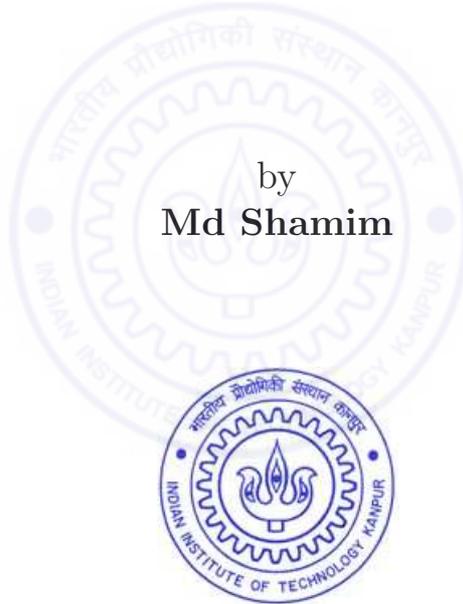


**Construction of Exchange and Correlation Energy
Functionals for Excited States in Time-independent
Density Functional Theory.**

*A Thesis Submitted
in Partial Fulfillment of the Requirements
for the Degree of*
Doctor of Philosophy

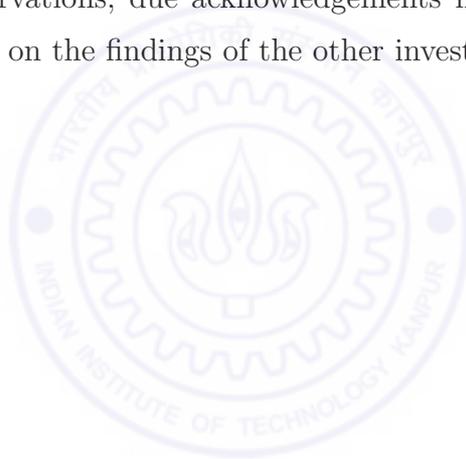
by
Md Shamim



to the
**DEPARTMENT OF PHYSICS
INDIAN INSTITUTE OF TECHNOLOGY KANPUR**
July 2013

STATEMENT

I hereby declare that the matter embodied in this thesis entitled "*Construction of Exchange and Correlation Energy Functionals for Excited States in Time-independent 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 the general practice of reporting scientific observations, due acknowledgements has been made everywhere the work described in based on the findings of the other investigators.



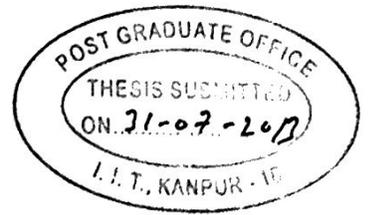
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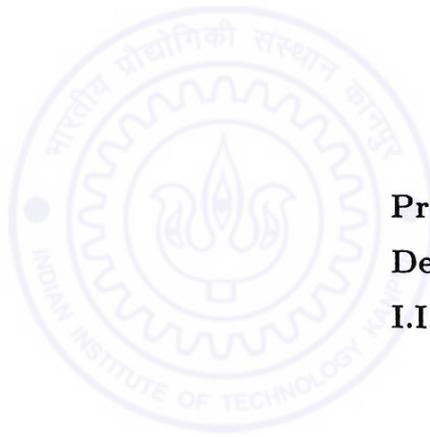
July 2013



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CERTIFICATE

It is certified that the work contained in the thesis entitled "*Construction of Exchange and Correlation Energy Functionals for Excited States in Time-independent Density Functional Theory.*", by *Md Shamim*, has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.



M. K. Harbola
30-7-2013

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July 2013

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July 2013

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Synopsis

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Density Functional Theory (DFT) for excited states has been taking shape over the years. In this theory, energy of an excited state is expressed as bi-functional of the excited state and ground state densities. Application of excited state DFT in practical calculation requires exchange and correlation energy functionals for excited states. In the work presented in this thesis we have made attempts to construct exchange and correlation energy functional for excited states. We also present exchange potentials for excited states.

We begin the study of excited states with the analysis of excited state electron density of real systems. We theoretically investigate the asymptotic decay of density for excited states including the auto-ionizing states. To support our theoretical finding, we present numerical results obtained from densities that have been generated using accurate Monte-Carlo calculations on some atomic excited states.

Construction of exchange and correlation energy functional for excited states is necessary if we want to apply density functional theory (DFT) to study excited states. Preliminary work on exchange energy functional by our group has led to the LDA exchange energy functional for excited states. This functional leads to accurate results for excitation energies of atoms and also accurate band gap for a range of solids. Therefore, in order to test the generality of such functional, in the present work, we use the same idea to construct exchange energy functional for higher excited states having set of two gaps in the occupation of orbitals. We perform calculations of excitation energy for the cases involving up to four electrons and show that the functional is accurate in these cases. This shows the generality of our functional.

Having demonstrated the generality of constructing LDA for excited states energies, we next ask if the functional can be made more accurate by including gradient correction in it. For this we include Becke and Perdew-Wang correction into the LDA functionals and show that accurate exchange and total energies for excited states are obtained with the incorporation of these corrections.

Mathematically, the exchange potential is given by the functional derivative of the exchange energy functional. However it is not easy to take the functional derivative of the proposed functional. At present, LDA exchange potential for excited states is not known. In the past, most of the calculation for excited states has been done by employing ground state local spin density approximation(LSDA) for exchange potential which is nothing but Dirac's exchange potential. Therefore, in this work we also address the problem of obtaining exchange potential for excited states. Owing to difficulty in calculating the functional derivative of the excited state energy functional, exchange potential has to be either obtained directly or modeled. We explore both the approaches in this thesis.

In the following, chapter wise description of the thesis is presented briefly.

The first chapter 1 of the thesis is an introduction to density functional theory covering the ground states, the excited states, important issues in excited state density

functional theory and the motivation for our work.

In chapter 2, we first analytically show that the asymptotic decay of density for the excited state including the auto-ionizing states is also dictated by the first allowed ionization energy of the system. We support our theoretical finding with numerical results obtained by employing accurate Monte-Carlo densities for excited states.

In chapter 3 we test the generality of the idea invoked in construction of exchange functional for excited states by our group. For this, we construct similar exchange energy functional for higher excited states having a set of two gaps in the occupation of orbitals. We apply the exchange energy functional so obtained to calculate excitation energies of such excited states of atoms. The cases considered here involve excitation of one to four electrons.

In chapter 4, we demonstrate that very accurate exchange energy and total energy for excited states are obtained within density functional formalism if Becke correction to exchange energy or Perdew Wang type correction is incorporated into the LDA exchange energy functional for excited states. We show that exchange and total energies obtained with this approach are very close to the Hartree Fock results.

In chapter 5, we apply the idea of splitting the k-space which has been used to construct exchange energy functionals, to write the exchange potential for excited states. We have constructed an accurate exchange potential by approximately calculating the functional derivative of the exchange energy functional described in the previous chapter. We arrive at the same exchange potential for excited states through a different route which involves calculation of Hartree-Fock exchange potential for excited states in split k-space. Further, we make changes in the potential based on the analysis of results to make it more accurate. This gives a model exchange potential.

We also present an exchange potential for excited states in local density approximation which is obtained from the work function formalism. Here also we employ the idea of splitting the k-space. Although this potential is totally different from the previous one,

this also leads to reasonably accurate results.

In chapter 6, we end the thesis with summary and brief discussion on further scopes in excited state density functional theory.

In appendix A, we discuss calculation of correlation energies for excited states. We describe our approach which is basically an extension of Colle-Salvetti's expression for correlation energy to the excited states constructed by us. Here we split the kinetic energy functional to obtain appropriate expression for correlation energy for excited states. The preliminary calculation of correlation energy shows that excited state correlation energy functional obtained by in this manner leads to similar results as the ground state functional. Therefore, this requires further exploration which we hope to do in our future work.



List of Publications

1. Study of asymptotic decay of electronic density for excited states including auto-ionizing states of many-electron systems: Md. Shamim and M K Harbola, Chem. Phys. Lett. **464**, 135 (2008).
2. Application of an excited state LDA exchange energy functional for the calculation of transition energy of atoms within time-independent density functional theory : Md. Shamim and M K Harbola, J. Phys B: At. Mol.Opt.Phys. **43**, 215002 (2010).
3. Exchange Potential for excited states: A self consistent DFT calculation (arXiv:1103.4043): Md. Shamim and M K Harbola
4. Accurate total energy for excited states: Inclusion of gradient corrections (arXiv:1201.5970): Md Shamim and M K Harbola,
5. Excited-state density functional theory: Manoj K. Harbola, M. Hemanadhan, Md. Shamim, P. Samal J. Phys.: Conf. Ser. 388, Number 1, 012011-626 (2012)
6. Time-independent excited-state density-functional theory: M.K. Harbola, Md. Shamim, P. Samal, M. Rahman, S. Ganguly and A. Mookerjee AIP Conference Proceedings 1108, 54 (2009).
7. Energy functionals for excited states: M.K. Harbola, M. Hemanadhan, Md. Shamim and P.Samal *In Concepts and Methods in Modern Theoretical Chemistry, Vol.1: Electronic Structure and Reactivity* Editors: S.K. Ghosh and P.K. Chattaraj, CRC Presss, 99-118(2013)

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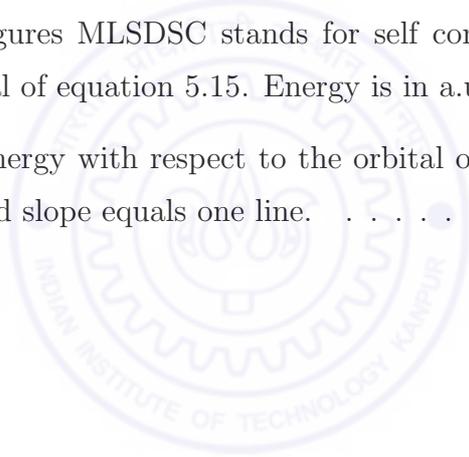
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Chapter 1

Introduction to density functional theory

Thomas(1927) and Fermi(1928) [1, 2] were the first to introduce the concept of density based theory for atomic systems. However, their idea was not formalized until 1964 when P. Hohenberg and W. Kohn [3] gave a boost to it expressing variational principle in terms of the density. They not only showed that ground state density alone fixes a system exactly but also proved that density of a system can be used as a variational parameter. This is known as the Hohenberg-Kohn theorem. Later in 1965 Kohn and Sham [4] gave a scheme which reduces the tedious task of dealing with many particle Schrödinger equation of real systems to a relatively easy to solve set of one-particle equations of a virtual system. Riding on the above mentioned theorem, the proposed theory, now known as density functional theory(DFT), has evolved to become one of the most widely used techniques in condensed matter physics and in quantum chemistry [5,6,82,83]. DFT has been employed to study wide range of problems involving calculations of various quantities such as stable configuration of molecules, bond length, bond angle, band structure of solids, excitation energies.

The popularity gained by DFT has come due to simplicity of the idea invoked in its formulation and due to ease of its implementation [7,43] . DFT provides an alternative

to wave function based approach where one is faced with difficult task of dealing with particle-particle interaction term in the Hamiltonian of a many particle system to which Kohn referred [8] as insurmountable barrier. Due to presence of the particle-particle interaction term, the many-electron Schrödinger equation cannot be solved exactly even for two particle systems, such as He, and difficulty goes on multiplying as the number of particles increases. Many theories have been developed to approximately solve the Schrödinger equation for many particle system. Some of these are Hartree theory, Hartree-Fock theory and configuration interaction method. In Hartree theory, wave function of many particle system is taken to be the product of the individual wave function of the particles [9]. Thus it is an independent particle model in which electrons move in an average potential created by other electrons. Hartree-Fock theory takes the Pauli exclusion principle into account, which demands that wave function of Fermions must be antisymmetric with respect to the exchange of two Fermions. In Hartree-Fock theory many particle wave function is approximated by a single Slater determinant [10,11] made up of single particles orbitals. Thus, Hartree-Fock theory takes only Fermi correlation into account. It does not incorporate the correlation effect among the electrons arising due to Coulomb interaction. Therefore, exact treatment of electronic systems requires one to go beyond HF theory. This is done by expressing the wave function as a linear combination of various possible Slater determinants. This leads to what is known as configuration interaction technique [12]. However as the number of determinants increases, doing CI becomes difficult. Therefore a more feasible technique is needed for doing many particle calculations. In such unmanageable situation, DFT proves to be handy [13] .

The Hohenberg-Kohn formulation of DFT does variational minimization of energy with respect to the density. This in principle leads to the true ground state of the system. However, for its direct implementation one is required to express energy as functional of density. So far it has not been possible to do so. Therefore one resorts to some approximations. Thomas Fermi energy functional is the first of such approximations.

In Kohn-Sham formulation of density functional theory problem of dealing with

particle-particle interaction term is tackled by replacing the effect of non local particle-particle interaction by an effective local potential. Therefore, in Kohn-Sham density functional theory an interacting many particle system gets mapped onto a non-interacting many particle system where particles move in a local effective potential. Thus major focus of DFT research is to find an appropriate energy functional and the corresponding local effective potential which will give the same density as the actual one. This appears to be more tractable path compared to solving the Schrödinger equation with the N-particle interaction term in it.

In DFT various quantities are expressed as functional of density. However these functionals are not known exactly. To construct them approximately, ideas are borrowed from wave-functional approach. For example, to construct exchange energy functional one uses the Hartree-Fock theory results of many particle system. To construct correlation energy functional one employs results of Monte Carlo calculations [14] for homogeneous electron gas. Thus, in DFT one does not have to worry much about constructing functional as far as ground states are concerned. We have the luxury of using various expressions developed in various theories which precede DFT. Since it is always difficult to derive expressions for quantities of a real system, expressions are developed for model systems and those expressions are used in approximate sense for the real system. In DFT, one of the most widely used approximation is the local density approximation (LDA) [15]. Here one uses the formulae derived for homogeneous electron gas (HEG). For inhomogeneous system one replaces the HEG density by the local density of the real system. This gives approximate estimation in calculation of various quantities.

LDA functionals are simple to construct but these functionals fail to satisfy certain conditions [16] such as asymptotic limit of energy density and potential and the correct one particle limit. Density of Coulombic electron system falls off exponentially in the asymptotic limit for a bound system [17]. Therefore LDA potential also has exponential fall in the asymptotic limit, which is not correct. For example, in the asymptotic limit exchange energy density actually falls as $-\frac{1}{2r}$ [18] whereas the LDA approximation for

it gives exponential decay. Incorrect asymptotic limit for exchange potential affects the orbital energies of the system significantly.

To improve the LDA one needs to take into account the spatial variation in density as well. This is done by systematically including gradient correction to density. It is known as gradient expansion approximation (GEA) [19]. It has been shown that accurate density functionals can be constructed by including gradient terms in such a way that the resulting functionals satisfy certain exact properties. This approach has led to what is known as generalized gradient approximation (GGA) [20]. Inclusion of Laplacian of density gives meta-generalized approximation (meta-GGA) [23]. As noted above, in these approximation gradient of density is included into the existing LDA functionals semi-empirically.

GGA and meta-GGA have been constructed in such a manner that these functionals satisfy many of the conditions mentioned above. Therefore, such corrections are expected to improve the results in most of the cases. Becke empirical correction for exchange energy [24] and van Leeuwen Baerend's [27] and Umezawa's [28] correction for exchange potential are such examples.

An important issue with density functionals is related to the one particle limit of the exchange correlation functionals. In the one particle limit exchange and correlation energy functionals and Hartree term in the expression for total energy should cancel each other. However this does not happen with most of the approximate functionals. That means functionals have self interaction error. Therefore as pointed out by Fermi and Amaldi [29], one needs to incorporate the self interaction correction (SIC) for each electron while employing such approximations.

Exact density functionals are also expected to show derivative discontinuity [31] and produce correct shell structure [30].

For calculating ground state properties, DFT pervades all fields. It is being used in physics, chemistry, biology, material engineering; i.e; in most of the present day research

related to materials. Now the question arises, can there be a DFT for excited-states also? The answer is in affirmative but extension of DFT to excited-states is more involved in comparison to ground states. For excited-states one has to look for an alternative to Hohenberg Kohn theorem because one-to-one correspondence between density of excited-state and potential may not exist. Furthermore, ground state functionals cannot not be applied to excited-states. Therefore, in excited-state, one has to first construct functionals specific to excited-states. We discuss more about the construction of functionals for excited-states in the following chapters.

