(\rho(\vec{r})) + \mathcal{E}_c^{hom}(\rho(\vec{r})) \right\} d^3r = \int \mathcal{E}_{xc}^{hom}[\rho(\vec{r})] d^3r. \quad (1.55)$$

This approximation for  $E_{xc}[\rho]$  has proved amazingly successful, even when applied to systems that are quite different from the electron liquid that forms the reference system for the LDA. For many decades the LDA has been applied in, for example, calculations of band structures and total energies in solid-state physics. In quantum chemistry it is much less popular, because it fails to provide results that are accurate enough to permit a quantitative discussion of the chemical bond in molecules (so-called ‘chemical accuracy’ requires calculations with an error of not more than about 1 kcal/mol = 0.0434eV/particle). Some further improvements on the LDA includes the gradient correction (GEA), the generalized gradient approximation (GGA) [67–71] and meta-GGA [73–77]. The latter are accurate enough to give chemical accuracy.

With the possibility of writing a local exchange potential in terms of the orbitals, functionals based on the exact expression for the exchange energy in terms of the orbitals are also employed to do exact-exchange only (EXX) DFT calculations. The method is known as optimized effective potential (OEP) [49–51] or optimized potential method [78]. As noted above, it utilizes the exact expression for the exchange energy in terms of the orbitals and considers electrons to be moving in a local effective potential. The minimization of the orbital functional with respect to the density is achieved by repeated application of the chain rule for functional differentiation,

$$v_{xc}([\rho]; \vec{r}) = \frac{\delta E_{xc}^{orb}[\{\phi_i\}]}{\delta \rho(\vec{r})} = \int \int \sum_i \left[ \frac{\delta E_{xc}^{orb}[\{\phi_i\}]}{\delta \phi_i(\vec{r}')} \frac{\delta \phi_i(\vec{r}')}{\delta v_s(\vec{r}'')} \frac{\delta v_s(\vec{r}'')}{\delta \rho(\vec{r})} + c.c. \right] d^3r' d^3r'', \quad (1.56)$$

where  $E_{xc}^{orb}$  is the orbital dependent functional (e.g., the Fock term). Further evaluation of Eq. (1.56) gives rise to an integral equation that determines the  $v_{xc}[\rho]$  belonging to the chosen orbital functional  $E_{xc}[\{\phi_i[\rho]\}]$  [79, 80]. The high accuracy attained in applications of the OEP, and the fact that it is easier to devise orbital functionals than explicit density functionals, makes the OEP concept attractive, but the computational cost of solving the OEP integral

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<sup>8</sup>Sometimes people use the per particle instead of the per volume energy of the homogeneous system in writing the LDA. Since the conversion factor between both is the number of particles per volume, i.e., the density, an additional  $\rho(\vec{r})$  then appears under the integrals in (1.55).

equation is a major drawback.

## 1.4 Excited-States in Time-Independent DFT

In this section we will present an overview of some of the techniques developed to calculate excitation energies that have appeared in the context of DFT over the past thirty years. The degree of success varies considerably among the different techniques. The HK theorem ensures that every observable quantity of a physical system of interest is a functional of its ground-state density. Therefore all electronic excitation energies are also functionals of the ground-state density (*i.e.* from the ground-state density the Hamiltonian can be obtained from which every property of the system can be determined including the excited-states.) (e.g.  $E_k[\rho_0]$  for the first excitation above the ground state). However, in contrast to the developments for the ground-state energy functional very little is known about the functionals for the excited states of the system under consideration. The best known failure is for an infinite system: band gap is underestimated. To date there are four distinct density functional based routes to excitation energies of electronic systems which will be discussed briefly in the following sections. So far the most successful of all is certainly TDDFT compared to other time-independent density-functional techniques, that has become the standard for the calculation of excitations for finite systems.

As a first approximation to the excitation energies, one can simply take the differences between the ground-state KS eigenvalues. This procedure, although not entirely justifiable, is often used to get a rough idea of the excitation spectrum. But the KS eigenvalues (as well as the KS wave-functions) do not have any physical interpretation, except that the eigenvalue of the highest occupied state is equal to minus the ionization potential of the system [81]. The second scheme is based on the observation that the HK theorem and the KS scheme can be formulated for the lowest excited-states of each symmetry [39, 40, 64]. In fact, the single modification to the standard proofs is to restrict the variational principle to wave-functions of a specific symmetry. The unrestricted variation will clearly yield the ground-state. The states belonging to different symmetry classes will correspond to excited states. The excitations can then be calculated by simple total energy differences. This approach suffers from two serious drawbacks: (i) Only the lowest lying excitation for each symmetry class is obtainable. (ii) The XC-functional that now enters the KS equations should depend on the particular symmetry

being chosen. However, specific approximations for a symmetry dependent  $XC$  functional are not available, one is relegated to use ground-state functionals. Unfortunately the excitation energies calculated in this way are only of moderate quality. With all this background now we will explore the excited-state DFT in the following sections.

### 1.4.1 $\Delta$ SCF Method

One possibility is to calculate excitation energies from the ground-state energy functional. In fact, it was proved by Perdew and Levy [82] that "every extremum density  $\rho_k(\vec{r})$  of the ground-state energy functional  $E_v[\rho]$  yields the energy  $E_k$  of a stationary state of the system." The problem is that not every excited-state density,  $\rho_k(\vec{r})$ , corresponds to an extremum of  $E_v[\rho]$ , which implies that not all excitation energies can be obtained from this procedure. Ziegler, Rauk and Baerends [40] and von Barth [39] have borrowed the idea from multi-configuration Hartree-Fock to calculate energies of multiplets. This is well known as  $\Delta$ SCF method. Perhaps this is the oldest approach for calculating the excitation energies in DFT. In this approach a many-particle state with good symmetry,  $\Psi_k$ , is constructed by taking finite superposition of states

$$\Psi_k = \sum_{\alpha} c_{k\alpha} \Phi_{\alpha}, \quad (1.57)$$

where  $\Phi_{\alpha}$  are Slater determinant of KS orbitals and the expansion coefficients  $c_{k\alpha}$  are determined from group theory. By inverting the above equations for the Slater determinant one will have a relationship

$$\Phi_{\beta} = \sum_j a_{\beta j} \Psi_j. \quad (1.58)$$

If  $E_j$  is the energy of the many-particle state  $\Psi_j$ , expectation value of the Hamiltonian with respect to  $\Phi_{\beta}$  will be

$$\langle \Phi_{\beta} | \hat{H} | \Phi_{\beta} \rangle = \sum_j |a_{\beta j}|^2 E_j. \quad (1.59)$$

The key point to calculate the excitation energies from the above equation is then: (i) Construct  $\Phi_\beta$  from  $n$  KS orbitals (not necessarily the lowest ones);(ii) Make KS calculation for each  $\beta$  and associate the corresponding density-functional total energy  $E_\beta$  with  $\langle \Phi_\beta | \hat{H} | \Phi_\beta \rangle$ ; (iii) Now determine  $E_j$  by solving the system of linear equation (1.59). Instead of resorting to the complex calculations involved in finding out  $E_j$  one can approximate the excitation energy as the difference between the ground-state energy and the energy of the excited-state configurations using functional similar to the ground-state functional in the KS system. For example the first excitation of the Carbon atom would in this approach be obtained by evaluating the ground state energy functional at a self consistent density  $\rho$  which corresponds to the excited configuration  $1s^2 2s^1 2p^3$  and subtracting the ground-state energy of the Carbon atom, i.e.

$$\Delta E = E_0[\rho] - E_0[\rho_0] \quad (1.60)$$

This is not quite correct since exchange and correlation pieces on the right hand side are evaluated at different densities  $\rho$  and  $\rho_0$ . It is natural that the  $XC$  functional must be different from one another as the configurational behavior of ground and excited-states differs significantly. One such  $x$ -only functional has recently been constructed for excited-state by taking into account of the state dependence, which will be discussed in detail in the third chapter.

## 1.4.2 Ensemble Theory for Excited-States

The DFT was first rigorously generalized for excited-state by Theophilou [41]. Similar attempts were made by Pathak [84], Fritsche [85] and English *et al.* [86] for providing formalism for excited-states in DFT. Later Gross *et al.* [42] provided a general approach to calculate excitation energies in DFT through ensemble density functional theory, where the ensemble density  $\rho_{ensemble}$  is a weighted sum of the ground-state density and the density of the first excited-state

$$\rho_{ensemble} = w_0 \rho_0 + w_1 \rho_1 \quad (1.61)$$

The weights have to be chosen as

$$w_0 = \eta \ ; \ w_1 = 1 - \eta \ , \ \eta = \frac{1}{2} \quad (1.62)$$

to ensure that the ensemble density is normalized to  $N$ . The  $w_i$  can be chosen equal, i.e.  $\eta = 1/2$ , which is then called an equal ensemble or  $\eta$  can be adjusted by temperature to give a thermal ensemble. The ensemble energy has the form

$$\mathcal{E}(\eta) = (1 - \eta)E_0 + \eta E_1 . \quad (1.63)$$

Note that (Eq. 1.63) gives the ground-state energy for the choice  $\eta = 0$ . It follows from the general Rayleigh-Ritz principle for ensembles that the total-energy functional has the variational properties

$$E^\eta[\rho_{ensemble}] = \mathcal{E}(\eta) , \quad (1.64)$$

and

$$E^\eta[\rho] > \mathcal{E}(\eta) \quad \text{for} \quad \rho(\vec{r}) \neq \rho_{ensemble}(\vec{r}) , \quad (1.65)$$

i.e. the exact ensemble energy  $\mathcal{E}(\eta)$  can only be obtained for the exact ensemble density. For all other densities the inequality in (1.65) is strictly obeyed. By subtracting now  $\mathcal{E}(\eta = 0)$  from (1.63) and dividing by the first excitation energy can be calculated

$$\frac{1}{\eta} \{\mathcal{E}(\eta) - \mathcal{E}(\eta = 0)\} = E_1 - E_0 . \quad (1.66)$$

This shows that the ensemble energy  $\mathcal{E}(\eta)$  has to be known for only one value with  $\eta > 0$  to obtain together with the ground state energy  $\mathcal{E}(\eta = 0)$  the first excitation energy. The scheme can be extended to ensembles of arbitrary size and to the case of degenerate levels. Very little, however, is known about the particular dependence of the ensemble energy functional  $E^\eta[\rho]$  on the parameter  $\eta$  and in practice the functional is replaced by LDA or a commonly used GGA ground-state energy functional. A relativistic density-functional theory for ensembles of unequally weighted states is formulated by Nagy [83]. This is the relativistic generalization of the formalism discussed above. In this theory accurate excitations are obtained using the relativistic  $X\alpha$  calculation.

### 1.4.3 Orbital Dependent Methods and Work Formalism

The first exact exchange only theory is the optimized potential method [49–51]. OPM has also been extended for calculation of excitation energies [87]. This method is already described in one of the section 1.3 of the present chapter. We now describe another theory that has also been implemented extensively in the exchange only approximation to calculate excited-states of atoms.

Harbola and Sahni proposed a nice interpretation of the exchange-correlation potential in Hohenberg-Kohn-Sham density-functional theory. The theory is for full exchange correlation potential. It has been implemented in exchange only situation. Like the HF theory in this formalism also one is able to perform DFT based calculations for ground as well as excited-states. According to this formalism exchange-correlation potentials is the work required to move an electron against the electric field of its Fermi-Coulomb charge distribution plus a kinetic energy contribution. The field can be rigorously defined from the differential virial theorem [88]. Thus

$$v_{ee}(\vec{r}) = \mathcal{W}_{ee}(\vec{r}) + \mathcal{W}_{tc}(\vec{r}) \quad , \quad (1.67)$$

where

$$\begin{aligned} \mathcal{W}_{ee}(\vec{r}) &= - \int_{\infty}^{\vec{r}} \vec{\mathcal{E}}_{ee}(\vec{r}') \cdot d\vec{l}' \quad , \\ \mathcal{W}_{tc}(\vec{r}) &= - \int_{\infty}^{\vec{r}} \vec{\mathcal{E}}_{tc}(\vec{r}') \cdot d\vec{l}' \quad . \end{aligned} \quad (1.68)$$

The electric field  $\mathcal{E}_{ee}(\vec{r})$  is a sum of the classical Coulomb  $\mathcal{E}_J(\vec{r})$  and the exchange correlation  $\mathcal{E}_{xc}(\vec{r})$  terms:

$$\mathcal{E}_{ee}(\vec{r}) = \mathcal{E}_J(\vec{r}) + \mathcal{E}_{xc}(\vec{r}) \quad , \quad (1.69)$$

where the terms on the right hand side are respectively the Coulomb and  $XC$  energy and is given by

$$\begin{aligned} \mathcal{E}_J(\vec{r}) &= \int \frac{\rho(\vec{r}')(\vec{r} - \vec{r}')}{|\vec{r} - \vec{r}'|^3} d\vec{r}' \\ \mathcal{E}_{xc}(\vec{r}) &= \int \frac{\rho_{xc}(\vec{r}, \vec{r}')(\vec{r} - \vec{r}')}{|\vec{r} - \vec{r}'|^3} d\vec{r}' \quad , \end{aligned} \quad (1.70)$$

and kinetic energy field is given as

$$\mathcal{Z}_{t_c}(\vec{r}) = \frac{1}{\rho(\vec{r})} \{z([\gamma_s]; \vec{r}) - z([\gamma]; \vec{r})\} \quad . \quad (1.71)$$

The exchange only potential derived using the Fermi hole combined with LDA for correlation has been employed extensively for calculation of excited-states by Sen [52] and Singh and Deb [53]. For details on Harbola-Sahni interpretation, we refer the reader to a recent book [35].

#### 1.4.4 Stationary-State Theory for Excited-States.

Levy's Constrained search procedure [59–61] successfully employed to the ground as well as excited-states in DFT. Using constrained-search approach, orbitals and the corresponding local potentials of non-interacting KS systems can be obtained that lead to a given exact ground or excited-state density with a configuration of one's choice. Thus on the basis of constrained-search formulation Görling [54] has demonstrated that all densities, irrespective of whether they belong to the ground state or an excited state, can be treated on equal footing. Work in this direction has been further pursued by Sahni *et al.* [89], Harbola [90], Gaudoin *et al.* [91] and two more attempts in this direction will be described in the second chapter of this thesis. This has direct relevance to the time-independent excited -state density-functional theory, which could make excited-state calculations as easy as they are for the ground states. Görling has put forth a stationary-state formulation of general density-functional theory based on the constrained-search formulation and generalized adiabatic connection (GAC). According to it density for the ground as well as an excited-states of an electronic system can be generated by a non-interacting system in which the particles move in a local potential. Görling's constrained wavefunction search looks for an energy functional

$$E[\rho, \nu, \alpha] = \langle \Psi[\rho, \nu, \alpha] | \hat{T} + \alpha \hat{V}_{ee} + \hat{v} | \Psi[\rho, \nu, \alpha] \rangle \quad , \quad (1.72)$$

where

$$F[\rho, \nu, \alpha] = \mathbf{stat}_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \alpha \hat{V}_{ee} | \Psi \rangle \quad . \quad (1.73)$$

In Eqs.1.72,1.73 the parameter  $\nu$  labels all existing wavefunctions  $\Psi$  that gives the density  $\rho$  in some arbitrary order. These states are called the  $\rho$ -stationary states. For any arbitrary

coupling constant  $\alpha$  the HK functional  $F[\rho, \alpha]$  is contained in the set of functional  $F[\rho, \nu, \alpha]$  because the absolute minimum  $\min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \alpha \hat{V}_{ee} | \Psi \rangle$  of Eq.1.73 is also a stationary point. Also the functional derivative of the functional  $F[\rho, \nu, \alpha]$  with respect to density for a fixed  $\nu$  and  $\alpha$  will be functions that differ from one another by additive constants. This is because only if they differ by additive constants the variation around the  $\rho$ -stationary states guarantees particle number conservation  $\int \delta\rho(\vec{r})d\vec{r} = 0$  and the reverse is also true.

In this stationary-state formalism the  $\rho$ -stationary state  $\Psi$  and the functional  $F[\rho, \nu, \alpha]$  are related to the eigenstates and potentials of the electronic systems. According to it each eigenstate of an electronic system are  $\rho$ -stationary state. This follows directly from the basic stationarity principle of quantum mechanics where the eigenstates of the Hamiltonian  $\hat{H}$  being generated by making  $\delta\langle \hat{H} \rangle = 0$  with the constraint that the particle number remains conserved. In the second step this theory states that for each  $\rho$ -stationary there exists an external potential  $\nu(\vec{r})$  so that the state is an eigenstate of an electronic system. This can be shown as follows:

For any  $\rho$ -stationary state  $\Psi$  (for simplicity of presentation from here onwards we drop the indices  $[\rho, \nu, \alpha]$ ) an arbitrary variation  $\delta\Psi$  will accompany a corresponding variation  $\delta\rho$  in the density but the particle number remains constant (*i.e.*  $\delta\Psi$  is of the type  $\delta_{\Psi \rightarrow N}$ ). Now the variation  $\delta\rho$  of the density is decomposed to

$$\delta\Psi = \delta\Psi_1 + \delta\Psi_2 \quad , \quad (1.74)$$

with

$$\delta\Psi_1 = \Psi[\rho + \delta\rho, \nu, \alpha] - \Psi[\rho, \nu, \alpha] \quad (1.75)$$

and

$$\delta\Psi_2 = \delta\Psi - \delta\Psi_1 \quad . \quad (1.76)$$

By bifurcating the arbitrary variation in  $\Psi$  [54], the first variation  $\delta\Psi_1$  changes the  $\rho$ -stationary

state  $\Psi[\rho, \nu, \alpha]$  to another  $\rho$ -stationary state  $\Psi[\rho + \delta\rho, \nu, \alpha]$ , for the density  $\rho + \delta\rho$ . Whereas the second variation  $\delta\Psi_2$  by construction is such that it does not change the density in first order (*i.e.*  $\delta\Psi_2$  is of the type  $\delta_{\Psi \rightarrow \rho}$ ). So with a fixed label  $\nu$ , the two variations together keeps the particle number again to be constant (*i.e.*  $\delta\Psi$  is of the type  $\delta_{\Psi \rightarrow N}$ ). Now by stationarity principle

$$\begin{aligned} \delta E[\rho, \nu, \alpha] &= \langle \delta\Psi | \hat{T} + \alpha \hat{V}_{ee} + \hat{v} | \Psi \rangle + \langle \Psi | \hat{T} + \alpha \hat{V}_{ee} + \hat{v} | \delta\Psi \rangle \\ &= \langle \delta\Psi_1 | \hat{T} + \alpha \hat{V}_{ee} + \hat{v} | \Psi \rangle + \langle \Psi | \hat{T} + \alpha \hat{V}_{ee} + \hat{v} | \delta\Psi_1 \rangle \\ &= \langle \delta\Psi_1 | \hat{T} + \alpha \hat{V}_{ee} | \Psi \rangle + \langle \Psi | \hat{T} + \alpha \hat{V}_{ee} | \delta\Psi_1 \rangle + \langle \delta\Psi_1 | \hat{v} | \Psi \rangle + \langle \Psi | \hat{v} | \delta\Psi_1 \rangle \\ &= \delta F[\rho, \nu, \alpha] + \int v(\vec{r}) \delta\rho(\vec{r}) d\vec{r} = \int \{f[\rho, \nu, \alpha] + v(\vec{r})\} \delta\rho(\vec{r}) d\vec{r} = 0 \quad , \end{aligned} \quad (1.77)$$

where we have used the functional defined in Eq.1.73 and its functional derivative by  $\frac{\delta F[\rho, \nu, \alpha]}{\delta\rho(\vec{r})} = f[\rho, \nu, \alpha]$ . Now using the Eq.1.77 with a Lagrange multiplier  $\mu$  to ensure the particle number preserving constraint for the  $\rho$ -stationary states will lead to the Euler-Lagrange equation

$$\int \{f[\rho, \nu, \alpha] + v(\vec{r})\} \delta\rho(\vec{r}) d\vec{r} - \mu \int \delta\rho(\vec{r}) d\vec{r} = 0 \quad . \quad (1.78)$$

As the  $\delta\rho$  is an arbitrary variation so

$$\left\{ \frac{\delta F[\rho, \nu, \alpha]}{\delta\rho(\vec{r})} + v(\vec{r}) \right\} = \mu \quad . \quad (1.79)$$

Through the generalized adiabatic connection (GAC) the density  $\rho$  establishes a connection between the  $\rho$ -stationary wavefunctions of KS (*i.e.*  $\alpha = 0$ ) and exact interacting system (*i.e.*  $\alpha = 1$ ) but with the label  $\nu$  remains intact. Now depending upon the nature of the  $\rho$ -stationary wavefunctions whether they are ground or excited state the energies will be obtained through the GAC KS scheme. Unlike the Levy-Nagy formalism to be discussed in the following section, within Górling's construction the state index,  $\nu$  is merely a label for the stationary value of  $F[\Psi]$ ,  $\nu$  is not generally same as the degree of excitation  $k$  of the Levy-Nagy formalism to be discussed next.

### 1.4.5 Levy-Nagy Variational Theory for Excited-States

Levy and Nagy have recently shown, [56] that there exists a variational KS density-functional theory, with a minimum principle, for the self-consistent determination of an individual excited-state energy and density. Functional in this variational theory are bi-functionals unlike the universal functional in the ground-state theory (*i.e.* they are functionals of not only the given excited-state density  $\rho_k(\vec{r})$ , but of the ground-state density  $\rho_0(\vec{r})$  as well). So in this theory the constrained-search variational energy density-functional can be expressed as

$$E_k = \min_{\rho} \min_{\Psi \rightarrow \rho ; \Psi \perp \Psi_0, \Psi_1, \dots, \Psi_{k-1}} \langle \Psi | \hat{H} | \Psi \rangle . \quad (1.80)$$

The constrained minimization is done in two steps: first, given a density the search is over all wave functions giving the density  $\rho_k(\vec{r})$  and being orthogonal to the lower  $(k - 1)$  states of the many-particle Hamiltonian  $\hat{H}$ . Then the search is for the density. Explicit expression for the energy functional is:

$$E_k = \min_{\rho_k} \left\{ \int \rho(\vec{r}) v(\vec{r}) d\vec{r} + F_k[\rho, \rho_0] \right\} = \int \rho_k(\vec{r}) v(\vec{r}) d\vec{r} + F_k[\rho_k, \rho_0] , \quad (1.81)$$

where the universal bi-density functional  $F_k[\rho, \rho']$  is given by

$$F_k[\rho, \rho'] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle = \langle \Psi[\rho, \rho'] | \hat{T} + \hat{V}_{ee} | \Psi[\rho, \rho'] \rangle . \quad (1.82)$$

Then Levy-Nagy define the KS system that should represent the interacting excited-state have the kinetic energy  $T_k = [\rho_k, \rho_0]$  given by

$$T_k[\rho_k, \rho_0] = \min_{\Phi \rightarrow \rho_k ; \Phi \perp \Phi_0, \Phi_1, \dots, \Phi_{m-1}} \min_{\int (\rho_0^k - \rho_0)^2 d^3r} \langle \Phi | \hat{T} | \Phi \rangle = \langle \Phi[\rho_k, \rho_0] | \hat{T} | \Phi[\rho_k, \rho_0] \rangle , \quad (1.83)$$

where  $\Phi$  is orthogonal to the first  $(m - 1)$  states of the non-interacting Hamiltonian  $\hat{H}_w^k$  if  $\rho_k$  is the density of the  $m^{\text{th}}$  state of the non-interacting system  $\hat{H}_w^k$ . It then follows that  $\Phi[\rho_k, \rho_0]$  is that non-interacting excited-state wave function of  $\hat{H}_w^k$  whose density is  $\rho_k$ . Moreover the corresponding minimum principle for the total energy reads as follows

$$T_k [\rho_k, \rho_0] + \int \rho_k(\vec{r}) w_k([\rho_k, \rho_0]; \vec{r}) d\vec{r} = \min_{\rho} \left\{ T_k [\rho, \rho_0] + \int \rho(\vec{r}) w_k([\rho, \rho_0]; \vec{r}) d\vec{r} \right\}, \quad (1.84)$$

with the non-interacting Hamiltonian

$$\hat{H}_w^k = \hat{T} + \sum_k^N w_k([\rho_k, \rho_0]; \vec{r}). \quad (1.85)$$

The excited-state KS Hamiltonian  $\hat{H}_w^k$  is identified as the one whose ground-state density  $\rho_0^k$  resembles the true ground-state  $\rho_0$  most closely in least square sense. This means from all those non-interacting excited-states (if there are more than one) for which the excited-state density is  $\rho_k$ , we select the one for which  $\int (\rho_0^k - \rho_0)^2 d^3r$  is minimum, where  $\rho_0^k$  is the ground-state density of the Hamiltonian  $\hat{H}_w^k$ . The KS equations have the form

$$\left[ -\frac{1}{2} \nabla^2 + w_k([\rho_k, \rho_0]; \vec{r}) \right] \phi_j^k(\vec{r}) = \varepsilon_j^k \phi_j^k(\vec{r}), \quad (1.86)$$

where the orbitals are occupied as necessary, so that the excited-state density is given by

$$\rho_k(\vec{r}) = \sum_j f_j^k |\phi_j^k(\vec{r})|^2. \quad (1.87)$$

The occupation numbers  $f_j^k$  will be 0, 1 or 2 for a non-degenerate system. Since  $\rho_k$  is the excited-state density for  $\hat{H}_w^k$ , at least one of the lower orbitals should remain unoccupied. As usual to begin the KS procedure  $w_k$  is obtained by first approximating it with a starting guess for  $\rho_k$  in the KS potential, and then the KS equations are solved in a self-consistent manner. The total excited-state energy is

$$E_k = \int \rho_k(\vec{r}) v(\vec{r}) d\vec{r} - \frac{1}{2} \sum_j f_j^k \langle \phi_j^k | \nabla^2 | \phi_j^k \rangle + G_k[\rho, \rho_0], \quad (1.88)$$

where

$$G_k[\rho, \rho_0] = F_k[\rho, \rho_0] - T_k[\rho, \rho_0], \quad (1.89)$$

is the sum of the Coulomb and exchange-correlation energy. In practice  $G_k[\rho, \rho_0]$  has to be approximated. Nagy [43], (2003) has generalized the optimized potential method and KLI

approximation to approximate  $G_k$  and KS potential  $w_k$ . It is convenient to partition  $G_k[\rho, \rho_0]$  into

$$G_k[\rho, \rho_0] = Q_k[\rho, \rho_0] + E_c^k[\rho, \rho_0] , \quad (1.90)$$

where the first term  $Q_k$  on the right hand side is the Coulomb plus exchange and  $E_c^k$  is the correlation component of  $G_k$ . Where the Levy-Nagy theory gives a formal description of variational excited-state DFT, it does not give a prescription how to construct the associated functionals. We will describe our work in this direction in the second chapter of this thesis.

## 1.5 Time-Dependent Density-Functional Theory (TDDFT)

Ground-state DFT is concerned with systems subject to a static external potential, which are described by the time-independent Schrödinger equation. However, there are many situations of interest that fall outside this category such as: an atom or a molecule under the influence of an external electromagnetic field (like a laser field), electron or proton scattering, etc. These systems are correctly described by the time-dependent Schrödinger equation. TDDFT is an extension of ordinary ground-state DFT designed to tackle such problems from a density functional perspective. The roots of TDDFT date back to the time-dependent Thomas-Fermi model proposed by Bloch [58]. The first time-dependent KS equations were obtained by Peuckert [92] and Zangwill and Soven [93]. The first approach was by Zangwill and Soven [93] to calculate the photoabsorption cross section. The rigorous foundation of the TDDFT was started by the work of Deb and Ghosh [94] and Bartolotti [95]. The theoretical foundations of TDDFT were laid by Runge and Gross [96] in 1984, who proved the time-dependent analogue of HK theorem [8] and developed a KS scheme [9] for the time-dependent case. The technique has now become a standard tool to calculate the excitation and optical absorption spectra of finite systems. In the following we will discuss how excited-states are obtained using TDDFT [36].

Hohenberg-Kohn-Sham DFT is based on the Rayleigh-Ritz variation principle. In the case of a time-dependent external potential, however, no minimum principle exists. Instead, there is a stationary-action principle. The starting point of studying time-dependent systems

is the Schrodinger equation

$$i\frac{\partial\Psi(\vec{r},t)}{\partial t} = \hat{H}\Psi(\vec{r},t) , \quad (1.91)$$

where the Hamiltonian

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{v}(\vec{r},t) , \quad (1.92)$$

includes the kinetic  $\hat{T}$ , electron-electron repulsion  $\hat{V}_{ee}$  and the external potential  $\hat{v}(t) = \sum_i^N v(\vec{r}_i, t)$  operators. The densities of the system evolves from a fixed initial state  $\Psi(t_0) = \Psi_0$  (for simplicity we drop the spatial argument). The initial state,  $\Psi_0$ , is arbitrary, its not required to be the ground-state or some other eigenstate of the initial potential  $v(\vec{r}, t_0) = v_0(\vec{r})$ . The potentials are required to be Taylor expandable about  $t_0$ . Then it is possible to have a equivalent theorem for time-dependent systems like the HK theorem (Runge-Gross (RG) theorem). The RG theorem states that there exists an one-to-one correspondence between the time-dependent external potential,  $v(\vec{r}, t)$ , and the time-dependent electron density,  $\rho(\vec{r}, t)$ , for a systems evolving from a fixed initial many-body state. According to it the density determines the external potential and subsequently helps in obtaining the time-dependent many-body wavefunctions. As this wave-function determines all observables of the system, so the conclusion is that all observables are functionals of the time-dependent density,  $\rho(\vec{r}, t)$ . The statement of the theorem is: "the densities  $\rho(\vec{r}, t)$  and  $\rho'(\vec{r}, t)$  evolving from the same initial state  $\Psi_0$  under the influence of two potentials  $v(\vec{r}, t)$  and  $v'(\vec{r}, t)$  are always different provided that the potentials differ by more than a purely time-dependent function :  $v(\vec{r}, t) = v'(\vec{r}, t) + C(t)$  . The theorem is proved with the assumption that the initial time  $t_0$  is finite and the potentials are Taylor expandable around  $t_0$ . This implies that only sudden switching is included in the formalism. On the other hand potentials which are switched-on adiabatically from  $t_0 = -\infty$  are automatically excluded by the Taylor-expandability condition.

### 1.5.1 Time-Dependent Kohn-Sham Scheme

Analogous to the case of ground-state, the time-dependent density can also be calculated by considering an auxiliary system of non-interacting electrons in which the electrons move in an effective time-dependent potential. This potential is unique by virtue of the Runge-Gross theorem applied to the KS system. Thus the equation of motion is

$$i\frac{\partial}{\partial t}\phi_i(\vec{r}, t) = \left\{ -\frac{\nabla^2}{2} + v_{KS}(\vec{r}, t) \right\} \phi_i(\vec{r}, t) \quad . \quad (1.93)$$

The density of the interacting system can be obtained from the time-dependent KS orbitals

$$\rho(\vec{r}, t) = \sum_i^{occ} |\phi_i(\vec{r}, t)|^2 \quad . \quad (1.94)$$

The KS equation above having the form of one-particle equation, is relatively easier to solve numerically. Like the steady-state DFT the KS potential in this case can be separated in the following way:

$$v_{KS}(\vec{r}, t) = v_{ext}(\vec{r}, t) + v_{Hartree}(\vec{r}, t) + v_{xc}[\rho; (\vec{r}, t)] \quad , \quad (1.95)$$

where the terms have their usual meaning. The last term, the exchange-correlation (*XC*) potential, comprises all the non-trivial many-body effects. Inevitably, the exact functional form of *XC* potential is unknown. Like the stationary-state DFT this has to be approximated in TDDFT. In contrast to the stationary-state DFT, where very good approximations of the *XC* functional exists, approximations to  $v_{xc}(\vec{r}, t)$  are still in their infancy. The first and simplest of these is the adiabatic local-density approximation (ALDA), reminiscent of the LDA. No doubt, recently several other functionals like time-dependent exact-exchange (EXX) and functional with memory have been proposed. Instead of going into the details of these proposed functionals our aim is to discuss the utility of the TDDFT approach to calculate excitation energies will be discussed in the following section.

## 1.5.2 Excited-States within TDDFT

The formal development of TDDFT, review in the last two sections, opened the way for a sound treatment of time-dependent properties in DFT. In particular, here we will describe properties involving linear response of the charge density to an applied field [33,97,100,101]. Not only this will allow the treatment of response properties such as dynamic polarizabilities, but, since excitation energies and oscillator strengths can be obtained as the poles and residues of the dynamic polarizability [97]. This makes possible a formally well founded treatment of excited-states within TDDFT.

The starting point is the time-dependent KS equation given by Eq.1.93. The exchange correlation potential appearing in the Eq.1.93 by adiabatic local density approximation [93] is given by

$$v_{xc}[\rho; (\vec{r}, t)] = \frac{\delta E_{xc}[\rho; (\vec{r}, t)]}{\delta \rho; (\vec{r}, t)} , \quad (1.96)$$

where  $E_{xc}[\rho; (\vec{r}, t)]$  is the exchange-correlation energy functional from the TD theory. Now consider a system initially in its ground electronic state. The linear response to a perturbation  $v(t)$  turned on slowly at some time in the distant past is given by

$$\delta \rho(\vec{r}, \omega) = \sum_{ij} \phi_i^\dagger(\vec{r}) \delta P_{ij}(\omega) \phi_j(\vec{r}) , \quad (1.97)$$

where  $\delta P_{ij}(\omega)$  is the linear response of the KS/HF density matrix in the basis of unperturbed molecular orbitals. By writing the effective TD potential as

$$v^{eff}(t) = v^{appl}(\vec{r}, t) + \delta v^{SCF}(\vec{r}, t) . \quad (1.98)$$

Here the field  $\delta v^{SCF}$  is the last two terms of the Hamiltonian in Eq.1.93. The response of the KS density matrix to the perturbation  $v^{eff}$  is then given by the generalized susceptibility for a system of independent particles,

$$\frac{\partial P_{ij}}{\partial v_{i'j'}^{eff}} = \delta_{i'i} \delta_{j'j} \frac{f_j - f_i}{\omega - (\epsilon_i - \epsilon_j)} . \quad (1.99)$$

Thus

$$\delta P_{ij}(\omega) = \frac{f_j - f_i}{\omega - (\epsilon_i - \epsilon_j)} \left[ v_{ij}^{appl}(\omega) + \sum_{kl} \mathcal{K}_{i,j,kl} \delta P_{kl}(\omega) \right] , \quad (1.100)$$

where the coupling matrix  $\mathcal{K}$  is the linear response of the self-consistent field to changes in the charge density,

$$\delta v_{ij}^{SCF}(\omega) = \sum_{kl} \mathcal{K}_{i,j,kl} \delta P_{kl}(\omega) , \quad (1.101)$$

$$\begin{aligned} \mathcal{K}_{ij,kl} &= \frac{\partial P_{ij}}{\partial v_{kl}^{SCF}} = \int \int \phi_i^\dagger(\vec{r}) \phi_j(\vec{r}) \frac{1}{|\vec{r} - \vec{r}'|} \phi_k(\vec{r}') \phi_l^\dagger(\vec{r}') d\vec{r} d\vec{r}' \\ &+ \int \int \int \int \phi_i^\dagger(\vec{r}) \phi_j(\vec{r}) f_{xc}[\rho; (\vec{r}, t)] \phi_k(\vec{r}') \phi_l^\dagger(\vec{r}') d\vec{r} d\vec{r}' \quad , \end{aligned} \quad (1.102)$$

where

$$f_{xc}[\rho; (\vec{r}, t)] = \frac{\delta^2 E_{xc}[\rho; (\vec{r}, t)]}{\delta^2[\rho; (\vec{r}, t)]} \quad (1.103)$$

is the time-dependent exchange-correlation kernel. Solving Eq. 1.100 for  $\delta P$  and separating the real imaginary parts one obtains after some algebra [98]

$$\left[ \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} - \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right] \begin{pmatrix} \delta P \\ \delta P^* \end{pmatrix} = \begin{pmatrix} -\delta v_{appl} \\ -\delta v_{appl}^* \end{pmatrix} \quad , \quad (1.104)$$

where the matrices  $\mathbf{A}$  and  $\mathbf{B}$  are defined as

$$A_{ij,kl} = \delta_{ik} \delta_{jl} (\varepsilon_i - \varepsilon_k) + \mathcal{K}_{ij,kl} \quad (1.105)$$

and

$$B_{ij,kl} = \mathcal{K}_{ij,kl} \quad . \quad (1.106)$$

In the response theory, excitation energies corresponds to the poles of the response function. So at the excitation energies  $\omega = \omega_I = E_I - E_0$ ,  $\delta P$  blows up. In Eq.1.104, as  $\delta P$  blows up at the excitation and  $\delta v_{appl}$  is finite, this implies that the matrix multiplying  $\delta P, \delta P^*$  should vanish, leading to zero eigenvalues on the left hand side of Eq.1.104. Thus the excitation energies can be determined as solutions of the non-Hermitian eigenvalue problem

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{bmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} \quad , \quad (1.107)$$

where  $X_{ij} = \delta P_{ij}(\omega)$  and  $Y_{ij} = \delta P_{ji}(\omega)$ . In the lowest order the excitation energies are obtained with a correction  $\mathcal{K}_{ij,ij}$  to the Kohn-Sham transition energies  $\omega_{ij} = \varepsilon_j - \varepsilon_i$ , which follows from Eq.1.105. To date most applications of the time-dependent KS formalism falls into the linear response regime [28, 102, 103]. In [99], Vasiliev *et al.* have derived an equation identical to the single pole approximation (SPA) proposed by Petersilka *et al.* [100, 101]. In this also the excitation energies are obtained as correction to the KS excitation energies  $\omega_{ij}$ . Why and under which circumstances SPA is so successful is discussed in [104, 105]. To conclude, it

is the choice of the static  $XC$  potential used to obtain the KS orbitals and eigenvalues, is the most crucial approximation to obtain the excitation energies in TDDFT. In the third chapter we report values of excitation energies obtained using SPA [106] for several atoms and ions.