Excited-state density functional theory has been formulated in various ways namely, Theophilou's equiensemble approach [38] and its extension to include weighted ensemble by Gross *et al* [37], Görling's [93] constrained search formulation, constrained search formulation of Levy Nagy [55] , Fritch's method which is based on partitioning of the wave function [96]. Finally Görling and Levy-Nagy formulations have been combined nicely by Samal and Harbola [75] and this forms the basis of present work. Formulation by Görling, Levy-Nagy and their fine tuning by Samal and Harbola has put excited-state density functional theory on a firm footing. To apply the theory, however, requires functionals for excited-states.

In the absence of excited-state functionals, normal trend has been to use ground state functionals for the excited-states [32]. But except for the lowest excited-states for given symmetry, this does not work for other excited-states, nor is it justified to apply it to other excited-states. The work presented in this thesis is concerned about the construction of exchange and correlation functionals and corresponding potentials for excited-states. We have constructed exchange functional and potential for excited-states and have made an attempt to construct correlation functional for excited-states by extending Lee Yang Parr correlation energy functional [104] to excited-states.

As stated at the beginning, functionals are developed using their various limits. An important aspect of this has been the asymptotic limits of density as that determines the

effective potential in that region. A study of asymptotic behaviour of density therefore also forms part of this thesis.

In the following a brief overview of basics of density functional theory is presented.

1.1 Density as a variable

Density of a system of particles is an observable. We can get density profile of electrons in a material through XRD, TEM, STM etc. Therefore density is good choice as variable to describe an electronic system. An advantage of using density as a variable instead of wave function is that, wave-function of a system of N particles is a function of $3N$ variables while density of the same system is a function of only 3 variables. Therefore, irrespective of the number of the particles, use of density provides some ease in computation. A related quantity of physical importance is probability density. Density of a system of particles is given as,

$$\rho(\mathbf{r}) = N \int \Psi_N^*(\mathbf{r}_1 = \mathbf{r}, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N) \Psi_N(\mathbf{r}_1 = \mathbf{r}, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N) d\mathbf{r}_2 d\mathbf{r}_3 \dots d\mathbf{r}_N \quad (1.1)$$

where Ψ_N is wave function of the particles. For Fermions the wave function has to be antisymmetric with respect to exchange of coordinates. Therefore, (ignoring spin)

$$\Psi_N(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N) = -\Psi_N(\mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_3, \dots, \mathbf{r}_N) \quad (1.2)$$

Having discussed that it is desirable to use density as variable, one can ask, is it really possible to formulate a theory in terms of density? The answer is in the affirmative. We will come to a detailed discussion about it later in this thesis. Right now, we first discuss the use of density as a basic variable for ground states. This began with the work of Thomas and independently that of Fermi. Idea of Thomas and Fermi (TF) was to express the total energy of the system as a functional of density. For this, they used the expressions derived for homogeneous electron gas (HEG) to approximately write the

energy functional for atomic system. Therefore if $\epsilon(\rho)$ is the energy per particle of HEG of density ρ and $\rho(\mathbf{r})$ be the local density of the given system then total energy of the system can be written as,

$$E[\rho] = \int \epsilon(\rho)\rho(\mathbf{r})d\mathbf{r} \quad (1.3)$$

Using kinetic energy per particle for HEG $t(\rho) = \frac{3}{10}(3\pi^2)^{\frac{2}{3}}\rho^{\frac{2}{3}}$, the total kinetic energy of electrons in an interacting systems as a functional of local electron density is written as,

$$T[\rho] = \frac{3}{10}(3\pi^2)^{\frac{2}{3}} \int \rho^{\frac{5}{3}}(\mathbf{r})d\mathbf{r} \quad (1.4)$$

Throughout the thesis we use atomic units. Coulomb energy for interacting particles having density $\rho(\mathbf{r})$ is given by,

$$E_{coul} = \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \quad (1.5)$$

and interaction energy with an external potential v_{ext} is given by,

$$E_{ext} = \int \rho(\mathbf{r})v_{ext}(\mathbf{r})d\mathbf{r} \quad (1.6)$$

Thus total energy of a system of electrons in TF theory is written as,

$$\begin{aligned} E[\rho] &= T[\rho] + E_{coul}[\rho] + E_{ext}[\rho] \\ &= \frac{3}{10}(3\pi^2)^{\frac{2}{3}} \int \rho^{\frac{5}{3}}(\mathbf{r})d\mathbf{r} + \int \rho(\mathbf{r})v_{ext}(\mathbf{r})d\mathbf{r} + \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \end{aligned} \quad (1.7)$$

The extended version of TF theory which also includes exchange energy is known as Thomas Fermi Dirac (TFD) theory. Using exchange energy per particle for HEG $\epsilon_x = -\frac{3k_f}{4\pi}$ where, $k_f = (3\pi^2\rho)^{1/3}$ is Fermi wave vector, we get the exchange energy for an interacting particle system to be,

$$E_X[\rho] = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{\frac{1}{3}} \int \rho^{\frac{4}{3}}(\mathbf{r})d\mathbf{r} \quad (1.8)$$

Thus total energy of a system of electrons in extended TF theory is written as,

$$E[\rho] = T_s[\rho] + E_{coul}[\rho] + E_{ext}[\rho] + E_X[\rho]$$

$$\begin{aligned}
&= \frac{3}{10}(3\pi^2)^{\frac{2}{3}} \int \rho^{\frac{5}{3}}(\mathbf{r})d\mathbf{r} + \int \rho(\mathbf{r})v_{ext}(\mathbf{r})d\mathbf{r} + \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}d\mathbf{r}' \\
&- \frac{3}{4} \left(\frac{3}{\pi}\right)^{\frac{1}{3}} \int \rho^{\frac{4}{3}}(\mathbf{r})d\mathbf{r}
\end{aligned}$$

Thus, from the knowledge of density of electrons total approximate energy is calculated. This is the first step towards density functional theory.

Thomas and Fermi [1,2] applied density based energy functionals to calculate ground state energy of atoms. Although the calculations were only approximate and did not yield very good results, it laid down the the idea of using density as a variable in quantum chemical calculations.

In addition to inaccurate numerical results for atoms, Thomas-Fermi model has some serious problems such as, non-existence of molecular binding, zero chemical potential, no shell structure in density profile, divergence of density at the nucleus et. Some attempts were made to improve upon the TFD theory by inclusion of Weizsacker's correction [25] to kinetic energy term. This does rectify some of the drawbacks of TFD model but is still far from being completely satisfactory. For example, in TFD-W model density is no more divergent at the nucleus, asymptotically density shows exponential decay and there is glimpse of molecular binding but other features are still missing. Therefore, one needs to go beyond TFD model [26].

1.2 Hohenberg Kohn formulation of DFT for ground state

In 1964 P. Hohenberge and W. Kohn enunciated and proved two theorems which laid the foundations of modern density functional theory. In the following we state the two theorems and also present proof for them.

Theorem 1: It states that ground state electron density of a system uniquely fixes

the external potential up to an additive constant and thus determines the Hamiltonian of the system.

$$\rho_{ground} \rightarrow v_{ext}(unique) \quad (1.9)$$

Thus, ground state electron density of a system determines all the properties of the system. For example expectation value of an operator $\langle \hat{O} \rangle$ can be written in terms of the density as

$$\langle \hat{O} \rangle = O[\rho] \quad (1.10)$$

In essence, we can say that this theorem talks about the invertibility of the equation 1.1. That is,

$$\Psi = \Psi[\rho] \quad (1.11)$$

Therefore, expectation value of Hamiltonian can also be written similarly,

$$\langle \hat{H} \rangle = E[\rho] \quad (1.12)$$

More explicitly we can write as,

$$E[\rho] = T[\rho] + E_{ee}[\rho] + E_{ext}[\rho] \quad (1.13)$$

Where, $T[\rho]$, $E_{ee}[\rho]$ and $E_{ext}[\rho]$ represent kinetic energy functional, energy functional corresponding to electron-electron interaction and energy functional corresponding to interaction of electrons with the external potential. Since in all materials the operator for the kinetic energy and electron-electron interaction energy is the same and their value changes only because of the external potential, $T[\rho] + E_{ee}[\rho]$ is a universal functional of the density. It is denoted by $F[\rho]$. Therefore,

$$F[\rho] = \langle \Psi[\rho] | -\frac{1}{2} \sum_i \nabla_i^2 | \Psi[\rho] \rangle + \langle \Psi[\rho] | \frac{1}{2} \sum_{ij} \frac{1}{r_{ij}} | \Psi[\rho] \rangle \quad (1.14)$$

If v_{ext} is the external potential then $E_{ext} = \int v_{ext}(\vec{r})\rho(\vec{r})d\mathbf{r}$. Therefore,

$$E[\rho] = F[\rho] + \int v_{ext}(\vec{r})\rho(\vec{r})d\mathbf{r} \quad (1.15)$$

Theorem2 : This theorem establishes variational principle in terms of the ground state density. It states that value of the energy density functional is a minimum for the exact ground state density. Therefore if ρ represents density of some configuration of the system and ρ_0 the ground state density then,

$$E_{ground} = E[\rho_0] \leq E[\rho] \quad (1.16)$$

The first Hohenberg Kohn theorem has been illustrated in many ways. One interesting illustration is through Kato's theorem [7]. It says that, since electronic density profile of a system fixes the locations of all the nuclei and gives the atomic number of atom corresponding to the cusp in density profile, therefore density fixes the Hamiltonian itself. Kato's theorem is given as,

$$Z_n = -\frac{a_0}{2n(\mathbf{r})} \frac{dn}{dr} \Big|_{\mathbf{r} \rightarrow \mathbf{R}_n} \quad (1.17)$$

A rigorous proof of Hohenberge Kohn theorem follows from *reductio ad absurdum* as given below.

Let us suppose that a density ρ of the system corresponds to two different external potentials v_1 and v_2 differing by more than a constant. And let Ψ_1 and Ψ_2 be the ground state wave functions corresponding to the two potentials respectively and E_1 and E_2 be the corresponding ground state energies. Then by the variational principle;

$$\begin{aligned} E_1 &< \langle \Psi_2[\rho] | H_1 | \Psi_2[\rho] \rangle \\ &< \langle \Psi_2[\rho] | [H_2 + (v_1 - v_2)] | \Psi_2[\rho] \rangle \\ &< E_2 + \int (v_1 - v_2)\rho d\mathbf{r} \end{aligned} \quad (1.18)$$

similarly,

$$\begin{aligned}
 E_2 &< \langle \Psi_1[\rho] | H_2 | \Psi_1[\rho] \rangle \\
 &< \langle \Psi_1[\rho] | [H_1 + (v_2 - v_1)] | \Psi_1[\rho] \rangle \\
 &< E_1 + \int (v_2 - v_1) \rho d\mathbf{r}
 \end{aligned} \tag{1.19}$$

adding equations 1.18 and 1.19 we get,

$$E_1 + E_2 < E_1 + E_2 \tag{1.20}$$

This is illogical! Thus we see that our assumption that two different potentials can give the same density is wrong. It means no density is ground state density for more than one external potential [66, 68, 69]. Restriction to ground state density arises from the use of variational principle for energy. Proof for the second Hohenberg Kohn theorem follows directly from the equation 1.11. As ground state wavefunction gives minimum energy so will the ground state density.

How does one move ahead with these two theorems and develop a theory that can be implemented? To study a given system we first look for a density which minimizes the energy and also gives correct number of electrons. Therefore we minimize $E[\rho]$ with the constraint that [67],

$$\int \rho(\mathbf{r}) d\mathbf{r} = N \tag{1.21}$$

We thus have the following variational equation,

$$\delta \{ E[\rho] - \mu \int \rho(\mathbf{r}) d\mathbf{r} \} = 0 \tag{1.22}$$

which gives,

$$\frac{\delta E[\rho]}{\delta \rho(\mathbf{r})} = \mu \tag{1.23}$$

or using equation 1.15 we get,

$$\frac{\delta F[\rho]}{\delta \rho(\mathbf{r})} + v_{ext}(\mathbf{r}) = \mu \tag{1.24}$$

This is called the Euler-Lagrange equation for the density; μ comes in the equation as Lagrange's undetermined multiplier. However it can be shown that $\mu = \frac{\delta E[\rho]}{\delta \rho} = \frac{\delta E[\rho]}{\delta N}$. Therefore, it is identified to be the chemical potential of the system [7]. Euler Lagrange equation can be used for determining the ground state density of the system and thereby one can calculate other properties of a system. TF density functional theory is an approximate version of the Euler-Lagrange equation. However this is not a very practical approach because the functional form of the universal energy functional $F[\rho]$ is not known exactly. Therefore one looks for some alternative. The breakthrough comes from Kohn-Sham formulation of DFT which we discuss in the following section.

1.3 Kohn-Sham formulation of DFT

This formulation of density functional theory again brings wave function into picture but that corresponding to N non-interacting Fermions. Kohn-Sham theory is briefly explained in the following.

Total energy of system of an interacting Fermionic system is written as,

$$E[\rho] = T[\rho] + E_{ee}[\rho] + E_{ext}[\rho] \quad (1.25)$$

This can be re-written as,

$$= T_s[\rho] + E_{Hartree}[\rho] + E_{ext}[\rho] + \{T[\rho] - T_s[\rho] + E_{ee}[\rho] - E_{Hartree}[\rho]\} \quad (1.26)$$

where $T_s[\rho]$ is non-interacting kinetic energy corresponding to density ρ . Thus we see that the kinetic energy functional $T[\rho]$ has been replaced by non-interacting kinetic energy term $T_s[\rho]$ and Hartree term has been separated; other extra terms have been written at the end. Therefore energy functional remains the same. The first three terms in above expression are the major terms quantitatively. Whereas, the last term inside curly bracket is a small term but it is a significant term. Advantage of this regrouping of terms is that first three terms can be treated exactly. The last term which requires approximation is about 10%

of the total energy. Therefore an approximation of reasonable accuracy is acceptable for this part as far as energy calculation is concerned. However for getting correct description of a system, accurate treatment of the last part is necessary. In HF theory the last term is only approximately treated so HF theory predicts unstable H^- ion whereas actually it is stable with respect to H atom.

$T_s[\rho]$ in above expression is expressed as,

$$T_s[\rho] = -\frac{1}{2}\langle\Psi_s[\rho]|\nabla^2|\Psi_s[\rho]\rangle \quad (1.27)$$

where, Ψ_s is Slater determinant formed from single particle orbitals ϕ_i 's. It is given as,

$$\Psi_s = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(x_1) & \phi_1(x_2) & \cdots & \phi_1(x_{N-1}) & \phi_1(x_N) \\ \phi_2(x_1) & \phi_2(x_2) & \cdots & \phi_2(x_{N-1}) & \phi_2(x_N) \\ \vdots & \vdots & \cdots & \vdots & \vdots \\ \phi_{N-1}(x_1) & \phi_{N-1}(x_2) & \cdots & \phi_{N-1}(x_{N-1}) & \phi_{N-1}(x_N) \\ \phi_N(x_1) & \phi_N(x_2) & \cdots & \phi_N(x_{N-1}) & \phi_N(x_N) \end{vmatrix} \quad (1.28)$$

The electrons density obtained from Ψ_s is given as,

$$\rho(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2 \quad (1.29)$$

The last term in equation 1.26 carries the effects arising due to Pauli exchange [79] and correlations and due to Coulombic correlation and it is called exchange correlation energy $E_{XC}[\rho]$. It is this part which draws most of the attention of DFT researchers.

Thus,

$$E[\rho] = -\frac{1}{2} \sum_i \langle\phi_i[\rho]|\nabla^2|\phi_i[\rho]\rangle + \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + \int v_{ext}\rho d\mathbf{r} + E_{XC}[\rho] \quad (1.30)$$

Minimizing above expression for energy with respect to the orbitals and using the condition $\int |\phi_i(\mathbf{r})|^2 = 1$, we get

$$\left[-\frac{1}{2}\nabla^2 + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + v_{ext} + v_{xc} \right] \phi_i = \epsilon_i \phi_i \quad (1.31)$$

where ϵ_i 's come into the equation as Lagrange multiplier. The second term in the above equation is the functional derivative of Hartree energy term. This equation is DFT coun-

terpart of Schrödinger equation and is known as the Kohn-Sham equation. Here ϕ_i 's are the Kohn-Sham orbitals and ϵ_i 's enter into the equation as the Lagrange undetermined multipliers and are the Kohn-Sham orbital energies. v_{ext} and v_{xc} are, respectively, external potential and the exchange correlation potential. For atoms, molecules and solids, nuclear potential is the external potential for the electrons. Exchange correlation potential is obtained as the functional derivative of exchange correlation energy as,

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})} \quad (1.32)$$

In practice exchange correlation energy is split into exchange and correlation parts separately. Therefore we have,

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho] \quad (1.33)$$

Corresponding potentials are also defined separately as, $v_x(\mathbf{r}) = \frac{\delta E_x[\rho]}{\delta \rho(\mathbf{r})}$ and $v_c = \frac{\delta E_c[\rho]}{\delta \rho}$. Exchange part constitutes about 10% of total energy while correlation part constitutes less than one percent of the total energy for majority of systems. Correlation effects, although small, become important in certain cases such as in formation of negative ions. Therefore, it is very important that accurate exchange and correlation energy functionals be available for density functional calculations. Total energy of the system is also expressed as,

$$E = \sum_{i=1}^N \epsilon_i - \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' - \int v_{ext}\rho(\mathbf{r})d\mathbf{r} + E_{XC}[\rho]. \quad (1.34)$$

The Kohn-Sham calculation proceeds as follows. We start with a density and solve the Kohn-Sham equation self-consistently to generate a set of Kohn-Sham orbitals from which then we calculate physical quantities of interest. The density chosen to start with should satisfy equation 1.21.

1.3.1 Implementation of Kohn-Sham theory

To apply Kohn-Sham equation to atomic and molecular calculations, we need to have exchange and correlation potentials. These potentials are obtained by taking functional

derivative [58] of corresponding energy functionals. In exchange-only approximation correlation part is omitted. Therefore in this approximation one deals only with exchange part of the exchange-correlation potential. A widely used approximation for exchange potential is the Dirac exchange potential in local density approximation. As stated above, we obtain exchange potential by taking functional derivative of exchange energy with respect to density. The exchange energy functional in local density approximation(LDA) is given by equation 1.8. Therefore LDA exchange potential is given by

$$\begin{aligned} v_x^{LDA} &= \frac{\delta E_x^{LDA}}{\delta \rho} \\ &= -\frac{k_f}{\pi} \end{aligned} \quad (1.35)$$

Where, k_f is Fermi wave vector and is given by, $k_f = (3\pi^2\rho(\mathbf{r}))^{2/3}$. For correlation part there is no such exact and simple approximation even in the LDA. However for ground state various approximations for correlation part are due to Gunnarson and Lundqvist and others [33, 59] which are constructed by parametrization of results obtained from Monte-Carlo calculations [48]. We discuss more about correlation in appendix A.

With approximate form of exchange and correlation potentials, K-S equation is solved self consistently to obtain orbitals ϕ_i 's for a given system. From these orbitals one gets density of the system through the relation $\rho = \sum_i |\phi_i|^2$. Once density of the system has been obtained, various quantities of interest can be calculated using their functional forms.

To explore spin-dependent quantities such as magnetization, multiplet structure etc we must incorporate spin dependence of the density of electrons. A further advantage of doing this is that spin dependent densities ρ^α and ρ^β for up and down spin give more flexibility in constructing density functionals. Thus functionals written in terms of the spin dependent densities are more accurate than their spin-independent counterpart. With spin dependent generalization of density we get,

$$E[\rho^\alpha, \rho^\beta] = \frac{1}{2}E^{(0)}[2\rho^\alpha] + \frac{1}{2}E^{(0)}[2\rho^\beta] \quad (1.36)$$

where ρ^α is density of up-spin electrons and ρ^β is density of down-spin electrons and $E^{(0)}$ is the spin-unpolarized functional.

1.4 DFT for excited-states

Success of density functional theory for ground states has motivated researchers to use it for studying excited-states also [35–37, 42, 57]. In principle this can be done. Because in accordance with Hohenberg Kohn theorem, ground state density fixes the Hamiltonian. Thus, ground state density should determine all the properties of a system. Application of equation 1.31 to excited-states with LDA approximation for exchange potential does not give correct results except for the lowest states of each symmetry. Thus application is limited only to those excited-states whose non-interacting counterpart can be represented by a single Slater determinant. However by using von Barth scheme [32] of constructing single determinant state from the linear combination of all degenerate excited-states of a particular symmetry, lowest excited-state of any given symmetry can be calculated [34]. The reason for failure of equation 1.31 in giving excited-state properties is that, excited-state density of a system does not provide complete information about a particular symmetry of the state. What it means is that a given excited-state density can be generated by different excited-states. Therefore, for doing density functional calculations for excited-states, mere knowledge of excited-state density is not sufficient. One needs to incorporate more information about excited-states in addition to its density. Such as, total spin quantum number S , total angular momentum quantum number L etc.

Development of time-independent DFT for general excited-state has been a challenging task [56]. This is because there are some issues in excited-states that make handling of excited-states more complex than ground states. We mention these in the following.

Following are the theoretical limitations related to excited-state density functional theory.

- There is no Hohenberg Kohn theorem for excited-states. As a result,
- Observables for excited-states cannot be expressed as the functional of excited-state density alone;

And following are the difficulties one faces in excited-state density functional theory.

- Because of point(2) above, there do not exist accurate energy functionals and exchange and correlation potentials for excited-states. It is only recently that a systematic method for developing excited-state functional has been presented.
- Energy functional and exchange correlation potential (if any) for excited-states are state dependent;

Non-existence of Hohenberg Kohn theorem implies that, for excited-states, a particular density can be generated from more than one local potential [40,65]. Thus, one-to-one correspondence between density of system and external potential does not hold.

$$\rho \rightarrow v_{ext}(\text{not unique}) \quad (1.37)$$

Therefore one has to be cautious in selecting a particular local potential in KS DFT for excited-states. How this is done is discussed in the following.

For determining external potential of a system, knowledge of ground state is essential. This requirement is analogous to the wave function based variational principle for excited-states, which demands that a wave function that minimizes the excited-state energy has to be orthogonal to all lower states. Thus in excited-states expectation value of an observable is bi-functional of excited-stated density and ground state density. i.e;

$$\langle \hat{O} \rangle = O[\rho, \rho_0] \quad (1.38)$$

Application of ground state functional to excited-states leads to erroneous results except for the lowest states of given symmetry. This happens because ground state functionals fail to incorporate the specific details of an excited-state. In particular a functional

for the excited-state should bear the state dependence to be able to distinguish between two states of the same symmetry. For different types of excited-states the functionals have to be different. Further more, to be able to perform a Kohn-Sham calculation, one should be able to obtain derivative of the functionals easily. The two limitations outlined above have been dealt [65,92] but the two difficulties mentioned here have not yet been circumvented. This is the main cause behind the poor performance of DFT. Work presented in thesis discusses method for constructing exchange and correlation potential for excited states.

1.4.1 Formulation of excited-state density functional theory(e-DFT)

Slater's transition state theory [10] was the first attempt to build an approach to excited-state on a line different from the ground state DFT . It occupies the orbitals with fractional number of electrons and does calculation of energy of the system using ground state functionals. Thus equations are the same as KS equation but density corresponds to fictitious system in which orbitals have fractional occupation. This concept was used by Theophilou in formulation of equiensemble approach to excited-state density functional theory [38]. Later the equiensemble approach was extended to unequiensemble theory by Gross, Oliviera and Kohn [39].

Recent work on excited-state density functional theory by us is based on the following works.

- Variational formulation of excited-state density functional theory due to Levy and Nagy. [92]
- ρ -stationary state formulation of excited-state density functional theory due to Görling [93]
- Development of excited-states functional by Samal and Harbola [75].

In the following section we discuss these formulations and follow it with a discussion of the extension of these ideas by our group [74].

1.4.2 Variational formulation of e-DFT

Levy and Nagy have given variational formulation of excited-states which is based on constrained search approach. In this formulation one looks for all wave functions Ψ 's which produce a given excited-state density $\rho(\mathbf{r})$ with a condition that wave functions Ψ_k of the given excited-state (k) must be orthogonal to all the lower states $\Psi_{k-1}, \Psi_{k-2}, \Psi_{k-3} \cdots \Psi_0$. This is essentially the variational principle for excited-state. Thus it leads to minimization of excited-state energy functional.

1.4.3 ρ -stationary state formulation of e-DFT

Based on generalized adiabatic connection (GAC) and constrained search formulation, Görling [93] has given ρ -stationary state description of density functional theory. It is quite general in that it is applicable to ground as well as excited-states. Further more, it provides theoretical basis for Kohn-Sham approach to e-DFT. It involves following steps.

- For a given density $\rho(\mathbf{r})$ look for wave functions Ψ 's that can give this density and construct the energy functional using the wave function.

$$\Psi's \rightarrow \rho \quad (1.39)$$

$$E[\rho, \lambda, v] = \langle \Psi[\rho, \lambda, v] | \hat{T} + \lambda \hat{V}_{ee} + \hat{v} | \Psi[\rho, \lambda, v] \rangle \quad (1.40)$$

- Search for density which minimizes the functional,

$$F[\rho, \lambda, v] = \min_{\rho} \langle \Psi[\rho, \lambda, v] | \hat{T} + \lambda \hat{V}_{ee} | \Psi[\rho, \lambda, v] \rangle \quad (1.41)$$

In the limit $\lambda \rightarrow 0$ we get Kohn-Sham system. Thus Görling's formulation of e-DFT states that density of ground state as well as excited-state can be generated from wave

function of non-interacting system moving in a local potential. It essentially means that interacting electronic system can be replaced by a non-interacting system moving in a local potential.

1.4.4 Selection of a Kohn-Sham system for excited-state

In the absence of Hohenberge-Kohn theorem for excited-states, selection of Kohn-Sham system corresponding to a given excited-state of a real system is tricky. A method suggested is the Levy-Nagy criterion which states that ground state density ($\tilde{\rho}_0$) of auxiliary Kohn-Sham system should match within a certain limit with ground state density (ρ_0) of real system. This is mathematically expressed as,

$$\Delta[\rho_0, \tilde{\rho}_0] = \int \{\rho_0 - \tilde{\rho}_0\}^2 d\mathbf{r} = \textit{smallest} \quad (1.42)$$

However this criterion has been shown not to reproduce excited-state configuration correctly in all cases. A more appropriate method for selection of Kohn-Sham system has been given by Samal and Harbola [75]. In this approach instead of density, comparison of excited-state kinetic energy of Kohn-Sham system is done with the true system. This is mathematically expressed as,

$$|T - T_{KS}| = \textit{smallest} \quad (1.43)$$

Above criterion leads to a Kohn-Sham system consistent with the excited-state configuration. Thus in principle a Kohn-Sham system can be constructed for an excited-state.

1.4.5 Semi-empirical approach to excited-states

For ground states, accurate energy functionals and exchange potential have been constructed semi-empirically. For example Becke exchange energy functional [84], van Leeuwen Baerend's exchange potential [27] incorporate the gradient of the density and satisfy certain exact properties satisfied by exact potential. In construction of these functionals and

potential, LDA expressions have been empirically modified. These have been parametrized to give correct result and correct limits. Such an approach has to be employed because it is not easy to derive functionals which give accurate results as well as give correct asymptotic limits. Situation is the same for excited-states as well. Therefore, taking motivation from the ground state, the idea may be employed for excited-states also. Thus we can develop functional and potential based on rigorous theory and then modify them to make them more accurate.

1.5 Concluding remarks

Density functional theory (DFT), which treats the ground-state density as the basic variable, has grown to become a theoretical technique of choice for ground state calculations. This is because of its versatility and comparatively less computational cost. It is founded on two Hohenberg-Kohn theorems which rigorously show that the ground-state density alone determines all the properties of the system and variational principle can be expressed in terms of density, respectively. However building the theory based only on density is not found to be so satisfactory. Therefore one takes a rather different route in DFT. This alternate formulation was give by Kohn-Sham in 1965. Significance of this approach is that here one reduces a real interacting system into a virtual non-interacting system. Thus, insurmountable task of dealing with many particle interacting term in the Hamiltonian is bypassed. However, one is faced with another difficult task of constructing exchange-correlation energy functionals. This however has proven to be relatively easy compared to solving the many particle Schrödinger equation.

Kohn-Sham approach to DFT requires one to solve a single particle equation for N orbitals instead of one equation for N particles. The N orbitals for auxiliary system are used to calculate density. Then to calculate quantities of interest from density, one needs to have accurate functionals. This is what constitutes major part of current research work. i.e construction of accurate energy functionals in density functional theory. For ground

state, approximate but accurate functionals have been constructed based on local density approximation (LDA), generalized gradient approximation (GGA) and meta-generalized gradient approximation (m-GGA). This renders density functional theory very successful for ground states.

Excited-state problem belongs to a different regime. Here one-to-one correspondence between excited-state density and potential does not exist. However, in principle DFT is applicable to excited-states also. Since ground state density determines Hamiltonian, it should determine all the excited-state properties of the system as well. Formulation of excited-state density functional theory is based on the works of Levy and Nagy; Görling; and Samal and Harobla. Based on these works, it has been concluded that excited-state functionals are bi-functionals of both ground state and excited-state densities. Further a Kohn-Sham system also exists for excited-states.

Construction of functionals for excited-states is also not as simple as it is for the ground states. This is because for excited-states functionals are state dependent. Same is the case for corresponding exchange correlation potential. This is one major reason behind the relatively slow development in the field of excited-state density functional theory. The work presented in this thesis addresses these issues. In this thesis we have studied exchange energy functional as well as exchange potential for excited-states. Some preliminary work on correlation energy functional for excited-states is also reported.

1.6 Outline of the thesis

Major portion of the work presented in this thesis is concerned with the studies of exchange energy functional and exchange potential for excited-states. We have also performed an analysis of excited-state density in the second chapter to show the asymptotic behaviour of excited-state density. We have shown that asymptotic decay of density of all excited-states including autoionizing states is governed by the smallest ionization energy. This

work is presented in the chapter 2.

In the third chapter we discuss construction of exchange energy functional for excited-states. Based on the work earlier pursued in our group [62, 72–74] we show that exchange functional can be constructed for the excited-states involving more than one gap. Through calculation of excitation energy for various type of cases involving transition of 1 to 4 electrons we show that the functional is highly accurate and does not impose any restriction on number of electrons involved in transition. In chapter 4 we add gradient correction to it to make it more accurate. This leads to very accurate results for the total energy of excited-states as well as for the corresponding excitation energies.

In chapter 5 we construct exchange potential for excited-states. Exchange potential is given by functional derivative of exchange energy functional. But for excited-states functional proposed, functional derivative cannot be calculated exactly. Therefore we have to resort to some sort of approximation. We follow two approaches for this, leading to the same final result. To make the exchange potential more accurate we further make some modification in the potential based on our analysis. This makes the potentials semi-empirical. To calculate exchange energy from exchange potential we use Levy-Perdew theorem. We have studied various types of excitation in different atoms using this potential. Results that we get for excitation energy are comparable to standard results.

In the last chapter we briefly summarize the work presented in the thesis and discuss the work that that should follow.

In appendix-A attempt is made to construct correlation energy functional. We have tried to extend the Colle-Salvetti functional to excited-states. This is done by using the idea of splitting k – *space*. We argue that since these functionals have been constructed to satisfy some general condition which is also equally applicable to excited-states, it should work for excited-states too when kinetic energy terms are replaced by corresponding excited-state terms. We look to improve it further since preliminary results are not encouraging.

Chapter 2

Study of Asymptotic Decay of Density for Excited States Including Auto-ionizing States.

2.1 Introduction

In developing a theory in terms of the density, it is important that as much exact information about the density be obtained as possible from analytical methods or from available densities. For example, for the ground-state densities, it is well known that their asymptotic behaviour is determined by the ionization potential of the system. This leads immediately to asymptotic behaviour and derivative discontinuity of the exchange-correlation potential. As such in this chapter we obtain, employing techniques similar to those used for studying ground state-densities, the asymptotic behaviour of an excited state density. We show that for excited states also asymptotic decay of density is determined by the ionization potential of the system.