## 1.6 Concluding Remarks

The density-functional formalism is a fundamental tool for the calculation of electronic structure of atoms, molecules and solids. Though it is an exact theory, one has to use approximations as the exact form of the exchange-correlation ( $XC$ ) functional is not known. The accuracy of the calculations depends on the quality of the approximated functionals. Various relations and criteria required to be fulfilled by the density functionals help a lot in the construction of new reliable functionals. In this connection, Levy's co-ordinate scaling [107] and functional expansion proposed by Parr *et al.* [108] are the two very powerful techniques for improving the functionals.

Treating excited-states is an emerging field of research in density-functional theory. In most of the attempts made so far for the treatment of excited-states and some of the proposed theories described in this chapter, the ground-state  $XC$  potentials were used in calculating excitation energies. The study of the several ground-state approximations for determining excitation energies leads to the conclusion that the excitation energy cannot generally be obtained as a difference of the one electron or total energies. Research on the exact exchange potentials has already been proposed by Nagy [87]. The ground-state adiabatic connection formula is extended to the ensemble  $XC$  energy.

One can apply the theories discussed in this chapter for a large variety of calculations. The ground-state calculations are not so problematic because the  $XC$  functionals are universal by nature. In the excited-state calculations, on the other hand, one of course will have different exchange correlation functionals for the different excited-states or for different ensembles. It is believed that these functionals can be constructed as orbital dependent functionals, *i.e.* the difference between the excited-state functionals is revealed in the  $XC$  functional only through the electronic configurations (the occupation numbers). This can be realized by the exact exchange only theories like OPM or the HS method. For that purpose one only requires the correlation functional as the functional of the orbitals and then the way of derivation and calculations is exactly same as the  $x$  - *only* method. Unfortunately, so far we do not have

ensemble or excited-state correlation functionals. In the third chapter we will describe an attempt made by us for the construction of *x - only* functionals for excited-states within LDA. Not only excited states, in ground-state theory also it's fundamentally tough to find an appropriate correlation functional. Gross *et al.* [80] found that among the existing correlation functionals the Colle-Slavetti [109] is the best. In a lot of cases KLI + Colle-Slavetti gives results better than any other functional. The study of correlation in excited-state calculation remains as a challenge for future research.

To conclude, in this chapter we have presented a brief overview of time-independent excited-state DFT and TDDFT. In the linear response regime, TDDFT has become a standard tool to calculate excitation energies within DFT, and is by now implemented in most of the major DFT codes. In the non-linear regime, TDDFT is able to describe extremely non-linear effects like higher harmonic generation and multiphoton ionization. However, the problem of double excitation and knee structure in multiphoton ionization remain as challenges. The time-independent theories in the present chapter and those evolving from these which will be discussed in the next two chapters of this thesis can be regarded as complementary to the powerful TDDFT approach for the calculation of excitation energies. Undoubtedly, the challenges that will arise in due course of studying excited-states will definitely help the future generation *density - functionalist* for providing a complete shape to the excited-states within DFT.

## 1.7 Outline of the Thesis

In the second chapter we will describe the density-to-potential mapping of the time independent excited-states. The chapter will have a rigorous description of Görling and Levy-Nagy formalism for excited-states based on which the proposed theory fixes the density-to-potential mapping. Constrained search method for generating potentials for a given excited-state density through Zhao-Morrison-Parr method will also be discussed. We will also present adaptation of van-Leeuwen-Baerends method to generate potentials for non-interacting systems and implement it. Results obtained by studying several atomic systems will be presented at the end of the chapter.

In the third chapter procedure for developing new *XC* functionals within the LDA for excited-states will be described. This will include a brief introduction to the *homogeneous*

*electron gas* (HEG) model, which is used for the LDA. After describing LDA we will show how state-dependence of the  $XC$  functionals in case of the excited-states plays the key role for the construction of the  $XC$  functionals. Exchange only functionals for three different classes of excited-states will be included for discussion. We will show that not only the  $XC$  functional but the Thomas-Fermi kinetic energy and self-energy plays a significant role in obtaining accurate excitation energies. We have also found out the energies for double excitation which cannot be obtained in TDDFT.

In the fourth chapter we have analyzed the Floquet formulation of TDDFT in light of the recent criticism to density-to-potential mapping for quasienergy eigenstates. Our analysis shows that steady-state DFT is a complete theory and its earlier criticism has overlooked the subtle difference between Floquet and Runge-Gross formalism of TDDFT. Based on our analysis we have shown that it is actually the steady-state rather the Runge-Gross formalism being used in calculating the excitation and oscillator strengths.

## Chapter 2

# Foundations of Time-Independent Excited-State DFT

### 2.1 INTRODUCTION

In the previous chapter we have discussed the evolution of DFT as an alternative quantum many-body approach for the ground as well as excited-states. So far as the electronic structure calculation is concerned the Hohenberg-Kohn-Sham (HKS) density functional theory (DFT) [8,9,23] has emerged as the most successful theory for the ground-state. It is a theory for dealing with the ground states and its properties [21,24]. Applications of the Hohenberg-Kohn theorem and the Kohn-Sham construction is limited to the ground-state because it is the ground-state density of an electronic system that determines the Hamiltonian, and consequently other physical observables of the electronic system. This suggests both the ground as well as excited-state properties can be determined from the ground-state density through the Hamiltonian operator since it characterizes all the states of a system. However, in order to develop an excited-state DFT akin to its ground-state counterpart, it is important to describe an excited-state of a system in terms of the density of that state. Almost for the last two and half decade researchers have investigated [39–43, 52, 53, 64, 82, 84, 86, 110] the possibility of giving a formal foundation to the time-independent excited-state DFT similar to the HKS DFT for the ground-states, but it is yet to come to its full fruition because of the complexity involved in establishing the density-to-potential mapping and the construction of excited-state functionals.

In order to develop the excited-state DFT analogous to the ground-state density func-

tional formalism there are two open questions to be answered: (i) Existence of the unique mapping between the excited-state density and the external potential like the ground-states (*i.e.* the excited-state counterpart of Hohenberg-Kohn theorem) ? (ii) Secondly, for the determination of the excited-state energies, is it possible to construct reasonably accurate exchange-correlation ( $XC$ ) energy functionals? In our discussion in the previous chapter for excited-states in DFT we have noticed that the  $XC$  functionals for excited-states are non universal unlike the ground-states because of the state-dependence. We note that although the exact form of the  $XC$  functional is unknown for the ground-states, there are several accurate and approximate functionals<sup>1</sup> [67–69, 71–73] in traditional DFT. The issue of finding such approximate functionals for the excited-states remains. In this thesis we address both the questions in the present chapter and in the one following it. We start with the issue of mapping an excited-state density to the external potential in the following sections.

## 2.2 Earlier Attempts for Establishing Density-to -Potential Mapping

The question of whether there exists a mapping from an excited-state density  $\rho(\vec{r})$  to a potential  $v(\vec{r})$  or the many-body wavefunction  $\Psi(\vec{r})$  is central to performing density-functional calculations for excited states. In the context of Kohn-Sham systems, the issue has been addressed in a series of works by Sahni *et al.* [89], Harbola [90], and Gaudoin and Burke [91]. In the work of [89] and [90], it is shown that a given ground- or excited-state density can be generated as a non-interacting system density by a configuration of one's choice. Sahni *et al.* obtained the potentials using the differential virial theorem [88], whereas Harbola did the same using the constrained-search approach [59–62]. It is clear that because of the multiplicity of potentials that could lead to a given density, one needs an additional condition for mapping a density  $\rho(\vec{r})$  to a unique potential  $v_{ext}(\vec{r})$ . The additional criterion would be of help in finding  $v_{ext}(\vec{r})$  corresponding to a given excited-state density as well as finding a Kohn-Sham system. For the ground-state density the Hohenberg-Kohn (HK) theorem [8] fixes the Kohn-Sham (KS) system [9] uniquely; it is that system where the lowest energy orbitals are occupied. For the excited-state density a different criterion is needed. As described in the previous chapter the issue to select a unique potential (KS system) for a given excited-state

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<sup>1</sup>The detailed description is available in the section 1.3 of Chapter 1

density has been addressed earlier by Levy and Nagy (LN) [56]. They have proposed a qualitative criterion, which has been investigated quantitatively by us and will be described later in this chapter. However, in depth investigation of the LN criterion shows that this criterion is insufficient.

A brief account of the attempts having been made so far in this direction is as follows: The first step in establishing a mapping from an excited-state density to a many electron wavefunction is taken by looking for  $\rho$ -stationary states [54] as described by Görling's  $\rho$ -stationary state formulation for excited-states. These are states  $\Psi$  that reproduces a given density  $\rho_k$  (density of the  $k^{\text{th}}$ - excited-state) and simultaneously make the expectation value  $\langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$  stationary. However, for a given density there are many  $\rho$ -stationary states and thus establishing a one-to-one mapping requires an additional input. Variational density functional theory of Levy and Nagy for excited-states [56] provides this by requiring that  $\Psi$  be orthogonal to  $\Psi_j$  ( $j < k$ ), which are to be determined by the ground-state density  $\rho_0$  for the system under study. Thus the knowledge of the ground-state density is essential to define a map  $\rho_k \rightarrow \Psi_k$ . This is reasonable because it is the ground-state density that really fixes the Hamiltonian of a system uniquely. Levy and Nagy then go on to construct a Kohn-Sham system of non-interacting electrons whose  $m^{\text{th}}$  excited-state produces the given excited-state density. Further they put forth a criterion that the ground-state density of the Kohn-Sham system is closest to the true ground state density of the system in the least square sense.

However, recently Gaudoin and Burke [91] have suggested that a unique mapping from an excited-state density to an external potential may not exist since a given excited-state density can be generated by more than one potentials either by using different configurations [89, 90] or the same configuration [91]. But in their study Gaudoin and Burke did not take into account the Levy-Nagy criterion [56] stated above - that the ground-state density should also be taken into consideration when considering such mapping. In Levy-Nagy theory there is a unique mapping from density-to- potential for excited-states of non-interacting systems as discussed later in this chapter.

## 2.3 Present Investigation

We have studied the issues of mapping from an excited-state density to the potential [89–91] based on rigorous analysis of Görling's stationary-state theory [54] and Levy-Nagy varia-

tional theory [56] for constructing the Kohn-Sham system for excited-states. We present our investigation in the following sections. We show :

- (i) an explicit construction of the external potential from an excited-state density using Görling's stationary state approach [54],
- (ii) that the Levy-Nagy criterion [56] of constructing the Kohn-Sham system does not in general hold good. We give reasons why it does not do so,
- (iii) that for a given excited-state the Kohn-Sham system exists and is given by comparison of the kinetic energies of the true and the non-interacting (KS) systems.

For our work, we generate the potentials corresponding to a given density using the constrained search approach [111] as well as the van-Leeuwen-Baerends approach [112]. These are discussed in the appendices. We will start with a discussion of Görling and Levy-Nagy theory.

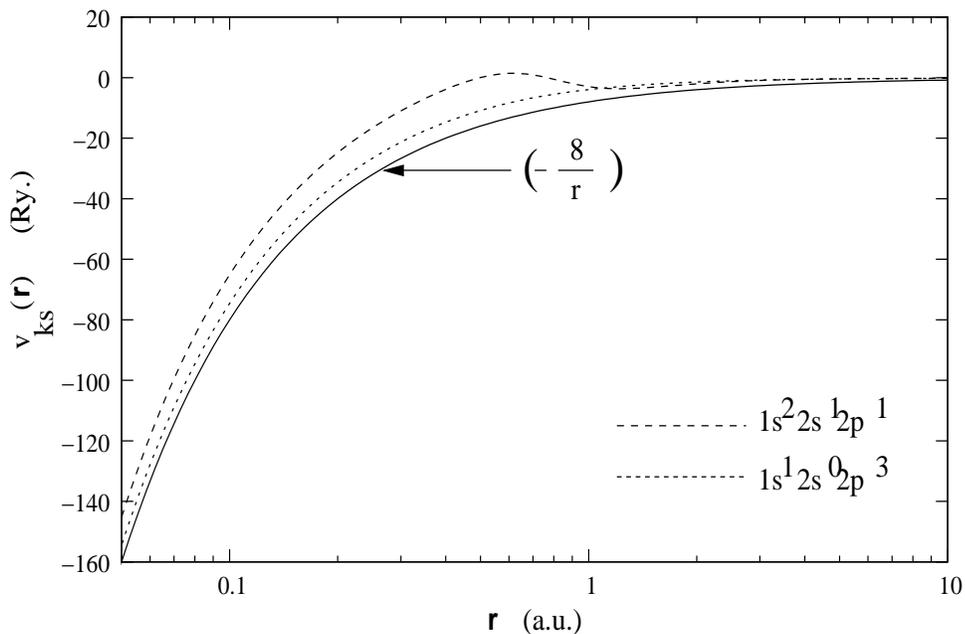


Figure 2.1: Shown in the figure are the KS potentials for the excited-state density of  $1s^1 2s^0 2p^3$  ( $^5S$ ) state of *Be* generated for the original and one alternative configuration.

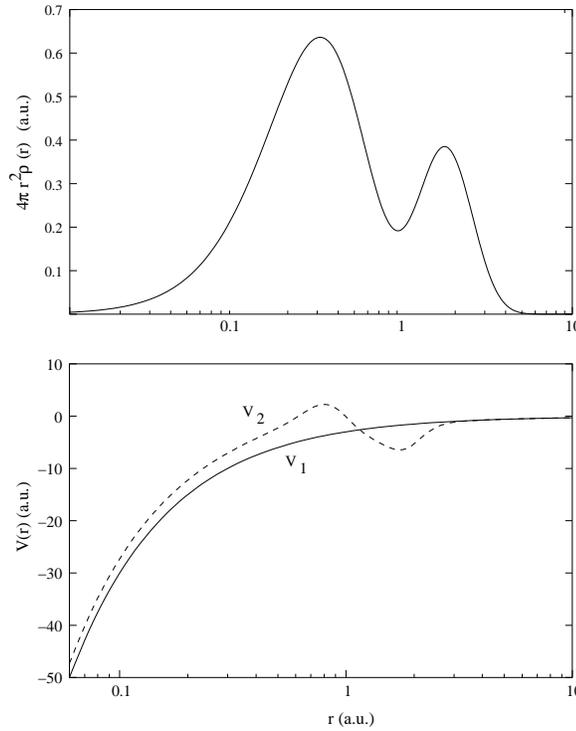


Figure 2.2: Two potentials (lower panel) yielding the same excited state density (upper panel) for  $1s^12s^2$  state of a model *Li* atom of non-interacting electrons. Note that the x-axis scale in the upper and the lower panel is different.

### 2.3.1 Understanding Görling/Levy-Nagy Formalism

### 2.3.2 Görling's Stationary-State Approach

Let us begin with Görling's formulation [54] of the excited-state problem. The formulation is based on the constrained-search approach [59–62] and provides a map from an excited-state density to a many-body wavefunction. For a given excited-state density  $\rho(\vec{r})$  a  $\rho$ -stationary state  $\Psi(\vec{r})$  is given by making the expectation value  $\langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$  stationary with the constraint that the many-particle wavefunction  $\Psi(\vec{r})$  yield the density  $\rho(\vec{r})$ . Corresponding to each  $\rho$ -stationary state  $\Psi(\vec{r})$  there is an external potential  $v_{ext}(\vec{r})$ , which has been shown by Görling. The stationary state formulation can be realized in a manner different from that of Görling. The proof is given below with the external potential  $v_{ext}(\vec{r})$  arising as the Lagrange multiplier to ensure the constraint of generating the density  $\rho(\vec{r})$ .

A  $\rho$ -stationary wavefunction  $\Psi$  gives, by the quantum mechanical stationarity principle

$$\langle \delta\Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle + \langle \Psi | \hat{T} + \hat{V}_{ee} | \delta\Psi \rangle = 0 \quad (2.1)$$

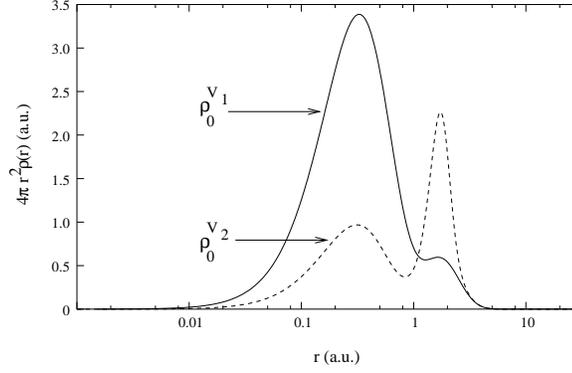


Figure 2.3: Shown are the ground-state densities for the two potentials  $v_1$  and  $v_2$  of Fig. 2.2 .

with the constraint of density conservation:

$$\delta\rho(\vec{r}) = \int \{\Psi\delta\Psi^\dagger + \Psi^\dagger\delta\Psi\} d\vec{r}_2\dots\dots d\vec{r}_N = 0 . \quad (2.2)$$

Writing Eq. 2.1 explicitly, we get

$$\int \{\delta\Psi^\dagger (\hat{T} + \hat{V}_{ee})\Psi + \Psi^\dagger (\hat{T} + \hat{V}_{ee})\delta\Psi\} d\vec{r}_1 d\vec{r}_2\dots\dots d\vec{r}_N = 0 . \quad (2.3)$$

Because  $\delta\Psi$  are arbitrary variations in  $\Psi$  except that they obey the condition (Eq. 2.2) above, Eq.2.3 will be satisfied if

$$\int (\hat{T} + \hat{V}_{ee})\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) d\vec{r}_2\dots\dots d\vec{r}_N = \int f_1(\vec{r}_1)\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) d\vec{r}_2\dots\dots d\vec{r}_N . \quad (2.4)$$

Thus in general  $\rho$ -stationarity of  $\Psi$  implies that it satisfies

$$(\hat{T} + \hat{V}_{ee})\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \left( \sum_i f_i(\vec{r}_i) \right) \Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) . \quad (2.5)$$

However, since  $\hat{T}, \hat{V}_{ee}$  are symmetric operators and  $\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$  is antisymmetric, it is necessary that  $(\sum_i f_i(\vec{r}_i))$  also be symmetric. Thus all  $f_i$ 's must be the same function  $f(\vec{r})$ . Identifying this function as  $f(\vec{r}) = -v(\vec{r}) + E$ , where  $\lim_{\vec{r} \rightarrow +\infty} v(\vec{r}) = 0$ , we get  $\Psi$  satisfying

$$\left\{ \hat{T} + \hat{V}_{ee} + \sum_i v(\vec{r}_i) \right\} \Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = E\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) . \quad (2.6)$$

It is important to note that for a given density different  $\rho$ -stationary states give different  $v_{ext}(\vec{r})$ . Thus by applying the constrained search method one will get many  $\rho$ -stationary states and the corresponding external potentials. The question is which one of these should correspond to a given system. Levy and Nagy identify [56] this system as the one where  $\Psi$  is orthogonal

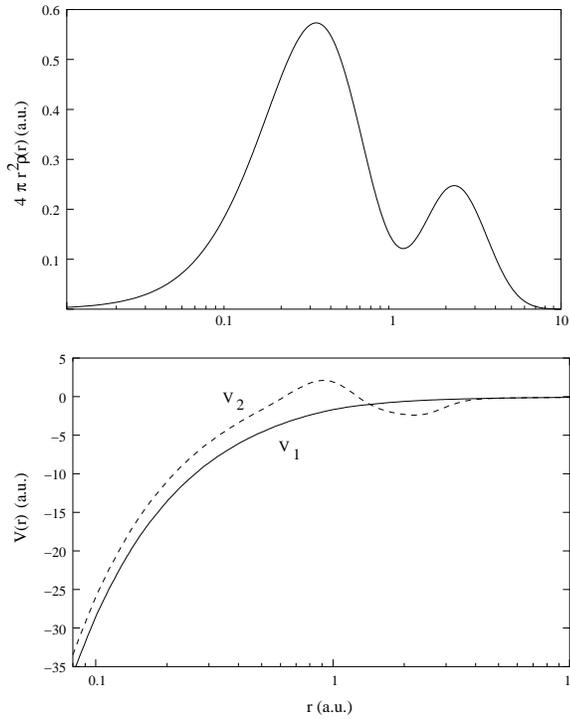


Figure 2.4: Two potentials (lower panel) yielding the same excited state density (upper panel) for the  $1s^1 2s^2 2S$  state of the *Li* atom. Note that the x-axis scale in the upper and the lower panel is different.

to  $\Psi_j$  ( $j < k$ ) for a given ground-state density  $\rho_0$ . Thus in the Levy-Nagy theory [56], the wavefunction  $\Psi[\rho; \rho_0]$  is a bi-functional of  $\rho$  and  $\rho_0$ . One subtle point about the Levy-Nagy theory is that if the search for  $\Psi$  is restricted to the space orthogonal to  $\Psi_j$  ( $j < k$ ), the variational principle becomes a minimum principle. The prescription above also makes the functional  $F[\rho; \rho_0] = \min_{\Psi \rightarrow \rho(\mathbf{r})} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$  a bi-functional of the excited-state density  $\rho(\vec{r})$  as well as the ground-state density  $\rho_0(\vec{r})$ .

Now the question is how a Kohn-Sham (KS) system can be realized for an excited-state density? To get a KS system, the mapping from a given excited-state density to a non-interacting wavefunction is established by making the expectation value  $\langle \Phi | \hat{T} | \Phi \rangle$  stationary with respect to variations in  $\Phi$  with  $\Phi$  giving the excited-state density. This is done using either the Zhao-Morrison-Parr (ZMP) [111] (see Appendix C) or van Leeuwen-Baerends (LB) [112] (see Appendix D) approach. As is the case for the interacting systems, there may be several  $\Phi$ 's and the corresponding KS potentials  $v_{KS}$  that give rise to an excited-state den-

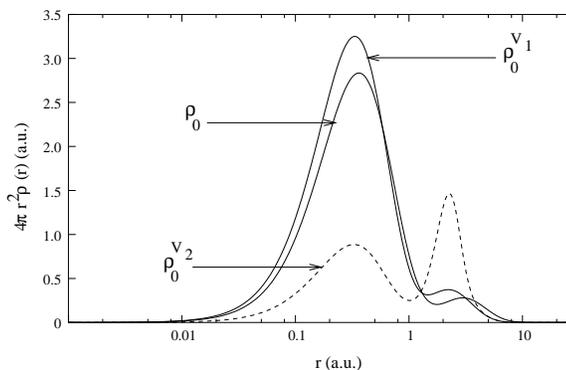


Figure 2.5: Shown are the noninteracting ground-state densities for the two potentials  $v_1$  and  $v_2$  of Fig. 2.4 along with the interacting (exact) one.

sity and make  $\langle \Phi | \hat{T} | \Phi \rangle$  stationary. Two such potentials for the density of  $1s^1 2s^0 2p^3$  ( $^5S$ ) of *Be* are shown in Fig. 2.1. The excited-state density used is obtained by solving the excited-state KS equation with the Harbola-Sahni (HS) [48] exchange-only potential where the density is essentially the same as Hartree-Fock (HF) density and also close to the true density. The question that arises again is how do we choose one particular KS system to represent a system in its excited-state. An intuitive way would be by comparing the ground-state densities, as was done for the interacting systems. However, the ground-state density of a non-interacting system that reproduces an excited-state density may not be the same as that of the true system (it will be the same only if the electron-electron interaction were absent). Thus Levy and Nagy propose [56] that of the many Fermionic non-interacting systems that give the same excited-state density, the one whose ground-state density resembles the exact one in the least square sense be identified as the Kohn-Sham system. The criterion is obviously exact for systems with no electron-electron interaction, as stated above. For interacting-electron systems, the criterion appears to give the true Kohn-Sham for some systems, consistent with the orbitals to which the electrons have been excited, as we will discuss it next.

### 2.3.3 Levy-Nagy Criterion

Similar to the ground-state theory, the LN formulation [56] provides a variational DFT approach for excited-states. In this the  $k^{\text{th}}$ -excited state of an  $N$ -electron interacting system is described by defining a unique universal functional  $F_k[\rho, \rho_0]$  such that the energy  $E_k$  and the

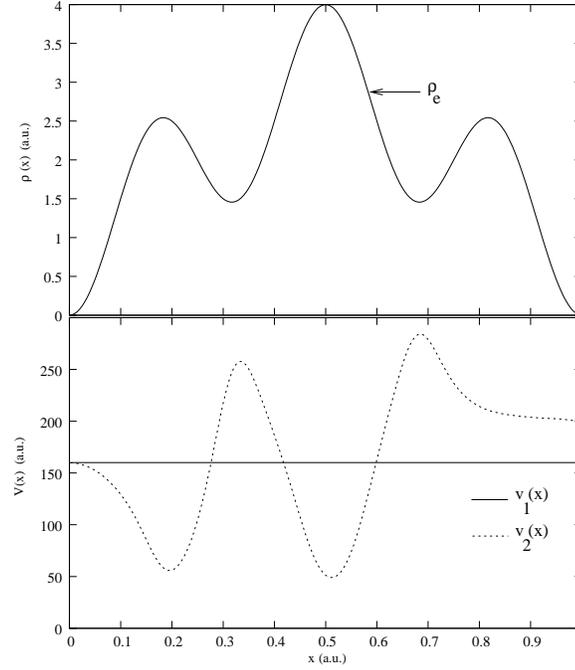


Figure 2.6: Two potentials (lower panel) yielding the same excited-state density (upper panel) for an excited state of the two same spin non-interacting electrons in a one-dimensional infinitely deep well. This model system is same as that discussed in [91].

density  $\rho_k(\vec{r})$  of this state are given by

$$\begin{aligned}
 E_k &= \min_{\rho(\vec{r}) \rightarrow N} \left\{ \int d^3r v_{ext}(\vec{r}) \rho(\vec{r}) + F_k[\rho, \rho_0] \right\} \\
 &= \int d^3r v_{ext}(\vec{r}) \rho_k(\vec{r}) + F_k[\rho_k, \rho_0]
 \end{aligned} \tag{2.7}$$

Here  $v_{ext}(\vec{r})$  is the external potential,  $\rho_0(\vec{r})$  is the ground-state density of this system. Due to the HK [8] theorem,  $v_{ext}$  is a unique functional of  $\rho_0$ . The bi-density functional for excited-states is defined in a manner different from the HK functional for ground-states. In the definition of the bi-density functional

$$F_k[\rho, \rho_0] = \min_{\Psi \rightarrow \rho, \{\langle \Psi | \Psi_j \rangle = 0, j < k\}} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle, \tag{2.8}$$

the  $N$ -electron trial wave function  $\Psi$  belongs to the space which is orthogonal to the space spanned by all lower  $j^{th}$ -state functions  $\Psi_j$  of the system,  $j < k$ .  $\hat{T}$  and  $\hat{V}_{ee}$  are the  $N$ -electron operators of the kinetic and electron-electron interaction energies. In this formulation, the mapping from the  $k^{th}$  excited-state density  $\rho_k(\vec{r})$  to the corresponding wave function  $\Psi_k$  of the system follows from Eq. (2.8) after inserting there  $\rho = \rho_k$  — the minimizer in Eq. (2.7),

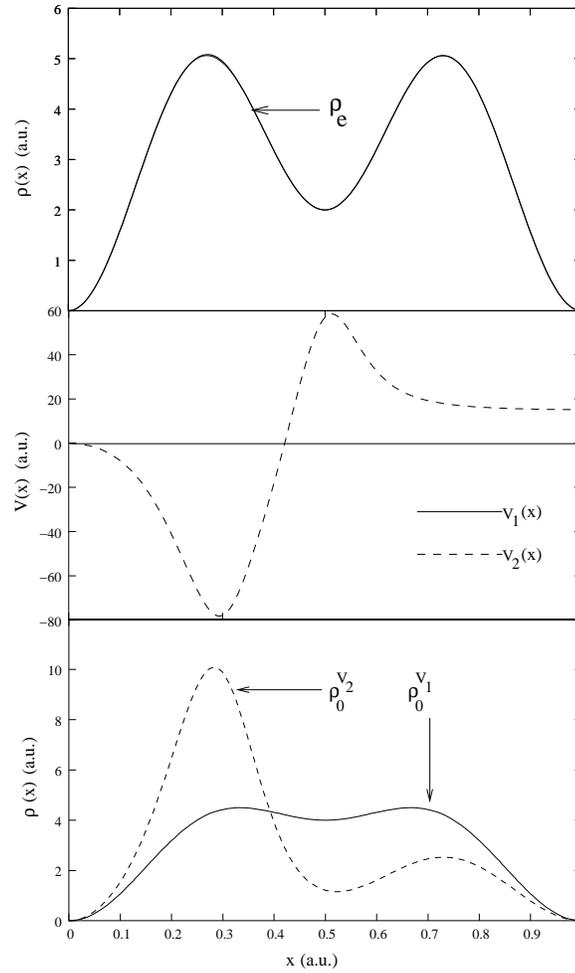


Figure 2.7: Two potentials (middle panel) yielding the same excited-state density (upper panel) along with their corresponding ground-state densities (lower panel) for an excited state of the three-electron 1D infinitely deep well model system of non-interacting electrons.

because then  $\Psi_k$  is the minimizer in Eq. (2.8). Since the lower states  $\Psi_j$  ( $j < k$ ) in Eq. (2.8) are determined by  $v_{ext}[\rho_0]$ , a functional of  $\rho_0$ , it is clear that the ground-state density  $\rho_0$  plays an important role in the DFT for excited states.

For each original, interacting system, one can introduce a corresponding noninteracting system such that their densities are the same. In the constrained-search approach, this is done by minimizing the expectation value  $\langle \Phi | \hat{T} | \Phi \rangle$ , where  $\Phi$  is now a single Slater determinant of one-electron spin orbitals that gives the density of interest. However, many different noninteracting systems (potentials) can be related with the given excited-state density  $\rho_k(\vec{r})$  of the interacting system. Of the many  $\Phi$ 's (many systems) that may give the same density

Table 2.1: Shown in the table are  $\varepsilon_{max}$  and the expectation values  $\langle \frac{1}{R} \rangle$ ,  $\langle R \rangle$  and  $\langle R^2 \rangle$  for various configurations giving the same density as that of  $1s^1 2s^0 2p^3, ^5S$  state of *Be*. The self-consistently determined values of these physical quantities are :  $\varepsilon_{max} = -0.658$  Ry,  $\langle \frac{1}{R} \rangle = 5.818$ ,  $\langle R \rangle = 6.755$  and  $\langle R^2 \rangle = 17.309$ .

configurations	$\lambda$	$\varepsilon_{max}(Ry.)$	$\langle \frac{1}{R} \rangle$	$\langle R \rangle$	$\langle R^2 \rangle$
$1s^1 2s^0 2p^3$	5000	-0.649	5.818	6.755	17.312
$1s^2 2s^0 2p^2$	5000	-0.649	5.819	6.755	17.312
$1s^2 2s^1 2p^1$	5000	-0.655	5.819	6.755	17.312
$1s^1 2s^1 2p^2$	30,000	-0.626	5.818	6.755	17.310

$\rho_k$ , a unique one, the KS system, is chosen by comparing the ground-state densities of the corresponding noninteracting systems and the true ground-state density  $\rho_0$ , and checking if the LN criterion for identifying the Kohn-Sham system for an excited-state is satisfied. Thus, let in a particular noninteracting system [characterized by its potential  $v(\vec{r})$ ] the density of its  $m^{th}$  state,  $\rho_m^v(\vec{r})$ , be the same as  $\rho_k(\vec{r})$ . Its ground-state density will be denoted accordingly as  $\rho_0^v(\vec{r})$ . Then the KS system connected with  $\rho_k$  is identified among the above noninteracting systems as the one whose  $\rho_0^v(\vec{r})$  resembles  $\rho_0(\vec{r})$  most closely in a least-squares sense. The LN [56] criterion intuitively defines the KS system consistent with the adiabatic connection to the  $k^{th}$  excited-state of the interacting system (characterized in DFT by  $F_k[\rho, \rho_0]$ ). What it means is if the electron-electron interaction in an interacting system is turned off slowly, keeping the excited-state density unchanged, the corresponding ground-state density of the resulting system will remain close to the true ground-state density of the interacting system. Thus of the many noninteracting systems that give the same excited-state density, the one whose ground-state density remains closest to the true ground-state density of a given system is identified as the KS system representing the excited-state of that system. The noninteracting system so chosen should best resemble the true system because, within the constraint of the equality of their excited-state density, their ground-state densities match most closely. This should also make their external potential resemble each other by the HK theorem.

Table 2.2: Value of  $\Delta$  (see Eq. 2.10) for different configurations ( $3^{rd}$  column) giving the same excited-state density as that for the original configuration ( $2^{nd}$  column). Systems where the LN criterion is not satisfactory are indicated with a ‘\*’ against them.

atoms/ions	<i>true.config.</i>	<i>alt.config.</i>	$\Delta [\rho_0(\vec{r}), \tilde{\rho}_0(\vec{r})]$
*Be	$1s^1 2s^0 2p^3$	$1s^1 2s^1 2p^2$	0.0662
		$1s^1 2s^0 2p^3$	0.1627
		$1s^2 2s^1 2p^1$	0.8758
B	$1s^2 2s^0 2p^3$	$1s^2 2s^0 2p^3$	0.0002
		$1s^2 2s^1 2p^2$	0.0065
		$1s^2 2s^2 2p^1$	0.0286
C	$1s^2 2s^1 2p^3$	$1s^2 2s^1 2p^3$	0.0008
		$1s^2 2s^2 2p^2$	0.0156
		$1s^2 2s^0 2p^4$	0.0181
N	$1s^1 2s^0 2p^6$	$1s^1 2s^0 2p^6$	0.2903
		$1s^2 2s^0 2p^5$	6.8461
		$1s^2 2s^1 2p^4$	8.8409
O	$1s^1 2s^1 2p^6$	$1s^1 2s^1 2p^6$	0.3875
		$1s^2 2s^0 2p^6$	8.9609
		$1s^2 2s^1 2p^5$	12.1269
F	$1s^2 2s^1 2p^6$	$1s^2 2s^1 2p^6$	0.0002
		$1s^2 2s^2 2p^5$	0.0621
*F	$1s^2 2s^2 2p^3 3s^2$	$1s^2 2s^2 2p^4 3s^1$	0.0521
		$1s^2 2s^2 2p^3 3s^2$	0.2704
*Ne	$1s^1 2s^1 2p^6 3s^2$	$1s^1 2s^2 2p^6 3s^1$	0.7138
		$1s^1 2s^1 2p^6 3s^2$	1.6176

Table 2.3: Caption is the same as in Table 2.2.

atoms/ions	<i>true.config.</i>	<i>alt.config.</i>	$\Delta [\rho_0(\vec{r}), \tilde{\rho}_0(\vec{r})]$
$*B^+$	$1s^1 2s^0 2p^3$	$1s^1 2s^1 2p^2$	0.0402
		$1s^1 2s^0 2p^3$	0.1931
		$1s^2 2s^1 2p^1$	2.0261
$*Ne^{6+}$	$1s^1 2s^0 2p^3$	$1s^1 2s^1 2p^2$	0.1465
		$1s^1 2s^0 2p^3$	0.3463
$Mg$	$1s^2 2s^2 2p^6 3s^0 3p^2$	$1s^2 2s^2 2p^6 3s^0 3p^2$	0.0007
		$1s^2 2s^2 2p^6 3s^1 3p^1$	0.0014
		$1s^2 2s^2 2p^6 3s^2 3p^0$	0.0039
$Al$	$1s^2 2s^2 2p^6 3s^0 3p^3$	$1s^2 2s^2 2p^6 3s^0 3p^3$	0.0008
		$1s^2 2s^2 2p^6 3s^1 3p^2$	0.0022
		$1s^2 2s^2 2p^6 3s^2 3p^1$	0.0073
$Si$	$1s^2 2s^2 2p^6 3s^1 3p^3$	$1s^2 2s^2 2p^6 3s^1 3p^3$	0.0007
		$1s^2 2s^2 2p^6 3s^2 3p^2$	0.0027
		$1s^2 2s^2 2p^6 3s^0 3p^4$	0.0078
$Si^+$	$1s^2 2s^2 2p^6 3s^0 3p^3$	$1s^2 2s^2 2p^6 3s^0 3p^3$	0.0004
		$1s^2 2s^2 2p^6 3s^1 3p^2$	0.0042
		$1s^2 2s^2 2p^6 3s^2 3p^1$	0.0148
$P^+$	$1s^2 2s^2 2p^6 3s^1 3p^3$	$1s^2 2s^2 2p^6 3s^1 3p^3$	0.0005
		$1s^2 2s^2 2p^6 3s^2 3p^2$	0.0053
		$1s^2 2s^2 2p^6 3s^0 3p^4$	0.0099
$P$	$1s^2 2s^2 2p^6 3s^0 3p^5$	$1s^2 2s^2 2p^6 3s^0 3p^5$	0.0006
		$1s^2 2s^2 2p^6 3s^1 3p^4$	0.0055
		$1s^2 2s^2 2p^6 3s^2 3p^3$	0.0207

We reiterate that in general a particular density can be generated by a multitude of potentials; and for each potential the associated energy functional is different [89, 90] due to the difference in the noninteracting kinetic energy of each system. However, to keep the structure of these functionals and the corresponding potentials simple, it is important that we have a criterion to choose one particular system. In this connection we note that for the ground-state densities of noninteracting electrons too, there exist [89, 90] more than one noninteracting systems that give the same density  $\rho_0$ . However, the one where the lowest energy orbitals are occupied, i.e.  $\rho_0^v(\vec{r}) = \rho_0(\vec{r})$ , is the chosen KS system, and it is unique due to the HK theorem. For the excited-states the uniqueness should be provided by the LN criterion. But, before applying it in practice, this qualitative LN [56] criterion that “ $\rho_0^v(\vec{r})$  resembles  $\rho_0(\vec{r})$  most closely in a least-squares sense” needs to be transformed into some quantitative form.

### 2.3.4 Testing the LN Criterion

The LN criterion has been investigated by adopting the ZMP constrained search procedure (Appendix C). In the ZMP constrained search procedure the global Lagrange multiplier  $\lambda$  is chosen to be large enough so that not only do the densities match to a high degree of accuracy, the highest occupied eigenvalues  $\varepsilon_{max}$  also matches with the original  $\varepsilon_{max}$  to a great accuracy (to within 5%; in fact it is better than within 2% in many of the cases). For example, for the  $1s^1 2s^0 2p^3$  excited-state of *Be*, we have generated the density of this configuration with three other configurations:  $1s^2 2s^0 2p^2$ ,  $1s^2 2s^1 2p^1$  and  $1s^1 2s^1 2p^2$ . The  $\varepsilon_{max}$  and the expectation values  $\langle \frac{1}{R} \rangle$ ,  $\langle R \rangle$  and  $\langle R^2 \rangle$  for different configurations are compared in Table 2.1. To further check the numerical accuracy of our ZMP program, we also generate the excited-state density with the original configuration and compare numbers obtained with the original numbers. The comparison shows that with the original configuration, the  $\varepsilon_{max}$  comes to within 2% of the original value with  $\lambda = 5000$  whereas the various expectation values are essentially exact. For the three alternative configurations, the accuracy of  $\langle \frac{1}{R} \rangle$ ,  $\langle R \rangle$  and  $\langle R^2 \rangle$  is about the same but the  $\varepsilon_{max}$  values differ slightly more depending on the configuration. The worst case is the  $1s^1 2s^1 2p^2$  for which  $\varepsilon_{max} = -0.626 Ry$  for  $\lambda = 30000$ . To make sure that the eigenvalue will eventually converge to  $\varepsilon_{max} = -0.658 Ry$ , we performed calculations for different values of  $\lambda$  for this configuration and found that  $\varepsilon_{max} = -0.621 Ry$ ,  $-0.624 Ry$  and  $-0.626 Ry$  for  $\lambda = 10000$ ,  $14000$  and  $30000$ , respectively, thereby shifting towards the true eigenvalue, albeit

very slowly. We also mention that for the configuration  $1s^2 2s^1 2p^1$ , the uppermost orbital is  $2s$  and not  $2p$ . The local potential in which the electrons move is then given as:

$$v_{KS}(\vec{r}) = \lambda \int \frac{[\sum_j n_j |\phi_j(\vec{r}')|^2 - \rho(\vec{r}')] }{|\vec{r} - \vec{r}'|} d\vec{r}', \quad (2.9)$$

where  $n_j$  are the occupation numbers of orbitals  $\phi_j$  and  $\rho(\vec{r})$  is the given density. Having found the potential above, we obtain the ground-state density,  $\rho_0^v(\vec{r}) = \tilde{\rho}_0(\vec{r})$  of this potential by occupying the lowest energy orbitals with the given number of electrons. One of the ways that the difference between the two densities  $\tilde{\rho}_0(\vec{r})$  and  $\rho_0(\vec{r})$  can be characterized quantitatively is by the squared distance in the functional space :

$$\Delta [\rho_0(\vec{r}), \tilde{\rho}_0(\vec{r})] = \int_{\infty} \{\rho_0(\vec{r}) - \tilde{\rho}_0(\vec{r})\}^2 d^3r. \quad (2.10)$$

We note that it may be possible to measure the closeness between the two densities by quantifying them in an way different from the above equation. However, we consider the LN criterion as representing the least-square deviation of the alternative ground-state density,  $\tilde{\rho}_0(\vec{r})$  from the exact ground-state density,  $\rho_0$ . Then, according to the LN criterion, the noninteracting system having the smallest  $\Delta$  would be chosen as the KS system. We will now show through few examples how the proposed quantitative version of the LN criterion chooses the KS system in agreement with intuitive expectations in the cases considered. What it means is if the excitation corresponds (i) to a fixed external potential with several configurations (Sahni *et al.* [89] and Harbola [90]) or (ii) to a particular configuration with different potentials (Gaudoin and Burke [91]), then the minimum deviation occurs only for the true configuration for the exact potential. It is also shown that if some particular, different quantitative measure of the distance between densities is used in the LN criterion, it may lead to erroneous choice of the KS system.

As the first example let us consider a model *Li* atom:  $N = 3$  noninteracting electrons moving in the external potential  $v_{ext}(\vec{r}) = -Z/r$ ,  $Z = 3$ , resulting in the hydrogen-like orbitals. The  $k = 1s^1 2s^2$  excited-state configuration of the model system is considered. The exact potential,  $v_1(\vec{r}) = v(\vec{r})$  and the alternative potential  $v_2(\vec{r})$  with the same occupation along with the excited-state density  $\rho(\vec{r}) = \rho_k(\vec{r})$  are shown in Fig. 2.2 . Both potentials are generated using the non-interacting ZMP [111] method with the excited-state density  $\rho_k$  as the

input. Since the potentials  $v_1$  and  $v_2$  are different, their ground-state densities cannot be the same according to the HK theorem [8]. Whereas the ground-state density corresponding to  $v_1 = -Z/r$  is the true ground-state density of the system, that corresponding to  $v_2$  should be different — they are shown in Fig. 2.3 . Indeed, the two densities are dissimilar. If  $v_2$  also were to represent the KS system connected with the same excited-state density, the difference in the ground-state densities for these two potentials should vanish.

The same argument also works well in the case of interacting systems. To test the LN criterion further let us consider the true *Li* atom:  $N = 3$  interacting electrons moving in the external potential  $v_{ext}(\vec{r}) = -Z/r$ ,  $Z = 3$ , and consider its  $k = 1s^1 2s^2 \ ^2S$  excited-state configuration. The density  $\rho_k(\vec{r})$  of this state is represented by the density calculated self consistently using the exchange-only Harbola-Sahni (HS) [48] potential for this configuration. As described in the previous chapter, this density is a good approximation to the exact solution and very close [52, 53] to the Hartree-Fock (HF) density of this state. Shown in Fig. 2.4 are the two different potentials  $v_1(\vec{r})$  and  $v_2(\vec{r})$  reproducing the same density  $\rho_k(\vec{r})$  as the  $1s^1 2s^2$  excited-state densities of noninteracting systems;  $v_1$  coincides with the HS effective potential,  $v_1(\vec{r}) = -Z/r + v_H(\vec{r}) + v_x^{HS}(\vec{r})$ . The ZMP procedure was employed to generate both  $v_1(\vec{r})$  and  $v_2(\vec{r})$ . Although the excited-state densities of the two potentials are the same, the ground-state densities of the two potentials are different — that is what discriminates the two potentials from one another. In Fig. 2.5 we plot the noninteracting ground-state densities  $\rho_0^v(\vec{r})$  for potentials  $v = v_1$  and  $v = v_2$ , along with the interacting ground-state density  $\rho_0(r)$ . The latter is obtained in the same approximation as applied for  $\rho_k$ , namely with the HS [48] potential, now for the ground-state  $1s^2 2s$  configuration. As expected, the three densities are different. However, the noninteracting ground-state density produced by  $v_1$  is quite similar to the “*exact*” HS ground-state density of *Li* . On the other hand, that corresponding to  $v_2$  is very different from the “*exact*” one. We introduce also the potential  $v_3(\vec{r})$  (not shown), which reproduces  $\rho_k(\vec{r})$  as the ground-state density of a noninteracting system. This  $v_3$  is unique according to the HK theorem. Thus the density shown in the upper panel of Fig. 2.4 can also be labeled with  $\rho_0^{v_3}$  in analogy with Fig. 2.5. To apply the LN criterion, the squared distance, Eq. (2.10), between ground-state densities is evaluated, giving  $\Delta[\rho_0^v, \rho_0] = 0.111, 1.467, 0.460$  for  $v = v_1, v_2, v_3$ , respectively. Thus, according to this criterion, the KS system connected with the  $k^{th}$ -excited state of the *Li* atom is given by the potential  $v_1$ . This result implies that the LN criterion may have the potential to establish a  $\rho(\vec{r}) \rightarrow v(\vec{r})$  for excited-states.

As the third example let us discuss the singlet excited-state  $1s2s$  of  $He$  atom, with the density  $\rho_k$  taken from [113]. This example was examined, by Harbola [90] in the same context. Two potentials were obtained that reproduce the density  $\rho_k$ :  $v_1(\vec{r})$  as the density of the  $1s2s$  excited state of a noninteracting system, and  $v_2(\vec{r})$  as the density of the  $1s^2$  ground state. To make use of the LN criterion, the quantity  $\bar{\Delta}[\rho_0^v, \rho_0] = \int_0^\infty dr \{\rho_0^v(\vec{r}) - \rho_0(\vec{r})\}^2$  (for spherical densities) was defined, and evaluated with  $\rho_0(\vec{r})$ , the ground-state density of the true  $He$  atom, taken from [114]. On the basis of the results  $\bar{\Delta} = 0.273, 0.140$  for  $v = v_1, v_2$ , respectively, Harbola [90] concluded that the LN criterion [56] might not be proper for finding the KS potential of the excited-state DFT. However, if the distance between the ground-state densities is evaluated applying the definition (Eq.2.10), the result  $\Delta = 0.086, 0.091$  for  $v = v_1, v_2$ , respectively, is obtained. Thus on the basis of the LN criterion, we find that indeed the  $1s2s$   $^1S$  state of  $He$  is properly represented by the KS system with the potential  $v_1$  that reproduces  $\rho_k$  as the density of its  $1s2s$  configuration, in agreement with LN criterion. Carrying forward these investigations, we have also tested the LN criterion for non-interacting electrons in an infinitely deep well. Here also different potentials are generated by LB method.

The above arguments apply equally well to the one-dimensional (1D) case considered by Gaudoin and Burke [91]. Using another conventional approach — the van-Leeuwen and Baerends [112] method — for obtaining the potentials for the noninteracting-system, we have reproduced not only the results of Gaudoin and Burke as shown in Fig. 2.6 but have also done many other calculations. The second (1D) example we give in this chapter is for the following 1D model system:  $N = 3$  noninteracting electrons in an infinitely deep box of unit length, in the excited state obtained by putting one electron in the lowest-energy state and two electrons in the second-lowest one. The excited-state density ( $\rho_e$ ) and the corresponding two potentials that reproduce this density in the same configuration are shown in Fig. 2.7 . Also shown are the ground state densities  $\rho_0^{v_1}$  and  $\rho_0^{v_2}$  corresponding to these potentials. Again the ground-state density given by the potential  $v_2(x)$  is not the same as that given by  $v_1(x)$ . Thus  $v_2(x)$  can not represent the excited-state density of the model.

Our investigations so far show that the Levy-Nagy criterion is exact for non-interacting systems. However, for interacting system, we have taken only two examples; The investigation is far from being exhaustive. Keeping this in mind we have investigated many more excited states of atomic systems and find that there are exceptions to the Levy-Nagy criterion giving an appropriate Kohn-Sham system. We present these investigations next.

We have studied a large number of excited-states of atomic systems. The results obtained using the quantified LN criterion ( $\Delta$ ) Eq. 2.10 for a number of atoms and their excited-states are shown in Tables 2.2 and 2.3. It is seen from the results that for most of the cases  $\Delta$  is the smallest for the original configuration but there are cases where  $\Delta$  is the smallest for a different configuration. For example, there is the excited-state  $1s^1 2s^0 2p^3$  of *Be* for which the configuration  $1s^1 2s^1 2p^2$  gives the smallest  $\Delta$ . Similarly for the state  $1s^2 2s^2 2p^3 3s^2$  of *F*,  $1s^1 2s^1 2p^6 3s^2$  of *Ne* and  $1s^1 2s^0 2p^3$  of  $B^+$ ,  $1s^1 2s^0 2p^3$  of  $Ne^{6+}$   $\Delta$  is the smallest for a configuration other than the original configuration of the system. So one can notice that the Levy-Nagy criterion, as quantified by Eq. 2.10 above, is not satisfactory in that it leads to a KS system where an excited-state configuration is not consistent with the original system. To get over this inconsistency we first propose an alternative criterion within the Levy-Nagy scheme of comparing the ground-state densities. We then perform further analysis.

### 2.3.5 Alternative Way to Compare Ground-States

In the previous section we found that the LN criterion as quantified by Eq.(2.10) is not fully satisfactory to identify a KS system. So there may exist other ways for selecting a KS system for a given density. One such alternative has been explored by us remaining within the Levy-Nagy proposal of comparing the ground-state densities. In this alternative approach instead of comparing densities directly, we compare them energetically as follows. After obtaining many different non-interacting systems for an excited-state density, construct the corresponding ground-states from their orbitals and calculate the expectation value of the true ground-state Kohn-Sham Hamiltonian (constructed using the HS exchange potential) with respect to these ground-states. Its implementation is described below.

The sequential steps that are adopted are as follows: first solve the HS equation for the ground-state of a system and obtain the ground-state Kohn-Sham Hamiltonian  $H_0$ . The expectation value  $\langle H_0 \rangle$  with respect to the true ground-state orbitals is designated as  $\langle H_0 \rangle_{true}$ ; This is the sum of the eigenvalues of the ground-state orbitals. Next let us take the different non-interacting systems giving an excited-state density obtained using the HS potential, consider their ground-states and calculate the expectation value  $\langle H_0 \rangle_{alt.}$  with respect to these states. Because of the variational principle  $\langle H_0 \rangle_{alt.}$  should always be above  $\langle H_0 \rangle_{true}$ . We then identify the true KS system as that for which  $\langle H_0 \rangle_{alt.}$  is closest to  $\langle H_0 \rangle_{true}$ . This comparison is

Table 2.4: Comparison of the expectation value  $-\langle H_0 \rangle_{alt.}$  and  $-\langle H_0 \rangle_{exact}$  for various configurations corresponding to a given excited-state density. The first column displays the atoms/ions, the second column the original configuration, fourth column the alternative configurations considered. In the third and last column are given the expectations values  $-\langle H_0 \rangle_{exact}$  and  $-\langle H_0 \rangle_{alt.}$  respectively.

atoms/ions	<i>exact config.</i>	$-\langle H_0 \rangle_{exact}$ <b>a.u.</b>	<i>alt. config.</i>	$-\langle H_0 \rangle_{alt.}$ <b>a.u.</b>
*Be	$1s^1 2s^0 2p^3$	8.9272	$1s^2 2s^1 2p^1$	7.4302
			$1s^1 2s^0 2p^3$	8.8051
			$1s^1 2s^1 2p^2$	8.8601
Be	$1s^2 2s^1 2p^1$	8.9237	$1s^1 2s^1 2p^2$	6.1351
			$1s^2 2s^1 2p^1$	8.9217
B	$1s^2 2s^0 2p^3$	15.1482	$1s^2 2s^2 2p^1$	15.0828
			$1s^2 2s^0 2p^3$	15.1471
			$1s^2 2s^1 2p^2$	15.1365
C	$1s^2 2s^1 2p^3$	22.9759	$1s^2 2s^2 2p^2$	22.9556
			$1s^2 2s^1 2p^3$	22.9723
			$1s^2 2s^0 2p^4$	22.9473
N	$1s^2 2s^1 2p^4$	32.6951	$1s^2 2s^2 2p^3$	32.6682
			$1s^2 2s^1 2p^4$	32.6949
			$1s^2 2s^0 2p^5$	32.6712
O	$1s^2 2s^0 2p^6$	43.3618	$1s^2 2s^2 2p^4$	43.2215
			$1s^2 2s^0 2p^6$	43.3608
			$1s^2 2s^1 2p^5$	43.3252
F	$1s^2 2s^2 2p^3 3s^2$	55.8686	$1s^2 2s^2 2p^4 3s^1$	55.4295
			$1s^2 2s^2 2p^3 3s^2$	55.6436
Ne	$1s^1 2s^1 2p^6 3s^2$	70.1743	$1s^1 2s^2 2p^6 3s^1$	69.2101
			$1s^1 2s^1 2p^6 3s^2$	69.4399

made in Tables 2.4 & 2.5 for the same systems as in Tables 2.2 and 2.3 . As is clear from the table the alternate criterion is better in that the correspondence between the original system and the Kohn-Sham system is restored for  $F, Ne$  and  $Ne^{6+}$ . However, new inconsistencies arise in  $Al, Si$  and  $P^+$  although in these cases the difference in the numbers for the original and the alternative configuration is very small. On the other hand, the inconsistency in  $Be$  and  $B^+$  remains. One thing is for sure that this criterion is very sensitive to the exchange potential. If calculations are done with KLI-OPM exchange potential, the inconsistency remains only in  $Be$  and  $B^+$  systems.

It is clear from the discussion in the two sections above that a criterion based on comparison of ground-state densities of excited-state Kohn-Sham systems cannot be satisfactory. So one requires a different criterion which replaces the one proposed by LN for describing the excited-states.

## 2.4 Present Theory for Excited-State DFT

With all the discussion so far we conclude that the direct or indirect comparison of ground-states are not sufficient to obtain  $\rho(\vec{r}) \rightarrow v_{ext}(\vec{r})$  (or KS system) for excited-states. Given the background above, we now present a consistent theory of excited-states within the rubric of density-functional approach. The principal tenets of the theory are:

(i) There is a straightforward way of mapping an excited-state density  $\rho(\vec{r})$  to the corresponding many-electron wavefunction  $\Psi(\vec{r})$  or the external potential  $v_{ext}(\vec{r})$  using the  $\rho$ -stationary wavefunctions. The wavefunction depends upon the ground-state density  $\rho_0$  implicitly.

(ii) The Kohn-Sham system is defined through a comparison of the kinetic energy for the excited-states. This avoids any comparison of the ground-state densities which, as seen above, does not give a satisfactory way of defining a KS system.

Let us now discuss these two points one by one. To describe the mapping from an excited-state density  $\rho_k(\vec{r})$  to a many-body wavefunction, we take recourse to the constrained search approach. This gives, as discussed earlier, many different wavefunctions  $\Psi_k(\vec{r})$  and the corresponding external potential  $v_{ext}^k(\vec{r})$ . If in addition to the excited-state density we also know the ground-state density  $\rho_0$  then  $v_{ext}(\vec{r})$  is uniquely determined by the Hohenberg-Kohn

Table 2.5: Caption is the same as in Table 2.4.

atoms/ions	<i>exact config.</i>	$-\langle H_0 \rangle_{exact}$ <b>a.u.</b>	<i>alt. config.</i>	$-\langle H_0 \rangle_{alt.}$ <b>a.u.</b>
<i>*B<sup>+</sup></i>	$1s^1 2s^0 2p^3$	16.6626	$1s^1 2s^1 2p^2$	16.6106
			$1s^1 2s^0 2p^3$	16.5501
			$1s^2 2s^1 2p^1$	14.2959
<i>Ne<sup>6+</sup></i>	$1s^1 2s^0 2p^3$	93.0672	$1s^1 2s^1 2p^2$	92.9276
			$1s^1 2s^0 2p^3$	92.9699
<i>Mg</i>	$1s^2 2s^2 2p^6 3s^0 3p^2$	110.9422	$1s^2 2s^2 2p^6 3s^2 3p^0$	110.9091
			$1s^2 2s^2 2p^6 3s^0 3p^2$	110.9368
			$1s^2 2s^2 2p^6 3s^1 3p^1$	110.9341
<i>*Al</i>	$1s^2 2s^2 2p^6 3s^0 3p^3$	137.1905	$1s^2 2s^2 2p^6 3s^1 3p^2$	137.1856
			$1s^2 2s^2 2p^6 3s^0 3p^3$	137.1853
			$1s^2 2s^2 2p^6 3s^2 3p^1$	137.1655
<i>*Si</i>	$1s^2 2s^2 2p^6 3s^1 3p^3$	166.2441	$1s^2 2s^2 2p^6 3s^2 3p^2$	166.2411
			$1s^2 2s^2 2p^6 3s^1 3p^3$	166.2393
			$1s^2 2s^2 2p^6 3s^0 3p^4$	166.2201
<i>Si<sup>+</sup></i>	$1s^2 2s^2 2p^6 3s^0 3p^3$	170.5966	$1s^2 2s^2 2p^6 3s^2 3p^1$	170.5714
			$1s^2 2s^2 2p^6 3s^0 3p^3$	170.5941
			$1s^2 2s^2 2p^6 3s^1 3p^2$	170.5923
<i>*P<sup>+</sup></i>	$1s^2 2s^2 2p^6 3s^1 3p^3$	203.2722	$1s^2 2s^2 2p^6 3s^2 3p^2$	203.2693
			$1s^2 2s^2 2p^6 3s^1 3p^3$	203.2687
			$1s^2 2s^2 2p^6 3s^0 3p^4$	203.2522
<i>P</i>	$1s^2 2s^2 2p^6 3s^0 3p^5$	198.1074	$1s^2 2s^2 2p^6 3s^2 3p^3$	198.0818
			$1s^2 2s^2 2p^6 3s^0 3p^5$	198.1058
			$1s^2 2s^2 2p^6 3s^1 3p^4$	198.1025
<i>S</i>	$1s^2 2s^2 2p^6 3s^0 3p^6$	232.1008	$1s^2 2s^2 2p^6 3s^2 3p^4$	232.0761
			$1s^2 2s^2 2p^6 3s^0 3p^6$	232.0996
			$1s^2 2s^2 2p^6 3s^1 3p^5$	232.0957

[8] theorem. Thus with the knowledge of  $\rho_0$  it is quite straightforward to select a particular  $\Psi$  that belongs to a  $[\rho, \rho_0]$  combination by comparing  $v_{ext}^k(\vec{r})$  with  $v_{ext}(\vec{r})$ . Alternatively, one can think of it as finding  $\Psi$  variationally for a  $[\rho, v_{ext}]$  combination because the knowledge of  $\rho_0$  and  $v_{ext}$  is equivalent. Through the constrained search above a functional

$$F[\rho; \rho_0] = \langle \Psi[\rho; \rho_0] | \hat{T} + \hat{V}_{ee} | \Psi[\rho; \rho_0] \rangle \quad (2.11)$$

is also defined. The prescription above is similar to that of Levy and Nagy [56] but avoids the orthogonality condition imposed by them.

The densities for different excited-state for a given ground-state density  $\rho_0$  or external potential  $v_{ext}$  can thus be found as follows: take a density and search for  $\Psi$  that makes  $\langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$  stationary; check whether any one of the corresponding  $v_{ext}$  matches with the given  $\rho_0$  (or  $v_{ext}$ ); if not, take another density and repeat the procedure until the correct  $\rho$  is found. For a density near  $(\rho + \delta\rho)$ , again perform constraint search to find  $\Psi[\rho + \delta\rho; \rho_0]$ ; In this case choose that  $(v_{ext} + \delta v_{ext})$  that converges to  $v_{ext}$  as  $\delta\rho \rightarrow 0$ . This then is used to define the functional derivative  $\frac{\delta F}{\delta\rho}$ . Now because of the proof given by Görling [54], the Euler equation for the excited-state density is

$$\frac{\delta F[\rho, \rho_0]}{\delta\rho(\vec{r})} + v_{ext}(\vec{r}) = \mu \quad , \quad (2.12)$$

where  $\mu$  is the Lagrange multiplier to ensure that  $\rho_k(\vec{r})$  integrates to the proper number of electrons.

The prescription above for the excited-states in terms of their densities is quite straightforward, particularly because it's development is parallel to that for the ground-states. On the other hand, to construct a Kohn-Sham [9] system for a given density is non-trivial; and to carry out accurate calculations for excited-states it is of prime importance to construct a KS system. Further, a KS system will be meaningful if the orbitals involved in an excitation match with the corresponding excitations in the true system. We have shown above that the Kohn-Sham system constructed using the Levy-Nagy criterion fails in this regard. We next discuss if a Kohn-Sham system can be defined for an excited-state.

In principle, obtaining a Kohn-Sham system is quite easy. Define the non-interacting kinetic energy  $T_s[\rho, \rho_0]$  and use it to further define the exchange-correlation functional as

$$E_{xc}[\rho, \rho_0] = F[\rho, \rho_0] - \frac{1}{2} \int \int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}d\vec{r}' - T_s[\rho, \rho_0] . \quad (2.13)$$

Then the Euler equation for the excited-state densities will read

$$\frac{\delta T_s[\rho, \rho_0]}{\delta \rho(\vec{r})} + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + \frac{\delta E_{xc}[\rho, \rho_0]}{\delta \rho(\vec{r})} + v_{ext} = \mu . \quad (2.14)$$

which is equivalent to solving

$$\left\{ -\frac{1}{2}\nabla^2 + v_{KS}(\vec{r}) \right\} \phi_i(\vec{r}) = \varepsilon_i \phi_i(\vec{r}) \quad (2.15)$$

with

$$v_{KS}(\vec{r}) = v_{ext}(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + \frac{\delta E_{xc}[\rho, \rho_0]}{\delta \rho(\vec{r})} . \quad (2.16)$$

However, it is defining  $T_s[\rho, \rho_0]$  that is not easy in the excited-state problem. For the ground-states,  $T_s[\rho_0]$  is easily defined as the minimum kinetic energy for a given density obtained by occupying the lowest energy orbitals for a non-interacting system. On the other hand, for the excited-states it is not clear which orbitals to occupy for a given density, particularly because a density can be generated by many different non-interacting systems. Levy-Nagy select one of these systems by comparing the ground-state density of the excited-state non-interacting system with the true ground-state density. However, this criterion is not satisfactory as we have pointed out earlier. Therefore some other criterion has to be evolved to construct the excited-state Kohn-Sham system.

Before searching for other ways of constructing a Kohn-Sham system, we look for reasons that may be responsible for the Levy-Nagy criterion not being fully satisfactory. We argue that we are not being consistent while comparing the ground-state density of an excited-state KS system with the true ground-state density. This is because the ground-state density of the excited-state KS system is not the self-consistent ground-state density of the  $v_{ext}(\vec{r})$  obtained for the excited-state density but of a potential different from  $v_{ext}(\vec{r})$ . In comparing the ground-state densities, we are thus not comparing the  $v_{ext}(\vec{r})$  of the excited-state KS system

with the true  $v_{ext}(\vec{r})$ , and this at times leads to inconsistent results.

In light of the above remarks, it is important that in constructing the Kohn-Sham system only the self-consistently determined quantities corresponding to a given excited-state density be compared. Thus our proposition is that the KS system be so chosen that it is energetically very close to the original system. To ensure this, we define the KS system as that system for which the non-interacting kinetic energy, obtained through constrained search over the non-interacting wavefunctions, is closest to  $T[\rho, \rho_0]$ , already obtained through the full constrained search. This then gives the functional  $T_s[\rho, \rho_0]$ . Thus  $T_s[\rho, \rho_0]$  is defined as the kinetic energy that is closest to the true kinetic energy  $T[\rho, \rho_0]$  obtained for a given excited-state density  $\rho$ . Defining  $T_s[\rho, \rho_0]$  in this manner also keeps the DFT exchange-correlation energy close to the conventional quantum chemical exchange-correlation energy. An added advantage of keeping the difference between the two kinetic energies  $T_s[\rho, \rho_0]$  and  $T[\rho, \rho_0]$  smallest is that the structure of the Kohn-Sham potential is simple; it is known that contribution of  $\underbrace{T - T_s}$  gives more structure to the KS potential.

We will now discuss how for a given density  $\rho$  one can have different exchange correlation and external potentials. Our argument is based on differential virial theorem (DVT) [88]<sup>2</sup>. The KS potential corresponding to a given excited-state density  $\rho(\vec{r})$  satisfies

$$-\nabla v_{ks} = -\frac{1}{4\rho} \nabla \nabla^2 \rho + \frac{\vec{Z}_{ks}(\vec{r}; [\Gamma_{1,ks}])}{\rho}, \quad (2.17)$$

where  $\Gamma_1$  ( $\Gamma_2$ ) is the first (second) order density matrix and the vector field  $\vec{Z}_{KS}$  is related to the Kohn-Sham kinetic energy density tensors similar to the field  $\vec{Z}$  for the true kinetic energy respectively. Similarly for the interacting system there are many external potentials that gives the excited-state density at hand with  $v_{ext}$  satisfies

$$-\nabla v_{ext} = -\frac{1}{4\rho} \nabla \nabla^2 \rho + \frac{\vec{Z}(\vec{r}; [\Gamma_1])}{\rho} + \nabla v_{Hxc}, \quad (2.18)$$

where the last term in Eq. 2.18 is the field  $\mathcal{E}_{hxc}$  for Hartree plus exchange-correlation potential.

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<sup>2</sup>For detailed discussion on differential virial theorem [88] please see Appendix B of this thesis.

In other words

$$-\nabla v_{ext} = -\frac{1}{4\rho} \nabla \nabla^2 \rho + \frac{\vec{Z}(\vec{r}; [\Gamma_1])}{\rho} + 2 \int \Gamma_2[\rho] \nabla \left( \frac{1}{|\vec{r} - \vec{r}'|} \right) d\vec{r}' . \quad (2.19)$$

Now for a given  $v_{ext}(\vec{r})$ ,  $\vec{Z}$  and  $\Gamma_2$  are fixed. Thus for a given ground-state density  $\rho_0(\vec{r})$ , in addition to the excited-state density  $\rho$ ,  $\Gamma_1$  and  $\Gamma_2$  are also fixed. This is because the ground-state density automatically fixes the external potential by HK theorem. So the  $[\rho, \rho_0]$  combination gives a many-body state for which there can be several KS systems. *i.e.*

$$\begin{aligned} [\rho, \rho_0] &\rightarrow \Psi_1 \rightarrow \{\Gamma_2, \vec{Z}\} \rightarrow \{\vec{Z}_{ks}^1, v_{xc}^1\} \\ [\rho, \rho_0] &\rightarrow \Psi_2 \rightarrow \{\Gamma_2, \vec{Z}\} \rightarrow \{\vec{Z}_{ks}^2, v_{xc}^2\} \\ [\rho, \rho_0] &\rightarrow \Psi_i \rightarrow \{\Gamma_2, \vec{Z}\} \rightarrow \{\vec{Z}_{ks}^i, v_{xc}^i\} \end{aligned} \quad (2.20)$$

By fixing the external potential ( or  $\rho_0$ ) then the different configuration arises as a result of the difference between the KS  $\vec{Z}_{ks}$  and original  $\vec{Z}$  kinetic energy density tensors. This difference leads to different exchange-correlation potentials. All the statements in the paragraph above are justified on the basis of the differential virial theorem [88]. Using this theorem the exchange-correlation potential for a given density and the corresponding many body wavefunction  $\Psi$  can be written as

$$-\nabla v_{xc}(\vec{r}) = \frac{\{\vec{Z}_{KS}(\vec{r}; [\Gamma_1^{KS}]) - \vec{Z}(\vec{r}; [\Gamma_1]) + \int [\nabla u(\vec{r}, \vec{r}')] [\rho(\vec{r})\rho(\vec{r}') - 2\Gamma_2(\vec{r}, \vec{r}')] d\vec{r}'\}}{\rho(\vec{r})} . \quad (2.21)$$

A given non-interacting effective potential can be thought of as arising from the sum of an external potential  $\tilde{v}_{ext}$ , coulomb potential and the exchange correlation potential given by Eq. 2.21 with  $\vec{Z}$ ,  $\Gamma_1$  and  $\Gamma_2$  corresponding to  $\tilde{v}_{ext}$ . Now the different configurations can be thought of as arising from a different external potential (as is shown below) or from a different exchange-correlation potential [89, 90]. Suppose a given density  $\rho$  is generated through an  $i^{th}$  KS system, then

$$-\nabla v_{ks} = -\frac{1}{4\rho} \nabla \nabla^2 \rho + \frac{\vec{Z}_{ks}^i(\vec{r}; [\Gamma_1 ks])}{\rho} . \quad (2.22)$$

If the density is generated through a  $j^{th}$  external potential. Then

$$-\nabla v_{ext}^j = -\frac{1}{4\rho} \nabla \nabla^2 \rho + \frac{\vec{Z}^j(\vec{r}; [\Gamma_1^j])}{\rho} + 2 \int \Gamma_2^j[\rho] \nabla \left( \frac{1}{|\vec{r} - \vec{r}'|} \right) d\vec{r}' . \quad (2.23)$$

Which implies

$$-\nabla v_{xc}^{jj} = \frac{\vec{Z}_{ks}^i - \vec{Z}^j}{\rho} + \vec{\mathcal{E}}_{xc}^j , \quad (2.24)$$

where  $\vec{\mathcal{E}}_{xc}^j$  is the field due to the Fermi-Coulomb field hole of the  $j^{th}$  system  $[\Gamma_2^j]$ . In any case kinetic energy difference between the true and Kohn-Sham system is [115, 116]

$$\Delta T = \frac{1}{2} \int \vec{r} \cdot \{ \vec{Z}_{KS}(\vec{r}; [\Gamma_1^{KS}]) - \vec{Z}(\vec{r}; [\Gamma_1]) \} d\vec{r} . \quad (2.25)$$

It is this difference that we propose be kept the smallest for the true KS system, and as we show below, it gives the Kohn-Sham system consistent with the original system.