In the next section we first present analytical discussion on the asymptotic decay of excited state density. Then we give numerical results using accurate Monte Carlo densities to support our analytical findings. This work has been published [17]

2.2 Analytical Study

For a non-interacting electron system which is described by the Hamiltonian,

$$H_N = -\frac{1}{2} \sum_i^N \nabla_i^2 + \sum_i^N V_{ext}(\vec{r}_i) \quad (2.1)$$

If the external potential $V_{ext}(\mathbf{r})$ vanishes as $r \rightarrow \infty$ then, density for both ground and excited states in asymptotic limit goes as,

$$\rho(r) \sim e^{-2\sqrt{-2\epsilon_{max}}r}, \quad (2.2)$$

Here ϵ_{max} is the orbital energy of the highest occupied orbital. Since for non-interacting systems $\epsilon_{max} = -I$, where I is first ionization energy the asymptotic decay of the density can be written as,

$$\rho(r) \sim e^{-2\sqrt{2I}r}, \quad (2.3)$$

The result is true for both the ground-state and excited state densities of non-interacting particles represented by the Hamiltonian of equation 2.1.

Our aim is to find asymptotic decay of density for interacting electron systems. Therefore, let us ask the question, whether the density of interacting systems, like atoms and molecules also has similar decay as given by equation 2.3 in the asymptotic limit or has some other form?. This question has been addressed extensively in the past for the ground states of an electronic system [18, 44–47, 49]. However, from these studies it is not clear how the density for excited states will decay in the asymptotic limit. Evidently, equation 2.3 does not work for the auto-ionizing excited states. For an auto-ionizing state the ionization potential is negative. Therefore from equation 2.3 we get an oscillatory density in the asymptotic limit, which is not the case in reality. In our treatment of excited states of many-electrons system we address such issues also. In the following

we analytically derive the asymptotic behaviour of the excited state density, essentially following the method of references [18, 44–47, 49] mentioned above.

To derive the asymptotic form for the excited state densities we consider a system with N electrons. It may be in its ground-state or in any of its excited states. In the Born-oppenheimer approximation the Hamiltonian for the electrons is,

$$H_N = \sum_i h_i + \frac{1}{2} \sum_{ij(i \neq j)} \frac{1}{r_{ij}} \quad (2.4)$$

with,

$$h_i = -\frac{1}{2} \nabla_i^2 + V_{ext}(\vec{r}_i) \quad (2.5)$$

where $V_{ext}(\vec{r})$ is the electron-nuclear interaction potential. Now in terms of the $(N-1)$ -electron Hamiltonian, H_N can be written as,

$$H_N = H_{N-1} + h_i + \sum_{j(i \neq j)} \frac{1}{r_{ij}}. \quad (2.6)$$

If $\psi_N(x_1, x_2, \dots, x_N)$ and $\psi_{N-1}(x_2, x_3, \dots, x_N)$, where $x = (\vec{r}, \sigma)$ with σ denoting the spin variable, are the exact eigenfunctions of H_N and H_{N-1} respectively, we have

$$H_N \psi_N(x_1, x_2, \dots, x_N) = E_N \psi_N(x_1, x_2, \dots, x_N) \quad (2.7)$$

and

$$H_{N-1} \psi_{N-1}(x_2, x_3, \dots, x_N) = E_{N-1} \psi_{N-1}(x_2, x_3, \dots, x_N) \quad (2.8)$$

Multiplying equation 2.7 on the left by $\psi_{N-1}^{s*}(x_2, x_3, \dots, x_N)$, where s denotes the s th eigenstate of the $N-1$ electron system, and integrating over $\vec{r}_2, \dots, \vec{r}_N$, and summing over the spins $\sigma_2, \sigma_3 \dots \sigma_N$, we get,

$$\left[-\frac{1}{2} \nabla_1^2 + V_{ext}(\vec{r}_1) \right] f_s(x_1) + \langle \psi_{N-1}^s | \sum_{i>1} \frac{1}{r_{i1}} | \psi_N \rangle = (E_N - E_{N-1}^s) f_s(x_1) \quad (2.9)$$

where,

$$f_s(x) = \int \psi_{N-1}^{s*}(x_2, x_3, \dots, x_N) \psi_N(x, x_2, \dots, x_N) dx_2, \dots, dx_N \quad (2.10)$$

with dx denoting the integral over the spatial variables and summation over the spin variable. The quantities $f_s(x)$ are known as the quasi particle amplitudes. The integration in the second bracket on the left-hand side of equation 2.9 is over variables x_2, x_3, \dots, x_N . Further, E_{N-1}^s is the energy value of the s th eigenstate of the $(N-1)$ electrons system. From equation 2.9 of quasi particle amplitudes, it is clear that in the limit of $r \rightarrow \infty$, these should decay exponentially as $\exp(-\sqrt{2(E_{N-1}^s - E_N)}r)$.

The first-order density matrix $\gamma(x, x')$ [52, 53] and the density $\rho(\vec{r})$ of the system can both be expressed in terms of quasi-particle amplitude as follows.

$$\gamma(x, x') = \sum_s f_s^*(x) f_s(x') \quad (2.11)$$

and

$$\rho(\vec{r}) = \sum_\sigma \sum_s |f_s(x)|^2 \quad (2.12)$$

This is easily proved by the completeness of eigenfunctions ψ_{N-1}^s as we show below,

$$\begin{aligned} \gamma(x, x') &= \int \psi_N^{s*}(x, x_2, \dots, x_N) \psi_N(x', x_2, \dots, x_N) dx_2, \dots, dx_N \\ &= \int \psi_N^{s*}(x, x_2, \dots, x_N) \delta(x_2 - x'_2) \cdots \delta(x_N - x'_N) \psi_N(x', x'_2, \dots, x'_N) \\ &\quad \times dx'_2, \dots, dx'_N dx_2, \dots, dx_N \\ &= \int \psi_N^{s*}(x, x_2, \dots, x_N) \left(\sum_s \psi_{N-1}^{s*}(x'_2, \dots, x'_N) \psi_{N-1}^s(x_2, \dots, x_N) \right) \psi_N \\ &\quad \times (x', x'_2, \dots, x'_N) dx'_2, \dots, dx'_N dx_2, \dots, dx_N \\ &= \sum_s f_s^*(x) f_s(x'). \end{aligned} \quad (2.13)$$

The formula for density follows by taking the diagonal term of the density-matrix above

and summing over the spin index.

It is clear from the expression above that the asymptotic behaviour of the density is determined by the most slowly decaying quasi-particle amplitude. Following Refs. [18,44–47,49], we show below that for any excited-state of an N -electron system, the decay of all quasi-particle amplitudes is determined by the least value of positive $(E_{N-1}^s - E_N)$. This makes the study of asymptotic behaviour of excited-state densities interesting since even for multiplets arising from a single electronic-configuration, the states of the $(N - 1)$ electron system that dictate the decay of the corresponding density can be different.

To obtain the asymptotic behaviour of quasi-particle amplitudes, we employ the expansion

$$\sum_{i=2}^N \frac{1}{|\vec{r} - \vec{r}_i|} = \sum_{i=2}^N \sum_l \frac{r_i^l}{r^{l+1}} P_l \cos(\theta_i) \quad (2.14)$$

and substitute it in the equation 2.9. In doing so we keep only the leading order terms with $l = 0$ and $l = 1$ to get

$$\left(-\frac{\nabla^2}{2} + V_{ext}(\vec{r}) + \frac{N-1}{r} \right) f_s(x) + \frac{1}{r^2} \int \psi_{N-1}^{s*} \left(\sum_{i=2}^N r_i \cos \theta_i \right) \psi_N dx_2 \cdots dx_N = \epsilon_s f_s(x), \quad (2.15)$$

where $\epsilon_s = E_N - E_{N-1}^s$. Using completeness of eigenfunctions ψ_{N-1}^s again, we get

$$\left(-\frac{\nabla^2}{2} + V_{ext}(\vec{r}) + \frac{N-1}{r} \right) f_s(x) + \frac{1}{r^2} \sum_{s'} D_{ss'} f_{s'}(x) = \epsilon_s f_s(x), \quad (2.16)$$

where, $D_{ss'}$ is the dipole matrix element between states s and s' of the $(N - 1)$ electron system. To understand how each quasi-particle amplitude decays, we take $s = 0$ in the equation above to get

$$\left(-\frac{1}{2} \frac{\nabla^2 f_0}{f_0} + V_{ext}(\vec{r}) + \frac{N-1}{r} - \epsilon_0 \right) = -\frac{1}{r^2} \frac{\sum_{s'} D_{0s'} f_{s'}(x)}{f_0}, \quad (2.17)$$

where, f_0 is the quasi-particle amplitude corresponding to the eigenvalue ϵ_0 of smallest

magnitude. Since each of the quasi particle amplitudes in the equation above decays exponentially, the decay constant for all of them must be the same. If it were not, the left hand side of the equation will be finite but the right hand side will become infinitely large as $r \rightarrow \infty$ because of the quasi-particle amplitudes f_s that decay slower than f_0 .

To see how the solutions for the quasi particle amplitudes go asymptotically, we first assume that as $r \rightarrow \infty$ the fastest growing f_s behaves like $r^n f_0$ where n is a positive integer and then find the solution for f_s iteratively. Substituting $f_s = r^n f_0$ in Eq. 2.17 gives to the leading order

$$\left(-\frac{1}{2} \frac{\nabla^2 f_0}{f_0} + v_{ext}(\mathbf{r}) + \frac{N-1}{r} - \epsilon_0 \right) = -r^{n-2} D_{0s} \quad (2.18)$$

To be consistent with the left hand side the value of n can be at most 1. Thus the fastest that a quasi particle amplitude can grow is as $r f_0$. Let us now rewrite Eq. 2.16 for f_s , substituting for it $r f_0$ in the term involving dipole matrix element to get

$$\left(-\frac{1}{2} \nabla^2 + v_{ext}(\mathbf{r}) + \frac{N-1}{r} - \epsilon_s \right) f_s(\mathbf{x}) = -\frac{1}{r} D_{ss} f_0(\mathbf{x}) - \frac{1}{r^2} D_{s0} f_0(\mathbf{x}) - \frac{1}{r^2} \sum_{s', s' \neq s, 0} D_{ss'} f_{s'}(\mathbf{x}) \quad (2.19)$$

this equation implies that f_s is of the order of $\frac{f_0}{r}$. Substituting this again in equation 2.16, we find,

$$\left(-\frac{1}{2} \nabla^2 + v_{ext}(\mathbf{r}) + \frac{N-1}{r} - \epsilon_s \right) f_s(\mathbf{x}) = -\frac{1}{r^2} D_{ss} f_0(\mathbf{x}) - \frac{1}{r^2} D_{s0} f_0(\mathbf{x}) - \frac{1}{r^2} \sum_{s', s' \neq s, 0} D_{ss'} f_{s'}(\mathbf{x}) \quad (2.20)$$

this equation implies that f_s is of the order of $\frac{f_0}{r^2}$. Substituting this again in equation 2.16, we find,

$$\left(-\frac{1}{2} \nabla^2 + v_{ext}(\mathbf{r}) + \frac{N-1}{r} - \epsilon_s \right) f_s(\mathbf{x}) = -\frac{1}{r^3} D_{ss} f_0(\mathbf{x}) - \frac{1}{r^2} D_{s0} f_0(\mathbf{x}) - \frac{1}{r^2} \sum_{s', s' \neq s, 0} D_{ss'} f_{s'}(\mathbf{x}) \quad (2.21)$$

this equation also implies that f_s is of the order of $\frac{f_0}{r^2}$ in the asymptotic limit. Therefore we conclude that asymptotically f_s goes as $\frac{f_0}{r^2}$. Thus in effect it is the $1/r^2 D_{s0}$ term that determines f_s . To get its exact form we take asymptotic limit in the equation 2.20 to get,

$$\left(-\frac{1}{2} \nabla^2 - \epsilon_s \right) f_s = -\frac{D_{s0}}{r^2} f_0 \quad (2.22)$$

using $f_s \sim \frac{f_0}{r} \sim \frac{\exp(-\sqrt{-\epsilon_0}r)}{r}$, we get,

$$f_s(r) = -\frac{1}{r^2} \frac{D_{s0}f_0}{(\epsilon_0 - \epsilon_s)} \quad (2.23)$$

It is instructive to make a comparison of the quasi-particle amplitudes for electrons with quasi-particle amplitudes of noninteracting particles moving in an external potential. It is a simple exercise to show that the quasi-particle amplitude for a non-interacting system is the same as orbital from which the particle is removed to create the $(N-1)$ particle excited state. Thus higher the value of s , faster the quasiparticle amplitude decays with the decay constant corresponding to its own eigenvalue. On the other hand, because of the inhomogeneous term arising from electron-electron interaction, quasi-particle amplitudes corresponding to all ionic excited states get coupled with the same decay constant in the exponential term but their values are smaller by a factor of r^2 in comparison to the lowest energy amplitude.

2.3 Numerical Results

On the basis of the derivation above it is clear that far away from a system, density decays depending upon the lowest value of positive value of $(E_{N-1}^s - E_N)$ for which $f_s \neq 0$, irrespective of whether a system is in the ground or in an excited-state. We now demonstrate this for excited-state densities corresponding to some excited states of boron isoelectron series. The densities in the asymptotic region is expected to have the functional form

$$\rho(r) = Cr^{2\beta} \exp(-2\kappa r) \quad (2.24)$$

with

$$\kappa = \sqrt{-2\epsilon_0} \quad (2.25)$$

and

$$\beta = \frac{Z - N + 1}{\kappa} - 1, \quad (2.26)$$

where Z is the nuclear charge and N is the number of electrons. For our study we employ accurate densities for the $2p^3(^4S)$, $2p^3(^2D)$ and $2p^3(^2P)$ states obtained from quantum Monte-Carlo calculations [50, 51][We thank A. Sarsa for providing us accurate Monte-Carlo densities.]. We fit the density to the form given in equation 2.24 with C and κ as fitting parameters. The value of parameter β is calculated from the energy difference $\epsilon_0 = E_{N-1}^s - E_N$ using equation 2.26 and kept fixed during the fitting. We start by presenting our results for the $2p^3(^4S)$ case.

2.3.1 Results for $2p^3(^4S)$ states:

For the $2p^3(^4S)$ state of B-like ions parity is -1 and $L = 0$, the lowest energy states of corresponding Be-like ions that lie above this energy(starting from the lowest energy) are $:2s^2(^1S)$ (except for B^+), $2s2p(^3P)$, $2s2p(^1P)$ and $2p^2(^3P)$. However when an electron is removed, the multiplicity of the state can change by only 1. Thus the quasi-particle amplitudes corresponding to the $2s^2(^1S)$ and $2s2p(^1P)$ state will be zero. That leaves us the with the choice of either $2s2p(^3P)$, parity=-1, $L = 1$ or $2p^2(^3P)$, parity=+1, $L = 1$ states that determine the asymptotic decay of the density. For these states the angular momentum of the quasi-particle amplitude would correspond to $L = 1$, so that its parity is -1. The product $\psi_{N-1}(x_2 \cdots x_N)\psi_N(x_1 = x, x_2 \cdots x_N)$ should therefore also have the same parity. This requirement therefore rules out $2s2p(^3P)$ state from giving a non-zero quasi-particle amplitude. Thus the decay of the density of $2p^3(^4S)$ state of B-like ions should be determined by the difference in the energy of this state and that of the $2p^2(^3P)$ state of the corresponding Be-like system. This is shown in the Table 2.1 where we display the value of β of Equation 2.26 calculated from this energy difference, and the value of $\kappa^2/2$ where κ is determined by fitting the density to the form given by equation 2.25. The fitting is done over varying range of distances from the nucleus. In the Table we also

give the average value of $\kappa^2/2$ over the different ranges considered and the corresponding standard deviation. First, it is seen that the standard deviation is small except in the cases of O^{3+} and Ne^{5+} . This indicates that the density should decay with the decay constant κ as given in the Table for distances beyond the largest value of r considered. Further, it is evident from the results that except for the cases of O^{3+} and Ne^{5+} , in all other cases the decay constant κ and the energy difference $\Delta E = E [2p^2(^3P)] - E [2p^3(^4S)]$ are related as expected. Incidentally, the standard deviation in the value of κ is also relatively larger in these two cases. We suspect on the basis of our results that densities of O^{3+} and Ne^{5+} may not be accurate asymptotically.

2.3.2 Results for $2p^3(^2D)$ state:

Next we consider the case of the states $2p^3(^2D)$. Parity of this state is -1 and $L = 2$. In this case the quasi-particle amplitude would be non-zero for both the triplet and the singlet states. Thus all the low lying states $-2s^2(^1S)$, $2s2p(^3P)$, $2s2p(^1P)$ and $2p^2(^3P)$ - of the Be-like ions with energy higher than that of the $2p^3(^2D)$ state may give non-zero f_s . However, the quasi-particle amplitude corresponding to the $2s^2(^1S)$ state will be zero because for this state, parity is +1 and $L=0$ therefore from angular momentum algebra we get that for f_s $L=2$ that is $f - s$ has d-orbital like character which has parity value of 1. On the other hand, $\psi_{N-1} [2s^2(^1S)] \psi_N [2p^3(^2D)]$ does not have this parity. Therefore, the angular momentum and parity considerations allow non-zero amplitudes for only $2s2p(^3P)$ and $2s2p(^1P)$ ionic states with the character of f_s being d-orbital like for these states and for the $2p^2(^3P)$ with p-orbital like character for f_s . As such the density decay should be governed by the energy difference $\Delta E = E [2s2p(^3P)] - E [2p^3(^2D)]$ of the $2s2p(^3P)$ and the $2p^3(^2D)$ states because this is the lowest energy difference for which quasi particle amplitude is not zero. We have tried to fit the density of $2p^3(^2D)$ state of B-like ions of carbon to Ne to the form given by equation 2.24 with the above given energy difference. We find that the density decay is not governed by this energy difference. The reason for this, we believe, is the following. Although the density corresponding to the $2p^3(^2D)$



Table 2.1: The energy difference ΔE and the quantity $\kappa^2/2$, where 2κ is the decay constant of the asymptotic density, for the $2p^3(^4S)$ multiplet of the $2p^3$ excited-state of Boron isoelectronic series

A/I	ΔE	β	$\kappa^2/2$					Avg $\kappa^2/2(\sigma)$	Deviation(%)
B	0.313	0.264	0.353(2-7)	0.342(2.5-7)	0.335(3-7)	0.333(3.5-7)	0.344(4.5-7)	0.341(0.007)	8.9
C^+	0.874	0.513	0.920(2-7)	0.920(2.2-7)	0.921(3-7)	0.936(3.5-7)	0.984(4.5-7)	0.936(0.028)	7.0
N^{2+}	1.690	0.632	1.757(2-7)	1.757(2.-7)	1.763(3-7)	1.781(3.5-7)	1.778(4-7)	1.767(0.012)	4.6
O^{3+}	2.758	0.703	1.370(1-7)	1.678(1.5-7)	1.905(2-7)	2.087(2.5-7)	2.186(3-7)	1.845(0.329)	-
F^{4+}	4.076	0.751	4.279(0.7-7)	4.299(1-7)	4.222(1.5-7)	4.259(2-7)	4.223(2.5-7)	4.242(0.025)	4.2
Ne^{5+}	5.643	0.786	2.374(0.5-7)	3.367(1-7)	3.926(1.5-7)	4.181(2-7)	4.474(2.5-7)	3.664(0.828)	

should be non spherical, we are actually finding the decay rate of the spherical average of this density. Such averaging of a density makes it spherical and gives it the character corresponding to an $S(L = 0)$ state. As such the decay of such spherically averaged density should also be governed by the energy difference $\Delta E = E [2p^2(^3P)] - E [2p^3(^2D)]$ as was the case for the density of $2p^3(^4S)$ state. This is precisely what we find. The corresponding parameters for these states are displayed in Table 2.2. It is again seen that except for the case of O^{3+} , the decay for the spherically averaged densities of the $2p^3(^2D)$ state is governed by the energy difference $\Delta E = E [2p^2(^3P)] - E [2p^3(^2D)]$.

2.3.3 Results for $2p^3(^2P)$ state:

Next we discuss the case of $2p^3(^2P)$ state. In this case all the four states, viz. $2s^2(^1S)$, $2s2p(^3P)$, $2s2p(^1P)$ and $2p^2(^3P)$, give non-zero quasi particle amplitudes as can be easily seen. However taking spherical average of the density again makes the density of this state decay according to the energy difference $\Delta E = E [2p^2(^3P)] - E [2p^3(^2P)]$ rather than the difference $\Delta E = E [2s^2(^1S)] - E [2p^3(^2P)]$ which is the smallest. This is shown clearly in Table 2.3. Again we see that the ion O^{3+} does not satisfy the trend observed for the other systems.

To demonstrate that the density corresponding to an auto-ionizing state also decays according to the discussion above, we look at the Hartree-Fock (HF) density of the $2s2p(^3P)$ state of He . The energy of this state is -0.745 a.u. and the eigen energies of the orbitals are $\epsilon_{2s} = -0.265$ a.u. and $\epsilon_{2p} = -0.262$ a.u. The value of ϵ_{2p} is very close to the energy difference of $E [He^+(2s)] - E [He(2s2p;^3P)] = 0.254$ a.u. This demonstrates decay of density and its relationship with the ionization energy for auto-ionizing states also.



Table 2.2: The energy difference ΔE and the quantity $\kappa^2/2$, where 2κ is the decay constant of the asymptotic density, for the $2p^3(^2D)$ multiplet of the $2p^3$ excited-state of Boron isoelectronic series

A/I	ΔE	β	$\kappa^2/2$					Avg $\kappa^2/2(\sigma)$	Deviation(%)
C^+	0.836	0.547	0.896(1.8-7)	0.881(2.1-7)	0.870(2.5-7)	0.874(3-7)	0.890(3.5-7)	0.882(0.011)	5.5
N^{2+}	1.616	0.669	1.737(1.5-7)	1.694(1.8-7)	1.661(2.1-7)	1.552(2.5-7)	1.541(3-7)	1.637(0.087)	1.3
O^{3+}	2.650	0.738	1.353(1-7)	1.636(1.5-7)	1.802(2-7)	1.885(2.5-7)	1.986(3-7)	1.732(0.248)	-
F^{4+}	3.935	0.782	4.217(0.8-7)	4.166(1-7)	4.147(1.8-7)	4.065(2.2-7)	3.815(2.6-7)	4.082(0.159)	3.7
Ne^{5+}	5.470	0.814	5.784(0.8-7)	5.743(1-7)	5.836(1.5-7)	5.866(2-7)	5.576(2.2-7)	5.761(0.114)	5.0

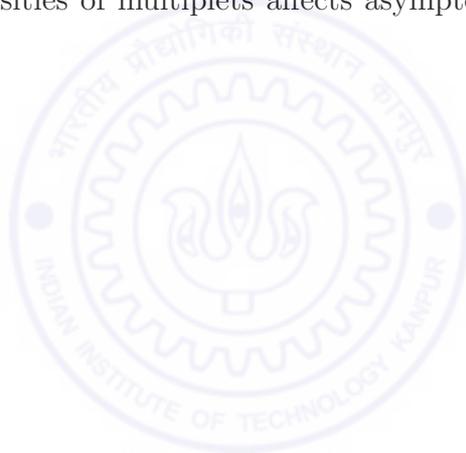


Table 2.3: The energy difference ΔE and the quantity $\kappa^2/2$, where 2κ is the decay constant of the asymptotic density, for the $2p^3(^2P)$ multiplet of the $2p^3$ excited-state of Boron isoelectronic series

A/I	ΔE	β	$\kappa^2/2$					Avg $\kappa^2/2(\sigma)$	Deviation(%)
N^{2+}	1.492	0.737	1.721(1.5-7)	1.654(1.8-7)	1.611(2-7)	1.542(2.3-7)	1.461(2.6-7)	1.598(0.100)	7
O^{3+}	2.496	0.790	1.320(1-7)	1.470(1.3-7)	1.620(1.8-7)	1.656(2.3-7)	1.634(2.6-7)	1.540(0.143)	-
F^{4+}	3.752	0.825	4.251(0.8-7)	4.040(1.2-7)	3.947(1.8-7)	3.947(2.3-7)	3.330(2.6-7)	3.903(0.344)	4
Ne^{5+}	5.258	0.850	6.116(0.5-7)	5.793(0.8-7)	5.781(1.2-7)	5.751(1.5-7)	5.780(1.8-7)	5.844(0.152)	11

2.4 Discussion and concluding remarks.

We have shown in this chapter that decay of the density far away from an electronic system is determined by the difference between its energy and the energy of its ion lying above its own energy. This is true for the ground as well as the excited-state densities including the auto-ionizing states. This is demonstrated using the excited state densities of B-like ions. We see that ΔE which is calculated from the data available in literature and $\kappa^2/2$ which is calculated numerically, has an average difference less than 6% and maximum difference between the two values obtained from calculation is 11 % which perhaps occur due to fluctuation in the density used for the calculation. It is also observed that taking spherical average of densities of multiplets affects asymptotic behaviour of their density significantly.



Chapter 3

Exchange Energy Functional for Excited States: Application to Two-gap Systems.

3.1 Introduction

The work presented in this chapter has been published as *J. Phys. B* **43**, 215002, (2010). In this chapter we generalize the approach proposed by our group for construction of exchange energy functional for excited states to the cases involving more than one gap. We construct exchange energy functional for the more general cases of excited states having two gaps and apply it to calculate energies for excitations involving multiple electrons. We also discuss some subtle points about self interaction correction in excitation energy calculation. Before we go on to describe the new functional, we give a brief account of the work that precedes the present exposition.

There have been early attempts to tackle excited state problem using DFT by Gunnarson and Lundqvist [33] and von Barth [88]. They applied ground state functional for the excited state energy calculations. As the functional employed was constructed for the ground states, it could give energies of only the lowest excited state of each symme-

try. Therefore we need to develop functional for excited states which will overcome such limitations.

As discussed in chapter 1, According to excited state density functional theory of individual excited-states the total energy of the k^{th} excited state of a system is a bi-functional of the excited state density $\rho(\mathbf{r})$ and the ground state density $\rho_0(\mathbf{r})$ of the system. Thus,

$$E[\rho, \rho_0] = F[\rho, \rho_0] + \int \rho(\mathbf{r})v_{ext}(\mathbf{r})d\mathbf{r} \quad (3.1)$$

Here,

$$F[\rho(\mathbf{r}), \rho_0] = \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle \quad (3.2)$$

In any case, the excited-state density $\rho(\mathbf{r})$ for a system specified by the ground-state density $\rho_0(\mathbf{r})$ is given [65,93] by the Euler equation

$$\frac{\delta F[\rho, \rho_0]}{\delta \rho(\mathbf{r})} + v(\mathbf{r}) = \mu \quad (3.3)$$

Here $v(\mathbf{r})$ is the external potential and μ is the Lagrange multiplier to ensure that the total number of electrons is equal to the specified value. We note, however, that like in the ground-state DFT the bi functional $F[\rho, \rho_0]$ is not known and has to be approximated. How this is done within the local-density approximation will be discussed in the following section.

The density for an excited-state can also be obtained by solving the corresponding Kohn-Sham equation. To obtain the Kohn-Sham system, functional $F[\rho, \rho_0]$ is split into the kinetic energy functional $T_s[\rho, \rho_0]$ of a system of noninteracting electrons of the same density as ρ , the classical Coulomb energy of the electrons and the exchange-correlation energy $E_{xc}[\rho, \rho_0]$. The Kohn-Sham system for a given configuration of excited state is defined as the one with exactly the same configuration as the true system. Thus the Kohn-Sham system has the kinetic energy and the exchange-correlation energy close to the true system [65, 71]. The ordering of the levels and excited-state configurations are

dictated by the ground-state Kohn-Sham system given by ρ_0 .

To do calculations for excited-states, energy functionals and corresponding potential have to be constructed first. In the next section we discuss a method developed by us for constructing excited-states energy functional.

3.2 Excited state functional by splitting the k-space

In this section we outline the concept of splitting the k -space to construct the functionals for excited states. Our aim is to develop LDA for excited-state energy functionals. We note that we cannot write the excited-state energy functional in terms of excited-state density of atom. The reason for this is quite straightforward: the LDA is based on the homogeneous electron gas (HEG) and for the HEG, the excited-state density is exactly the same as the ground-state density. This is because in a homogeneous electron gas of N electrons in volume V , the density is always $\frac{N}{V}$ irrespective of how the plane-wave orbitals are occupied. Therefore one needs more information to write the excited-state energy functional for the HEG. If we have the knowledge of occupied orbitals and the unoccupied orbitals between them, it is easy to write the energy in terms of the densities corresponding to the occupied and unoccupied states. For example consider an excited-state of the HEG shown in figure 3.1(a).

Here the plane-wave orbitals from $k = 0$ to $k = k_1$ are occupied, orbitals from $k = k_1$ to $k = k_2$ are unoccupied and orbitals from $k = k_2$ to $k = k_3$ are again occupied. For this system density is given as,

$$\rho = \rho_1 - \rho_2 + \rho_3 \quad (3.4)$$

where,

$$\rho_1 = \frac{k_1^3}{3\pi^2} \quad (3.5)$$

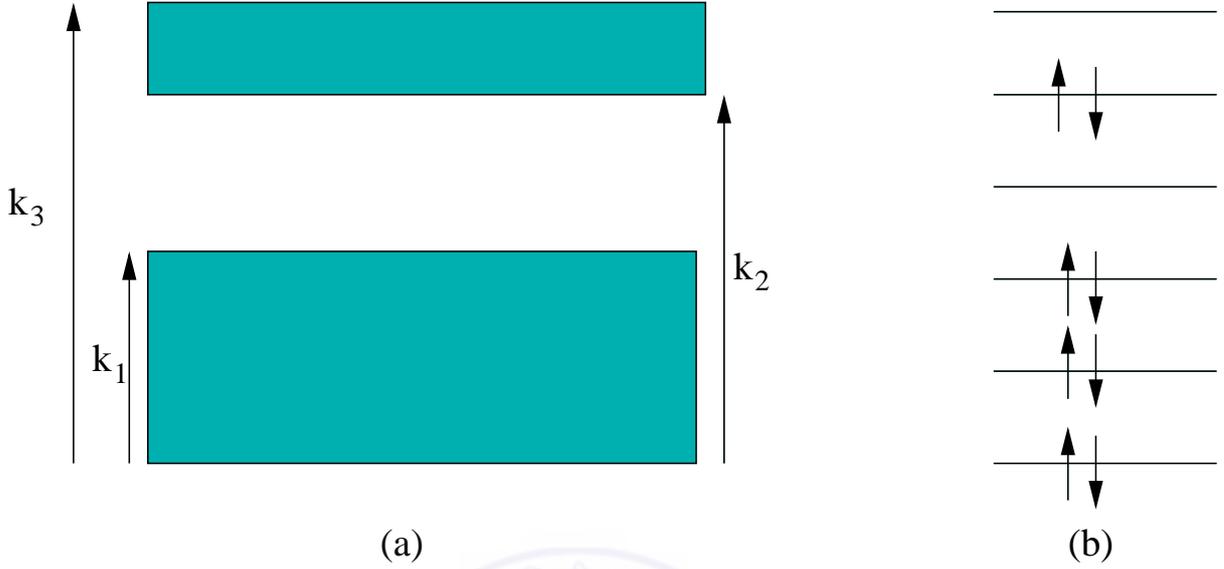


Figure 3.1: k - space occupation for homogeneous electron gas (HEG) (a), and the corresponding orbital occupation (b), in the excited state configuration of a one-gap system

is the core density,

$$\rho_2 = \frac{k_2^3}{3\pi^2} \quad (3.6)$$

is the sum of the core density and the density corresponding to unoccupied orbitals in the range k_1 to k_2 and

$$\rho_3 = \frac{k_3^3}{3\pi^2} \quad (3.7)$$

is the sum of the core, the unoccupied and the shell orbital densities outside k_2 . Non-interacting Kinetic energy functional [100] of this system is given as,

$$\begin{aligned} T^*(k_1, k_2, k_3) &= V \frac{1}{10\pi^2} (k_1^5 + k_3^5 - k_2^5) \\ &= V \frac{3}{10} (3\pi^2)^{2/3} (\rho_1^{5/3} + \rho_3^{5/3} - \rho_2^{5/3}) \end{aligned} \quad (3.8)$$

where V is the volume of the system. Similarly the exchange energy for this one-gap system is given as

$$E_X^* = E_X^{core} + E_X^{shell} + E_X^{core-shell} \quad (3.9)$$

where

$$E_X^{core} = V \left[-\frac{k_1^4}{4\pi^3} \right] \quad (3.10)$$

is the exchange energy of the core electrons,

$$E_X^{shell} = -\frac{V}{8\pi^3} \left[2(k_3^3 - k_2^3)(k_3 - k_2) + (k_3^2 - k_2^2)^2 \ln \left(\frac{k_3 + k_2}{k_3 - k_2} \right) \right] \quad (3.11)$$

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

$$E_X^{core-shell} = -\frac{V}{8\pi^3} \left[2(k_3 - k_2)k_1^3 + 2(k_3^3 - k_2^3)k_1 + (k_2^2 - k_1^2)^2 \ln \left(\frac{k_2 + k_1}{k_2 - k_1} \right) - (k_3^2 - k_1^2)^2 \ln \left(\frac{k_3 + k_1}{k_3 - k_1} \right) \right] \quad (3.12)$$

represents the exchange energy of interaction between the core and the shell electrons.