We have discussed above that for a proper Kohn-Sham system for the excited-states, it is important that its kinetic energy  $T_s[\rho, \rho_0]$  be closest to the true Kinetic energy  $T[\rho, \rho_0]$ . We will demonstrate this in next section through examples. The discussion, however, should not give the impression that to do a KS calculation we should know the exact kinetic energy beforehand. That would make doing a KS calculation meaningless. Rather through the analysis above we have learned that smallest magnitude of the difference between the true and KS kinetic energies  $\Delta T = (T - T_s)$  gives a proper KS system. The question is how do we make sure of this in a density-functional calculation. We discuss this next.

As noted above defining  $T_s[\rho, \rho_0]$  as that KS kinetic energy which is closest to the true kinetic energy  $T[\rho, \rho_0]$  also keeps the DFT exchange correlation (XC) energy  $E_{xc}$  close to the conventional quantum mechanical exchange correlation energy. Now let us use this fact to construct an XC energy functional by approximating it by its quantum chemical expression for a given state for some known systems such as the homogeneous electron gas as is done for obtaining the ground-state functional. In that case we would be taking  $\Delta T = (T - T_s)$  to be zero. This is what we have done recently in constructing an exchange only energy functional for the excited-states which is discussed in the third chapter. The exchange energy expression employed in the OPM or HS calculations also falls in this category, although the

expression for energy is not a density functional but is given in terms of the orbitals. Further the functionals for the ground-state are also in the same category. With such functionals employed, a given excited-state of the KS system would correspond to a similar state for the true system. This is then the prescription for constructing excited-state energy functionals and performing the corresponding KS calculations.

## 2.5 Demonstration of Present Theory

In this section we demonstrate the ideas presented above by implementing them to various atomic systems. Since we do not know how to perform the general constrained search  $\rho \rightarrow \Psi, \delta \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle = 0$ , we take an indirect path for the purpose of demonstration. In the following we demonstrate with atomic excited-state densities generated by the HS exchange-only potential and take these as the excited-state density. The densities and the energies obtained by the HS formalism are essentially the same as those of Hartree-Fock (HF) [117] theory for both the ground as well as the excited-states. Similarly the HS exchange potential is very close to the true local exchange potential of the optimized potential method (OPM). Thus the formalism is well suited for testing the ideas presented above. Thus we start with this given  $[\rho, v_{ext}]$  combination.

We first demonstrate that an excited-state density is generated by different external potentials depending on the configurations chosen to generate the density. For this we use the ZMP method to get the non-interacting potential giving the density  $\rho(\vec{r})$  and subtract from it the Coulomb  $v_{coul}(\vec{r})$  and the exchange  $v_x^{HS}(\vec{r})$  potential to get the external potential  $v_{ext}(\vec{r})$  (i.e.  $v_{ext}(\vec{r}) = v_{KS}(\vec{r}) - v_{coul}(\vec{r}) - v_x^{HS}(\vec{r})$ ). Choosing  $v_x^{HS}(\vec{r})$  as the exchange potential amounts to taking  $\Delta T$  of Eq. 2.25 to be zero since  $v_x^{HS}(\vec{r})$  is calculated from only the expression under the integral sign in Eq. 2.21. The exchange potential for a given set of occupied orbitals is obtained using the Harbola-Sahni formula [118] for it. (We note the alternate possibility of thinking of this effective potential arising from the combination of the original external potential  $-\frac{Z}{r}$ , the Coulomb potential and an exchange potential with non-zero ( $\vec{Z} - \vec{Z}_{KS}$ ) component and therefore different from  $v_x^{HS}$ ). Shown in Fig.2.8 are different external potentials thus generated for the  $1s^1 2s^0 2p^3$  ( $^5S$ ) density of *Be*. To check our consistency, we first obtain  $v_{ext}(\vec{r})$  for the original configuration ( $1s^1 2s^0 2p^3$ ) and find it correctly to be  $-\frac{8}{r}$  Ry. The other config-

Table 2.6: Shown in the table are atoms/ions with the original excited-state configuration in the second column and density of this generated by various alternative configurations shown in the fourth column. In the third and fifth column are given the values of the kinetic energies corresponding to the original and alternative configurations respectively

atoms/ions	<i>true config.</i>	$T[\rho]$ a.u.	<i>alt. config.</i>	$T_s[\rho]$ a.u.
<i>Be</i>	$1s^1 2s^0 2p^3$	10.1489	$1s^1 2s^1 2p^2$	10.0177
			$1s^1 2s^0 2p^3$	10.1481
			$1s^2 2s^1 2p^1$	8.1357
<i>B</i>	$1s^2 2s^0 2p^3$	24.1249	$1s^2 2s^2 2p^1$	23.7627
			$1s^2 2s^0 2p^3$	24.1211
			$1s^2 2s^1 2p^2$	23.9238
<i>C</i>	$1s^2 2s^1 2p^3$	37.5938	$1s^2 2s^2 2p^2$	37.2985
			$1s^2 2s^1 2p^3$	37.5922
			$1s^2 2s^0 2p^4$	37.9299
<i>N</i>	$1s^1 2s^0 2p^6$	38.5551	$1s^2 2s^0 2p^5$	30.5856
			$1s^1 2s^0 2p^6$	38.5525
			$1s^2 2s^1 2p^4$	30.6238
<i>O</i>	$1s^1 2s^1 2p^6$	54.7136	$1s^2 2s^1 2p^5$	44.6244
			$1s^1 2s^1 2p^6$	54.7095
			$1s^2 2s^0 2p^6$	44.5899
<i>F</i>	$1s^2 2s^1 2p^6$	98.5267	$1s^2 2s^2 2p^5$	97.8733
			$1s^2 2s^1 2p^6$	98.5212
<i>F</i>	$1s^2 2s^2 2p^3 3s^2$	98.2631	$1s^2 2s^2 2p^4 3s^1$	97.8746
			$1s^2 2s^2 2p^3 3s^2$	98.2393
<i>Ne</i>	$1s^1 2s^1 2p^6 3s^2$	94.6521	$1s^1 2s^2 2p^6 3s^1$	93.4337
			$1s^1 2s^1 2p^6 3s^2$	94.6364

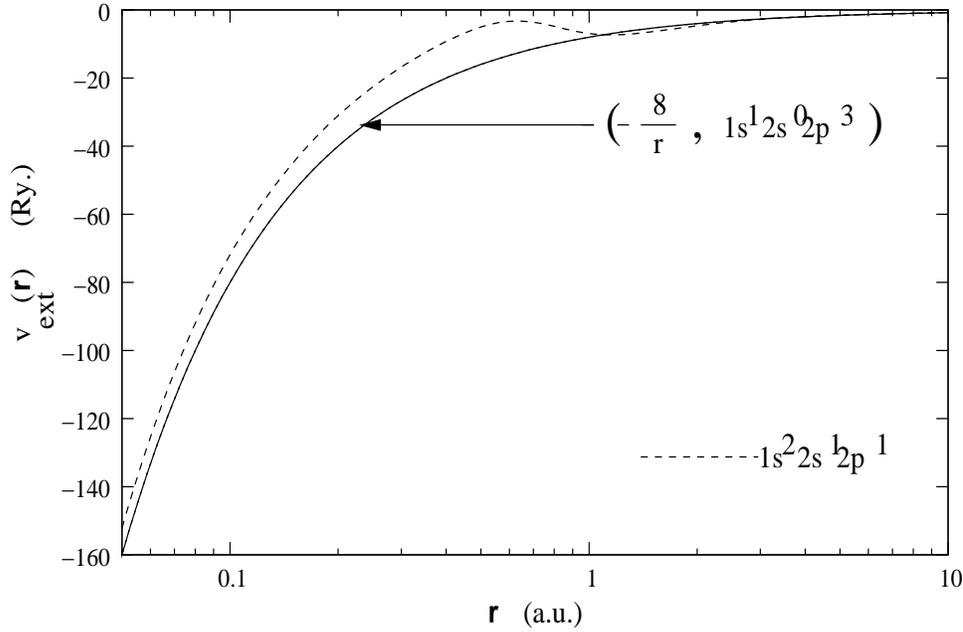


Figure 2.8: Shown in the figure are the external potentials for the excited-state density of  $1s^1 2s^0 2p^3$  ( $^5S$ ) state of  $Be$  corresponding to the original and one alternative configuration.

urations that we use to obtain the same density are  $1s^2 2s^0 2p^2$ ,  $1s^2 2s^1 2p^1$ ,  $1s^1 2s^1 2p^2$ . We have shown only two potentials corresponding to the configurations  $1s^2 2s^1 2p^1$  and  $1s^1 2s^0 2p^3$ , and compared them with the true external potential  $v_{ext}(\vec{r}) = -\frac{8}{r} Ry$ . As discussed earlier, only one of these - that corresponding to the original configuration - matches with the true external potential.

Question is now what the external potentials or the ground-state densities corresponding to various excited-state KS system will be? In our study we have shown that the external potentials corresponding to the ground-state density of excited-state KS systems are different from the external potential for the excited-state density. This, as pointed out earlier, sometimes leads to non-satisfaction of the Levy-Nagy criterion. Shown in Fig. 2.9 are the  $\tilde{v}_{ext}(\vec{r})$  corresponding to the ground-state densities of different configurations for the excited-state density of  $1s^1 2s^0 2p^3$  ( $^5S$ ) state of  $Be$ . These potential are also obtained by subtracting from the Kohn-Sham potential  $v_{KS}$  the Coulomb and the Harbola-Sahni exchange potential calculated by occupying the corresponding KS orbitals in the ground-state configuration. One can see that whereas the true external potential is  $-\frac{8}{r} Ry$ , the external potentials corresponding to the ground-states are different even for the original configuration  $1s^1 2s^0 2p^3$  ( $^5S$ ). It is this

Table 2.7: Caption is the same as in Table 2.6.

atoms/ions	<i>true config.</i>	$T[\rho]$ a.u.	<i>alt. config.</i>	$T_s[\rho]$ a.u.
$B^+$	$1s^1 2s^0 2p^3$	16.8390	$1s^1 2s^1 2p^2$	16.6581
			$1s^1 2s^0 2p^3$	16.8378
			$1s^2 2s^1 2p^1$	13.2701
$Ne^{6+}$	$1s^1 2s^0 2p^3$	76.5893	$1s^1 2s^1 2p^2$	76.3318
			$1s^1 2s^0 2p^3$	76.5837
$Mg$	$1s^2 2s^2 2p^6 3s^0 3p^2$	199.3771	$1s^2 2s^2 2p^6 3s^1 3p^1$	199.2404
			$1s^2 2s^2 2p^6 3s^0 3p^2$	199.3661
			$1s^2 2s^2 2p^6 3s^2 3p^0$	199.1455
$Al$	$1s^2 2s^2 2p^6 3s^0 3p^3$	241.5112	$1s^2 2s^2 2p^6 3s^1 3p^2$	241.3098
			$1s^2 2s^2 2p^6 3s^0 3p^3$	241.4967
			$1s^2 2s^2 2p^6 3s^2 3p^1$	241.1428
$Si$	$1s^2 2s^2 2p^6 3s^1 3p^3$	288.7507	$1s^2 2s^2 2p^6 3s^2 3p^2$	288.4802
			$1s^2 2s^2 2p^6 3s^1 3p^3$	288.7335
			$1s^2 2s^2 2p^6 3s^0 3p^4$	288.9977
$Si^+$	$1s^2 2s^2 2p^6 3s^0 3p^3$	288.0463	$1s^2 2s^2 2p^6 3s^1 3p^2$	287.7594
			$1s^2 2s^2 2p^6 3s^0 3p^3$	288.0259
			$1s^2 2s^2 2p^6 3s^2 3p^1$	287.5146
$P^+$	$1s^2 2s^2 2p^6 3s^1 3p^3$	340.1993	$1s^2 2s^2 2p^6 3s^2 3p^2$	339.8495
			$1s^2 2s^2 2p^6 3s^1 3p^3$	340.1796
			$1s^2 2s^2 2p^6 3s^0 3p^4$	340.5202
$P$	$1s^2 2s^2 2p^6 3s^0 3p^5$	339.8574	$1s^2 2s^2 2p^6 3s^1 3p^4$	339.5241
			$1s^2 2s^2 2p^6 3s^0 3p^5$	339.8390
			$1s^2 2s^2 2p^6 3s^2 3p^3$	339.2355

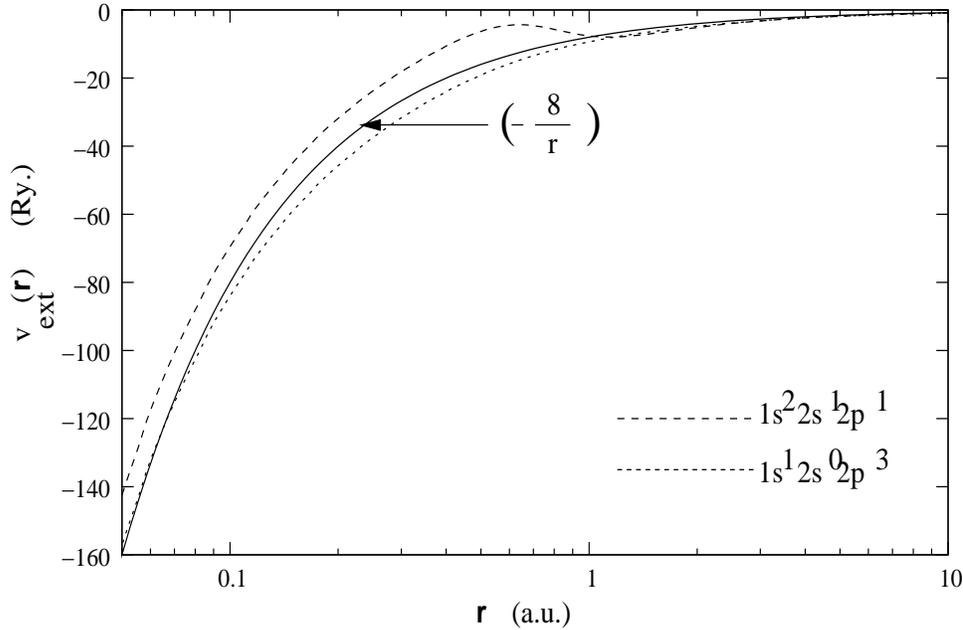


Figure 2.9: Shown in the figure are the external potentials corresponding to the ground-state densities of excited-state non-interacting systems for  $1s^1 2s^0 2p^3$  ( $^5S$ ) state of *Be*. The potentials are compared with the true external potential  $v_{ext} = -\frac{8}{r}$ .

difference that leads to the ground-state densities different from the true one, and also sometimes to inconsistencies between the KS and the true systems.

As proposed earlier the comparison of the kinetic-energies (KE) should lead to the appropriate Kohn-Sham system. We demonstrate this with the densities generated using the HS exchange potential and with one example with correlated density. Whether it is exchange only or exchange and correlation together taken into account the theory should work. The numbers for the noninteracting kinetic energy for different configurations corresponding to the same excited-state densities as considered earlier are shown in Tables 2.6 and 2.7 and are compared with their original kinetic energy. Since the HS potential itself is a local potential, the correct configuration should give  $\Delta T_s = 0$  (slight difference arising due to numerical calculations) and wrong ones a value of larger magnitude, as is evident from the numbers in the Tables 2.6 and 2.7. We see that unlike the Levy-Nagy criterion, a comparison of excited-state KE leads to a proper KS system in all the cases. Of course when we use the correlated densities, the difference  $\Delta T$  is not going to vanish for the proper configuration but should be the smallest. This is clearly seen in the example of  $1s2s(^1S)$  state of He atom where the

true  $T[\rho]$  is 2.146 *a.u.*. We have used the ZMP procedure to obtain the KS potentials in this case also and see that KE for the  $1s^2$  and the  $1s2s$  configurations is 2.044 *a.u.* and 2.153 *a.u.*, respectively. In the latter case it is closer to the true kinetic energy of the system. Thus the configuration  $1s2s$  represents the KS system for the  $1s2s(^1S)$  *He* density. Our demonstration here shows that a Kohn-Sham system for excited-states can be defined uniquely

## 2.6 Discussion and Concluding Remarks

Building on the work of Görling and Levy and Nagy, we have presented in this chapter a consistent theory of excited states within the density-functional formalism. Like the earlier approaches the proposed theory is based on constrained-search and defines a bi-density functional  $F[\rho, \rho_0]$  without the orthogonality constraint of Levy-Nagy. Further the theory gives a clear definition of the excited-state Kohn-Sham systems as that whose kinetic and exchange-correlation energy components are closest to those of the true system. This avoids the problem of comparing the non-self-consistent ground-state densities, as proposed in the LN theory, so no inconsistency arises in identifying an excited-state Kohn-Sham system.

The proposed theory leads to a map from an excited-state density to the corresponding Kohn-Sham potential that is consistent with the configuration of excitation in the known cases. Thus we have provided the theoretical foundations of excited-state time-independent density-functional theory and have put Kohn-Sham calculations for excited-states on a rigorous footing. It is clear from the discussion so far, that an excited-state configuration of the KS system corresponds to a similar excited-state of the true system (with the major component of the excited-state wavefunction involving the same orbitals as the KS system). Our definition for the KS system should help in providing guidance for the construction of the excited-state exchange-correlation energy functionals to facilitate self-consistent determination of the excited-state energies and other quantum mechanical quantities of interest.

## Chapter 3

# Development of Exchange-Correlation Functionals for Excited-States within the Local-Density Approximation

### 3.1 INTRODUCTION

Having established in the previous chapter that a consistent Hohenberg-Kohn-Sham density-functional theory can be established for excited-states also, in this chapter we look for possible ways of constructing the exchange-correlation functionals for excited states. The simplest of the exchange-correlation energy functional in the ground state theory is the local-density approximation (LDA). The proposition for the construction of an excited-state exchange-correlation functional is indeed a difficult task since the functional is non-universal and state-dependent. Thus a general functional form for it may not exist. In this chapter we will construct functionals analogous to the LDA for exchange energy for different classes of excited-states. We first argue how the  $k$  - space of a homogeneous electron gas (HEG) should be occupied differently for different classes of excited-states unlike the ground-state and then implement our idea using different methods. One particular functional proposed by us is shown to be highly accurate. The development of this chapter may pave the way to constructing accurate excited-state exchange-correlation (XC) energy functionals in DFT.

### 3.2 Homogeneous Electron Gas (HEG)

Simple systems always play an important paradigmatic role in science. Starting from the Hydrogen atom, which is a paradigm for all atomic systems to the *uniform electron gas* (*i.e.*

well known as *homogeneous electron gas*) [33, 119], which is the paradigm for solid-state physics and also for DFT. The homogeneous electron gas or liquid is a hypothetical system which has no true counterpart in the real world. Nevertheless, a great deal of work has been devoted to it. Various approximation to the kinetic and exchange-correlation functional described in the sections 1.3 start from the HEG concept. The interacting homogeneous electron gas, also known as the free electron gas or the jellium model, is an example of a translationally invariant system. This is because the electron density  $\rho(\vec{r})$  is uniform or constant over space, and thus the electron number is infinite. This particular system can be taken as a model for many metals, if we deal with the assumption that the charge density of the positive "background" of the metal is uniformly smeared out over the volume of the system so that the electrons can move practically freely through the material. The positive "background" of the model system must be taken as ions with hard core electrons forming closed shell. The valence electrons are then weakly bound and are therefore only weakly localized in the crystal lattice.

By symmetry, the Kohn-Sham potential must be uniform or constant for the HEG. Now by imposing the boundary condition within a cube of volume  $\mathcal{V} \rightarrow \infty$  so that the orbitals repeat from one face of the cube to the opposite face, the KS orbitals are plane waves  $\phi_k(\vec{r}) = \frac{e^{i\vec{k}\cdot\vec{r}}}{\sqrt{\mathcal{V}}}$ , with momenta or wavevector  $\vec{k}$  and energy  $k^2/2$ . The number of orbitals of both spins in a volume  $d^3k$  of the Fourier space is  $2 \left[ \frac{\mathcal{V}}{2\pi^3} \right] d^3k$  [120] by geometric argument. If  $N$  be the total number of electrons in  $\mathcal{V}$ , then these electrons will occupy  $N$  lowest KS spin orbitals, i.e., those with  $k < k_f$ . Thus

$$N = 2 \sum_k \theta(k_f - k) = 2 \left[ \frac{\mathcal{V}}{2\pi^3} \right] \int_0^{k_f} 4\pi k^2 dk = \mathcal{V} \frac{k_f^3}{3\pi^2}, \quad (3.1)$$

where  $k_f$  is the Fermi wavevector having wavelength  $\lambda_f = \frac{2\pi}{k_f}$ , which is the shortest de-Broglie wavelength for non-interacting electrons. The above equation leads to

$$\rho = \frac{k_f^3}{3\pi^2} = \frac{3}{4\pi r_s^3}, \quad (3.2)$$

where  $r_s$  is the Seitz radius– the radius of the sphere which on an average contains one electron. The kinetic energy of an electron having wavevector  $\vec{k}$  is  $k^2/2$ , and the average kinetic energy per electron will be

$$\tau_s[\rho] = \frac{2}{N} \sum_k \theta(k_f - k) \frac{k^2}{2} = 2 \left[ \frac{\mathcal{V}}{2\pi^3} \right] \int_0^{k_f} 4\pi k^2 \frac{k^2}{2} dk = \frac{3}{5} \frac{k_f^2}{2} = \frac{3}{5} \mathcal{E}_f, \quad (3.3)$$

where  $\mathcal{E}_f$  is the Fermi energy. In other notation,

$$\tau_s[\rho] = \frac{3}{10} \left\{ 3\pi^2 \rho \right\}^{\frac{2}{3}} = \frac{3}{10} \frac{(9\pi/4)^{\frac{2}{3}}}{r_s^2}. \quad (3.4)$$

Similarly the average exchange energy per particle is

$$\mathcal{E}_x[\rho] = -\frac{3}{4\pi} \left\{ 3\pi^2 \rho \right\}^{\frac{1}{3}} \quad (3.5)$$

But the exact analytic expressions for the correlation energy of the electron,  $\mathcal{E}_c[\rho]$  of the uniform electron gas, are known only in the extreme limits. In the high density or weak coupling limit ( $r_s \rightarrow 0$ ):

$$\mathcal{E}_c[\rho] = c_0 \ln r_s - c_1 + c_2 r_s \ln r_s - c_3 r_s + \dots \quad (3.6)$$

which is obtained by many-body perturbation theory [121]. The two positive constants  $c_0 = 0.031091$  [121] and  $c_1 = 0.046644$  [122]. In the high density limit ( $r_s \rightarrow 0$ ) the correlation energy given above does not quite tend to a constant because the excited-state of the non-interacting systems lie arbitrarily close in energy to the ground-state. Whereas, in the low density or strong-coupling limit ( $r_s \rightarrow \infty$ ) the uniform fluid phase is unstable against the formation of the close-packed Wigner lattice of localized electrons. Because in the limiting situation ( $r_s \rightarrow \infty$ ) the energies of the two phases remains nearly degenerate as they have the same kind of dependence on  $r_s$  [123] and the correlation energy per particle is:

$$\mathcal{E}_c[\rho] = -\frac{d_0}{r_s} + \frac{d_1}{r_s^{\frac{3}{2}}} + \dots, \quad (3.7)$$

where the constants  $d_0 \approx -\frac{9}{10}$  and  $d_1$  in the above equation can be estimated from the Madelung electrostatic and zero-point vibrational energies of the Wigner crystals respectively. For a brief derivation of the total energy of a uniform electron gas and the evaluation of exchange integrals please refer to Appendix A.

### 3.3 Construction of Exchange-Correlation (XC) Functionals

We start by elaborating upon why using the same (ground-state LDA functional) results in an underestimate of the excitation energies. As the electrons are excited in a system, the overlap between the orbitals decreases resulting in less of exchange effect compared to the ground-state. This is because now the electrons of the same spin are relatively less likely to come close. However, when we employ the ground-state functional to excited states also, this effect is ignored and consequently within the local approximation we make one more approximation. The latter gives larger magnitude of the exchange energy than what the correct local approximation for the excited-states should give, and this results in smaller excitation energies. The idea to construct accurate exchange energy functionals for excited-states is based on the following observation<sup>1</sup>. Since the orbital occupation in an excited-state is different from the ground-state Fermi distribution so the corresponding  $k$  - space occupation should also be different. This accounts for the non-universality and state-dependence of exchange-correlation functional described in the previous chapter. We now consider three different classes of excited-states, which are shown pictorially in the following in Figs. 3.1,3.2 and 3.3.

#### Shell Systems

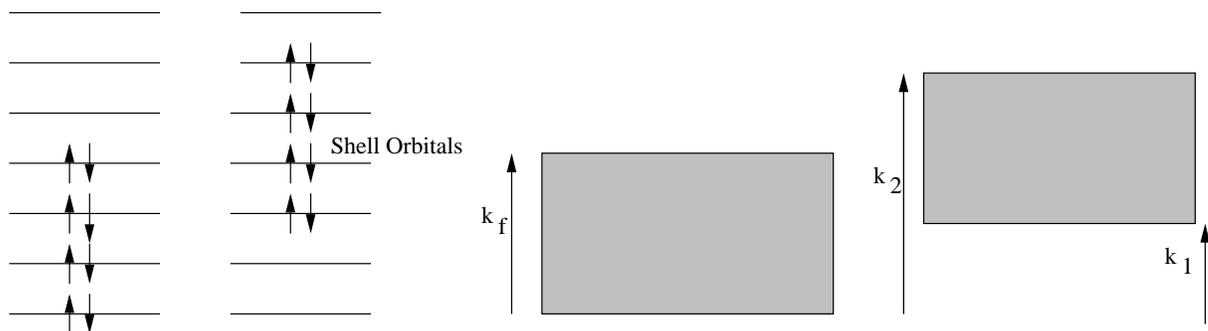


Figure 3.1: Orbital and the corresponding  $k$  - space occupation in the ground and the excited state configuration of a homogeneous electron gas.

<sup>1</sup>In this chapter we will show how to construct exchange only functionals for excited-states and hope is that the correlation functionals can be constructed in an analogous manner.

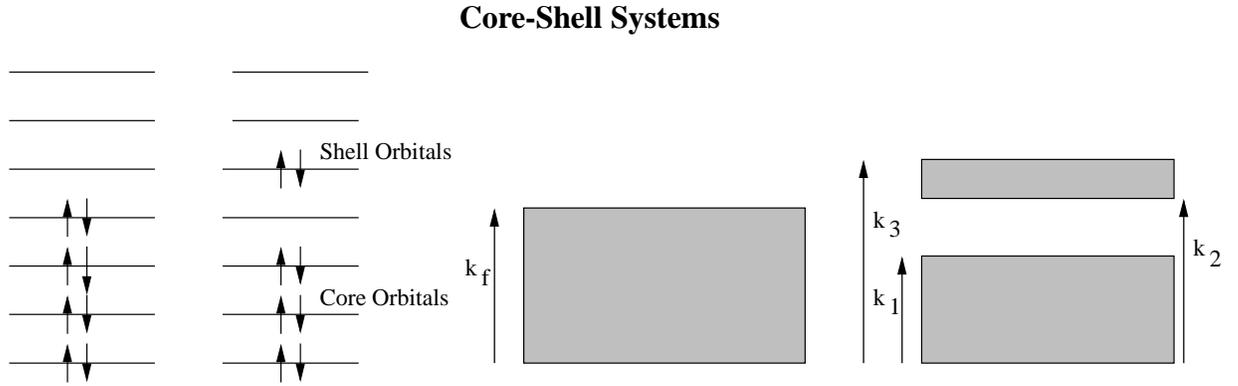


Figure 3.2: Orbital and the corresponding  $k$ -space occupation in the ground and the excited state configuration of a homogeneous electron gas.

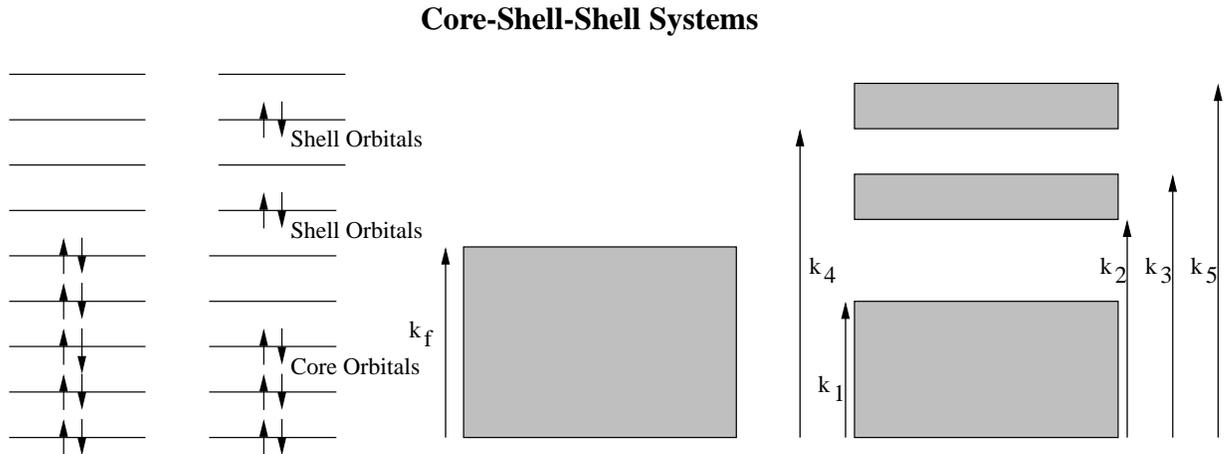


Figure 3.3: Orbital and the corresponding  $k$ -space occupation in the ground and the excited state configuration of a homogeneous electron gas.

### 3.3.1 Construction of Excited-State Exchange Energy Functionals

The exact exchange energy for a set of occupied orbitals is given as

$$E_X = -\frac{1}{2} \sum_{\sigma} \sum_i^{occ} \sum_j^{occ} \left\langle \phi_{i\sigma}(\mathbf{r}_1) \phi_{j\sigma}(\mathbf{r}_2) \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \phi_{j\sigma}(\mathbf{r}_1) \phi_{i\sigma}(\mathbf{r}_2) \right\rangle . \quad (3.8)$$

We now make LDA-like approximation for the excited-state exchange energy so that the excited-state exchange energies remain close to that given by the exact expression (Eq.3.8)

above. One point to note is that the exchange energy in the cases shown in the figures earlier (the expressions for the exchange energy is given below) is smaller in magnitude than the ground-state exchange energy. However, if we approximate it by the expression for the ground-state, its magnitude is overestimated, leading to an excited-state energy more negative than its correct value.

As the first step towards an excited-state functional, we make the correspondence between the excited-states that we are considering and similar excitations in a homogeneous electron gas. If the HEG is in its ground state, the electrons are filled up to the Fermi level so that the electrons occupy wave-vectors in  $k$  - space from  $k = 0$  to  $k_f = (3\pi^2\rho)^{\frac{1}{3}}$ , where  $\rho$  is the electron density. On the other hand, in an excited state of the system the electrons will occupy  $k$  - space differently compared to the ground state.

Here we will discuss three classes of excited-states as shown in Fig. 3.1, Fig. 3.2, Fig. 3.3 and describe how to construct exchange energy functionals for them and then obtain the corresponding accurate excitation energies using two different approaches: (1) first, through the comparison of non-interacting kinetic energy and its local density counterpart, which will be the content of the the current section. (2) by inclusion of self energies of the electrons responsible for the excitation to be described later.

To elaborate on this, let us take the example of a homogeneous electron gas. As already described if it is in its ground-state, the electrons occupy wave-vectors in the  $k$  - space from  $k = 0$  to  $k_F = (3\pi^2\rho_0(\mathbf{r}))^{\frac{1}{3}}$ . On the other hand, in the three classes of excited-states considered the electronic  $k$  - space occupation will be very different from the ground-state.

In the first case (Fig. 3.1): Electronic occupation is such that electrons in the lowest energy states and states just near to it are excited to virtual orbitals. Thus the corresponding  $k$  - space occupation is from  $k_1$  to  $k_2$  (forming a *shell* structure) so that the excited-state density  $\rho(\mathbf{r})$  is given by

$$k_2^3 - k_1^3 = 3\pi^2\rho(\mathbf{r}) \quad . \quad (3.9)$$

Now within LDA the total exchange energy for electrons forming the shell is given by

$$E_X^{total} = E_X^{shell} = -\frac{V}{8\pi^3} \left[ 2(k_2^3 - k_1^3)(k_2 - k_1) + (k_2^2 - k_1^2)^2 \ln \left( \frac{k_2 + k_1}{k_2 - k_1} \right) \right] . \quad (3.10)$$

In the second case (*core – shell* systems) the occupation of the orbitals is such that the electrons occupy some core orbitals and some shell orbitals, leaving the orbitals between the core and the shell region vacant. This is shown schematically in Fig. 3.2. Such an excited-state would be obtained, for example, if an electron from the filled orbitals of the ground-state is excited to just above the occupied levels. For this kind of excited-states (*core – shell* systems) that we consider here, the corresponding occupation in the  $k$  – *space* is as follows: The electrons occupy orbitals from  $k = 0$  to  $k_1$  and  $k_2$  to  $k_3$  with a gap in between as shown in Fig. (3.2). So the excited state density is given by

$$\rho = \rho_c + \rho_s , \quad (3.11)$$

with

$$k_1^3 = 3\pi^2 \rho_c , \quad (3.12)$$

$$k_2^3 - k_1^3 = 3\pi^2 \rho_m , \quad (3.13)$$

$$k_3^3 - k_2^3 = 3\pi^2 \rho_s . \quad (3.14)$$

In Eq. (3.11)  $\rho_c$  and  $\rho_s$  are the core and shell electron density, and in Eq. (3.13),  $\rho_m$  is the density of the vacant orbitals that lie between the core and the shell regions of occupied orbitals. The exchange energy for the HEG that occupies the  $k$  – *space* as described above can be obtained exactly and is given as (MLDA stands for modified local-density approximation)

$$E_X^{MLDA} = E_X^{core} + E_X^{shell} + E_X^{core-shell} , \quad (3.15)$$

where

$$E_X^{core} = V \left[ -\frac{k_1^4}{4\pi^3} \right] , \quad (3.16)$$

is the exchange energy of the core electrons,

$$E_X^{shell} = -\frac{V}{8\pi^3} \left[ 2(k_3^3 - k_2^3)(k_3 - k_2) + (k_3^2 - k_2^2)^2 \ln \left( \frac{k_3 + k_2}{k_3 - k_2} \right) \right], \quad (3.17)$$

is the exchange energy of the electrons in the shell, and

$$E_X^{core-shell} = -\frac{V}{8\pi^3} \left[ 2(k_3 - k_2)k_1^3 + 2(k_3^3 - k_2^3)k_1 + (k_2^2 - k_1^2)^2 \ln \left( \frac{k_2 + k_1}{k_2 - k_1} \right) - (k_3^2 - k_1^2)^2 \ln \left( \frac{k_3 + k_1}{k_3 - k_1} \right) \right], \quad (3.18)$$

represents the exchange energy of interaction between the core and the shell electrons. Here  $V$  is the volume of the HEG.

In the third class of excited-states (Fig. 3.3): Electrons occupy wave-vector from 0 to  $k_1$  from  $k_2$  to  $k_3$  and also from  $k_4$  to  $k_5$  (forming the *core – shell – shell* structure) so that

$$\rho = \rho_c + \rho_{s1} + \rho_{s2}, \quad k_1^3 = 3\pi^2\rho_c, \quad k_3^3 - k_2^3 = 3\pi^2\rho_{s1}, \quad k_5^3 - k_4^3 = 3\pi^2\rho_{s2}. \quad (3.19)$$

In Eq. 3.19  $\rho_c, \rho_{s1}$  and  $\rho_{s2}$  be the core, first and second shell electron densities with the excited density being  $\rho$ .

Similar to previous two classes of excited-states, proper local-density approximation should be made for the *core – shell – shell* systems (Fig. 3.3), where there will be some more electron-electron interaction term in addition to those present in the *shell* and *core – shell* cases and x-only functional for it will be:

$$E_X^{total} = E_X^{core} + E_X^{shell1} + E_X^{shell2} + E_X^{core-shell1} + E_X^{core-shell2} + E_X^{shell1-shell2}, \quad (3.20)$$

where  $E_X^{core}, E_X^{shell1}, E_X^{shell2}, E_X^{core-shell1}, E_X^{core-shell2}, E_X^{shell1-shell2}$  exchange interaction due to electrons present in core, first shell, second shell, core and first shell, core and second shell between first shell and second shell respectively. In all the three cases the exchange expressions for various *core, shell, core – shell* are similar except the *shell – shell* interactions. One should be careful that the radii in  $k$ –space should also differ from one another in all the three cases. In Eq.3.20 shell-shell interaction is given by:

$$\begin{aligned}
E_X^{shell1-shell2} = & -\frac{V}{8\pi^3} \left[ 2(k_3 - k_2)(k_5^3 - k_4^3) + 2(k_3^3 - k_2^3)(k_5 - k_4) \right. \\
& + (k_4^2 - k_3^2)^2 \ln \left( \frac{k_4 + k_3}{k_4 - k_3} \right) - (k_5^2 - k_3^2)^2 \ln \left( \frac{k_5 + k_3}{k_5 - k_3} \right) \\
& \left. + (k_5^2 - k_2^2)^2 \ln \left( \frac{k_5 + k_2}{k_5 - k_2} \right) - (k_4^2 - k_2^2)^2 \ln \left( \frac{k_4 + k_2}{k_4 - k_2} \right) \right] . \quad (3.21)
\end{aligned}$$

Now for a given inhomogeneous electron gas of excited-state density  $\rho(\mathbf{r})$ , in case of *shell* systems (Fig. 3.1) the LDA is made by assigning two  $\mathbf{r}$ -dependent wavevectors  $k_1$  and  $k_2$  related through Eq. 3.9 above and calculating the exchange energy at that point from Eq. 3.10. For  $k_1 = 0$ , the expression above gives the ground-state LDA exchange energy functional

$$E_x[\rho] = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{\frac{1}{3}} \int \rho^{\frac{4}{3}}(\mathbf{r}) d\mathbf{r} . \quad (3.22)$$

Although the focus above has been on the exchange energy, dramatic effects of occupying the same region of  $k$ -space for both the ground- and the excited-states are seen when we compare the exact non-interacting kinetic energy and its local-density counterpart - the Thomas-Fermi kinetic energy [21, 24] - for a set of orbitals occupied in the ground- and an excited-state configuration. For a given set of occupied orbitals  $\{\phi_i\}$  with occupation numbers  $\{n_i\}$ , the former is given as

$$T_s = \sum_i^{occ} n_i \langle \phi_i | -\frac{1}{2} \nabla^2 | \phi_i \rangle , \quad (3.23)$$

whereas the Thomas-Fermi kinetic energy is

$$T_s^{TF}[\rho] = \frac{3}{10} (3\pi^2)^{\frac{2}{3}} \int \rho^{\frac{5}{3}}(\mathbf{r}) d\mathbf{r}, \quad (3.24)$$

where  $\rho(\mathbf{r})$  is given by

$$\rho(\mathbf{r}) = \sum_i^{occ} |\phi_i(\mathbf{r})|^2 . \quad (3.25)$$

As an example, consider the  $1s$ ,  $2s$  and  $3p$  orbitals for the  $Be^{2+}$  ion occupied in different

configurations. In the ground-state configuration ( $1s^2$ ), the exact kinetic energy is 13.2943 a.u. whereas the Thomas-Fermi functional gives it to be 12.0360 a.u. - an error of 9.5%. On the other hand, if we consider an excited-state with orbitals  $2s$  and  $3p$  to be occupied with one electron each, the kinetic energy comes out to be 1.2381 a.u. whereas the Thomas-Fermi functional now gives the kinetic energy to be 0.3090 a.u. - an error of about 75%! (This is for the  $2s$  and  $3p$  orbitals taken from the ground-state calculation; if we perform a self-consistent LSD calculation with these orbitals occupied, the answers are 2.5481 a.u. and 0.6163 a.u., respectively. The error again is about 75%). The error for the excited-state becomes much larger because in calculating the Thomas-Fermi kinetic energy for the excited-state as we are still occupying the  $k$ -space from  $k_1 = 0$  to  $k_2 = (3\pi^2\rho)^{1/3}$ . Better estimates of kinetic-energy via the Thomas-Fermi approach would be obtained if we instead consider the electrons to be occupying a shell of inner radius  $k_1$  and outer radius  $k_2$ . In the latter case the Thomas-Fermi kinetic energy density  $\tau$  is given as

$$\tau = \frac{k_2^5 - k_1^5}{10\pi^2} \quad (3.26)$$

or its spin-polarized version [21, 24]. For  $k_1 = 0$ , this leads to the expression in Eq. 3.24.

### 3.4 Fixing the $k$ – $space$ Radii Through Kinetic Energy Comparison

So far we have given only one relationship between  $k_1$  and  $k_2$ . We need one more relation connecting the two vectors to determine them. In this approach we use the difference between the exact and Thomas-Fermi kinetic energies for the ground and the excited-state configurations as the second relation. We now explain this. Let us take

$$k_1 = C \left( 3\pi^2 \rho(\mathbf{r}) \right)^{\frac{1}{3}} \quad (3.27)$$

where  $C$  is a constant. Thus at each point in the inhomogeneous electron gas, the inner radius of the shell in  $k$ -space is determined by the density at that point with the outer radius being given via Eq. 3.9 as

$$k_2 = \left( (1 + C^3) 3\pi^2 \rho(\mathbf{r}) \right)^{\frac{1}{3}} ; \quad (3.28)$$

$C = 0$  of course corresponds to the ground-state. Now with a given set of occupied and virtual orbitals for a given system, we fix  $C$  for an excited-state configuration by demanding that the corresponding Thomas-Fermi kinetic energy, given by Eq. 3.26 with  $C > 0$  for the excited-state, have the same error as it does for the ground-state (evaluated with  $C = 0$ ). In the example of  $Be^{2+}$  given above,  $C = 1.4$  gives an error of about 9.5% for the the  $2s3p$  configuration. Thus it is this value of  $C$  that we shall use to evaluate the LDA exchange-energy and the corresponding potential in the self-consistent Kohn-Sham calculation for the  $2s3p$  configuration. We note that this is one possible way of fixing the value of  $C$ ; better ways of doing so may also exist. However, as it will be shown below, the value of  $C$  determined in this manner works quite well for the majority of excited-states investigated.

Similarly for the second and third class of excited states (Fig. 3.2 and Fig. 3.3) also one needs more relationship to determine  $k - space$  wavevectors forming the core and shell structures. In these cases also we have introduced the parameter  $C$  for determination of core and shell radii. These parameters are then determined through kinetic energy comparison as was done in the *shell* systems discussed above. For *core - shell* systems the radii vectors are given by

$$k_1 = \left( \frac{N_c}{N} \right)^{\frac{1}{3}} (3\pi^2 \rho(\mathbf{r}))^{\frac{1}{3}} \quad (3.29)$$

$$k_2 = \left( \frac{N_c + (C - 1)N_s}{N} \right)^{\frac{1}{3}} (3\pi^2 \rho(\mathbf{r}))^{\frac{1}{3}} \quad (3.30)$$

$$k_3 = \left( \frac{N_c + CN_s}{N} \right)^{\frac{1}{3}} (3\pi^2 \rho(\mathbf{r}))^{\frac{1}{3}} \quad , \quad (3.31)$$

where  $N_c$  and  $N_s$  be the number of electrons present in the core and shell orbitals respectively. Similarly for *core - shell - shell* type excited states the radii vectors are given by

$$\begin{aligned}
k_1 &= \left(\frac{N_c}{N}\right)^{\frac{1}{3}} (3\pi^2\rho(\mathbf{r}))^{\frac{1}{3}} \\
k_2 &= \left(\frac{N_c + (C_1 - 1)N_s^1}{N}\right)^{\frac{1}{3}} (3\pi^2\rho(\mathbf{r}))^{\frac{1}{3}} \\
k_3 &= \left(\frac{N_c + C_1N_s^1}{N}\right)^{\frac{1}{3}} (3\pi^2\rho(\mathbf{r}))^{\frac{1}{3}} \\
k_4 &= \left(\frac{N_c + C_1N_s^1 + (C_2 - 1)N_s^2}{N}\right)^{\frac{1}{3}} (3\pi^2\rho(\mathbf{r}))^{\frac{1}{3}} \\
k_5 &= \left(\frac{N_c + C_1N_s^1 + C_2N_s^2}{N}\right)^{\frac{1}{3}} (3\pi^2\rho(\mathbf{r}))^{\frac{1}{3}} , \tag{3.32}
\end{aligned}$$

where  $N_c$ ,  $N_s^1$  and  $N_s^2$  be the number of electrons present in the core, first shell and second shell respectively.

We have performed self-consistent Kohn-Sham calculations for the three different classes of excited-states mentioned above within the local-spin-density approximation (LSDA) by taking the LSDA functional as

$$E_x^{LSDA}[\rho^\alpha, \rho^\beta] = \frac{1}{2}E_x^{LDA}[2\rho^\alpha] + \frac{1}{2}E_x^{LDA}[2\rho^\beta] . \tag{3.33}$$

The resulting exchange energy functional and the corresponding potential have structure similar to the ground-state LSDA functional but with a different coefficient given in terms of  $C$ . For LSDA calculations we need two different  $C$ s, one for each spin. As discussed earlier, these are fixed by keeping the error in the Thomas-Fermi kinetic energy the same for both the ground and the excited states. By performing these calculations within the exchange-only, we will show that for the excited states values closer to the  $\Delta$ -SCF Hartree-Fock excitation energies are obtained with non-zero  $C$ . Further, for a given system,  $C$  increases as one goes to higher excited states.

## 3.5 Results Obtained by Kinetic Energy Comparison

### 3.5.1 Shell Systems

Shown in Table 3.1 are the excitation energies of *He*. We show the energies for three different excited states ( $2s2p\ ^3P$ ), ( $2p^2\ ^3P$ ) and ( $2s3p\ ^3P$ ) of the helium atom calculated with  $C = 0$

Table 3.1: Total energies and the excitation energies (in atomic units) of three different excited-states of helium atom for  $C = 0$  (ground-state functional) and the value of  $C$  determined by comparison of the exact and Thomas-Fermi kinetic energies for up spin. The corresponding Hartree-Fock (HF) excitation energies determined by the  $\Delta$ -SCF method are given in the last line of each set. The last column gives in eV the magnitude of the difference between the HF and the DFT transition energies.

State	C	Total Energy(a.u.)	Excitation Energy(a.u.)	Error (eV)
<b>He atom</b>				
$1s^2(^1S)$	-	-2.7236	-	-
$2s2p(^3P)$	0.0	-0.7223	2.0014	2.90
	1.045	-0.6095	2.1141	0.16
			$\Delta E_{HF} = 2.1081$	
$2p^2(^3P)$	0.0	-0.6965	2.0271	3.62
	0.955	-0.5933	2.1303	0.81
			$\Delta E_{HF} = 2.1603$	
$2s3p(^3P)$	0.0	-0.5615	2.1621	3.47
	1.395	-0.4646	2.2590	0.83
			$\Delta E_{HF} = 2.2898$	

(i.e. the ground-state LSDA) and with  $C$  determined as described earlier. Since all three excited-states have only up spin electrons,  $C$  shown in the table corresponds to up spin. These are all states that can be represented by a single Slater-determinant so that the LSDA is expected to work well [39,40] for them. We compare our results with the exact  $\Delta$ -SCF results of Hartree-Fock theory. In all the excited states considered, it is seen that whereas the error in the excitation energy obtained from the regular LSDA is about  $3eV$ , with the proposed functional it only a fraction of an  $eV$ . Thus it is clear that non-zero value of  $C$  gives a better value for the excitation energy. Further, for the higher excited states the value of  $C$  is larger, although it is slightly smaller when one goes from  $(2s2p^3P)$  to  $(2p^2^3P)$ .

To further check the validity of our approach, we have also tested it on excited states of other systems. Shown in Table 3.2 are the excitation energies of the  $(2s2p^3P)$  state of the  $Li^+$  ion,  $(2s3p^3P)$  state of the  $Be^{2+}$  ion,  $(2p^3^4S)$  state of  $Li$  atom and the  $(1s^12s^22p^1^3P)$  state of the  $Be$  atom. In the first three of these states, up spin electrons are promoted to higher energy orbitals so the  $C$  given is that for the up spin. For the  $Be$  atom, the down spin electrons of  $1s$  state is flipped and promoted to the  $2p$  level. Thus it is the down spin electron in the  $2s$  state that has to be described by a shell in the k-space; thus  $C$  in this system is that for

Table 3.2: Total energies and the excitation energies (in atomic units) of an excited-state of lithium ion  $Li^+$ , beryllium ion  $Be^{2+}$ , lithium atom and beryllium atom for  $C = 0$  and the value of  $C$  determined by comparison of the exact and Thomas-Fermi kinetic energies. The corresponding Hartree-Fock excitation energy is given in the last line. The last column gives in eV the magnitude of the difference between the HF and the DFT transition energies.

State	C	Total Energy(a.u.)	Excitation Energy(a.u.)	Error (eV)
<b>Li<sup>+</sup> ion</b>				
$1s^2(^1S)$	-	-7.0086	-	-
$2s2p(^3P)$	0.0	-1.8228	5.1858	4.89
	1.06	-1.6361	5.3725	0.19
			$\Delta E_{HF} = 5.3655$	
<b>Be<sup>2+</sup> ion</b>				
$1s^2(^1S)$	-	-13.2943	-	-
$2s3p(^3P)$	0.0	-2.5488	10.7455	8.28
	1.421	-2.3253	10.9691	2.19
			$\Delta E_{HF} = 11.0499$	
<b>Li atom</b>				
$1s^22s(^2S)$	-	-7.1934	-	-
$2p^3(^4S)$	0.0	-2.1061	5.0873	7.32
	0.777	-1.9262	5.2672	2.43
			$\Delta E_{HF} = 5.3565$	
<b>Be atom</b>				
$1s^22s^2(^1S)$	-	-14.2233	-	-
$1s^12s^22p^1(^3P)$	0.0	-10.1470	4.0863	3.07
	1.062	-10.0582	4.1646	0.94
			$\Delta E_{HF} = 4.1991$	

Table 3.3: The table caption is the same as that for Table 3.2 except that the numbers are for fluorine atom and neon ion.

State	C	Total Energy(a.u.)	Excitation Energy(a.u.)	Error (eV)
<b>F atom</b>				
$1s^2 2s^2 2p^5(^2P)$	-	-98.4740	-	-
$1s^1 2s^2 2p^6(^2S)$	0.0	-73.9002	24.5738	8.47
	0.685	-73.4263	25.0477	4.42
			$\Delta E_{HF} = 24.8852$	
$1s^2 2s^1 2p^6(^2S)$	0.0	-97.8069	0.6671	5.74
	0.238	-97.7492	0.7248	4.17
			$\Delta E_{HF} = 0.8781$	
<b>Ne<sup>+</sup> ion</b>				
$1s^2 2s^2 2p^5(^2P)$	-	-126.7371	-	-
$1s^1 2s^2 2p^6(^2S)$	0.0	-95.8931	30.8440	9.47
	0.670	-95.3537	31.3834	5.20
			$\Delta E_{HF} = 31.1921$	
$1s^2 2s^1 2p^6(^2S)$	0.0	-125.9027	0.8344	6.76
	0.244	-125.8311	0.9060	4.81
			$\Delta E_{HF} = 1.0829$	

the down spin. Further, since in this case both up and down spin electrons are involved,  $C$  is fixed so that the error in the total Thomas-Fermi kinetic energy matches for the ground- and the excited-states. We again see that for non-zero positive values of  $C$ , determined with the prescription given above, excitation energies come out to be closer to the  $\Delta$ -SCF Hartree-Fock excitation energies than with  $C = 0$ .

Shown in Table 3.3 are the numbers for the  $F$  atom and  $Ne^+$  excited-states. One of the excited-states ( $1s^1 2s^2 2p^6\ ^2S$ ) in each system corresponds to a shell in the k-space, whereas the other one ( $1s^2 2s^1 2p^6\ ^2S$ ) does not. As pointed out earlier, a shell in k-space represents well an excited-state in which the lowest lying orbitals are vacant. Thus we see that for the ( $1s^1 2s^2 2p^6\ ^2S$ ) state of both the systems, the error in the excitation energy as given by the proposed functional is smaller by a factor of about two in comparison to the corresponding error in the LSDA excitation energy. The relative error in the case of LSDA is about 1.2% whereas our functional gives an error of 0.6%. Since the excitation in these cases involve single-electron being transferred, TDDFT calculation can also be performed to determine the excitation energy. For the fluorine atom, TDDFT gives the excitation energy from the ground

Table 3.4: Transition states of few elements and ions are shown in the first column. In the second column the value of  $C$  determined by comparison of exact and Thomas-Fermi kinetic energies are shown. In the third and fourth column given are the values of excitation energies obtained from regular ground state LSD calculation and from our modified LSD functional (Eq.3.18). The corresponding Hartree-Fock excitation energies is given in the last column. These are all single excitations.

Transition State	C	$\Delta E(\text{LSD})$	$\Delta E(\text{Mod.LSD})$	$\Delta E(\text{HF})$
$B(2s^2, 2p^1 \ ^2P \rightarrow 2s^1, 2p^2 \ ^2D)$	1.063	0.1993	0.2267	0.2172
$C^+(2s^2, 2p^1 \ ^2P \rightarrow 2s^1, 2p^2 \ ^2D)$	1.086	0.3078	0.3548	0.3290
$C(2s^2, 2p^2 \ ^3P \rightarrow 2s^1, 2p^3 \ ^3D)$	1.059	0.2878	0.3192	0.2942
$N^+(2s^2, 2p^2 \ ^3P \rightarrow 2s^1, 2p^3 \ ^3D)$	1.084	0.4149	0.4686	0.4140
$N(2s^2, 2p^3 \ ^4S \rightarrow 2s^1, 2p^4 \ ^4P)$	1.053	0.3905	0.4241	0.4127
$O^+(2s^2, 2p^3 \ ^4S \rightarrow 2s^1, 2p^4 \ ^4P)$	1.082	0.5397	0.6001	0.5530
$O(2s^2, 2p^4 \ ^3P \rightarrow 2s^1, 2p^5 \ ^3P)$	1.037	0.5243	0.5805	0.6255
$F(2s^2, 2p^5 \ ^2P \rightarrow 2s^1, 2p^6 \ ^2S)$	1.028	0.6671	0.7413	0.8781
$Ne^+(2s^2, 2p^5 \ ^2P \rightarrow 2s^1, 2p^6 \ ^2S)$	1.028	0.8334	0.9204	1.0830
$P(3s^2, 3p^3 \ ^4S \rightarrow 3s^1, 3p^4 \ ^4P)$	1.037	0.2934	0.3098	0.3023
$Cl(3s^2, 3p^5 \ ^2P \rightarrow 3s^1, 3p^6 \ ^2S)$	1.012	0.4301	0.4592	0.5653
$Li(2s^1 \ ^2S \rightarrow 2p^1 \ ^2P)$	1.050	0.0646	0.0768	0.0677
$Na(3s^1 \ ^2S \rightarrow 3p^1 \ ^2P)$	1.017	0.0751	0.0801	0.0725
$Mg^+(3s^1 \ ^2S \rightarrow 3p^1 \ ^2P)$	1.039	0.1585	0.1715	0.1578
$K(4s^1 \ ^2S \rightarrow 4p^1 \ ^2P)$	1.007	0.0556	0.0575	0.0516
$Si^+(3s^2, 3p^1 \ ^2P \rightarrow 3s^1, 3p^2 \ ^2D)$	1.049	0.2632	0.2831	0.2743
$Si(3s^2, 3p^2 \ ^3P \rightarrow 3s^1, 3p^3 \ ^3D)$	1.037	0.2356	0.2507	0.2343

to the  $(1s^1 2s^2 2p^6 \ ^2S)$  to be 23.7848 a.u. which is in error by 29.94 eV. Similarly for the neon ion, the excitation energy comes out to be 29.9615 a.u. which is in error by 33.48 eV.

### 3.5.2 Core-Shell and Core-Shell-Shell Systems

The other excited-states( $1s^2 2s^1 2p^6 \ ^2S$ ) shown in Table 3.3 are those in which the lowest lying orbitals are not vacant, since one of the  $2s$  electrons has been excited to the  $2p$  orbital in fluorine or in a mono-positive ion of  $Ne$ . In these cases, the corresponding wavevectors will not form a shell but will be distributed in some other manner; one possibility is an occupied sphere (of radius  $k_1$ ) representing the core states, then a vacant shell (from radius  $k_1$  to  $k_2$ ) for the unoccupied states followed again by an occupied shell (from  $k_2$  to  $k_3$ ) representing the outer electrons. Thus the functional of Eq. 3.10 is not expected to be as accurate for such excited-states as it is for those with empty lowest states; although it should still be

Table 3.5: The table caption is same as Table 3.4 except that the numbers are for double excitations of some atoms and ions.

Transition State	C	$\Delta E(\text{LSD})$	$\Delta E(\text{Mod.LSD})$	$\Delta E(\text{HF})$
$O(2s^2, 2p^4 \ ^3P \rightarrow 2p^6 \ ^1S)$	1.040	1.1333	1.3174	1.5032
$O^+(2s^2, 2p^3 \ ^4S \rightarrow 2p^5 \ ^2P)$	1.063	1.2552	1.4991	1.5444
$N^+(2s^2, 2p^2 \ ^3P \rightarrow 2p^4 \ ^3P)$	1.042	0.8369	0.9533	1.0234
$N(2s^2, 2p^3 \ ^4S \rightarrow 2p^5 \ ^2P)$	1.058	0.9440	1.1312	1.1789
$F^+(2s^2, 2p^4 \ ^3P \rightarrow 2p^6 \ ^1S)$	1.040	1.4381	1.6565	1.8983
$P(3s^2, 3p^3 \ ^4S \rightarrow 3p^5 \ ^2P)$	1.021	0.6927	0.7611	0.8539

Table 3.6: Excitation energies, in atomic units, for third class of excited-states (*core – shell – shell* systems). The parameters  $C_1$  and  $C_2$  are the corresponding factors to decide the first and second shell radii. These are determined through kinetic energy comparison.

atoms/ions	$C_1$	$C_2$	$\Delta E$ (LSD)	$\Delta E$ (Mod.LSD)	$\Delta E$ (HF)
$C(1s^2, 2s^2, 2p^2 \rightarrow 1s^2, 2s^0, 2p^2, 3s^2)$	1.0551	1.164	1.355	1.5013	1.4191
$N(1s^2, 2s^2, 2p^3 \rightarrow 1s^2, 2s^0, 2p^3, 3s^2)$	1.0580	1.261	1.8424	2.0872	1.9538
$N^+(1s^2, 2s^2, 2p^2 \rightarrow 1s^2, 2s^0, 2p^2, 3s^2)$	1.042	1.239	2.3971	2.6022	2.4924
$O(1s^2, 2s^2, 2p^4 \rightarrow 1s^2, 2s^0, 2p^4, 3s^2)$	1.040	1.359	2.2657	2.5628	2.5089
$O^+(1s^2, 2s^2, 2p^3 \rightarrow 1s^2, 2s^0, 2p^3, 3s^2)$	1.063	1.319	3.0412	3.3731	3.1939
$F^+(1s^2, 2s^2, 2p^4 \rightarrow 1s^2, 2s^0, 2p^4, 3s^2)$	1.040	1.426	3.5745	3.9556	3.8919
$Ne(1s^2, 2s^2, 2p^6 \rightarrow 1s^2, 2s^2, 2p^2, 3p^2, 4s^2)$	1.445	1.017	5.7722	6.1496	5.8247
$Si([Ne]3s^2, 3p^2 \rightarrow [Ne]3s^1, 3p^2, 4s^1)$	1.0101	1.081	0.4236	0.4564	0.4439
$Si([Ne]3s^2, 3p^2 \rightarrow [Ne]3p^2, 4s^2)$	1.021	1.057	0.9828	1.0415	1.0384
$P([Ne]3s^2, 3p^3 \rightarrow [Ne]3p^3, 4s^2)$	1.021	1.079	1.2775	1.3669	1.3813
$P^+([Ne]3s^2, 3p^2 \rightarrow [Ne]3p^2, 4s^2)$	1.026	1.073	1.5719	1.6531	1.6525
$S([Ne]3s^2, 3p^4 \rightarrow [Ne]3p^4, 4s^2)$	1.015	1.108	1.5176	1.6259	1.7164
$Cl^+([Ne]3s^2, 3p^4 \rightarrow [Ne]3p^4, 4s^2)$	1.016	1.135	2.2176	2.3549	2.4672

better than the ground-state LSDA. In this case one should use the  $x - only$  functional for *core - shell* systems. Now the result for this state in addition to some other excitation of various atoms/ions are reported in Table 3.4: we see that although the error in the excitation energy does become smaller, but not as much as in the cases discussed earlier, where the  $x - only$  functional for *shell* systems is used for *core - shell* systems. Also the relative error increases if one use the exchange energy functional for *shell* systems. So the exchange energy functional for the *core - shell* systems should be applicable to these cases. Results that we have obtained for the core-shell systems are mentioned in Tables 3.4,3.5 . TDDFT calculations in these cases gives quite accurate excitation energies [124]. In Table 3.5 we have calculated some of the double excitation energies which is quite difficult to get using TDDFT approach [125].

Similarly in Table 3.6 we have mentioned results for systems having one core and two shell structure. Here, one has to determine two parameters ( $C_1$  and  $C_2$ ) for the determination of the  $k - space$  radii through the kinetic energy comparison as is done for the *shell* and *core - shell* systems. Now it is somewhat difficult to determine the parameters  $C_1$  and  $C_2$  unlike the *shell* and *core - shell* systems where only one parameter ( $C$ ) needs to be adjusted. In this case, we first determined  $C_1$  so as to keep the error in the TF and KS kinetic energies of the core and inner shell orbitals of atoms forming the *core - shell - shell* systems same as that of the corresponding atoms in the *core - shell* systems. We note that  $C$  for each atom in the *core - shell* systems are different from the  $C_1$  of the same atom in the *core - shell - shell* systems (compare the values of  $C$  and  $C_1$  in Tables 3.5 and 3.6) . For example, in the case of  $N$  atom when the excitation is such that it forms a *core - shell* structure the parameter  $C = 1.053$ , but when one electron is further excited so that it forms the *core - shell - shell* system then the parameter  $C_1 = 1.058$  and similarly for other cases also. This is because in the *core - shell - shell* systems some electrons has been further excited to form the outer shell. Once the parameter  $C_1$  is fixed the second parameter  $C_2$  is determined by comparison of the TF and KS kinetic energies of the full *core - shell - shell* system (*i.e.* core, inner shell and outer shell orbitals are used for the comparison of kinetic energies.) so that the error in the ground and excited-state configuration remains the same.

### 3.6 Excited-State Functionals Without Parameter

As stated above, let us consider once more the particular kind of excited-states (*core – shell*) Fig. 3.2 systems. Here we will present an approach which include *self-interaction correction* (SIC) for electrons taking part in the transition process in calculating the excitation energies of *core – shell* systems. For these excited-state if we rewrite the exact exchange-energy functional given by Eq.3.8, when an electron is transferred from one of the occupied orbitals in the ground-state to the lowest unoccupied level then it will become

$$\begin{aligned}
E_X^{excited} &= E_X^{ground} + \sum_{j(\sigma_j=\sigma_{rem})} \left\langle \phi_{rem}(\mathbf{r}_1)\phi_j(\mathbf{r}_2) \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \phi_j(\mathbf{r}_1)\phi_{rem}(\mathbf{r}_2) \right\rangle \\
&\quad - \frac{1}{2} \int \int \frac{|\phi_{rem}(\mathbf{r}_1)|^2 |\phi_{rem}(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 - \frac{1}{2} \int \int \frac{|\phi_{add}(\mathbf{r}_1)|^2 |\phi_{add}(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \\
&\quad - \sum_{j(j \neq add)(\sigma_j=\sigma_{add})} \left\langle \phi_{add}(\mathbf{r}_1)\phi_j(\mathbf{r}_2) \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \phi_j(\mathbf{r}_1)\phi_{add}(\mathbf{r}_2) \right\rangle, \tag{3.34}
\end{aligned}$$

where  $\phi_{rem}$  represents the orbital from which the electron has been removed and  $\phi_{add}$  where the electron is added. The sum over the index  $j$  in the second term on the right hand side runs over all the orbitals, including  $\phi_{rem}$  and  $\phi_{add}$ , up to the highest occupied orbital in the excited-state. On the other hand the sum in the fifth term runs over all the orbital except  $\phi_{add}$ . We now attempt to make an LDA-like approximation for the excited-state exchange energy so that the difference (the last four terms in the equation above) between the approximate excited- and ground-state exchange energies is close to that given by the exact expression above. In making this approximation accurate, it is evident that the self-energy terms (third and fourth terms on the right hand side of Eq. 3.34) for the orbitals  $\phi_{rem}$  and  $\phi_{add}$  are to be treated accurately. Now the LDA approximation to Eq. 3.34 can also be written in the form

$$\begin{aligned}
E_X^{MLDA} &= \int \rho [\mathcal{E}_x(k_3) - \mathcal{E}_x(k_2) + \mathcal{E}_x(k_1)] d\mathbf{r} - \frac{1}{8\pi^3} \int \left[ (k_3^2 - k_2^2)^2 \ln \left( \frac{k_3 + k_2}{k_3 - k_2} \right) \right] d\mathbf{r} \\
&\quad - \frac{1}{8\pi^3} \int \left[ (k_2^2 - k_1^2)^2 \ln \left( \frac{k_2 + k_1}{k_2 - k_1} \right) \right] d\mathbf{r} \\
&\quad + \frac{1}{8\pi^3} \int \left[ (k_3^2 - k_1^2)^2 \ln \left( \frac{k_3 + k_1}{k_3 - k_1} \right) \right] d\mathbf{r}, \tag{3.35}
\end{aligned}$$

where  $\mathcal{E}_x(k_f)$  represents the exchange-energy per particle when the HEG is in its ground-state with the Fermi momentum equal to  $k_f$ . This can be easily inferred from Eqs.3.15,3.16,3.17

and 3.18. The equation above has a nice interpretation: The integral on the right-hand side represents the exchange energy of the system of electrons with density  $\rho$  when per electron energy is written as  $[\mathcal{E}_x(k_3) - \mathcal{E}_x(k_2) + \mathcal{E}_x(k_1)]$ , i.e. the per electron energy is given according to the occupation in the  $k$ -space (compare with Eq. (3.15)). The  $\log$ . terms, on the other hand, have no such simple interpretation. They have the kinetic energy density in them but we have not been able to write the terms in as easy a form as the first term. That the functional above has all the right limits if we take  $k_1 = k_2$  or  $k_2 = k_3$  is easily verified<sup>2</sup>. Finally, the modified local-spin density (MLSD) functional  $E_X^{MLS D}[\rho_\alpha, \rho_\beta]$  in terms of the spin densities  $\rho_\alpha$  and  $\rho_\beta$  is easily obtained from the functional above as

$$E_X^{MLS D}[\rho_\alpha, \rho_\beta] = \frac{1}{2}E_X^{MLDA}[2\rho^\alpha] + \frac{1}{2}E_X^{MLDA}[2\rho^\beta] \quad (3.36)$$

Having derived the exchange functional for the HEG, we now apply it to the excited-states of various atoms to check if the functional above gives exchange energy differences accurately. Through out this chapter the excited-states chosen are such that they can be represented by a single Slater determinant so that the LDA is expected to be a good approximation [39, 40] for them. The different radii in the  $k$ -space ( $k_1$ ,  $k_2$  and  $k_3$ ) needed to evaluate the exchange energy are found by Eqs. (3.12), (3.13) and (3.14). For each state (ground and excited), the same set of orbitals<sup>3</sup> is employed to get the Hartree-Fock and the LSD exchange energies. We calculate the LSD and MLSD exchange energies using spherical spin densities since the effect of non-sphericity on the total exchange energy should be small [126]. This is because of the fact that in the Levy-Nagy formalism [56], the excited-state energy is obtained through variational minimization. Therefore inclusion of non-sphericity in the density would not cause as large a change in the total excited-state energy as the use of an appropriate exchange energy functional. Indeed the results for the lowest lying multiplets also indicate this [126].

In Table 3.7, we show the difference between the excited-state exchange energy and the ground-state exchange energy for some atoms and ions. In the first column we give the difference as obtained by the Hartree-Fock expression for the exchange energy. In the second column, the numbers are given for both the excited-state and the ground-state exchange en-

<sup>2</sup>The limiting conditions is also satisfied for the constructed functionals described in the previous section.

<sup>3</sup>The orbitals employed are those obtained by solving the Kohn-Sham equations with the Harbola-Sahni exchange potential (ref. [48] above). These orbitals are very close (see, for example, [V. Sahni V, Y. Li and M. K. Harbola, Phys. Rev. A **45** 1434 (1992)] and refs. [52, 53] above) to the Hartree-Fock orbitals.

Table 3.7: Difference in the exchange energies of the ground- and excited-states of some atoms and ions. The First column gives the atom/ion and the transition, the second column the difference  $\Delta E_X^{HF}$  as obtained in Hartree-Fock theory, the third column the difference  $\Delta E_X^{LSD}$  given by the ground-state energy functional. The fourth and the fifth column describes the difference as obtained with the functional proposed in this thesis. The fourth column gives the exchange-energy difference  $\Delta E_X^{MLSD}$  obtained by employing the functional of Eq. (3.36) whereas the fifth column gives that given by the functional of Eq. (3.39),  $\Delta E_X^{MLS\text{DSIC}}$ . Numbers given are in atomic units.

atoms/ions	$\Delta E_X^{HF}$	$\Delta E_X^{LSD}$	$\Delta E_X^{MLSD}$	$\Delta E_X^{MLS\text{DSIC}}$
$Li(2s^1\ ^2S \rightarrow 2p^1\ ^2P)$	0.0278	0.0264	0.0587	0.0282
$B(2s^22p^1\ ^2P \rightarrow 2s^12p^2\ ^2D)$	0.0353	0.0319	0.0998	0.0412
$C(2s^22p^2\ ^3P \rightarrow 2s^12p^3\ ^3D)$	0.0372	0.0332	0.1188	0.0454
$N(2s^22p^3\ ^4S \rightarrow 2s^12p^4\ ^4P)$	0.0399	0.0353	0.1381	0.0503
$O(2s^22p^4\ ^3P \rightarrow 2s^12p^5\ ^3P)$	0.1582	0.0585	0.2634	0.1624
$F(2s^22p^5\ ^2P \rightarrow 2s^12p^6\ ^2S)$	0.3021	0.0891	0.3908	0.2765
$Ne^+(2s^22p^5\ ^2P \rightarrow 2s^12p^6\ ^2S)$	0.3339	0.0722	0.4397	0.3037
$S(3s^23p^4\ ^3P \rightarrow 3s^13p^5\ ^3P)$	0.1106	0.0475	0.1798	0.1252
$Cl^+(3s^23p^4\ ^3P \rightarrow 3s^13p^5\ ^3P)$	0.1257	0.0483	0.2050	0.1441
$Cl(3s^23p^5\ ^2P \rightarrow 3s^13p^6\ ^2S)$	0.2010	0.0603	0.2567	0.1969

ergies obtained by employing the ground-state LSD functional. The third column gives the exchange energy difference when the excited-state exchange energy is calculated using the functional of Eq. (3.36). It is clearly seen that the ground-state LSD approximation underestimates this energy difference. This is not surprising since the ground-state functional would give a larger exchange energy for the excited-state than what a proper excited-state functional should give. However, when the functional of Eq. (3.36) is employed to calculate the exchange energy for the excited-states we found, to our surprise, that for the majority of the atoms the functional overestimates the differences by a large amount, whereas we expected to find the error to be about 10% which is the general LDA exchange energy error. One can note that this large difference cannot come because we have spherical densities. If non-spherical densities are used, the difference may increase even further. For example, for the fluorine atom, the ground-state exchange energy will become more negative for non-spherical densities. On the other hand, the excited-state exchange energy will remain unchanged since the density is already spherical. This will result in an even larger difference in the exchange energies of the two states.