Using the expressions above for an inhomogeneous system leads to modified Thomas-Fermi (MTF) approximation for the excited-states kinetic energy and modified local-density approximation (MLDA) for the exchange. To see how this methodology will apply to non-interacting system, consider an excited-state of noninteracting electrons shown in figure 3.1(b) where a set of orbitals (core orbitals) starting from the lowest energy orbital of the system $\{\phi_i; i = 1, n_c\}$ are fully occupied, then there is a set of orbitals $\{\phi_i; i = n_c + 1, n_r\}$ that are unoccupied and finally there is another set of occupied orbitals $\{\phi_i; i = n_r + 1, n\}$. In this case

$$\begin{aligned} \rho_1(\mathbf{r}) &= \sum_{i=1}^{n_c} |\phi_i(\mathbf{r})|^2 \\ \rho_2(\mathbf{r}) &= \sum_{i=n_c+1}^{n_r} |\phi_i(\mathbf{r})|^2 \\ \rho_3(\mathbf{r}) &= \sum_{i=n_r+1}^n |\phi_i(\mathbf{r})|^2 \end{aligned} \quad (3.13)$$

and the excited-state density is given by

$$\rho(\mathbf{r}) = \rho_1(\mathbf{r}) + \rho_2(\mathbf{r}) + \rho_3(\mathbf{r}) \quad (3.14)$$

Kinetic energy of the system by applying the MTF approximation is given as

$$T^{MTF}(\rho_1, \rho_2, \rho_3) = \frac{3}{10} (3\pi^2)^{2/3} \int d\mathbf{r} \left(\rho_1^{5/3}(\mathbf{r}) + \rho_3^{5/3}(\mathbf{r}) - \rho_2^{5/3}(\mathbf{r}) \right) \quad (3.15)$$

Similarly in applying the MLDA for calculating the exchange energy for an inhomogeneous system, $k_1(\mathbf{r})$, $k_2(\mathbf{r})$ and $k_3(\mathbf{r})$ in equations 3.10, 3.11 and 3.12 correspond to densities $\rho_1(\mathbf{r})$, $\rho_2(\mathbf{r})$ and $\rho_3(\mathbf{r})$ of equation 3.13 and are given by equations 3.5, 3.6 and 3.7. The exchange energy is calculated by integrating the resulting expression over space. After some algebraic manipulations the MLDA for the exchange energy can be written as

$$\begin{aligned} E_X^{MLDA} &= \int \rho(\mathbf{r}) [\epsilon(k_3) - \epsilon(k_2) + \epsilon(k_1)] d\mathbf{r} + \frac{1}{8\pi^3} \int (k_3^2 - k_1^2)^2 \ln \left(\frac{k_3 + k_1}{k_3 - k_1} \right) d\mathbf{r} \\ &- \frac{1}{8\pi^3} \int (k_3^2 - k_2^2)^2 \ln \left(\frac{k_3 + k_2}{k_3 - k_2} \right) d\mathbf{r} - \frac{1}{8\pi^3} \int (k_2^2 - k_1^2)^2 \ln \left(\frac{k_2 + k_1}{k_2 - k_1} \right) d\mathbf{r} \end{aligned} \quad (3.16)$$

Here $\epsilon(k) = -\frac{3k}{4\pi}$ is the exchange energy per electron for the HEG in its ground-state with the Fermi wave-vector equal to k . The expression above is extended to local spin-density approximation as

$$E_X^{MLSD}[\rho_\alpha, \rho_\beta] = \frac{1}{2} [E_X^{MLDA}(2\rho_\alpha) + E_X^{MLDA}(2\rho_\beta)] \quad (3.17)$$

Here MLSD stands for modified local spin density approximation. In calculating exchange energy in this manner we are not calculating any overlap integral for the wavefunction. Thus the functional is as simple as the ground state functional but has more terms. The functional is made more accurate if the self-interaction energy of the orbitals where an electron is removed from and creates a gap and that where this electron is added is subtracted from the functional of Eq. (5.8) to make a self-interaction correction (SIC) [101]. If an excited electron does not create a gap, no SIC is made for it. So the final

expression for the exchange energy for excited state becomes

$$E_X^{MLSDSIC} = E_X^{MLSD} - \sum_i^{rem} E_i^{SIC}[\phi^{rem}] - \sum_i^{add} E_i^{SIC}[\phi^{add}] \quad (3.18)$$

where,

$$E_i^{SIC}[\phi_i] = \frac{1}{2} \int \int \frac{|\phi_i(\mathbf{r}_1)|^2 |\phi_i(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + E_X^{LSD}[\rho[\phi_i]] \quad (3.19)$$

Here i in the second term of equation 3.18 represents the orbitals from where electrons are removed and in the third term it represents the orbitals to which electrons are added and $E_X^{LSD}[\rho[\phi_i]]$ is the exchange energy of orbital ϕ_i in the local spin-density approximation.

Now consider a system with the ground-state density $\rho_0(\mathbf{r})$ and the density $\rho(\mathbf{r})$ for the n^{th} excited-state. The question arises: how do we get $\rho_1(\mathbf{r})$, $\rho_2(\mathbf{r})$ and $\rho_3(\mathbf{r})$ from these densities to employ the MLDA to calculate its exchange energy? The simplest way to do this is through the excited-state Kohn-Sham system. From the occupied and unoccupied orbitals of the ground-state Kohn-Sham system corresponding to $\rho_0(\mathbf{r})$, we consider the configuration corresponding to its n^{th} excited-state. Now we generate [40, 65, 71] the excited-state Kohn-Sham system for the excited-state density $\rho(\mathbf{r})$ in this configuration. Using the occupied and unoccupied orbitals of the latter system, we get $\rho_1(\mathbf{r})$, $\rho_2(\mathbf{r})$ and $\rho_3(\mathbf{r})$. Note that in constructing these densities, we have employed the ground- and the excited-state densities. Thus although the functional is finally written explicitly in terms of $\rho_1(\mathbf{r})$, $\rho_2(\mathbf{r})$ and $\rho_3(\mathbf{r})$, it is intrinsically a functional of $\rho(\mathbf{r})$ and $\rho_0(\mathbf{r})$. From ρ_i 's we get k_i 's which are used to calculate exchange energy of the system.

Next question that arises is how do we apply the energy functional derived above to obtain excited-state densities and energies using the Kohn-Sham method. That is, how to do self consistent calculation with it. This requires calculation of functional derivative of the energy functional with respect to the density. The problem of obtaining the functional derivative of this functional is a difficult one and will be dealt with in the next chapter. Here we are concerned with the accuracy of the functional itself. Thus for calculations in this paper, we employ the same form for the LDA exchange potential as for the ground-

state. Our calculations are therefore only partly self-consistent.

The MLSDSIC functional of equation 3.18 for one-gap systems has been applied [70] to calculate energies for such excited states i.e states with one set of unoccupied orbitals between two sets of occupied orbitals. The calculation is done as follows. We calculate the orbitals of an excited-state configuration by solving self-consistently the Kohn-Sham equation with the Dirac exchange potential [81]

$$v_X(\mathbf{r}) = -\frac{(3\pi^2\rho(\mathbf{r}))^{1/3}}{\pi} \quad (3.20)$$

and employ these orbitals to calculate the exchange energy of the excited-state by employing the MLSDSIC functional of equation 3.18 for the exchange energy. Our main aim is to calculate transition energies. Therefore, steps involved in calculation of the transition energies are:

(i) Perform a self-consistent LSD calculation for the ground-state within the exchange-only, i.e. with the potential of 3.20 and calculate the total ground-state energy with the exchange energy calculated by employing the LSD approximation for it. LDA for exchange is given by

$$E_X^{LDA} = \int d\mathbf{r}\rho(\mathbf{r})\epsilon(k_F(\mathbf{r})) \quad (3.21)$$

and its LSD generalization is given by equation 3.17.

(ii) Next, perform a self-consistent exchange-only LSD calculation for the excited-state with the potential of 3.20, and calculate the total excited-state energy with the exchange energy calculated by employing the MLSDSIC approximation given by equation 3.18. The densities $\rho_1(\mathbf{r})$, $\rho_2(\mathbf{r})$ and $\rho_3(\mathbf{r})$ for calculating the exchange energy are obtained from the orbitals of the LSD self-consistent calculation. We note that during the self-consistent calculations with the LSD approximation, sometimes orbitals may swap [76] during different iteration, particularly if their orbital energies are very close. In the cases reported in this paper, this does not happen.

(iii) Obtain the transition energy as the difference between the excited-state energy and

the ground-state energy.

The results for excited-state energies thus obtained are highly accurate. As such, they bring out the soundness of physics invoked in constructing the functional. Although the calculations are only partially self-consistent, the effect of full self-consistency is not expected to be as significant as that of employing the appropriate functional for the excited-states. The functional has also been employed to calculate accurately the band gaps [73] of semiconductors with a wide range of band gaps.

Although past studies [70, 73] have given good results for one-gap systems, these are not the only states of interest. This prompts us to ask whether the method adopted to construct the functional is specific to the one-gap excited-states or is it more general. To examine this, in the present chapter we extend the idea further by constructing the excited state energy functional for two-gap excited-states as shown in 3.2. In these system two set of orbitals are unfilled therefore corresponding k - *space* has two gaps as shown in the figure.

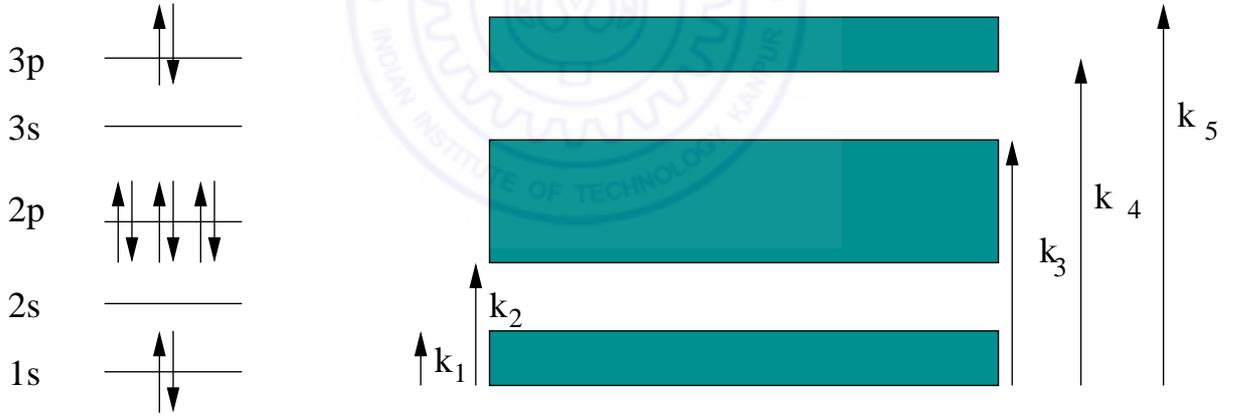


Figure 3.2: Orbital occupation and the corresponding k - *space* occupation for homogeneous electron gas(HEG) in the excited state configuration of two-gap system

An example of two-gap system is excited state configuration $1s^2 2s^0 2p^6 3s^0 3p^2$ of Ne(10) where the orbitals $2s$ and $3s$ constitute the first and the second gap, respectively, for both the up and down spin electrons and the $1s$ and $2p$ orbitals constitute the core

and the 1st shell and $3p$ orbitals constitute the second shell. Such excitations for heavy atoms have been studied [77] by using synchrotron radiation sources. Calculation of excitation energy for such systems subjects the functional proposed to a severe test for its accuracy. In the next section we describe how exchange energy functional is constructed for a two-gap excited states.

3.3 Exchange energy functional for excited states with two-gaps

To construct the MLDA exchange energy functional for a two gap excited-state, the state is represented in the k -space by occupation of electrons from $k = 0$ to $k = k_1$ (core), k_2 to k_3 (first shell) and again from k_4 to k_5 (second shell) as shown schematically in Fig. (3.2); states from k_1 to k_2 and from k_3 to k_4 are left unoccupied. We calculate the exchange energy by considering the exchange interaction of electrons in the filled levels.

The various \mathbf{k} -vectors for the homogeneous electron gas in a two-gap system are given as

$$k_1^3 = 3\pi^2 \rho_c \quad (3.22)$$

$$k_2^3 - k_1^3 = 3\pi^2 \rho_{v1} \quad (3.23)$$

$$k_3^3 - k_2^3 = 3\pi^2 \rho_{s1} \quad (3.24)$$

$$k_4^3 - k_3^3 = 3\pi^2 \rho_{v2} \quad (3.25)$$

$$k_5^3 - k_4^3 = 3\pi^2 \rho_{s2} \quad (3.26)$$

where ρ_c , ρ_{s1} and ρ_{s2} are the electron densities corresponding to the core and the first and the second shell orbitals. Similarly, ρ_{v1} is the electronic density corresponding to the first set of unoccupied orbitals and ρ_{v2} is the density for the second set of unoccupied orbitals.

The total electron density $\rho(\mathbf{r})$ is given as

$$\rho(\mathbf{r}) = \rho_c(\mathbf{r}) + \rho_{s1}(\mathbf{r}) + \rho_{s2}(\mathbf{r}) \quad (3.27)$$

The total exchange energy of this configuration is [74]

$$E_X^{MLDA} = E_X^{core} + E_X^{shell1} + E_X^{shell2} + E_X^{core-shell1} + E_X^{core-shell2} + E_X^{shell1-shell2} \quad (3.28)$$

where

$$E_X^{core} = V \left[-\frac{k_1^4}{4\pi^3} \right] \quad (3.29)$$

is the exchange energy of the core electrons;

$$E_X^{shell1} = -\frac{V}{8\pi^3} \left[2(k_3^3 - k_2^3)(k_3 - k_2) + (k_3^2 - k_2^2)^2 \ln \left(\frac{k_3 + k_2}{k_3 - k_2} \right) \right] \quad (3.30)$$

is the exchange energy of electrons in the first shell;

$$E_X^{shell2} = -\frac{V}{8\pi^3} \left[2(k_5^3 - k_4^3)(k_5 - k_4) + (k_5^2 - k_4^2)^2 \ln \left(\frac{k_5 + k_4}{k_5 - k_4} \right) \right] \quad (3.31)$$

is the exchange energy of electrons in the second shell;

$$\begin{aligned} E_X^{core-shell1} = & -\frac{V}{8\pi^3} \left[2(k_3 - k_2)k_1^3 + 2(k_3^3 - k_2^3)k_1 + (k_2^2 - k_1^2)^2 \ln \left(\frac{k_2 + k_1}{k_2 - k_1} \right) \right. \\ & \left. - (k_3^2 - k_1^2)^2 \ln \left(\frac{k_3 + k_1}{k_3 - k_1} \right) \right] \end{aligned} \quad (3.32)$$

is the exchange energy between the core and the first shell electrons;

$$\begin{aligned} E_X^{core-shell2} = & -\frac{V}{8\pi^3} \left[2(k_5 - k_4)k_1^3 + 2(k_5^3 - k_4^3)k_1 + (k_4^2 - k_1^2)^2 \ln \left(\frac{k_4 + k_1}{k_4 - k_1} \right) \right. \\ & \left. - (k_5^2 - k_1^2)^2 \ln \left(\frac{k_5 + k_1}{k_5 - k_1} \right) \right] \end{aligned} \quad (3.33)$$

is the exchange energy between the core and the second shell electrons; and

$$\begin{aligned} E_X^{shell1-shell2} = & -\frac{V}{8\pi^3} \left[2(k_3 - k_2)(k_5^3 - k_4^3) + 2(k_3^3 - k_2^3)(k_5 - k_4) \right. \\ & \left. + (k_4^2 - k_3^2)^2 \ln \left(\frac{k_4 + k_3}{k_4 - k_3} \right) - (k_5^2 - k_3^2)^2 \ln \left(\frac{k_5 + k_3}{k_5 - k_3} \right) \right. \\ & \left. + (k_5^2 - k_2^2)^2 \ln \left(\frac{k_5 + k_2}{k_5 - k_2} \right) - (k_4^2 - k_2^2)^2 \ln \left(\frac{k_4 + k_2}{k_4 - k_2} \right) \right] \end{aligned} \quad (3.34)$$

is the exchange energy between the first shell and the second shell electrons. Here V is the volume of the system. On adding all the terms together, the functional above takes a somewhat simpler form given below.