Let us now look for possible sources of error in the exchange-energy differences when

the functional of Eq. (3.36) is employed to get the exchange energy for the excited-states. For this we examine Eq. (3.34) in which the last four terms on the right hand side represent the exchange energy difference. Thus

$$\begin{aligned} \Delta E_X = & \sum_{j(\sigma_j=\sigma_{rem})} \left\langle \phi_{rem}(\mathbf{r}_1)\phi_j(\mathbf{r}_2) \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \phi_j(\mathbf{r}_1)\phi_{rem}(\mathbf{r}_2) \right\rangle \\ & - \frac{1}{2} \int \int \frac{|\phi_{rem}(\mathbf{r}_1)|^2 |\phi_{rem}(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \\ & - \frac{1}{2} \int \int \frac{|\phi_{add}(\mathbf{r}_1)|^2 |\phi_{add}(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \\ & - \sum_{j(j\neq add)(\sigma_j=\sigma_{add})} \left\langle \phi_{add}(\mathbf{r}_1)\phi_j(\mathbf{r}_2) \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \phi_j(\mathbf{r}_1)\phi_{add}(\mathbf{r}_2) \right\rangle . \end{aligned} \quad (3.37)$$

It is the LDA values to this term that are given in Table 3.7. The source of error in this term we suspect is the LDA treatment of the self-exchange energies of the orbitals  $\phi_{rem}$  and  $\phi_{add}$  involved in the electron transfer. To make the functional more accurate we make the self-interaction correction (SIC) for both these orbitals. This is done by subtracting [38]

$$E_X^{SIC}[\phi] = \frac{1}{2} \int \int \frac{|\phi(\mathbf{r}_1)|^2 |\phi(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + E_X^{LSD}[\rho(\phi)] , \quad (3.38)$$

where  $\rho(\phi)$  is the orbital density for the orbital  $\phi$ , from the  $E_X^{MLSD}$  functional. Thus the final expression for the exchange-energy that we have is

$$E_X^{MLS DSIC} = E_X^{MLSD} - E_X^{SIC}[\phi_{rem}] - E_X^{SIC}[\phi_{add}] \quad (3.39)$$

This gives the exchange energy difference between the excited-state and the ground-state to be

$$\Delta E_X = E_X^{MLSD}[\rho_{excited}] - E_X^{LSD}[\rho_{ground}] - E_X^{SIC}[\phi_{rem}] - E_X^{SIC}[\phi_{add}] . \quad (3.40)$$

We have also computed the exchange energy differences given by the functional in Eq. (3.39) and shown them in Table 3.7. As is evident from the numbers displayed there, the functional of Eq. (3.39) gives highly accurate exchange-energy differences for all the systems considered. When the exchange-energy difference between the ground- and the excited-state

is small, the HF, LSD and the functionals derived above, all give roughly the same results. However, when this difference is large, the LDA underestimates the magnitude of the difference by a large amount whereas the functional of Eq. (3.36) overestimates it. Only when the latter is corrected for the self-interaction then the difference is almost the same as the Hartree-Fock difference. Notice that SIC is made only for the orbitals involved in the transition. Thus despite this explicit orbital dependence, the functional is still quite simple and easy to deal with. Making the self-interaction correction may deceptively lead the reader to momentarily think that this approach may be nothing more than treating the exchange energy within the SICLDA approach for both the ground and the excited-states. However, this is not so. If the SICLDA exchange energy functional is used, the difference between the exchange energies for the two states would be (for keeping the expression simple, we are using the same set of orbitals for the two states):

$$\Delta E_X = E_X^{LSD}[\rho_{excited}] - E_X^{LSD}[\rho_{ground}] + E_X^{SIC}[\phi_{rem}] - E_X^{SIC}[\phi_{add}] \quad (3.41)$$

Expressions in Eqs. (3.40) and (3.41) differ in two significant ways: First, the exchange energy functionals used for the ground and excited states are different, and secondly  $E_X^{SIC}[\phi_{rem}]$  is subtracted in Eq. (3.40) whereas it is added in Eq. (3.41). A careful look at Eq. (3.41) also indicates that the excited-state energies in SICLDA scheme should not come out to be any different from those obtained from the LDA calculations, because  $E^{SIC}$  for the two orbitals involved in the transition would tend to cancel. This is what has been observed in the past [38, 127, 128].

We note that we do have a choice of writing the first and the second terms in Eq. (3.37) as

$$\sum_{j(j \neq rem)(\sigma_j = \sigma_{rem})} \left\langle \phi_{rem}(\mathbf{r}_1)\phi_j(\mathbf{r}_2) \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \phi_j(\mathbf{r}_1)\phi_{rem}(\mathbf{r}_2) \right\rangle + \frac{1}{2} \int \frac{|\phi_{rem}(\mathbf{r}_1)|^2 |\phi_{rem}(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \quad (3.42)$$

and then make the self-interaction correction for the orbital  $\phi_{rem}$ . However, that would bring  $E_X^{SIC}[\phi_{rem}]$  with a positive sign in  $E_X^{MLSDSIC}$ , and the resulting functional will not be as accurate. Although its not fully understood by us but we are able to give a qualitative argument as to why the functional of Eq. (3.39) gives accurate exchange energy differences. We feel that

Table 3.8: Transition energies, in atomic units, of an electron being excited from the  $2s$  orbital of some atoms to the  $2p$  orbital. The first column gives this energy as obtained in Hartree-Fock theory. The numbers in the second column are obtained by employing the ground-state LDA for both the ground- and the excited-state. The last column gives the energies given by employing the ground-state LDA for the ground-state and the functional of Eq. (3.39) for the excited-state.

atoms/ions	$\Delta E_{HF}$	$\Delta E_{LSD}$	$\Delta E_{MLS\text{DSIC}}$	$\Delta E_{TDDFT}$
$N(2s^2 2p^3 \ ^4S \rightarrow 2s^1 2p^4 \ ^4P)$	0.4127	0.3905	0.4014	0.4153
$O^+(2s^2 2p^3 \ ^4S \rightarrow 2s^1 2p^4 \ ^4P)$	0.5530	0.5397	0.5571	0.5694
$O(2s^2 2p^4 \ ^3P \rightarrow 2s^1 2p^5 \ ^3P)$	0.6255	0.5243	0.6214	0.5912
$F^+(2s^2 2p^4 \ ^3P \rightarrow 2s^1 2p^5 \ ^3P)$	0.7988	0.6789	0.8005	0.7651
$F(2s^2 2p^5 \ ^2P \rightarrow 2s^1 2p^6 \ ^2S)$	0.8781	0.6671	0.8573	0.7659
$Ne^+(2s^2 2p^5 \ ^2P \rightarrow 2s^1 2p^6 \ ^2S)$	1.0830	0.8334	1.0607	0.9546

the LDA should be reasonably accurate when the integral over  $k$  is continuous. As written in Eq. (3.37), the sum in the first term is continuous except for the exchange term involving  $\phi_{rem}$  and  $\phi_{add}$ . Thus the LDA to the first term should be reasonably accurate. This brings in the self-interaction energy of the electron removed with a negative sign in front. By including the self-interaction correction for the removed electron only, we found that the error in the exchange energy difference reduces to about 10% of the corresponding HF value. To make the difference even more accurate, we now consider the term for the orbital  $\phi_{add}$  where the electron is added. There, when the LDA is made, the electron comes in with its self-interaction so for the added orbital too  $E_X^{SIC}$  should be subtracted to make the results for the energy difference comparable to the Hartree-Fock results.

Having obtained the functional to calculate accurate exchange energy difference, we now apply it to a large number of excited-states of the class considered here and find that the transition energies very close to those given by the Hartree-Fock theory. The results will be described in the following sections.

### 3.6.1 Results Obtained Without Parametrization

We employ the exchange functional  $E_X^{MLS\text{DSIC}}$  (Eq.3.39) proposed earlier to obtain the transition energies for a variety of excitations in different atoms/ions. We find that for all the systems the transition energies obtained by employing Eq.3.39 are very close to the cor-

Table 3.9: The caption is the same as that for Table 3.8 except that we are now considering transitions from the outermost orbital to an upper orbital for weakly bound systems.

atoms/ions	$\Delta E_{HF}$	$\Delta E_{LSD}$	$\Delta E_{MLSDSIC}$	$\Delta E_{TDDFT}$
$Li(2s^1 \ ^2S \rightarrow 2p^1 \ ^2P)$	0.0677	0.0646	0.0672	0.0724
$Na(3s^1 \ ^2S \rightarrow 3p^1 \ ^2P)$	0.0725	0.0751	0.0753	0.0791
$Mg^+(3s^1 \ ^2S \rightarrow 3p^1 \ ^2P)$	0.1578	0.1585	0.1696	0.1734
$K(4s^1 \ ^2S \rightarrow 4p^1 \ ^2P)$	0.0516	0.0556	0.0580	0.0608

responding Hartree-Fock energies <sup>4</sup>. Our calculations proceed as follows: (a) We get the ground-state energy by solving the Kohn-Sham equation with the effective exchange potential calculated using the Dirac formula [4, 5]. (b) We then solve the Kohn-Sham equation with the same (corresponding to the ground-state) functional for the excited-state configuration. This gives us the excited-state energy  $E_{LSD}$ , and the LSD exchange energy  $E_X^{LSD}$  for the excited-state. The difference between  $E_{LSD}$  and the ground-state energy  $E_0$  gives us the transition energy  $\Delta E_{LSD}$ . (c) We then employ the Kohn-Sham orbitals from the excited-state LSD calculation to get the modified LSD exchange energy including SIC by employing the functional  $E_X^{MLSDSIC}$  of Eq. (3.39). (d) The modified transition energy  $\Delta E_{MLSDSIC}$  is then given as

$$\Delta E_{MLSDSIC} = \Delta E_{LSD} + E_X^{MLSDSIC} - E_X^{LSD} . \quad (3.43)$$

Although we have not performed self-consistent calculations with the new functional, self-consistency is not expected to affect the results significantly. This is because, as we shall see in the results, the major difference in the transition energies given by different functionals arises from the difference in the value of the exchange energy itself. We also compare our results with the transition energies obtained by the exchange-only time-dependent density-functional theory (TDDFT) applied within the single-pole approximation [33, 36, 97, 100, 124]. We find that our results are comparable to the TDDFT results. In the following, we have considered three different cases of electron transfer: electron making a transition from an ‘s’ to a ‘p’ orbital; from an ‘s’ to a ‘d’ orbital and from a ‘p’ to a ‘d’ orbital.

<sup>4</sup>The energies are calculated by solving the Kohn-Sham equation with the Harbola-Sahni potential. The resulting multiplet energies are essentially the same (see ref. [53]) as those of Hartree-Fock theory.

Table 3.10: Electron transition energy from the  $3s$  to the  $3p$  orbital in some atoms.

atoms/ions	$\Delta E_{HF}$	$\Delta E_{LSD}$	$\Delta E_{MLSDSIC}$	$\Delta E_{TDDFT}$
$P(3s^2 3p^3 \ ^4S \rightarrow 3s^1 3p^4 \ ^4P)$	0.3023	0.2934	0.3055	0.3183
$S(3s^2 3p^4 \ ^3P \rightarrow 3s^1 3p^5 \ ^3P)$	0.4264	0.3615	0.4334	0.4122
$Cl^+(3s^2 3p^4 \ ^3P \rightarrow 3s^1 3p^5 \ ^3P)$	0.5264	0.4482	0.5403	0.5113
$Cl(3s^2 3p^5 \ ^2P \rightarrow 3s^1 3p^6 \ ^2S)$	0.5653	0.4301	0.5630	0.4996
$Ar^+(3s^2 3p^5 \ ^2P \rightarrow 3s^1 3p^6 \ ^2S)$	0.6769	0.5174	0.6766	0.6007

Table 3.11: Electron transition energy from the  $2s$  to the  $3p$  orbital in the same atoms as in Table 3.10

atoms/ions	$\Delta E_{HF}$	$\Delta E_{LSD}$	$\Delta E_{MLSDSIC}$	$\Delta E_{TDDFT}$
$P(2s^2 3p^3 \ ^4S \rightarrow 2s^1 3p^4 \ ^4P)$	6.8820	6.4188	6.9564	6.1573
$S(2s^2 3p^4 \ ^3P \rightarrow 2s^1 3p^5 \ ^3P)$	8.2456	7.7337	8.3271	7.4533
$Cl^+(2s^2 3p^4 \ ^3P \rightarrow 2s^1 3p^5 \ ^3P)$	9.8117	9.2551	9.8997	8.9618
$Cl(2s^2 3p^5 \ ^2P \rightarrow 2s^1 3p^6 \ ^2S)$	9.7143	9.1653	9.8171	8.8686
$Ar^+(2s^2 3p^5 \ ^2P \rightarrow 2s^1 3p^6 \ ^2S)$	11.3926	10.8009	11.5061	10.4901

### 3.6.2 Electron transfer from an ‘s’ to a ‘p’ orbital

In this section we consider the cases when one or two electrons are transferred from an inner  $s$  orbital to an outer  $p$  orbital. Shown in Table 3.8 are the transition energies  $\Delta E_{HF}$ ,  $\Delta E_{LSD}$  and  $\Delta E_{MLSDSIC}$  for some light atoms and ions when one of their inner electrons is excited to the lowest available orbital. The excitation energy in these systems is such that for some of them  $\Delta E_{LSD}$  is close to  $\Delta E_{HF}$  but for others it is not. However,  $\Delta E_{MLSDSIC}$  is uniformly accurate for all the systems. We note that the error in  $\Delta E_{LSD}$  is almost fully from the error in the corresponding exchange energy difference. This is evident from a comparison of the numbers in Table 3.7 (for the exchange energy differences) and in Table 3.8. Thus major difference in  $\Delta E$  comes from the error in calculating the exchange energy. As noted earlier, self-consistency effects are much smaller compared to the differences arising from the use of the ground-state exchange energy functional for the excited-state also. Our results also match well with, and in some cases are better than, the TDDFT results shown in the last column of the table.

In Table 3.9, we look at the excitation energies of the alkali atoms and  $Mg^+$  by exciting an electron from the uppermost orbital to an outer orbital. These are weakly bound systems and as such their excitation energies are relatively smaller. Thus they provide a good test-

Table 3.12: Electron transition energy when the upper state is not the lowest energy multiplet.

atoms/ions	$\Delta E_{HF}$	$\Delta E_{LSD}$	$\Delta E_{MLSDSIC}$	$\Delta E_{TDDFT}$
$B(2s^2 2p^1 \ ^2P \rightarrow 2s^1 2p^2 \ ^2D)$	0.2172	0.1993	0.2061	0.2168
$C^+(2s^2 2p^1 \ ^2P \rightarrow 2s^1 2p^2 \ ^2D)$	0.3290	0.3078	0.3216	0.3325
$C(2s^2 2p^2 \ ^3P \rightarrow 2s^1 2p^3 \ ^3D)$	0.2942	0.2878	0.2967	0.3090
$N^+(2s^2 2p^2 \ ^3P \rightarrow 2s^1 2p^3 \ ^3D)$	0.4140	0.4149	0.4305	0.4433
$Si^+(3s^2 3p^1 \ ^2P \rightarrow 3s^1 3p^2 \ ^2D)$	0.2743	0.2632	0.2799	0.2864
$Si(3s^2 3p^2 \ ^3P \rightarrow 3s^1 3p^3 \ ^3D)$	0.2343	0.2356	0.2442	0.2567

ing ground for the proposed functional. An interesting point about these systems is that the LSD itself gives excitation energies close to the HF excitation energies. It is therefore quite gratifying to see that the transition energies obtained by the new functional also are of very good quality, although the present method tends to slightly overestimate the transition energies. The TDDFT method also gives similar numbers although it overestimates the transition energies by a slightly larger amount.

Next we consider some bigger atoms where we can excite the electron from more than one inner orbital. Shown in Tables 3.10 and 3.11 are the excitation energies for the atoms in the third row of the periodic table. In Table 3.10, we consider an electron being excited from the  $3s$  orbital to the  $3p$  orbital. In all these case  $\Delta E_{LSD}$  is smaller than the true energy difference whereas the present functional gives highly accurate estimates of the transition energy. Notice again that the error in the value of  $\Delta E_{LSD}$  arises mainly from the error in the exchange energy. The TDDFT results in these cases too are of quality comparable to the present method.

In Table 3.11, we show the transition energies for the same set of atoms and ions as in Table 3.10, but for the electron now being excited from the  $2s$  orbital to the  $3p$  orbital. Consequently the energy of excitation is much larger in this case. The LSD in all these cases underestimates the excitation energy, whereas the present functional gives accurate results although slightly overestimating them. However, the error with respect to the LSD is reduced by a factor of 5 or more. Thus the proposed functional is accurate for transitions from a shallow level as well as from a deep level. We find that the TDDFT results in the present case are not as accurate as in the cases studied above.

Shown in Table 3.12 are the excitation energies for a group of atoms for which the LSD gives transition energies very close to the HF excitation energies. In all the cases we find

Table 3.13: Excitation energies of some atoms when two electrons are excited.

atoms/ions	$\Delta E_{HF}$	$\Delta E_{LSD}$	$\Delta E_{MLS\text{DSIC}}$	$\Delta E_{TDDFT}$
$Be(2s^2\ ^1S \rightarrow 2p^2\ ^1D)$	0.2718	0.2538	0.2655	—
$B(2s^2 2p^1\ ^2P \rightarrow 2p^3\ ^2D)$	0.4698	0.4117	0.4798	—
$C^+(2s^2 2p^1\ ^2P \rightarrow 2p^3\ ^2D)$	0.6966	0.6211	0.7180	—
$C(2s^2 2p^2\ ^3P \rightarrow 2p^4\ ^3P)$	0.7427	0.5950	0.7312	—
$N^+(2s^2 2p^2\ ^3P \rightarrow 2p^4\ ^3P)$	1.0234	0.8369	1.0143	—
$N(2s^2 2p^3\ ^4S \rightarrow 2p^5\ ^2P)$	1.1789	0.9440	1.1785	—
$O^+(2s^2 2p^3\ ^4S \rightarrow 2p^5\ ^2P)$	1.5444	1.2552	1.5480	—
$O(2s^2 2p^4\ ^3P \rightarrow 2p^6\ ^1S)$	1.5032	1.1333	1.4736	—
$F^+(2s^2 2p^4\ ^3P \rightarrow 2p^6\ ^1S)$	1.8983	1.4381	1.8494	—
$Mg(3s^2\ ^1S \rightarrow 3p^2\ ^1D)$	0.2578	0.2555	0.2651	—
$S(3s^2 3p^4\ ^3P \rightarrow 3p^6\ ^1S)$	1.0273	0.7807	1.0266	—
$P(3s^2 3p^3\ ^4S \rightarrow 3p^5\ ^2P)$	0.8539	0.6927	0.8680	—
$Si^+(3s^2 3p^1\ ^2P \rightarrow 3p^3\ ^2D)$	0.5856	0.5377	0.6230	—
$Si(3s^2 3p^2\ ^3P \rightarrow 3p^4\ ^3P)$	0.5860	0.4928	0.5986	—
$Cl^+(3s^2 3p^2\ ^3P \rightarrow 3p^4\ ^3P)$	1.2535	0.9551	1.2516	—

that the functional proposed here is able to give accurate excitation energies. Thus we find that when the LSD results are accurate, so are the results given by the new functional. What is significant, however, is that when the LSD results are poor, the new functional properly corrects the error in the LSD.

Finally, we consider the cases where two electrons are excited to the higher orbitals. In this case the functional  $E_X^{MLS\text{DSIC}}$  is evaluated by subtracting the SIC energy from the  $E_X^{MLSD}$  for both the electrons. As already pointed out, double excitations are difficult to deal within the TDDFT approach to finding excitation energies, because the theory is based on the first-order perturbation theory of non-interacting particles. Results for different excitations for a variety of atomic systems are shown in Table 3.13. As is evident from the table, for all the systems, our method gives excellent results whereas the LSD underestimates the energies. In the case of double excitations, no comparison with the TDDFT results can be made because a satisfactory TDDFT of double excitations does not exist.

In all the cases above, we have compared our results with those of Hartree-Fock theory and those obtained from exchange-only TDDFT. We do so because in our work we have not taken into account the effect of correlations. We note that although in atoms Hartree-Fock theory gives total energies which are very close to the experimental energies, correlation effects

Table 3.14: Electron transition energy when an ‘s’ electron is transferred to a ‘d’ orbital.

atoms/ions	$\Delta E_{HF}$	$\Delta E_{LSD}$	$\Delta E_{MLSDSIC}$	$\Delta E_{TDDFT}$
$Sc(3s^23d^1\ ^2D \rightarrow 3s^13d^2\ ^2G)$	2.1562	1.8584	2.1223	1.8649
$Ti(3s^23d^2\ ^3F \rightarrow 3s^13d^3\ ^5F)$	2.2453	1.9740	2.2061	—
$Ti(3s^23d^2\ ^3F \rightarrow 3s^13d^3\ ^3H)$	2.3861	2.0827	2.3649	2.0951
$V(3s^23d^3\ ^4F \rightarrow 3s^13d^4\ ^4H)$	2.6098	2.3107	2.6106	2.3266
$Mn(3s^23d^5\ ^6S \rightarrow 3s^13d^6\ ^6D)$	3.1331	2.7860	3.1199	2.8062
$Fe(3s^23d^6\ ^5D \rightarrow 3s^13d^7\ ^5F)$	3.4187	3.0483	3.4527	3.0755
$Co(3s^23d^7\ ^4F \rightarrow 3s^13d^8\ ^4F)$	3.7623	3.3178	3.7955	3.3516
$Ni(3s^23d^8\ ^3F \rightarrow 3s^13d^9\ ^3D)$	4.1204	3.5949	4.1476	3.6351

become relatively more important in calculating transition energies which is the difference between total energies. Thus a comparison with experimental transition energies would be meaningful only after correlation effects are properly taken into account.

### 3.6.3 Electron transfer from an ‘s’ or a ‘p’ orbital to a ‘d’ orbital

In this section we consider the case when a  $3s$  or a  $3p$  electron is transferred to an incompletely filled  $3d$  orbital in transition metals  $Sc$ ,  $Ti$ ,  $V$ ,  $Mn$ ,  $Fe$ ,  $Co$  and  $Ni$ . The results for our calculations on these systems are shown in Tables 3.14 and 3.15.

In Table 3.14, numbers are shown for transitions from the  $3s$  orbital of these atoms to their  $3d$  orbital. As is clear from the table, whereas the LSD results underestimate the transfer energies, our results compare well with those of Hartree-Fock theory. On the other hand, we find that the TDDFT results also underestimate the transition energies in comparison to the Hartree-Fock theory results.

In Table 3.15, results for the transition  $3p \rightarrow 3d$  are shown. Since there are three down spin electrons in the  $3p$  orbital, two electrons are left in it after an electron is excited to the  $3d$  orbital. The question arises whether to treat these electrons as core electrons, as shell electrons or divide them in the core and the shell; the three possibilities give different answers. When the electrons are treated as the core electrons, the transition energy comes out to be the smallest and it is the largest when they are treated as the shell electrons. We have taken the smallest transition energy obtained by us and compared it to the energy of transition to the largest possible L value (so the smallest transition energy) excited-state for a given spin. In these cases too, we find that for  $Sc$ ,  $Ti$  and  $V$ , our method gives results which are better than

Table 3.15: Electron transition energy when a ‘p’ electron is transferred to a ‘d’ orbital.

atoms/ions	$\Delta E_{HF}$	$\Delta E_{LSD}$	$\Delta E_{MLSDSIC}$	$\Delta E_{TDDFT}$
$Sc(3p^6 3d^1 \ ^2D \rightarrow 3p^5 3d^2 \ ^2H)$	1.1295	1.1018	1.1245	1.2128
$Ti(3p^6 3d^2 \ ^3F \rightarrow 3p^5 3d^3 \ ^3I)$	1.2698	1.2478	1.2728	1.3586
$V(3p^6 3d^3 \ ^4F \rightarrow 3p^5 3d^4 \ ^4I)$	1.4153	1.3959	1.4227	1.5042
$Mn(3p^6 3d^5 \ ^6S \rightarrow 3p^5 3d^6 \ ^6F)$	1.7270	1.6431	1.6726	1.8073
$Fe(3p^6 3d^6 \ ^5D \rightarrow 3p^5 3d^7 \ ^5G)$	1.8785	1.8784	2.0061	1.9898
$Co(3p^6 3d^7 \ ^4F \rightarrow 3p^5 3d^8 \ ^4G)$	2.1178	2.0568	2.2778	2.1755
$Ni(3p^6 3d^8 \ ^3F \rightarrow 3p^5 3d^9 \ ^3F)$	2.4232	2.2402	2.5518	2.3656

the LSD results, but for systems with more than half filled  $d$ -shell, our method overestimates the transition energy whereas the LSD underestimates it. The three cases of  $Fe$ ,  $Co$  and  $Ni$  are where our results do not match with those of Hartree-Fock theory.

A tough problem in calculating transfer energies is that of electron transferring from the  $4s$  orbital to the  $3d$  orbital in the transition metals considered above. The problem has been well investigated [127, 128] in the past and as in all the cases considered so far, LSD underestimates these energies by large amount. We have applied our functional to obtain these transfer energies to see if we could get the correct answer. However, for these  $s \rightarrow d$  transfer energies, our method gives hardly any improvement over the LSD results; in fact for most of the systems, we get a transition energy which is lower than the LSD energy. Further investigations of this problem are being made.

### 3.7 Discussion and Concluding Remarks

In the present chapter, we have developed three functionals for three different classes of excited states and demonstrated that it is possible to construct excited-state energy functionals that are capable of giving transition energies close to the exact theory. While defining the bi-density functional for the excited-states through constrained search formulation [56] the wavefunctions involved in the minimization procedure are those which are orthogonal to the lower energy wavefunctions. The latter are supposed to be determined by the ground-state density  $\rho_0(\mathbf{r})$ . In constructing our functional, by looking at the orbital occupation in the excited-states, we occupy the  $k$ -space in a similar manner, representing the unoccupied orbitals by a gap in it. Thus in our case the orthogonality condition described above is taken

care of, to a large extent, by the gap in the  $k$ -space. This also reflects an implicit dependence on the ground-state density.

In the above we have constructed new LDA-like functional for obtaining the excitation energies. It has been employed to investigate over large number of excited states. The results show that the second procedure gives accurate excitation energies for all of them, whereas for most of the systems the LSD underestimates the energy difference. The results obtained using the kinetic approach are slightly inferior compared to the other proposed approach including SIC. We have worked within the exchange-only approximation and have chosen three particular class of excited-states. What we have learned through the study reported here is that a simple extension of the LDA to the excited-states overestimates the energy differences. This is due to the self-interaction of the electron inherent in the LDA. When corrected for the self-interaction through a careful analysis, the resulting functional gives highly accurate answers for the excited-states. In the first case, however excitations are obtained by fixing the  $k$ -space radii through the comparison of KE. Thus if more accurate functionals than the LDA are employed, our method of developing excited-state functionals should give good excited-state functionals.

As pointed out in the introduction, excited-state functionals are not universal and therefore have to be dealt with separately for different kinds of excited-states. In this chapter, we have also not looked at the correlation energy functionals. Can correlation energy functionals be developed along similar lines? We trust that it should be possible and in future such analogous attempts should continue so as to provide the time-independent excited-states DFT a complete shape.

# Chapter 4

## Analysis of Floquet Formulation of Time-Dependent Density-Functional Theory

### 4.1 INTRODUCTION

We have already discussed in the introductory chapter how DFT becomes a well established theory for the ground-states of Coulombic systems. It is conceptually simple and practically useful in various branches of physics, chemistry and material science. Based on the work of Hohenberg and Kohn (HK) [8] and Kohn and Sham (KS) [9], DFT has become a practical tool for the electronic structure calculation of atoms, molecules and solids [21]. Also discussed in previous chapters is the extension of time-independent density functional formalism to excited-states [44, 54, 56, 89–91]. On the other hand, time-dependent phenomena are not accessible through traditional DFT. Time-dependent density functional theory (TDDFT) [94–96] is the generalization of the ground-state DFT to time-dependent problems. The central result of modern TDDFT is a set of time-dependent Kohn-Sham equations which are structurally similar to the time-dependent Hartree-Fock equations but include in principle exactly all the many-body effects through a local time-dependent exchange-correlation potential. TDDFT allows access to lots of interesting and important phenomena which can not be easily dealt within static DFT. It has become popular for studying atoms and molecules in intense laser fields [129], calculating the excitation spectra and oscillator strengths [97, 100], frequency dependent polarizabilities, hyperpolarizabilities [130] and optical response of solids, etc. [33]. TDDFT is especially very useful for quantum control problems [131]. This is because for intense laser fields where correlation effects are quite crucial, TDDFT appears to be the only way of studying the quantum dynamics of a many-electron

system. In light of our investigation of the time-independent excited-state DFT which is discussed in the second chapter, we can now analyze the Floquet theory in a similar manner

## 4.2 Understanding the Density-to-Potential Mapping in TDDFT

Initial steps towards the rigorous foundation of TDDFT were taken by Deb and Ghosh [94] and by Bartolotti [95]. They formulated and explored HK and KS type theorems for the time-dependent density. Each of these derivations, however, was restricted to a particular class of allowable time-dependent potentials (to potentials periodic in time). Because of the periodicity of the potential in time, Deb and Ghosh developed TDDFT with the Floquet formulation. This is the formalism applicable to adiabatically switched on potentials. Further in recent times Floquet formulation for TDDFT has been extensively applied by Telnov and Chu [132–136] to many interesting time-dependent problems. Actually they have provided the "generalized" and new Floquet formulations of TDDFT and time-dependent current density functional theory (TDCDFT) which allows the inclusion of the "continuum" states for "nonperturbative" treatment of multiphoton ionization and dissociation processes in intense laser fields. Another new development is the "generalized" Floquet formulations of TDDFT for the treatment of multiphoton processes in intense non-periodic (quasi-periodic, polychromatic) laser fields [137]. Exact relations of the quasienergy functional and the exchange-correlation potential from the Floquet formulation of TDDFT has also been found [138]. A variational perturbation method based on the Floquet theory has also been developed and applied [139] to study optical properties of atoms within TDDFT.

However, a general proof of density to potential mapping [ $\rho(\vec{r}, t) \rightarrow v(\vec{r}, t)$ ] for a time-dependent density was given by Runge and Gross [96]. Runge and Gross (RG) [96] formally established the TDDFT by showing that for a given initial state the evolving density  $\rho(\vec{r}, t)$  uniquely determines the corresponding time-dependent potential  $v(\vec{r}, t)$ . Two features of RG formalism are noteworthy: one that the time-dependent wavefunction for a given density has functional dependence on both the density as well as the initial wavefunction  $\Psi_0$ . Secondly the formalism is valid for potentials that are Taylor series expandable at the initial time  $t = t_0$ . This makes the formalism applicable to suddenly switched-on potentials but not to the adiabatically switched-on potentials. We will discuss in the following two sections the two formalism in TDDFT.

### 4.2.1 Floquet Formalism in TDDFT

In wavefunctional formalism, Floquet theory is an attractive approach for studying of species in intense laser fields. A time-periodic potential, such as in the case of laser fields, allows for a complete set of ‘steady-state’, or Floquet solutions, in which the problem reduces to a matrix diagonalization, similar to the finding of Bloch states for spatially periodic problems [132,133,140,141]. The system is assumed to reach a Floquet state by adiabatic ramping of the time-dependent part of the potential [133]. Floquet theory is particularly useful because it is not limited to weak time-dependent fields. As is mentioned earlier Floquet theory has been successful in describing a variety of phenomena, including multiphoton ionization and detachment problems [134,142], two-colour ionization [135,143], analyzing microwave ionization experiments [144], higher harmonic generation [145], selective excitation of molecular vibrational states using short laser pulses [146]. Most applications consider a one-electron picture, although recently an R-matrix Floquet theory [147–149] has been developed to address multiphoton processes in many-electron systems. So let us consider problems in which the external potential is time-periodic, and the interacting system has reached a Floquet state, so that its density is time-periodic. It is natural to ask if the time-periodic density of a Floquet state uniquely determines the time-periodic potential. If it does, then all properties of the system are functionals of that density, which was the basis of [136,137].

Like in the case of static DFT, in TDDFT also an interacting many-electron system is mapped onto a fictitious non-interacting Kohn-Sham system with the same time-dependent density as the interacting system. In Floquet formulation [94,95,132–136,139], introduced above, the Kohn-Sham system is developed in terms of the periodic time-dependent density only. On the other hand, in the the RG formalism the Kohn-Sham wavefunction is a functional of both the time-dependent density and an initial state [150,151]. The uniqueness of the KS system follows from the one-to-one  $\rho(\vec{r},t) \rightarrow v(\vec{r},t)$  mapping. However, recently researchers has questioned [152] the foundations of Floquet formalism of TDDFT. So based on their investigation they went on to conclude that a KS system within the Floquet formalism is not unique. The non-uniqueness of the KS system has been attributed to its functional dependence on the initial state. Further, it has been suggested that the Hohenberg-Kohn like theorem [94] may not exist in Floquet theory of TDDFT because the “ground Floquet state” cannot be defined properly. This appears to have created some doubts [153] about the Floquet

theory in TDDFT. It is the purpose of this chapter to analyze the Floquet theory of TDDFT particularly in light of our work, reported in previous chapters, on excited-state problems. We show that it is perfectly valid. The present analysis also brings out subtle differences between the RG and Floquet theory and shows the two formulations to be distinct and founded on two different principles. As such Floquet theory of TDDFT cannot be thought of as a particular case of the RG theory and the RG arguments cannot be applied to Floquet formulation. We begin with a short description of the foundations of Floquet and RG theory in TDDFT.