For a space-dependent density $\rho(\mathbf{r})$, the corresponding core and shell densities $\rho_c(\mathbf{r})$, $\rho_{s1}(\mathbf{r})$ and $\rho_{s2}(\mathbf{r})$, and the density of unoccupied orbitals $\rho_{v1}(\mathbf{r})$ and ρ_{v2} , the MLDA exchange energy functional for two-gap excited-states is then given as

$$\begin{aligned}
E_X^{MLDA} &= \int \rho(\mathbf{r}) [\epsilon(k_5) - \epsilon(k_4) + \epsilon(k_3) - \epsilon(k_2) + \epsilon(k_1)] d\mathbf{r} \\
&- \frac{1}{8\pi^3} \int \left[(k_3^2 - k_2^2)^2 \ln \left(\frac{k_3 + k_2}{k_3 - k_2} \right) \right] d\mathbf{r} - \frac{1}{8\pi^3} \int \left[(k_5^2 - k_4^2)^2 \ln \left(\frac{k_5 + k_4}{k_5 - k_4} \right) \right] d\mathbf{r} \\
&- \frac{1}{8\pi^3} \int \left[(k_2^2 - k_1^2)^2 \ln \left(\frac{k_2 + k_1}{k_2 - k_1} \right) \right] d\mathbf{r} + \frac{1}{8\pi^3} \int \left[(k_3^2 - k_1^2)^2 \ln \left(\frac{k_3 + k_1}{k_3 - k_1} \right) \right] d\mathbf{r} \\
&- \frac{1}{8\pi^3} \int \left[(k_4^2 - k_1^2)^2 \ln \left(\frac{k_4 + k_1}{k_4 - k_1} \right) \right] d\mathbf{r} + \frac{1}{8\pi^3} \int \left[(k_5^2 - k_1^2)^2 \ln \left(\frac{k_5 + k_1}{k_5 - k_1} \right) \right] d\mathbf{r} \\
&+ \frac{1}{8\pi^3} \int \left[(k_5^2 - k_3^2)^2 \ln \left(\frac{k_5 + k_3}{k_5 - k_3} \right) \right] d\mathbf{r} - \frac{1}{8\pi^3} \int \left[(k_4^2 - k_3^2)^2 \ln \left(\frac{k_4 + k_3}{k_4 - k_3} \right) \right] d\mathbf{r} \\
&- \frac{1}{8\pi^3} \int \left[(k_5^2 - k_2^2)^2 \ln \left(\frac{k_5 + k_2}{k_5 - k_2} \right) \right] d\mathbf{r} + \frac{1}{8\pi^3} \int \left[(k_4^2 - k_2^2)^2 \ln \left(\frac{k_4 + k_2}{k_4 - k_2} \right) \right] d\mathbf{r}
\end{aligned} \tag{3.35}$$

$\epsilon(k) = -\frac{3k}{4\pi}$ represents energy per particle. Here the quantities k_1, k_2, k_3, k_4 and k_5 are calculated using equations 3.22-3.26 and are space-dependent. The functional obtained above is extended to MLSDSIC functional by using equations 3.17-3.19. We note that the two-gap functional reduces to that corresponding to one-gap if either $k_1 = k_2$ or $k_3 = k_4$. In the next section we present the results of employing the functional above to a range of systems using the steps given in section 3.2.

3.4 Results

Now we present the results for the excitation energies of many different atomic systems obtained with the exchange energy functional set up in the previous section. Since the

LDA or any of its modified form is expected [88] to be accurate only for single Slater determinants, in our calculations we calculate the excited-state energies for a given configuration rather than for a state. Further, the calculations are performed within the central-field approximation, i.e. we take the densities to be spherical, since the contribution of non-central components of the density to the total energy is in general relatively insignificant [6]. The excitation energies from the ground-state to this configuration are then given by the difference between the excited-state and the ground state energy of a system. As mentioned above, steps involved in the calculation of the transition energies are the same as those for the one-gap systems except that now the functional used for the exchange energy is that corresponding to the two-gap systems. Therefore calculation of transition energy involves following steps: (i) Self consistent Kohn-Sham calculation with Dirac exchange potential to generate orbitals for excited states; (ii) Calculation of k_i 's from orbitals and using k_i 's we calculate exchange energy employing the new functional. We use this exchange energy to calculate total energy of the system; (iii) Subtract the ground state energy to get the transition energy.

To check the accuracy of the functionals developed by us we compare the transition energies obtained by our calculation with accurate exchange-only excitation energies. The latter can be calculated by applying either the Hartree-Fock(HF) method [78], or the optimized potential method (OPM) [60] or the orbitals obtained by from the Harbola-Sahni (HS) exchange potential [61]. The energies obtained by the three methods are within parts per million of each other for the ground [79, 80] as well as excited-states [6, 64] of atoms. Since the HS potential can be obtained rather easily (in comparison to the HF or the OPM) for a large variety of atomic excited-states, in this work we compare our answers with the transition energies obtained through this method. The conclusions drawn are however equally applicable to comparison with the numbers calculated by the Hartree-Fock method or the OPM. To put the accuracy of numbers obtained in a proper perspective, we also calculate the energies of the excited-states using the regular LSD expression for the exchange energy and compare these to the results of the MLSDSIC

and the HS results. We see that the functional proposed by us gives results that are significantly better than those obtained using the regular LSD functional and are very close to the numbers corresponding to the exact exchange calculations. In the following subsections, we discuss one by one the excitation energies when one, two, three and four electrons are excited in such a manner that a two-gap excited-state is created. The number of electrons to be excited is not limited unlike the case of time-dependent density functional theory where adiabatic local density approximation is used [94,95]

3.4.1 Transitions involving one electron

In Table 3.1 excitation energy for excitation of single electron is given. In all the cases an electron from the 2s orbital is excited, as shown in figure 3.3 for the neon atom. In this case the electron is excited to the 4s orbital, therefore the 2s orbital for the spin down electron constitutes the first gap while the 3s and the 3p orbitals together form the second gap. Further, in calculating the exchange energy using Eq. (5.17) the self interaction correction is done for the 2s, from where the electron is removed, and the 4s orbital where the electron is added. In Table 3.1, the excitation energies obtained by

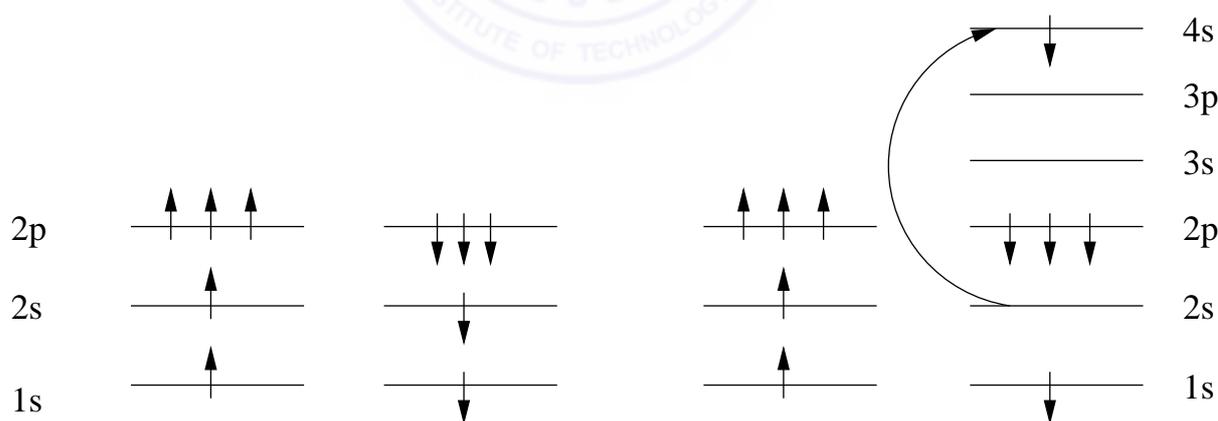


Figure 3.3: Excitation of one electron.

employing the MLSDSIC functional for excited states of different atoms are compared

to those given by the ground-state LSD functional and accurate exchange-only energies obtained using the orbitals obtained by employing the HS exchange potential [61]. It is evident that while the LSD leads to an error of about 5-10% in comparison to the HS results in all cases, the MLSDSIC gives energies that are very close to the actual excitation HS energies and brings the error down by roughly a factor of 3 except for boron where the LSD and the MLSDSIC give almost the same answers. To show the improvement that our approach yields, we have plotted in figure 3.3 the percentage difference of transition energies from the HS value for both the LSD and the MLSDSIC values for the cases considered in Table 3.1. The plot clearly displays the accuracy of our approach. For

Table 3.1: Excitation energy of two-gap systems (one electron excitation). Numbers given are in atomic units. The first column gives the atom and the configuration to which the system is excited from the ground-state. In the second column are given the transition energies obtained by employing the ground state LSD functional for both the ground-state and the excited-state. The third column gives transition energies obtained by employing the ground-state LSD for the ground-state and the MLSDSIC functional for the excited state. The percentage difference from the HS values, given in the fourth column, is also given in the brackets. The last column gives the difference between the eigenenergies, as calculated in the HS method, of the orbitals involved in the transition.

atoms	$\Delta E(LSD)$	$\Delta E(MLSDSIC)$	$\Delta E(HS)$	$\Delta\epsilon(HS)$
$B(2s^1 2p^1 3s^1 M_L = 1, M_S = 1/2)$	0.380(6.4)	0.437(7.9)	0.406	0.387
$C(2s^1 2p^2 3s^1 M_L = 1, M_S = 1)$	0.575(12)	0.706(7)	0.658	0.580
$O(2s^1 2p^4 3p^1 M_L = 2, M_S = 1)$	1.044(15)	1.313(6)	1.230	1.066
$F(2s^1 2p^5 3p^1 M_L = 2, M_S = 1/2)$	1.259(14)	1.556(7)	1.463	1.311
$Ne(2s^1 2p^6 4s^1 M_L = 0, M_S = 0)$	1.538(14)	1.837(2)	1.796	1.632
$Mg(2s^1 2p^6 3s^2 4s^1 M_L = 0, M_S = 0)$	3.170(9)	3.568(2)	3.490	3.036
$Si(2s^1 2p^6 3s^2 3p^2 4s^1 M_L = 1, M_S = 1)$	5.385(7)	5.914(2)	5.785	5.225
$P(2s^1 2p^6 3s^2 3p^3 4s^1 M_L = 0, M_S = 3/2)$	6.656(6)	7.186(1)	7.095	6.495
$S(2s^1 2p^6 3p^4 4s^1 M_L = 1, M_S = 1)$	8.069(6)	8.648(1)	8.547	7.865
$Cl(2s^1 2p^6 3s^2 3p^5 4s^1 M_L = 1, M_S = 1/2)$	9.548(6)	10.224(1)	10.114	9.359
average error	9.5%	3.7%		

one electron excitations, TDDFT approach to calculating excitation energies can also be applied within the adiabatic LDA to calculate excitation energies for one electron excitations. However, in the excitations reported in Table 3.1, the method does not lead to good results. For example, in the case of chlorine, the difference in the Kohn-Sham exchange-only orbital energies between the 2s and the 4s orbitals involved in the

transition is 9.186 atomic units. Further, the TDDFT correction to it within the single-pole approximation is negligibly small. This leads to the excitation energy of 9.186 atomic units that is about 9% in error compared to the 6% error in the LSD and 1% error in the MLSDSIC values with respect to the accurate exchange-only theory numbers. We conclude that TDDFT calculations may not be consistently reliable for calculations of one-electron transition energies when an electron is excited from a deep level. It has

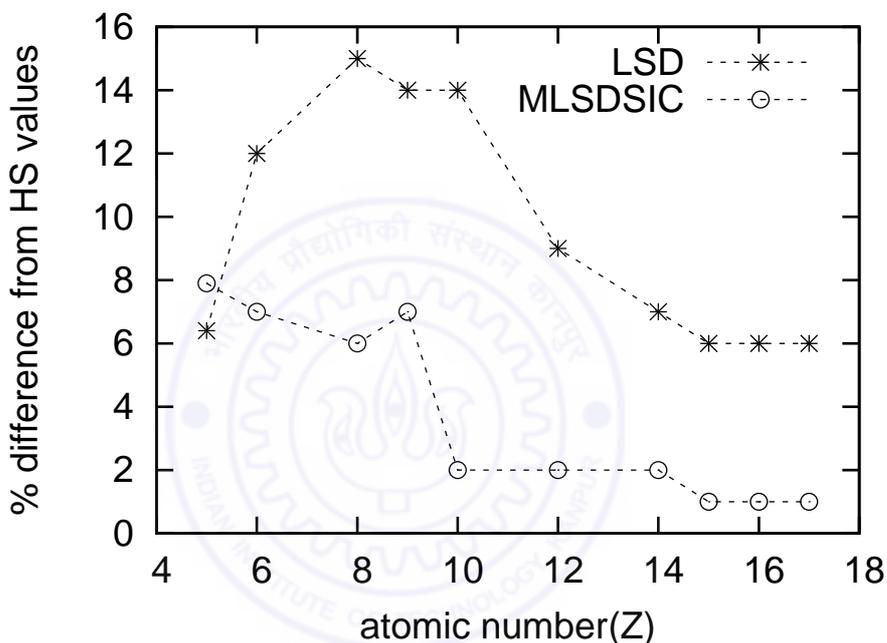


Figure 3.4: Error graph for one electron transitions.

been observed [63] that in an exact Kohn-Sham calculation, the difference between the orbital energies of the highest occupied orbital and an unoccupied orbital is very close to the corresponding excitation energy. In this connection it is interesting to compare the Δ SCF excitation energies with the orbital energy differences when an electron is excited from a deep level. We make such a comparison in Table 3.1 where we also show the orbital energy difference, as calculated in the HS theory, between the orbitals involved in the transition. We see that in the present case the orbital energy difference is not close to the Δ SCF numbers. Thus when electrons are excited from deep levels, only Δ SCF

method can give reliable transition energies.