For a time-dependent (TD) Hamiltonian  $\hat{H}(t)$  periodic in time, *i.e.*

$$\hat{H}(t) = \hat{H}(t + \tau) , \quad (4.1)$$

where the period  $\tau$  is positive with  $\omega = \frac{2\pi}{\tau}$ , the TD Schrödinger equation (atomic units are used throughout)

$$\left[ \hat{H}(t) - i \frac{\partial}{\partial t} \right] \Psi_n(\vec{r}, t) = 0 , \quad (4.2)$$

has solutions [140, 141] of the form

$$\Psi_n(\vec{r}, t) = \phi_n(\vec{r}, t) e^{-i\varepsilon_n t}; \phi_n(\vec{r}, t) = \phi_n(\vec{r}, t + \tau) , \quad (4.3)$$

where the time-periodic functions  $\phi_n(\vec{r}, t)$  are termed as the *quasienergy* eigenstates (QES) and  $\varepsilon_n$  are referred to as the *quasienergy* eigenvalues. The steady-state wavefunctions  $\phi_n(\vec{r}, t)$  are solutions of

$$\left[ \hat{H}(t) - i \frac{\partial}{\partial t} \right] \phi_n(\vec{r}, t) = \varepsilon_n \phi_n(\vec{r}, t) , \quad (4.4)$$

where  $\phi_n(\vec{r}, t)$  are square integrable and  $\varepsilon_n$  are real numbers. The quasienergies,  $\varepsilon_0, \varepsilon_1, \dots, \varepsilon_i, \dots$  are defined ‘modulo ( $\omega$ )’. However, they can be ordered in increasing order  $\varepsilon_0, \varepsilon_1, \dots$  by making sure that as the strength of the applied time-dependent potential goes to zero, each quasi-energy go to its unperturbed counterpart [154]. Thus as long as  $\omega$  is not one of the resonant frequencies, there exist the “ground-state energy”  $\varepsilon_0$  and “excited-state energies”  $\varepsilon_1, \dots, \varepsilon_n$  [154] in the steady-state formalism (see Appendix E for details). The theory of solutions in time-periodic Hamiltonian can be thought of like the stationary-state theory but in the composite Hilbert space ( $R + T$ ) [140, 141, 154] that includes in addition to the space

dependent function, time-periodic functions also. The operator

$$\mathcal{H}(t) = \hat{H}(t) - i\frac{\partial}{\partial t} , \quad (4.5)$$

is called the Hamiltonian for the steady states in the composite Hilbert space, which resembles in many way the Hamiltonian for bound-states. The scalar product in this space is defined as

$$\{\langle\phi|\psi\rangle\} = \frac{1}{\tau} \int_0^\tau dt \int \phi^*(\vec{r}, t)\psi(\vec{r}, t)d\vec{r} \quad (4.6)$$

*i.e.* in addition to the space integral, an integral <sup>1</sup> over time is also taken. Thus the quasienergy functional is given by

$$\varepsilon_n[\phi_n] = \{\langle\phi_n|\mathcal{H}(t)|\phi_n\rangle\} . \quad (4.7)$$

The most crucial point which is important from TDDFT point of view is that the steady-state solutions are obtained by an adiabatic switching of the periodic potential. Finally applying the variational principle, each state  $\phi_n(\vec{r}, t)$  can also be obtained [141] by making the expectation value  $\{\langle\phi_n|\hat{H}(t) - i\frac{\partial}{\partial t}|\phi_n\rangle\}$  stationary. The stationarity principle becomes a minimum principle for the "ground-state"<sup>2</sup> by assuming completeness of the set  $\{\phi_n\}$  over the composite  $(R + T)$  Hilbert space. The general proof of the minimum principle for the ground-Floquet state is given in Appendix E.

Using the minimum property of the ground-state quasienergy functional [see Appendix E] a Hohenberg-Kohn like theorem can be proved [94] for time-dependent periodic densities also. We reproduce the proof below. Let us consider the nondegenerate ground-state of a system characterized by the Hamiltonian  $\hat{H}(t)$ . Suppose there exist two different Floquet ground-states  $\phi$  and  $\phi'$  corresponding to the steady state Hamiltonians  $\mathcal{H}$  and  $\mathcal{H}'$ , or more specifically corresponding to the external potentials  $v(\vec{r}, t)$  and  $v'(\vec{r}, t)$ , both of which give rise to the same TD density  $\rho(\vec{r}, t)$ . Using the minimal property for the ground-state one will get

<sup>1</sup>Here the curly brackets '{ }' indicates the time average over a period.

<sup>2</sup>Here the "ground-state" is referred to a steady-state having lowest quasienergy.

$$\varepsilon' < \varepsilon + \frac{1}{\tau} \int_{t_1}^{t_2} dt \int [v'(\vec{r}, t) - v(\vec{r}, t)] \rho(\vec{r}, t) d^3r \quad , \quad (4.8)$$

where  $\tau = t_2 - t_1$ . Similarly for the ground-state of the Hamiltonian  $\mathcal{H}$

$$\varepsilon < \varepsilon' + \frac{1}{\tau} \int_{t_1}^{t_2} dt \int [v(\vec{r}, t) - v'(\vec{r}, t)] \rho(\vec{r}, t) d^3r \quad . \quad (4.9)$$

Adding Eqs. (4.8) and (4.9) results in the absurdity,

$$\varepsilon + \varepsilon' < \varepsilon' + \varepsilon \quad . \quad (4.10)$$

Hence two different potentials  $v(\vec{r}, t)$  and  $v'(\vec{r}, t)$  cannot give the same density  $\rho(\vec{r}, t)$ , which implies that the time-dependent potential  $v(\vec{r}, t)$  is a unique functional of the time-dependent density  $\rho(\vec{r}, t)$ . We refer to this as the Deb-Ghosh theorem [94]. Accordingly,  $\mathcal{H}$ ,  $H$  and  $\phi$  and indeed any "ground-state" property are all unique functional of  $\rho(\vec{r}, t)$ . Thus for Floquet states the HK theorem is [94]: "the density corresponding to the ground-state quasienergy of a time-periodic Hamiltonian determines the corresponding external time-periodic potential  $v_{ext}(\vec{r}, t)$  uniquely". For example in perturbation theory up to the second order in energy,  $E^{(2)}$  is minimum [139] with respect to  $\rho^{(1)}$  for frequencies less than the first excitation frequency (*i.e.*  $\omega < \omega_{10} = E_1 - E_0$ , where  $E_0$  and  $E_1$  are the unperturbed ground and excited-state energies). Thus in the linear response regime, the theorem would apply to  $\rho^{(1)}$  up to frequency  $\omega < \omega_{10}$ . This theorem is then the foundation of Floquet theory of TDDFT [132–136, 139]. We point out that the theory does not have any initial state dependence but requires adiabatic switching of the applied external potential. Assuming the  $v$ -representability, an equivalent Kohn-Sham system for an  $N$ -electron system can also be developed.

## 4.2.2 Runge-Gross Formalism in TDDFT

Runge and Gross had shown the one-to-one mapping between  $\rho(\vec{r}, t)$  and  $v(\vec{r}, t)$  using a two step procedure. In the first step they have established an unique mapping between TD density  $\rho(\vec{r}, t)$  to TD current  $j(\vec{r}, t)$  and in the second step they tried to establish the uniqueness of the mapping between  $j(\vec{r}, t)$  and the external potential  $v(\vec{r}, t)$  [33]. It is quite obvious to notice that the current plays a significant role for establishing mapping between the TD density and potential. The Runge and Gross proof [96] for time-dependent systems is based directly on

the Schrödinger equation:

$$i\frac{\partial}{\partial t}\Psi(t) = \hat{H}(t)\Psi(t) , \quad (4.11)$$

where

$$\hat{H}(t) = \hat{T} + \hat{V}(t) + \hat{U}(t) , \quad (4.12)$$

and

$$\hat{T} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 ; \quad \hat{U} = \frac{1}{2} \sum_{i,j=1,i \neq j}^N \frac{1}{|\vec{r}_i - \vec{r}_j|} . \quad (4.13)$$

Runge-Gross have assumed densities  $\rho(\vec{r}, t)$  of electronic systems evolving from fixed initial many-particle state  $\Psi(t = 0) = \Psi_0$  under the influence of different external potentials of the form  $\hat{V}(t) = \sum_{i=1}^N v(\vec{r}_i, t)$ . They have assumed the initial time  $t_0$  is to be finite and the potentials are required to be expandable in a Taylor series about that initial time  $t_0$ . No further assumptions concerning the size of the radius of convergence are made. It is sufficient that the radius of convergence is greater than zero. The initial state  $\Psi_0$  is not required to be the ground state or some other eigenstate of the initial potential  $v(\vec{r}, t_0) = v_0(\vec{r})$ . In Runge-Gross theory, potentials that are switched-on adiabatically from  $t_0 = -\infty$  are excluded because of the Taylor- expandability condition and the adiabatic switching involves an essential singularity at  $t_0 = -\infty$ .

With these preliminaries, one can formulate the following Hohenberg-Kohn-type theorem: The densities  $\rho(\vec{r}, t)$  and  $\rho'(\vec{r}, t)$  evolving from a common initial state  $\Psi_0 = \Psi(t_0)$  under the influence of two potentials  $v(\vec{r}, t)$  and  $v'(\vec{r}, t)$  (both Taylor expandable about the initial time  $t_0$ ) are always different provided that the potentials differ by more than a purely time-dependent (r-independent) function <sup>3</sup>:

$$v(\vec{r}, t) = v'(\vec{r}, t) + c(t) . \quad (4.14)$$

We will briefly describe the Runge-Gross proof below. As the potentials considered are Taylor expandable so one can easily express these in the following Taylor series

---

<sup>3</sup>If  $v$  and  $v'$  differ by a purely time-dependent function, the resulting wave functions  $\Psi(t)$  and  $\Psi'(t)$  differ by a purely time-dependent phase factor and, consequently, the resulting densities are identical. This trivial case is excluded by the condition (4.14), in analogy to the ground-state formalism where the potentials are required to differ by more than a constant.

$$\begin{aligned}
 v(\vec{r}, t) &= \sum_{m=0}^{\infty} \frac{1}{m!} v_m(\vec{r})(t - t_0)^m \quad , \\
 v'(\vec{r}, t) &= \sum_{m=0}^{\infty} \frac{1}{m!} v'_m(\vec{r})(t - t_0)^m \quad .
 \end{aligned}
 \tag{4.15}$$

The condition imposed on the external potentials Eq.(4.14) is equivalent to the statement that for the expansion coefficients  $v_m(\vec{r})$  and  $v'_m(\vec{r})$  there exists a smallest integer  $m \geq 0$  such that

$$v_m(\vec{r}) - v'_m(\vec{r}) = \frac{\partial^m}{\partial t^m} \{v(\vec{r}, t) - v'(\vec{r}, t)\} \Big|_{t=t_0} \neq \text{constant} \quad .
 \tag{4.16}$$

Since  $\Psi$  and  $\Psi'$  corresponding to the two potentials evolving from the same initial state (*i.e.*  $\Psi(t_0) = \Psi'(t_0) = \Psi_0$ ) one can correlate the current densities to the potentials in the following manner:

$$\begin{aligned}
 \frac{\partial}{\partial t} \{j(\vec{r}, t) - j'(\vec{r}, t)\} \Big|_{t=t_0} &= -i \langle \Psi_0 | [\hat{j}_p(\vec{r}), \hat{H}(t_0) - \hat{H}'(t_0)] | \Psi_0 \rangle \\
 &= -\rho_0(\vec{r}) \nabla \{v(\vec{r}, t_0) - v'(\vec{r}, t_0)\} \quad ,
 \end{aligned}
 \tag{4.17}$$

where  $\rho_0(\vec{r})$  is the initial density and  $j_p(\vec{r})$  be the current density operator. If the condition Eq.(4.16) is satisfied for  $m = 0$  the right-hand side of Eq.(4.17) cannot vanish identically and  $j$  and  $j'$  will become different infinitesimally later than  $t_0$ . If Eq.(4.16) holds for some finite  $k > 0$  then by taking the derivative of the above equation ( $k + 1$ ) times and obtain after some algebra:

$$\left( \frac{\partial}{\partial t} \right)^{k+1} \{j(\vec{r}, t) - j'(\vec{r}, t)\} \Big|_{t=t_0} = -\rho_0(\vec{r}) \nabla w_m(\vec{r}) \neq 0 \quad ,
 \tag{4.18}$$

with

$$w_m(\vec{r}) = \left( \frac{\partial}{\partial t} \right)^k \{v(\vec{r}, t) - v'(\vec{r}, t)\} \Big|_{t=t_0} \quad .
 \tag{4.19}$$

Which implies  $j(\vec{r}, t) \neq j'(\vec{r}, t)$  provided Eq.(4.16) holds for the two potentials. In the second step in order to prove that if the currents become different from one another so also the corresponding densities RG used the continuity equation:

$$\frac{\partial}{\partial t} \{\rho(\vec{r}, t) - \rho'(\vec{r}, t)\} = -\nabla \cdot \{j(\vec{r}, t) - j'(\vec{r}, t)\} \quad , \quad (4.20)$$

and again calculating the  $k + 1$  time derivative of Eq. (4.20) at  $t = t_0$  leads to

$$\left(\frac{\partial}{\partial t}\right)^{k+2} \{\rho(\vec{r}, t) - \rho'(\vec{r}, t)\}\Big|_{t=t_0} = \nabla \cdot (\rho_0(\vec{r})\nabla w_m(\vec{r})) \quad . \quad (4.21)$$

In order to prove that the densities  $\rho(\vec{r}, t)$  and  $\rho'(\vec{r}, t)$  will become different infinitesimally later than  $t_0$ , one has to demonstrate that the right-hand side of Eq. (4.21) cannot vanish identically. This is done by reductio ad absurdum by assuming  $\nabla \cdot (\rho_0(\vec{r})\nabla w_m(\vec{r})) \equiv 0$  and following some algebraic steps. With the above assumption one can easily obtain the following relation by Green's theorem

$$\int \rho_0(\vec{r}) [\nabla w_m(\vec{r})]^2 d^3r = \oint \{\rho_0(\vec{r})w_m(\vec{r})\nabla w_m(\vec{r})\} \cdot d\mathbf{S} - \int w_m(\vec{r})\nabla \cdot (\rho_0(\vec{r})w_m(\vec{r})) \quad (4.22)$$

The second integral on the right hand side of Eq.(4.22) vanishes by assumption. The surface integral on the other hand vanishes for any physically realistic potentials (*i.e* potentials arising from normalizable external charge densities). This is because for such potentials the quantities  $w_m(\vec{r})$  falls off at least as  $\frac{1}{r}$ . As the integrand on the left hand side is non-negative so  $\rho_0(\vec{r}) [\nabla w_m(\vec{r})]^2 \equiv 0$  in contradiction to  $w_m(\vec{r}) \neq \text{constant}$ . Which completes the proof of the theorem. It is important to note that introduction of the current  $j(\vec{r}, t)$  and assumption of the initial state-dependence plays the crucial role in establishing  $\rho(\vec{r}, t) \rightarrow v(\vec{r}, t)$  mapping in RG theory. The key point to be noted here is that the RG theory uses the fact: how the potential change depends upon the change of the current density with time. Which is well understood by the time-dependent analog of the differential virial theorem (DVT) (see Appendix B for review).

### 4.3 Comparison of Floquet and Runge-Gross Formalism

In order to understand what made the earlier researchers [152] to conclude that Floquet theory of TDDFT is incomplete, it is of prime importance that we figure out what are the subtle differences between Runge-Gross and Floquet formalism in TDDFT. As pointed out earlier,

Table 4.1: Comparison of Floquet theory and RG theory of TDDFT

Floquet Theory	RG Theory
<ul style="list-style-type: none"> <li>• Based on the minimum principle of the ground-state quasienergy.</li> <li>• Steady-state is reached by adiabatic switching of the time-periodic potential.</li> <li>• <math>v(\vec{r}, t)</math> is functional of <math>\rho(\vec{r}, t)</math> only.</li> </ul>	<ul style="list-style-type: none"> <li>• Based on the evolution of wavefunction from <math>t = t_0</math>.</li> <li>• Wavefunctions are obtained from potentials analytic at <math>t = t_0</math>. Adiabatic switching is ruled out.</li> <li>• <math>v(\vec{r}, t)</math> is functional of <math>\rho(\vec{r}, t)</math> as well as <math>\Psi_0</math>.</li> </ul>

in RG theory [96] the proof of the density-to-potential mapping for time-dependent systems is based directly on the TD Schrödinger equation. In this theory, it is assumed that the time-dependent potential  $v(\vec{r}, t)$  is turned on at a particular time  $t = t_0$  and all systems are taken to evolve from the same initial state wavefunction  $\Psi(t_0) = \Psi_0$ . It is then shown that if the potential has a Taylor series expansion around the initial time  $t = t_0$ , then the time-dependent density  $\rho(\vec{r}, t)$  determines the potential  $v(\vec{r}, t)$  uniquely. In turn  $\Psi(\vec{r}, t)$  is also determined by  $\rho(\vec{r}, t)$ . Thus the RG theory is quite distinct from the Hohenberg-Kohn theorem or its steady-state DFT counterpart (Deb-Ghosh theorem [94] proved above), which are based on the minimization of energy (or quasienergy in the Floquet formalism). Notice that because of the Taylor series expansion requirement of  $v(\vec{r}, t)$ , RG theorem is applicable to suddenly switched-on potentials but not to adiabatically switched-on potentials. Table 4.1 gives a comparison of the two theories.

It is clear from the comparison given in Table 4.1 that the two theories are quite distinct and their domain of application are also different. As such Floquet formulation of TDDFT [94, 95, 132–139] is not a particular case of the RG theory. In light of this let us now analyze the work by Maitra and Burke [152] and then go on to comment on what does the distinction between the Floquet and the RG theory mean in the context of calculation of quantities like polarizabilities  $\alpha(\omega)$  and excitation energies etc. using TDDFT.

## 4.4 Examples

Let us consider the example [152] of two non-interacting electrons in a one-dimensional harmonic oscillator potential subject to an adiabatically switched-on time periodic potential.

This is the example considered by Maitra and Burke (MB) in their analysis. Thus the Hamiltonian for this case will be

$$H = -\frac{1}{2} \frac{d^2}{dx^2} + \frac{1}{2} \omega_0^2 x^2 + \lambda x \sin(\omega t) . \quad (4.23)$$

The QESs for the above mentioned Hamiltonian are known analytically [155] to be

$$\phi_n(x, t) = \psi_n(\bar{x}(t)) e^{i(\omega A x \cos(\omega t) + \alpha(t))} , \quad (4.24)$$

where  $\psi_n$  are the eigenstates of the static Harmonic oscillator and  $\bar{x}(t) = x - A \sin(\omega t)$ . The parameters of the wavefunction are given as

$$A = \frac{\lambda}{\omega^2 - \omega_0^2} \quad (4.25)$$

and

$$\alpha(t) = \lambda^2 \frac{\left\{ \frac{\sin(2\omega t)}{8} + \cos(\omega t) - 1 - \omega^2 \cos(\omega t) \times \frac{\sin(\omega t)}{(\omega^2 - \omega_0^2)} \right\}}{\omega(\omega^2 - \omega_0^2)} . \quad (4.26)$$

The corresponding quasienergy for the QES  $\phi_n(x, t)$  is

$$\varepsilon_n = \left[ \left( n + \frac{1}{2} \right) \omega_0 + \frac{\lambda^2}{4(\omega^2 - \omega_0^2)} \right] \text{modulo}(\omega) \quad (4.27)$$

One thing to be pointed out here is that the quasienergies have been expressed in such a manner that as  $\lambda \rightarrow 0$ , the energy eigenvalues go to their respective time-independent eigenvalues. Thus energy defined ‘modulo( $\omega$ )’ does not create any difficulty. Secondly, as long as  $\omega \neq \omega_0$ , there is clearly a well defined ‘‘ground-state’’ in these solutions. Thus  $\varepsilon_0 = \frac{\omega_0}{2} + \frac{\lambda^2}{4(\omega^2 - \omega_0^2)}$  represents the ‘‘ground-state’’ energy of the system, whereas the other energies are the ‘‘excited-state’’ energies.

In [152] MB consider a singlet state with one electron occupying the ground-state (*i.e.*  $n = 0$ ) and the other the first excited-state (*i.e.*  $n = 1$ ) quasienergy orbitals. This gives the density of the system to be

$$\rho(x, t) = \sqrt{\frac{\omega_0}{\pi}} \left(1 + 2\omega_0 \bar{x}(t)^2\right) e^{-\omega_0 \bar{x}(t)^2} \quad (4.28)$$

Now MB generate the same density by another system with a different periodic potential. For doing this they consider a Floquet state which is also a spin singlet but with one doubly occupied steady state. Thus

$$\tilde{\Phi}(x_1, x_2, t) = \tilde{\phi}(x_1, t) \tilde{\phi}(x_2, t) e^{2i\tilde{\epsilon}t}, \quad (4.29)$$

with

$$\tilde{\phi}(x, t) = \sqrt{\frac{\rho(x, t)}{2}} e^{i\beta(x, t)}, \quad (4.30)$$

where  $\beta(x, t)$  is a real time-periodic function,  $\beta(x, t + \tau) = \beta(x, t)$ . By inverting the TD Schrödinger equation one will have a different potential given by

$$\tilde{v}(x, t) = \frac{1}{2} \frac{\tilde{\phi}''(x, t)}{\tilde{\phi}(x, t)} + i \frac{\dot{\tilde{\phi}}(x, t)}{\tilde{\phi}(x, t)} + \tilde{\epsilon}. \quad (4.31)$$

In this  $\tilde{\epsilon}$  is the orbital quasienergy for the second Floquet state. The function  $\beta(x, t)$  is determined by assuming the potential and quasienergy to be real. Now the new potential and phase for the second Floquet state are given by

$$\begin{aligned} \tilde{v}(x, t) &= \frac{1}{2} \omega_0^2 \bar{x}(t)^2 \left\{ 1 - \frac{4}{(1 + 2\omega_0 \bar{x}(t)^2)^2} - \frac{4}{1 + 2\omega_0 \bar{x}(t)^2} \right\} + \\ &\quad \frac{\omega_0}{1 + 2\omega_0 \bar{x}(t)^2} + \omega_0 - \frac{\omega_0^2 A^2 S \sin^2(\omega t)}{2} \\ \beta(x, t) &= A \omega \cos(\omega t) x - A^2 \left( \omega^2 - \frac{\omega_0^2}{2} \right) \frac{S \sin(2\omega t)}{4\omega} \end{aligned} \quad (4.32)$$

The phase  $\beta(x, t)$  is uniquely determined up to a purely time-dependent function. At large  $x$  both the potentials  $v(\bar{x}, t), v'(\bar{x}, t) \rightarrow \frac{\omega_0^2 x^2}{2} + \lambda x S \sin(\omega t)$  and the quasienergy is  $\tilde{\epsilon} = \frac{3\omega_0}{2} + \frac{A^2(\omega^2 - \omega_0^2/2)}{2} \text{ modulo}(\omega)$

The fact that MB have been able to generate one density from two different potentials, which let them to conclude that this is a manifestation of the initial state-dependence

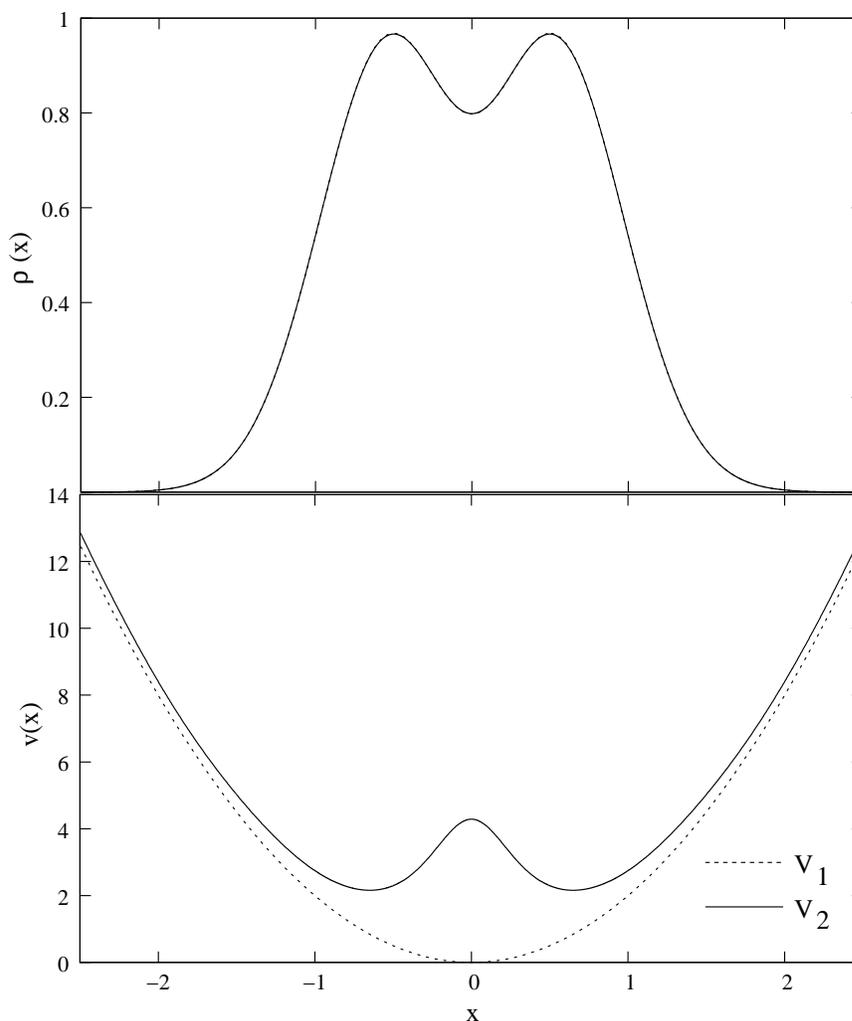


Figure 4.1: Shown in the figure are the two potentials (lower panel) giving rise to the same excited-state density (upper panel) of a harmonic 1D oscillator by putting one electron in the ground and other electron in the first excited-state.

of TDDFT. Thus MB find Floquet theory of TDDFT to be incomplete. We now show that MB are incorrect on two counts. First, they have considered a system in steady-state solution that is supposed to have been obtained by an adiabatic switching. Thus RG theory is not applicable to this system. Therefore one cannot talk about the dependence on the initial state which is a specific feature of the RG theory. The problem falls in the domain of steady-state solutions and as such should be looked at within the Floquet theory of TDDFT. As discussed earlier, the domain of applicability of the Floquet theory of TDDFT is precisely the kind of example that has been considered above. Secondly, the Floquet theory of TDDFT is similar to the stationary-state DFT and as the derivation earlier shows, it is applicable to only the

ground-states of the steady-states. On the other hand in the work [152] MB have applied it to an excited-state of the steady-state solution and shown that an excited-state density can be generated by two different potentials. That however, does not invalidate Floquet theory of TDDFT. This point needs further elaboration and we do that in the following.

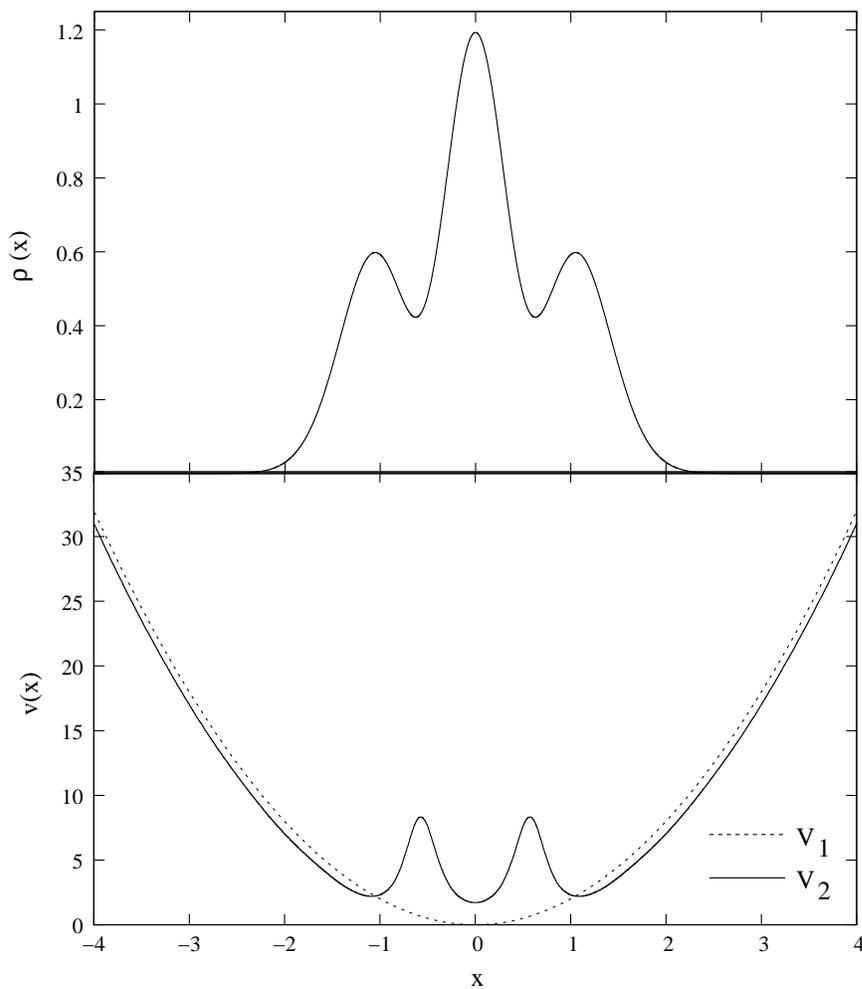


Figure 4.2: Two potentials (lower panel) yielding the same excited-state density (upper panel) for an excited state of the two-electron in an 1D harmonic oscillator.

#### 4.4.1 Discussion

For further discussion, we show that even in the stationary-state theory, one can always generate a given excited-state density by many different potentials [89–91] and also by us as is discussed in the second chapter. Again consider two electrons in a one-dimensional harmonic

oscillator potential. If the two electrons are in the ground-state, the potential is determined uniquely by the Hohenberg-Kohn theorem. However, for excited-states, there is no such theorem and more than one potentials can give the same density. For this let us consider one electron in  $n = 0$  and one in  $n = 1$  state. The corresponding density is shown in the upper panel of Fig.4.1. One potential corresponding to this density is obviously the harmonic potential  $v(x) = \frac{1}{2}\omega_0^2 x^2$  itself. Another potential can be generated by putting both the electrons in the ground-state orbital and then by inverting the Schrödinger equation or by using the van-Leeuwen-Baerends method [112] (see Appendix D). These two potentials are shown in the lower panel of Fig.4.1. We now consider one more example similar to that discussed above, where the excited-state density of two non-interacting electrons moving in a one-dimensional harmonic oscillator potential is obtained by putting one electron in  $n = 0$  and the other in  $n = 2$  state. Now this density (shown in the upper panel of Fig.4.2) is produced by an alternative potential, which is shown in the lower panel of Fig.4.2 along with the original potential. Thus if a system is in excited-state, more than one potentials can give the same density. On the other hand for the ground-state, occupation is uniquely defined and so is the potential. More examples of this kind have been discussed in the second chapter of this thesis and also in the literature [89–91]. Exactly in the same manner as in stationary-state theory, in Floquet theory of TDDFT also the "ground-state" gives the potential uniquely but for "excited-states" more than one potential can be found. This is precisely what has been done in [152]. Although in [152] the researchers have questioned the foundations of Floquet theory in TDDFT but they also admit at the same time that their results resemble those of excited-states in time-independent problems but they fail to make further connection with the latter.

Having explained the work of Maitra and Burke, we now also comment on the TDDFT calculations in light of the Floquet and RG theories of TDDFT. It is clear that in calculating frequency dependent polarizability  $\alpha(\omega)$ , it is the steady-state of a system that is employed. Thus in calculation of  $\alpha(\omega)$ , and related quantities such as excitation energies and oscillator strengths, [97] it is the Floquet theory of TDDFT rather than the RG theory that is being applied. Finally, one may raise a question if Floquet theory of TDDFT is applicable only to "ground-states". The answer is that even for steady-state "excited-states", a theory similar to the stationary-state excited-state DFT (analogous to that described in the second chapter of this thesis) [44, 54, 56, 89–91] can be developed. This work will be taken up in future.

## 4.5 Concluding Remarks

To conclude, we have shown that Floquet theory of TDDFT is well founded and is distinct from the RG theory. Further, its recent criticism by Maitra and Burke is easily explained on the basis of a careful analysis of Floquet theory and RG theory.

We now also comment on possible extension of arguments of second chapter to Floquet formulaion of TDDFT for the excited-state. As was shown by using the constrained search prescription one can generate various potentials for a given density in time-independent case. In a similar manner constrained search theory can also in principle be developed for TD cases. The question will arise as to which potentials be selected for a given TD density. Like in our time-independent situation discussed in the second chapter, probably one can do that through the comparison of the ground-states and kinetic energies, which will automatically establish an unique  $\rho(\vec{r}, t) \rightarrow v(\vec{r}, t)$  mapping.

# Chapter 5

## Summary and Outlook

In this thesis fundamental aspects of time-independent excited-state density-functional theory (DFT) and time-dependent density-functional theory (TDDFT) have been studied. This has resolved two important issues : density-to-potential mapping and construction of exchange-correlation functionals for excited-states. Another work described in this thesis answers the questions relating to the foundations of the Floquet formulation of TDDFT, which has been questioned recently. We will summarize in the following the attempts made by us to formulate excited-state DFT and how further possible developments can be made based on these.

The description of an interacting many-particle systems is, in general, very complicated and approximations need to be made. Several methods in quantum chemistry try to describe the motion of the electrons in such systems by the electronic wavefunction, the solution of either the time-independent or time-dependent Schrödinger equation. The computational effort involved in these methods, is very high. In contrast to density-functional theory, the computational costs are much lower. In DFT, the electronic wavefunction is not evaluated for a full description of the interacting many-particle system but it is sufficient to look at the electron density. The fundamental theorems for this theory were first formulated in the early 1960s by Hohenberg and Kohn (HK), and, for practical use, incorporated, shortly after, in a one-electron self-consistent field calculation scheme by Kohn and Sham (KS). In KS approach to density-functional theory, the interacting many-particle system is modelled in terms of an effective auxiliary non-interacting particle system, called the KS system. The effective external field, to which this KS system gives rise, incorporates the true external field and, in an effective way, the interparticle interactions. In the modelled system the effective potential, is constructed in such a way that the electron density of the non-interacting KS system exactly reproduces the electron density of the true interacting many-particle system.

Thus the KS potential is a functional of the electron density. However, this density can only be obtained if this KS potential is known. Both the electron density and the KS potential can be obtained in a self-consistent field scheme in which self-consistency is achieved for the electron density. The electron density and the KS potential are hereby updated in an iterative way. In time-dependent extension of DFT, the external potential varies in time, and consequently also the electron density and effective potential become time-dependent.

Density functional theory (DFT) within the local density (LDA) and gradient corrected (GGA, meta-GGA) approximations is most widely used for the investigation of the properties of complex systems ranging from atoms to large molecules and solids. This method has achieved considerable success in the prediction of structural properties and vibrational frequencies for a variety of systems. However, within the density functional framework there is no simple method for the estimation of electronic excitation energies. The importance of excitation energies derives from the existence of a large amount of experimental spectroscopic data and also from the fact that they contain information on the electronic dynamics.

According to the HK theorem, the ground state electron density determines (within an additive constant) the external potential. It is clear therefore that the ground-state density can, in principle, be used to calculate excitation energies. Unfortunately, the route from the ground state electron density to the excitation energies is not necessarily a simple one and, at least, it appears that the computation of electronic spectral properties is far more complicated in DFT than in the traditional schemes of quantum chemistry. In Hartree-Fock (HF), for instance, it is easy to prove the so called Koopmans theorem: "neglecting the electronic relaxation effects, electron removal energies are directly related to the eigenvalues of the HF single electron equations". In DFT a correspondence between KS eigenvalues and excitation energies is not valid, as discussed, for example, by Perdew and Zunger.

The simplest DFT scheme for the computation of excitation energies (and in particular, electron removal energies), has been the evaluation of the total energy difference between the initial and the final states. This method is also used in HF to compute excitation energies including relaxation effects, and for this reason it is known as  $\Delta$ SCF method. Obviously, this method can be applied when both the initial and the final state are within the reach of DFT. However, in general excited states cannot always be identified with a DFT solution. For these reasons, the search for simple schemes providing at the same time a reliable description

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of ground and excited state properties is an active subject of research. In this connection there happen to be several attempts as described in the introductory chapter of this thesis for the description of excited-states in DFT. Based on some of these attempts we have tried to formulate a complete theory for excited-states.

In the second chapter, we have described the basic foundation (*i.e.* the possibility of Hohenberg-Kohn like theorem or in other words density-to-potential mapping) of time-independent excited-state DFT. We demonstrate the point made by earlier researchers that information of both ground as well as excited-state density is a must for establishing the density-to-potential mapping for excited-states. Based on Görling's stationary state formulation there exists several external potentials and the corresponding KS potentials for each  $\rho$ -stationary state giving the excited-state density  $\rho$ . In order to select the appropriate KS system out of the many that gives the same excited-state density Levy and Nagy proposed the comparison of ground-state densities of the true and non-interacting systems. However, the criterion proposed by Levy-Nagy for constructing a Kohn-Sham system for excited-states is insufficient to handle the situation. We propose that comparing the kinetic energies of the original and non-interacting systems selects the appropriate Kohn-Sham system for a given excited-state density. So the present work provides a strong basis to time-independent excited-state DFT. To summarize, we have answered the issue regarding the existence of the excited-state counterpart of the Hohenberg-Kohn like theorem. In the chapter next to this we have described another important aspect of excited-state DFT, *i.e.* construction of exchange-correlation functionals.

In the third chapter, we have described the construction of accurate and approximate exchange only functionals for various classes of excited-states within the simple local-density approximation. As its obvious from the theory of excited-states described earlier that the functionals for it are non-universal and state-dependent unlike the ground-state theory so different classes of excited-states must have different functionals. We also note that why the ground-state functionals are insufficient for calculating the excitations. The key point in constructing the new exchange-correlation functionals is to take into account the state-dependence of these functionals. With the three different  $x$ -only functionals described in this chapter, we have shown the ease with which one can calculate the double excitations in addition to single ones. Although we have not constructed any correlation functionals but we trust it should be possible. As the electronic systems in excited-states are highly

inhomogeneous so in order to account for that gradient corrections to excited-state exchange-correlation functionals is a must, which could be the future direction for further development of these functionals. Lastly, we think functionals constructed in the manner similar to that being done in this chapter will also be helpful for calculation of band-gaps in solids.

In the fourth chapter, we have again addressed the basic foundations of Floquet formulation of TDDFT which has been questioned regarding its validity. In our analysis we have shown that criticism by earlier researchers has overlooked the key points of this formalism. In light of these issues we differentiate between the Floquet and Runge-Gross formalism of TDDFT and show that only the Floquet formalism is valid for systems evolving in time-periodic potentials rather than the latter. In fact its the Floquet formalism which has been employed for the calculation of excitations and dynamic polarizabilities instead of the Runge-Gross formalism. A theory analogous to the one presented in the second chapter is also possible for systems driven by time-periodic potentials. Further emphasis is that a more generalized version of TDDFT is also possible through the constrained search principle which should be applicable to all kind of time-dependent potentials.

To summarize in this thesis we have given excited-state DFT on a strong footing. Our work on the fundamental aspects of excited-state DFT will give some new directions for further developments and successful implementations that will naturally bring it into a complete shape like the ground-state DFT.

# Appendix A

## Ground-State of Homogeneous Electron Gas (HEG)

In this appendix, we present a brief derivation of the kinetic and exchange-correlation energy functionals for uniform electron gas. The complete Hamiltonian for the electron gas is given by

$$\hat{H} = \hat{H}_i + \hat{H}_e + \hat{v}_{ext} \quad , \quad (\text{A.1})$$

where  $\hat{H}_i$  represents the electrostatic energy of the background ions,  $\hat{H}_e$  is the total electronic energy operator and  $\hat{v}_{ext}$  be the mutual coulomb interaction between the ions and electrons. If the density  $\rho = \frac{N}{\mathcal{V}}$  of the uniform electron gas is known then it is quite simple to obtain energies arising due to the first and third term of Eq.A.1. Now it will be important to calculate the electronic part of the total energy which is

$$\hat{H}_e = -\frac{1}{2} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i,j=1, i \neq j}^N \frac{1}{|\vec{r}_i - \vec{r}_j|} \quad . \quad (\text{A.2})$$

Now by imposing periodic boundary condition over a cube of volume  $\mathcal{V}$  and and going to the Fourier space, the total HF energy of the spinpolarized electron gas in the ground-state is given by

$$E_e^{HF} = \frac{1}{10} \frac{\mathcal{V}}{2\pi^2} \{k_f^5\} - \frac{\mathcal{V}}{2} \int_0^{k_f} \int_0^{k_f} \frac{d^3k}{(2\pi)^3} \frac{d^3k'}{(2\pi)^3} \frac{4\pi}{|\vec{k} - \vec{k}'|^2} \quad . \quad (\text{A.3})$$

If we take the  $z$ -axis of integration to be coinciding with  $\vec{k}$  then the integrals in the second term of Eq.A.3 can be evaluated as

$$\frac{1}{(2\pi)^3} \int_0^{k_f} \frac{4\pi}{|\vec{k} - \vec{k}'|^2} d^3k' = \frac{4\pi}{(2\pi)^3} \int_0^{k_f} k' dk' \int_0^\pi \int_0^{2\pi} \frac{\sin\theta d\theta d\phi}{k^2 + k'^2 - 2kk' \cos\theta} . \quad (\text{A.4})$$

Now by elementary integration the total ground-state energy per particle of the HEG within  $x$ -only theory will be:

$$\varepsilon_{k_f} = \int_0^{k_f} \left\{ \frac{k^2}{2} - \frac{1}{\pi} \left[ k_f + \frac{k_f^2 - k^2}{2k} \ln \left| \frac{k_f + k}{k_f - k} \right| \right] \right\} \frac{d^3k}{(2\pi)^3} . \quad (\text{A.5})$$

It can be proved that the exchange term is the first order term in perturbation theory, if the entire interaction is regarded as a perturbation. The zeroth order terms immediately give us the kinetic energy of the electron gas [156]. At this point the question arises as to whether we can obtain parts of the correlation energy in the same way by including higher order terms in the perturbation expansion. It turns out that every order in perturbation theory beyond the first order diverges. Only in special cases one manages to get sensible results by diagrammatical methods for the limiting case of  $r_s \rightarrow 0$  e.g. The difficulty can be overcome in another way if we realize that the main reason of the divergence of the higher order perturbation terms originates in the long-range tail of the Coulomb potential. Hence, one thing that seems natural to do is to divide the total Coulomb interaction into a short-range and a long-range parts. The short-range part then can be calculated by perturbation theory, since this part does not give rise to divergent expressions. However, nonperturbative approach is required to calculate the long-range correlation energy.

# Appendix B

## Differential Virial Theorem

This theorem establishes the local relation between the density, potentials and the kinetic energy density tensors. The starting point is the Schrödinger equation

$$\hat{H}\Psi = E\Psi \quad . \quad (\text{B.1})$$

Because the Hamiltonian is real, this equation is satisfied separately by the real and imaginary parts of the wavefunction  $\Psi = \Psi^{re} + \Psi^{im}$ , *i.e.*

$$E = \frac{\hat{H}\Psi^{re}}{\Psi^{re}} = \frac{\hat{H}\Psi^{im}}{\Psi^{im}} \quad . \quad (\text{B.2})$$

So from the Eq.(B.1) one can obtain

$$\hat{V} + \hat{U} - E = -\frac{\hat{T}\Psi^{re}}{\Psi^{re}} = -\frac{\hat{T}\Psi^{im}}{\Psi^{im}} \quad , \quad (\text{B.3})$$

where

$$\hat{T} = \sum_{i=1}^N -\frac{1}{2}\nabla_i^2; \quad \hat{U} = \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{1}{|\vec{r}_i - \vec{r}_j|}; \quad \hat{V} = \sum_{i=1}^N v(\vec{r}_i) \quad . \quad (\text{B.4})$$

Now by differentiating both sides of the left hand side of E.(B.3) with respect to  $\vec{r}_{1\alpha}$ , we will get

$$v_{1\alpha}(\vec{r}_1) + \sum_{j=2}^N u_{1\alpha}(\vec{r}_1, \vec{r}_j) = \frac{1}{2\Psi^{re}} \sum_{i=1}^N \sum_{\beta} \Psi_{1\alpha \ i\beta \ i\beta}^{re} - \frac{1}{2}(\Psi^{re})^{-2}\Psi_{1\alpha}^{re} \sum_{i=1}^N \sum_{\beta} \Psi_{i\beta \ i\beta}^{re} \quad . \quad (\text{B.5})$$

Here we have adopted the notation for partial derivatives  $f_{1\alpha} = \frac{\partial f}{\partial r_{1\alpha}}$ . After multiplying both sides of Eq.(B.5) by  $(\Psi^{re})^2$  leads to

$$\begin{aligned} \left\{ v(\vec{r}_1) + \sum_{j=2}^N u(\vec{r}_1, \vec{r}_j) \right\}_{1\alpha} (\Psi^{re})^2 &= \sum_{i=1}^N \sum_{\beta} \left\{ \frac{1}{2} \Psi_{1\alpha i\beta}^{re} \Psi_{i\beta}^{re} - \frac{1}{2} \Psi_{1\alpha}^{re} \Psi_{i\beta}^{re} \right\} \\ &= \sum_{i=1}^N \sum_{\beta} \left\{ \frac{1}{4} (\Psi^{re} \Psi^{re})_{1\alpha i\beta i\beta} - (\Psi_{1\alpha}^{re} \Psi_{i\beta}^{re})_{i\beta} \right\} . \end{aligned} \quad (\text{B.6})$$

An equation similar to the above can also be obtained for the imaginary part  $\Psi^{im}$  of the total wavefunction  $\Psi$ . After adding the equations corresponding to the real and imaginary parts, one gets the following relation

$$\left\{ v(\vec{r}_1) + \sum_{j=2}^N u(\vec{r}_1, \vec{r}_j) \right\}_{1\alpha} |\Psi|^2 = \sum_{i=1}^N \sum_{\beta} \left\{ \frac{1}{4} (|\Psi|^2)_{1\alpha i\beta i\beta} - (\Psi_{1\alpha}^{re} \Psi_{i\beta}^{re} + \Psi_{1\alpha}^{im} \Psi_{i\beta}^{im})_{i\beta} \right\} . \quad (\text{B.7})$$

Again by multiplying both sides of Eq.(B.6) by  $N$ , then summing over spin  $s_1$  and integrating over  $dx_2 dx_3 \dots dx_N$ , we get

$$\begin{aligned} v_{1\alpha}(\vec{r}_1) \rho(\vec{r}_1) - 2 \sum_{j=2}^N N \sum_{s_1} \int u_{1\alpha}(\vec{r}_1, \vec{r}_j) |\Psi|^2 dx_2 dx_3 \dots dx_N &= \frac{1}{4} \nabla_{1\alpha}^2 \rho_{1\alpha}(\vec{r}_1) \\ &\quad - 2 \sum_{\beta} \left\{ N \sum_{s_1} \int \frac{1}{2} (\Psi_{1\alpha}^{re} \Psi_{1\beta}^{re} + \Psi_{1\alpha}^{im} \Psi_{1\beta}^{im}) \right\}_{1\beta} dx_2 dx_3 \dots dx_N \\ &\quad + \sum_{j=2}^N \sum_{\beta} N \sum_{s_1} \int \left\{ \frac{1}{4} (|\Psi|^2)_{1\alpha j\beta} - (\Psi_{1\alpha}^{re} \Psi_{j\beta}^{re} + \Psi_{1\alpha}^{im} \Psi_{j\beta}^{im}) \right\}_{j\beta} dx_2 dx_3 \dots dx_N , \end{aligned} \quad (\text{B.8})$$

where  $x_i = (\vec{r}_i, s_i)$ . The last integral on the right hand side of Eq.(B.8) vanishes after integration over  $dr_{j\beta}$ . By boundary condition, the wavefunction  $\Psi$  and its derivative vanishes for  $|r_{j\beta}| \rightarrow \infty$ . The expression inside the curly brackets in the other integral is nothing but the kinetic energy density tensor  $t_{\alpha\beta}(\vec{r}_1)$  which is in general defined by

$$t_{\alpha\beta}([\Gamma_1]; \vec{r}) = \frac{1}{4} \left\{ \frac{\partial^2}{\partial r'_\alpha \partial r''_\beta} + \frac{\partial^2}{\partial r''_\alpha \partial r'_\beta} \right\} \rho(\vec{r}'; \vec{r}'') \Bigg|_{\vec{r}=\vec{r}'=\vec{r}''} . \quad (\text{B.9})$$

Now the term involving  $u_{1\alpha}$  can be rewritten using the symmetry of  $\Psi$  and the definition of the second order reduced density matrix  $\Gamma_2$  as

$$N(N-1) \sum_{s_1} \int u_{1\alpha}(\vec{r}_1, \vec{r}_2) |\Psi|^2 dx_2 dx_3 \dots dx_N = 2 \int u_{1\alpha}(\vec{r}_1, \vec{r}_2) \Gamma_2(\vec{r}_1, \vec{r}_2) d^3 r_2 \quad . \quad (\text{B.10})$$

Finally, Eq.(B.8) will be reduced to the following equation

$$v_\alpha(\vec{r}) \rho(\vec{r}) + 2 \int u_\alpha(\vec{r}, \vec{r}') \Gamma_2(\vec{r}, \vec{r}') d^3 r' = \frac{1}{4} \nabla^2 \rho_\alpha(\vec{r}) - 2 \sum_{\beta} t_{\alpha\beta}(\vec{r}) \quad , \quad (\text{B.11})$$

which is termed as the differential virial theorem (DVT). This is an exact, local relation involving the external potential  $v(\vec{r})$ , the electron-electron interaction potential  $u_\alpha(\vec{r}, \vec{r}')$ , the diagonal elements of the first- and second order density matrices,  $\rho(\vec{r})$  and  $\Gamma_2(\vec{r}, \vec{r}')$ , and the first order density matrix  $\Gamma_1(\vec{r}_1; \vec{r}_2)$ . Using the DVT one can obtain gradient of the potential to be

$$\nabla v(\vec{r}) = \frac{\left\{ -\frac{1}{4} \nabla \nabla^2 \rho(\vec{r}) + \vec{Z}(\Gamma_1; \vec{r}) + 2 \int [\nabla u(\vec{r}, \vec{r}')] \Gamma_2(\vec{r}, \vec{r}') d^3 r' \right\}}{\rho(\vec{r})} \quad , \quad (\text{B.12})$$

where

$$\vec{Z}_\alpha(\Gamma_1; \vec{r}) = 2 \sum_{\beta} \frac{\partial}{\partial r_\beta} t_{\alpha\beta}(\Gamma_1; \vec{r}) \quad , \quad (\text{B.13})$$

is the vector field related to the kinetic energy density tensor. Similarly one can also obtain relation the gradient of potential in case of non-interacting systems [88]. We use this DVT in the second chapter of the thesis to establish the density to potential mapping for time-independent excited-states.

## Appendix C

# Zhao-Morrison-Parr (ZMP) Constrained Search Method and Its Application to Excited-States of Non-Interacting Systems

This is a method [111] to calculate the Kohn-Sham kinetic energies, orbitals, orbital energies and exchange correlation ( $XC$ ) potential from accurate electron densities. Now this method has been extensively used by us for the demonstration of density-to-potential mapping for time-independent excited-states which is described in the second chapter. We will briefly describe it here. The scheme is based on Levy's constrained search method [59–61] for determining KS kinetic energy. In addition, given correct total energies one can obtain the corresponding  $XC$  energies. In Levy's restricted search the kinetic energy is given by

$$T_s[\rho] = \min_{\Phi \rightarrow \rho_e(\mathbf{r})} \langle \Phi | \hat{T} | \Phi \rangle , \quad (\text{C.1})$$

where  $\hat{T}$  is the  $N$ -electron kinetic energy operator  $\Phi$ 's are the normalized  $N$ -electron Slater determinants that yield the exact density  $\rho_e$ . In the ZMP method the constraint associated with the above equation is modified to

$$C[\rho, \rho_e] = \frac{1}{2} \int \int \frac{[\rho(\vec{r}) - \rho_e(\vec{r})][\rho(\vec{r}') - \rho_e(\vec{r}')] }{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' = 0 . \quad (\text{C.2})$$

This follows from the fact that for a given density  $\rho_e$  when the density  $\rho$  associated with  $\Phi$  satisfies the constraint then  $\rho(\vec{r}) - \rho_e(\vec{r}) = 0$  for all spatial position  $\vec{r}$ . So the eq. C.2 is necessary and sufficient condition for the constraint ( $\rho = \rho_e$ ) to be satisfied. By the constrained search the orbitals obtained in this procedure are the KS orbitals. Again by introducing a global Lagrange multiplier  $\lambda$  conjugate to the constraint of Eq.C.2, and a set of non-interacting orbitals,  $\phi_i$ , leading to the density  $\rho(\vec{r}) = \sum_i |\phi_i(\vec{r})|^2$  and making the non-interacting kinetic-energy  $T_s = \sum_i \langle \phi_i | -\frac{1}{2}\nabla^2 | \phi_i \rangle$  stationary with respect to  $\phi_i^*$  the KS equations and the corresponding potentials can be generated. Since  $\hat{T}$  is positive definite operator, stationary point of  $\langle \phi_i | \hat{T} | \phi_i \rangle$  is also local minimum of  $\langle \phi_i | \hat{T} | \phi_i \rangle$ . The constrained-search variational principle becomes

$$\frac{\delta}{\delta \phi_i^*(\vec{r})} \left\{ \sum_j \langle \phi_j(\vec{r}) | -\frac{1}{2}\nabla^2 | \phi_j(\vec{r}) \rangle + \frac{\lambda}{2} \int \int \frac{[\rho(\vec{r}) - \rho_e(\vec{r})][\rho(\vec{r}') - \rho_e(\vec{r}')] }{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' \right\} = 0 . \quad (\text{C.3})$$

Now by defining the potential

$$v_c^\lambda(\vec{r}) = \lambda \int \frac{[\rho(\vec{r}') - \rho_e(\vec{r}')] }{|\vec{r} - \vec{r}'|} d\vec{r}' \quad (\text{C.4})$$

the KS type equations

$$\left\{ -\frac{1}{2}\nabla^2 + v_c^\lambda(\vec{r}) \right\} \phi_i(\vec{r}) = \varepsilon_i \phi_i(\vec{r}) , \quad (\text{C.5})$$

are obtained and the orbitals of this equation are going to give the exact density at hand. It is also possible to follow the same constrained search prescription by fixing the external potentials at a particular value. In that case the orbitals to be used in the constrained variational minimization procedure will be those whose Slater determinant minimizes the expectation value  $\langle \Phi | \hat{T} + v_{ext}(\vec{r}) | \Phi \rangle$  and satisfies the constraint in eq. C.2. For atomic systems  $v_{ext}(\vec{r}) = -\frac{Z}{r}$ . Again by using the constrained variational principle the KS type equation will be

$$\left\{ -\frac{1}{2}\nabla^2 + v_{ext}(\vec{r}) + v_c^\lambda(\vec{r}) \right\} \phi_i(\vec{r}) = \varepsilon_i \phi_i(\vec{r}) . \quad (\text{C.6})$$

Only in the limit  $\lambda \rightarrow \infty$  the desired constraint will be satisfied and the Eqs. C.5 and C.6 becomes the KS equations. To speed up the convergence of the self-consistent procedure,

improve numerical accuracy and satisfy the long-range asymptotic behavior of the exchange-correlation potential Fermi-Amaldi correction [21] to the electron-electron repulsion potential is implemented. In our work discussed in the second chapter of this thesis we have also used the ZMP procedure for non-interacting electrons. In that case the Fermi-Amaldi correction [57] is the term  $\frac{1}{N}v_j^\lambda(\vec{r})$  itself. So the modified one-particle equation in the Zhao-Morrisson-Parr scheme will be

$$\left\{ -\frac{1}{2}\nabla^2 + v_{ext}(\vec{r}) + \left(1 - \frac{1}{N}\right)v_j^\lambda(\vec{r}) + v_c^\lambda(\vec{r}) \right\} \phi_i(\vec{r}) = \varepsilon_i \phi_i(\vec{r}) . \quad (\text{C.7})$$

With the proposed Fermi-Amaldi correction the coulomb and exchange correlation potentials are given by

$$v_j(\vec{r}) = \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' \quad ; \quad v_{xc} = \lim_{\lambda \rightarrow \infty} \left( v_c^\lambda(\vec{r}) - \frac{1}{N}v_j^\lambda(\vec{r}) \right) \quad (\text{C.8})$$

For more details about Eq.C.6 over Eq.C.7 we refer the reader to a detailed description of ZMP method [111]. The method can also be used to generate various different non-interacting systems for a given density of interacting or non-interacting systems. We have used this to generate different potentials for model *Li* atom in the second chapter. Depending on the starting potential used to initialize this procedure, various potentials can be generated from the given input density  $\rho(\vec{r})$  for each assumed configurations. Thus this procedure is capable of generating all possible systems (potentials) that reproduce the density on hand. Evidently, the determined different potentials give different ground-state densities (by the Hohenberg-Kohn theorem [8]); the one which is the closest to the true ground-state density singles out the KS potential of the excited-state DFT.

## Appendix D

# Generating Potentials by van Leeuwen Baerends Iterative Procedure

In this appendix, we present an iterative scheme proposed by van Leeuwen and Baerends [112] for obtaining the Kohn-Sham potential from a given electron density  $\rho(\vec{r})$  no matter whether it corresponds to the ground or excited-state. This scheme is similar to the one proposed by Zhao-Morrison-Parr [111] and is capable of generating potentials for electronic systems with any number of electrons. As described in the introductory part of this thesis the Kohn-Sham equations for many-electronic systems are

$$\left\{ -\frac{1}{2}\nabla^2 + v_{ks}(\vec{r}) \right\} \phi_i(\vec{r}) = \varepsilon_i \phi_i(\vec{r}) , \quad (\text{D.1})$$

in which  $v_{ks}(\vec{r})$  be the Kohn-Sham potential. The Kohn-Sham orbitals  $\phi_i(\vec{r})$ 's are required to satisfy

$$\rho(\vec{r}) = \sum_i^N |\phi_i(\vec{r})|^2 , \quad (\text{D.2})$$

where  $N$  is the total number of electrons in the system. Now on multiplication of Eq. (D.1) by  $\phi_i^*(\vec{r})$ , summing it over  $i$  and after dividing by  $\rho(\vec{r})$  will give

$$v_{ks}(\vec{r}) = \frac{1}{\rho(\vec{r})} \sum_i^N \left\{ \frac{1}{2} \phi_i^*(\vec{r}) \nabla^2 \phi_i(\vec{r}) + \varepsilon_i |\phi_i(\vec{r})|^2 \right\} . \quad (\text{D.3})$$

van Leeuwen and Berends (LB) has defined an iterative scheme for generating the potential using Eq. (D.3). The calculated potential corresponds to the given density  $\rho(\vec{r})$ . The iterative procedure goes as follows: Suppose at some stage of the iteration we have calculated orbitals  $\phi_i^n(\vec{r})$  with eigenvalues  $\varepsilon_i^n$  and density  $\rho^n(\vec{r})$ . In the next step according to this procedure the new potentials is defined as

$$v^{n+1}(\vec{r}) = \frac{1}{\rho(\vec{r})} \sum_i^N \left\{ \frac{1}{2} \phi_i^{n*}(\vec{r}) \nabla^2 \phi_i^n(\vec{r}) + \varepsilon_i^n |\phi_i^n(\vec{r})|^2 \right\} = \frac{\rho^n(\vec{r})}{\rho(\vec{r})} v^n(\vec{r}) . \quad (\text{D.4})$$

The potential obtained by Eq. (D.4) will be further used to calculate new orbitals and a new density and define in the same way a new potential for the next iteration. This procedure is continued until the density calculated from the orbitals is the same as the given density. The procedure has to be continued until

$$\max_r \left| 1 - \frac{\rho^n(\vec{r})}{\rho(\vec{r})} \right| < \epsilon , \quad (\text{D.5})$$

with  $\epsilon$  as a given threshold. In order to achieve convergence one should take care to keep the prefactor in the last term of Eq. (D.4) in each iteration within an acceptable range:

$$1 - \delta < \frac{\rho^n(\vec{r})}{\rho(\vec{r})} < 1 + \delta . \quad (\text{D.6})$$

The scheme is not guaranteed to converge as there are densities which are not non-interacting  $v$ -representable. However, many such densities which are not  $v$ -representable by one determinant are  $v$ -representable by linear combination of determinants [60]. In any case if the procedure converges then its limit is unique as guaranteed by the Hohenberg-Kohn theorem [8] applied to non-interacting electronic systems [9].

For the first time we have successfully implemented the iterative procedure mentioned above for generating potentials for non-interacting electrons in one dimension. First solve the required 1D Schrödinger equation with a initial starting potential and obtain the density. Then use the density of the previous iteration to modify the starting potential for the next iteration using the van-Leeuwen-Baerends approach as discussed earlier. Care should be taken so that during the iterative procedure if at some particular iteration the potential has zero crossing then in the subsequent iterations there will be no further improvement of the potential. If it

is negative then it will become more and more negative further. So in order to avoid these the starting potential be such that it does not have any zero crossings or attain negative values during the iterative procedure. Our results using the LB approach is discussed in the second and third chapter of the thesis.

# Appendix E

## Variational Principle for Steady-States in Floquet Formalism

In this appendix, we show that if one confines the quasienergies to a range such that they go to their unperturbed counterpart when the time-periodic potential is turned off, then there is a well defined ground-state quasienergy satisfying the minimum variational principle. We first point out that defining the eigenenergies as suggested above is equivalent to taking the corresponding quasienergy state such that it has no free time-dependent factor of the form  $(\sum_p e^{ip\omega t})$ , where  $\{p = 0, \pm 1, \pm 2, \dots, \pm i, \dots\}$ , associated with it as the strength of the time-periodic potential goes to zero. Let us denote such quasienergy states as  $\phi_0(\vec{r}, t), \phi_1(\vec{r}, t), \dots, \phi_i(\vec{r}, t), \dots$  with the corresponding eigenvalues  $\varepsilon_0, \varepsilon_1, \dots, \varepsilon_i, \dots$  such that  $\varepsilon_0 < \varepsilon_1 < \dots < \varepsilon_i < \dots$ . The quasienergy states satisfy the normalization condition

$$\int \phi_m^\dagger(\vec{r}, t) \phi_n(\vec{r}, t) d\vec{r} = \delta_{mn} \quad , \quad (\text{E.1})$$

as is easily seen by the hermiticity of the Hamiltonian coupled with its adiabatic switching.

Let us consider a Hamiltonian  $\hat{H}(\vec{r}, t) = \hat{H}_0(\vec{r}) + \hat{v}(\vec{r}, t)$  with  $\hat{v}(\vec{r}, t)$  being time periodic. Now a trial periodic function  $\Phi(\vec{r}, t)$  can be expanded in terms of unperturbed states  $\bar{\phi}_i(\vec{r})$ 's of  $\hat{H}_0(\vec{r})$  and its associated states  $\bar{\phi}_i(\vec{r}) e^{ip\omega t}$  as

$$\begin{aligned}
\Phi(\vec{r}, t) &= a_0 \bar{\phi}_0(\vec{r}) + a_1 \bar{\phi}_1(\vec{r}) + \dots + a_i \bar{\phi}_i(\vec{r}) + \dots \\
&\quad + a_0^{(\omega)} \bar{\phi}_0(\vec{r}) e^{i\omega t} + a_1^{(\omega)} \bar{\phi}_1(\vec{r}) e^{i\omega t} + \dots + a_i^{(\omega)} \bar{\phi}_i(\vec{r}) e^{i\omega t} + \dots \\
&\quad + a_0^{(2\omega)} \bar{\phi}_0(\vec{r}) e^{i2\omega t} + a_1^{(2\omega)} \bar{\phi}_1(\vec{r}) e^{i2\omega t} + \dots + a_i^{(2\omega)} \bar{\phi}_i(\vec{r}) e^{i2\omega t} + \dots \\
&= \left( \sum_p a_0^{(p\omega)} e^{ip\omega t} \right) \bar{\phi}_0(\vec{r}) + \left( \sum_p a_1^{(p\omega)} e^{ip\omega t} \right) \bar{\phi}_1(\vec{r}) + \dots \\
&\quad + \left( \sum_p a_i^{(p\omega)} e^{ip\omega t} \right) \bar{\phi}_i(\vec{r}) + \dots
\end{aligned} \tag{E.2}$$

In the expansion above, each coefficient  $a_i^{(p\omega)}$  ( $p \neq 0$ ) should become zero as  $\hat{v}(\vec{r}, t) \rightarrow 0$ . Otherwise coefficient  $a_i^{(p\omega)}$  would have two components: one arising from the applied time-dependent potential causing unperturbed states to mix and the other is the coefficient of physically equivalent state  $\phi_i e^{ip\omega t}$ . To see this let us add  $\Phi(\vec{r}, t) e^{i\omega t}$  to  $\Phi(\vec{r}, t)$  to get

$$\begin{aligned}
\Phi'(\vec{r}, t) &= a_0 \bar{\phi}_0(\vec{r}) + a_1 \bar{\phi}_1(\vec{r}) + \dots + a_i \bar{\phi}_i(\vec{r}) + \dots \\
&\quad + (a_0^{(\omega)} + a_0) \bar{\phi}_0(\vec{r}) e^{i\omega t} + (a_1^{(\omega)} + a_0) \bar{\phi}_1(\vec{r}) e^{i\omega t} + \dots + (a_i^{(\omega)} + a_0) \bar{\phi}_i(\vec{r}) e^{i\omega t} + \dots \\
&= (1 + e^{i\omega t}) \Phi(\vec{r}, t)
\end{aligned} \tag{E.3}$$

For normalized wavefunctions the factor in front of  $\Phi(\vec{r}, t)$  gives rise to a purely time-dependent phase factor and can therefore be ignored. This is best illustrated if we look at the unperturbed time-independent problem in the Floquet formulation.

In the case of time-independent problem in Floquet formulation the time-dependent wavefunction corresponding to a state  $\phi_i(\vec{r})$  can be written in two equivalent forms as

$$\Psi_i(\vec{r}, t) = e^{-iE_i t} \phi_i(\vec{r}) \equiv e^{-i(E+p\omega)t} \underbrace{\phi_i(\vec{r}) e^{+ip\omega t}}_{= \phi_i(\vec{r}, t)} \quad , \tag{E.4}$$

where  $\phi_i(\vec{r}, t)$  are the Floquet states satisfies

$$\left( \hat{H}(t) - i \frac{\partial}{\partial t} \right) \phi_i(\vec{r}, t) = (E_i + p\omega) \phi_i(\vec{r}, t) \quad . \tag{E.5}$$

However, each  $\phi_i(\vec{r}, t)$  gives the same  $\Psi_i(\vec{r}, t)$ . So they are all physically equivalent. If we were to expand a trial Floquet function in terms of  $\{\phi_i(\vec{r})\}$ ,  $\{\phi_i(\vec{r}) e^{i\omega t}\}$ ,  $\dots$ ,  $\{\phi_i(\vec{r}) e^{ip\omega t}\}$ , all it

will do is give a complicated time-dependent phase factor in front of  $\phi_i(\vec{r})$ . How does this physical equivalence gets reflected variationally is discussed next.

Let us take a trial periodic wavefunction as [140] for the unperturbed problem as

$$\Phi(\vec{r}, t) = \sum_{ip} a_i^{(p)} \phi_i(\vec{r}) e^{ip\omega t} , \quad (\text{E.6})$$

with all  $\phi$ 's and their equivalent states included. The quasienergy of the system is

$$\begin{aligned} & \frac{1}{T} \int \left\langle \Phi(\vec{r}, t) \left| \hat{H}(t) - i \frac{\partial}{\partial t} \right| \Phi(\vec{r}, t) \right\rangle dt \\ &= \frac{1}{T} \int \sum_{ip, jq} a_i^{(p)*} \phi_i^*(\vec{r}, t) e^{-ip\omega t} (E_j + q\omega) a_j^{(q)} \phi_j(\vec{r}, t) e^{iq\omega t} d\vec{r} dt \\ &= \sum_{ip, jq} \delta_{ij} \delta_{pq} (E_j + q\omega) a_i^{(p)*} a_j^{(q)} \\ &= \sum_{ip} |a_i^{(p)}|^2 (E_i + p\omega) . \end{aligned} \quad (\text{E.7})$$

Since  $\Phi(\vec{r}, t)$  is normalized at all times, to obtain  $a_i^{(p)}$ , the functional above is made stationary [139] with the condition

$$\frac{1}{T} \int \langle \Phi(\vec{r}, t) | \Phi(\vec{r}, t) \rangle = \sum_{ip} |a_i^{(p)}|^2 = 1 . \quad (\text{E.8})$$

Using the techniques of Lagrange multipliers this leads to the equation

$$a_i^{(p)} [E_i + p\omega - \mu] = 0 , \quad (\text{E.9})$$

where  $\mu$  is the Lagrange multiplier and gives the quasienergy of the system. The equation above gives  $\mu = E_i + p\omega$  with  $a_i^{(p)} \neq 0$  but all other  $a_i^{(p)}$ 's vanishes. Thus stationary variational procedure picks Floquet states from only one particular zone (*i.e.* 'p' is fixed) to represent the system. However, irrespective of which 'p' we take, the final wavefunction is the same. Thus Floquet states from different zones do not represent different states. As such one may restrict oneself to only one zone in the expansion of the Floquet state. Question that arise is: does restricting oneself to one particular zone lead to a minimum principle? Actually, it does

as we will now show. It is best shown for  $p = 0$  zone but the result is true for any 'p'. Thus

$$\Phi(\vec{r}, t) = \sum_{i,p=0} a_i^{(0)} \phi_i(\vec{r}) , \quad (\text{E.10})$$

$$\langle \Phi | \hat{H} - i \frac{\partial}{\partial t} | \Phi \rangle = \sum_i |a_i^{(0)}|^2 \varepsilon_i > \sum_i |a_i^{(0)}|^2 \varepsilon_0 , \quad (\text{E.11})$$

by the standard variational argument.

Having discussed the time-independent case, we now discuss the time-dependent case. In this case the basis functions are the Floquet state  $\phi_i(\vec{r}, t)$  of the full Hamiltonian and their physically equivalent counterparts  $\phi_i(\vec{r}, t)e^{ip\omega t}$ . If we expand a trial Floquet state  $\Phi(\vec{r}, t)$  as

$$\Phi(\vec{r}, t) = \sum_{ip} c_i^{(p)} \phi_i(\vec{r}, t) e^{ip\omega t} , \quad (\text{E.12})$$

we again argue that including Floquet states from all zones does not really give us any new information. So the expansion should be restricted to only one zone. Mathematically it is again shown as was done above. The approximate quasienergy is given as

$$\frac{1}{T} \int \langle \Phi | \hat{H} - i \frac{\partial}{\partial t} | \Phi \rangle dt = \sum_{i,p'} |c_i^{(p')}|^2 (\varepsilon_i + p\omega) . \quad (\text{E.13})$$

So the stationarity [139] of the time averaged expectation value in Eq.E.13 under the constraint  $\frac{1}{T} \int \langle \Phi | \Phi \rangle dt = 1$  gives

$$c_i^{(p)} \{ \varepsilon_i + p\omega - E \} = 0 \quad (\text{E.14})$$

implying again that  $E = \varepsilon_i + p\omega$  with  $c_i^{(p)}$  - only in one zone. However, Floquet states from each zone give the same wavefunction  $\Psi = e^{-i(E+p\omega)t} \phi_i(\vec{r}, t)e^{ip\omega t}$ . Thus in expanding an approximate  $\Phi(\vec{r}, t)$  one can restrict oneself to one particular zone. This leads to a minimum principle following the standard arguments.

The question arises how do we make sure that the trial wavefunction comprises Floquet

states from one particular zone only. This is best done for  $p = 0$  zone by making sure that if we take  $v(\vec{r}, t) = 0$ , the trial wavefunction must be time-independent. If Floquet states from other zones are also present in the trial wavefunction, it will not become time-independent as the time-dependent potential becomes zero. With such a trial wavefunction the quasienergy follow a minimum principle as shown above.

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