3.4.2 Transitions involving two electrons

In Table 3.2 we give excitation energies obtained when two electrons are excited. In the cases considered, two electrons from different orbitals are excited to different higher orbitals. For instance, in the case of Na, as shown in figure 3.5, one electron from the 2s orbital and one from the 3s orbital are excited to the 3p orbitals with their spins remaining unchanged. Therefore the 2s and the 3s orbitals form the first and the second gap, respectively. In this case, for exchange energy calculation we do self interaction

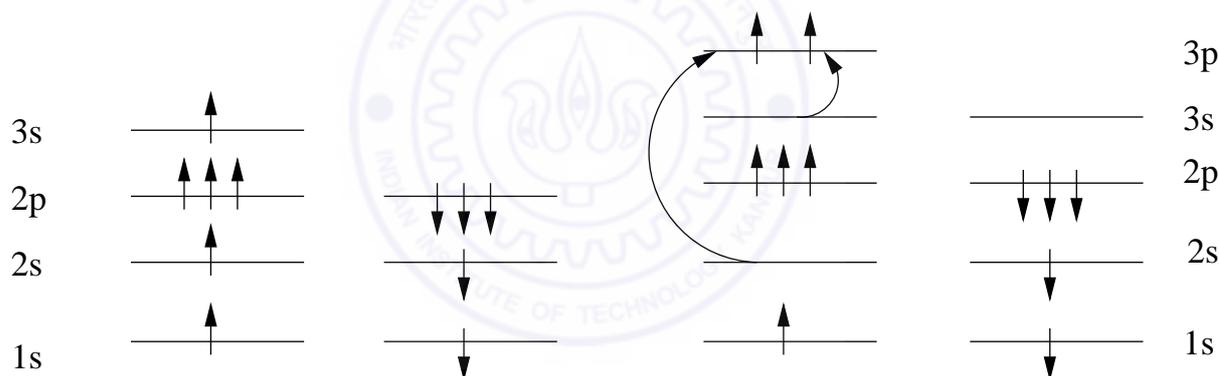


Figure 3.5: Excitation of two electrons.

correction for each of the 2s and 3s orbitals from where electrons are removed and for the two 3p orbitals where electrons are added. In Table 3.2, excitation energies obtained in this way by employing MLSDSIC functional are given together with the HS and the LSD values. It is seen that improvement over LSD values is substantial for all the cases, again reducing the error by roughly a factor of 3 or more. In figure 3.6 we display the errors of the LSD numbers and the MLSDSIC numbers with respect to their HS counterparts.

Table 3.2: Excitation energy of two-gap systems (two electron excitation). Numbers given are in atomic units.

atoms	$\Delta E(LSD)$	$\Delta E(MLSDSIC)$	$\Delta E(HS)$
$B(2p^1 3p^2 M_L = 3, M_S = 1/2)$	0.966(4.4)	1.053(4.3)	1.010
$C(2p^2 3p^2 M_L = 2, M_S = 2)$	1.286(9)	1.432(2)	1.409
$N(2p^4 3p^1 M_L = 2, M_S = 3/2)$	1.257(18)	1.501(4)	1.438
$F(2p^6 3p^1 M_L = 1, M_S = 1/2)$	1.945(18)	2.439(3)	2.371
$Ne(2p^6 3p^2 M_L = 1, M_S = 1)$	3.438(13)	4.122(4)	3.948
$Na(2s^1 2p^6 3p^2 M_L = 1, M_S = 1/2)$	2.318(11)	2.694(3)	2.615
$Al(2s^1 2p^6 3s^1 3p^3 M_L = 0, M_S = 1/2)$	4.254(10)	4.780(2)	4.702
$Ar(2p^6 3s^0 3p^6 4p^2 M_L = 2, M_S = 0)$	2.216(14)	2.703(4)	2.589
$K(2p^6 3s^1 3p^6 4p^2 M_L = 1, M_S = 1/2)$	1.407(13)	1.697(4)	1.626
$Cu(2p^6 3s^1 3p^3 3d^{10} 4s^2 4p^1 M_L = 1, M_S = 1/2)$	6.825(8)	7.846(6)	7.404
average error	11.1%	3.4%	

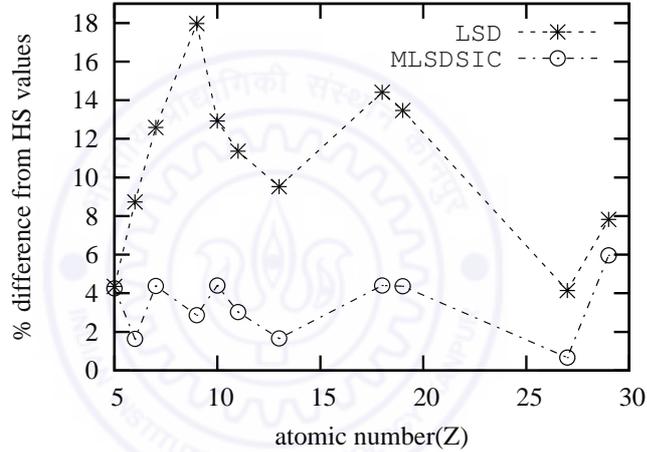


Figure 3.6: Error graph for two electron transitions.

3.4.3 Transitions involving three electrons

In Table 3.3 are given the excitation energies involving excitation of three electrons. We have excited three electrons from different orbitals in different cases considered here. For example, in the case of oxygen two up spin electrons from the 2s and 2p orbitals are excited to 3p orbitals and one down spin electron from 2p is excited to the 3p up spin orbital, as shown in figure 3.7. Here the 2s orbital forms the first gap while 2p and 3s orbitals together constitute the second gap. In these cases down spin electrons are transferred to up spin orbitals. Therefore, the process can be seen as taking place in two steps. For

O, we first transfer the down spin 2p electron into 3s orbital and then subsequently the electrons are moved to their final orbitals. The intermediate configuration involved here is just like the ground state configuration. Therefore self-interaction correction is done for one 2s orbital, one 2p orbital, one 3s orbital and for three 3p orbitals. In Table 3.3 we give excitation energies obtained in this way by employing MLSDSIC functional together with the HS and the LSD values. Two particular transitions that we wish to mention here in connection with SIC are $C(2s^2 2p^2 \ ^3P \rightarrow 2p^2 3p^2 \ M_L = 4, M_S = 0)$ and $O(2s^2 2p^4 \ ^3P \rightarrow 2p^4 3p^2 \ M_L = 4, M_S = 0)$. Here two electrons are excited to higher orbitals and one electron in the 2p orbital undergoes a spin flip. Although it may appear that no SIC has to be made for this electron, this is not so. Since this transition of electron creates a gap in the 2p orbital, SIC is made for this electron also. Like the previous two cases, the improvement over LSD values is substantial for all the systems. This is also evident from figure 3.8 where errors in the LSD and MLSDSIC values are shown.

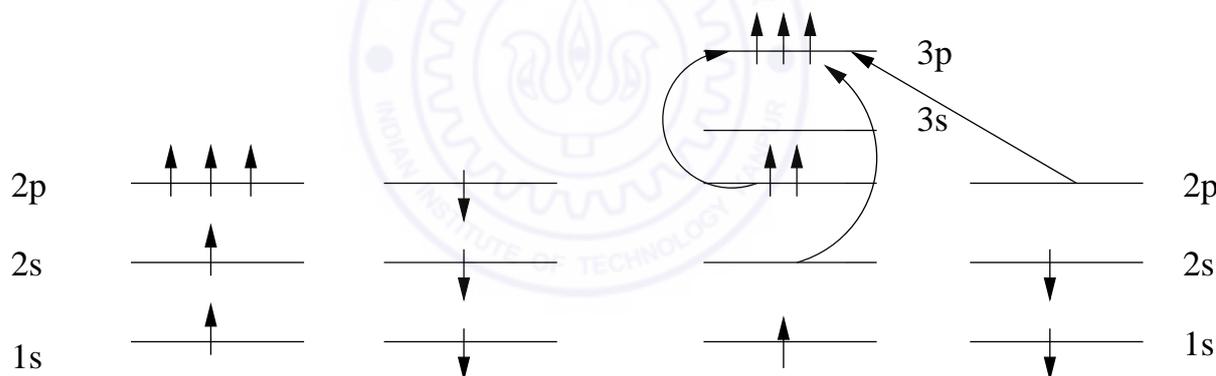


Figure 3.7: Excitation of three electrons.

3.4.4 Transition involving four electrons

In Table 3.4 excitation energies involving excitation of four electrons are given. Two of the four electrons excited come from the 2s orbitals and another two electrons from the 3s orbitals and enter into different orbitals in different atoms. For example in the case of

Table 3.3: Excitation energy of two-gap systems (three electron excitation). Numbers given are in atomic units.

atoms	$\Delta E(LSD)$	$\Delta E(MLSDSIC)$	$\Delta E(HS)$
$C(2p^1 3s^1 3p^2 M_L = 2, M_S = 2)$	1.961(3)	1.977(2.5)	2.028
$O(2s^1 2p^2 3p^3 M_L = 1, M_S = 2)$	2.868(7)	3.082(0.4)	3.070
$C(2p^2 3p^2 M_L = 4, M_S = 0)$	1.462(3.5)	1.562(3.0)	1.515
$O(2p^4 3p^2 M_L = 4, M_S = 0)$	2.424(8.4)	2.721(2.9)	2.645
$F(2s^2 2p^1 3p^1 3d^2 M_L = 5, M_S = 5/2)$	2.960(0.3)	3.013(1.4)	2.971
$Ne(2s^1 2p^4 3p^3 M_L = 1, M_S = 2)$	4.047(7)	4.456(2)	4.354
$Na(2s^1 2p^5 3p^3 M_L = 1, M_S = 1/2)$	4.046(9)	4.485(2)	4.399
$Mg(2s^1 2p^4 3s^2 3p^3 M_L = 1, M_S = 0)$	8.160(1)	8.176(1)	8.256
$P(2s^2 2p^6 3s^1 4p^3 4s^1 M_L = 1, M_S = 3/2)$	1.532(6)	1.669(2)	1.635
$Ar(2s^2 2p^6 3s^1 3p^4 4p^3 M_L = 1, M_S = 0)$	2.379(4.5)	2.528(1.5)	2.491
$Ca(2s^2 2p^6 3s^1 3p^6 4p^3 M_L = 0, M_S = 1)$	1.914(13)	2.241(2)	2.190
$Zn(3s^1 3p^4 3d^{10} 4s^2 4p^3 M_L = 1, M_S = 0)$	11.633(6)	12.935(4)	12.407
average error	5.7%	2.1%	

Mg, all the four electrons enter into the 3p orbitals, as shown in figure 3.9. Therefore, the resulting vacancies in the 2s orbitals and the 3s orbitals form the first and the second gaps respectively, for both the up and the down spin electrons. Again in all these cases, the excitation of four electrons is done by considering possible intermediate ground-state-like configurations. Therefore for exchange energy calculation self interaction correction is done only for those orbitals which are involved in creation of a gap. As such for Mg we do SIC correction for the two 2s orbitals, two 3s orbitals and four 3p orbitals. In Table 3.4 excitation energies obtained with MLSDSIC functional are compared with the HS and LSD values. As is clearly seen, for all the cases considered here improvement we get over the LSD values is large. In figure 3.10 we show the errors of the LSD and MLSDSIC numbers given in Table 3.4.

3.4.5 Some cases where results are not good

In Table 3.5, we also show three systems where the MLSDSIC functional does not improve results in comparison to the LSD functional. After investigating several possibilities, the

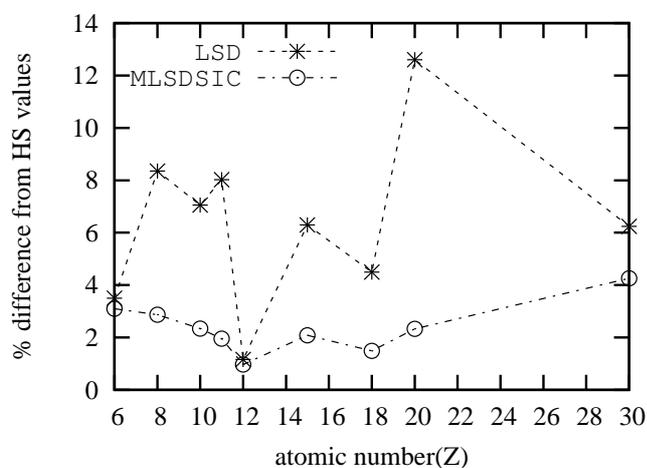


Figure 3.8: Error graph for three electron transitions.

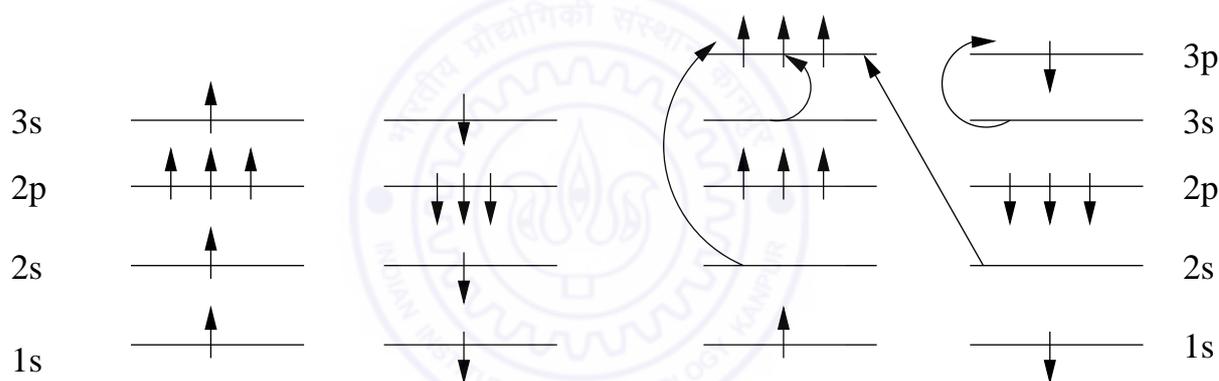


Figure 3.9: Excitation of four electrons.

only observation we make is when the excited electrons go to orbital with eigenvalues close to zero, the MLSDSIC results are worse than the LSD numbers. We have not been able to find a reason for this discrepancy.

3.5 Discussion and concluding remarks.

we have constructed exchange energy functional for excited states having two gaps. The functional is based on local-spin-density approximation and takes care of the configura-

Table 3.4: Excitation energy of two-gap systems (four electron excitation). Numbers given are in atomic units.

atoms	$\Delta E(LSD)$	$\Delta E(MLSDSIC)$	$\Delta E(HS)$
<i>Mg</i> ($2p^6 3p^4$ $M_L = 1, M_S = 1$)	7.053(10)	7.967(2)	7.805
<i>Al</i> ($2p^6 3p^5$ $M_L = 1, M_S = 1/2$)	9.219(9)	10.295(2)	10.116
<i>Si</i> ($2p^6 3p^6$ $M_L = 0, M_S = 0$)	11.609(8)	12.853(1.5)	12.666
<i>P</i> ($2p^6 3p^6 4s^1$ $M_L = 0, M_S = 1/2$)	14.595(7.6)	16.005(1.3)	15.799
<i>S</i> ($2p^6 3p^6 4s^2$ $M_L = 0, M_S = 0$)	18.031(7)	19.613(1)	19.387
<i>Ar</i> ($2p^6 3p^6 4s^2 3d^2$ $M_L = 4, M_S = 0$)	26.346(6)	28.289(1)	28.026
<i>K</i> ($2p^6 3p^6 4s^2 3d^3$ $M_L = 5, M_S = 1/2$)	30.748(6)	32.853(1)	32.555
<i>Ca</i> ($2p^6 3p^6 4s^2 3d^4$ $M_L = 6, M_S = 0$)	35.280(5)	37.551(0.9)	37.220
<i>Sc</i> ($2p^6 3p^6 4s^2 3d^5$ $M_L = 0, M_S = 5/2$)	39.672(5)	42.111(0.8)	41.783
<i>Ti</i> ($2p^6 3p^6 4s^2 3d^6$ $M_L = 2, M_S = 2$)	44.658(4.8)	47.319(1)	46.931
<i>V</i> ($2p^6 3p^6 4s^2 3d^7$ $M_L = 3, M_S = 3/2$)	49.892(4.6)	52.780(1)	52.294
<i>Cr</i> ($2p^6 3p^6 4s^2 3d^8$ $M_L = 3, M_S = 1$)	55.477(4.3)	58.640(1)	57.985
<i>Mn</i> ($2p^6 3p^6 4s^2 3d^9$ $M_L = 2, M_S = 1/2$)	61.128(4.3)	64.472(1)	63.887
<i>Fe</i> ($2p^6 3p^6 4s^2 3d^{10}$ $M_L = 0, M_S = 0$)	66.944(4.2)	70.517(1)	69.862
<i>Co</i> ($2p^6 3p^6 4s^2 3d^{10} 4p^1$ $M_L = 1, M_S = 1/2$)	73.557(4)	77.394(1)	76.594
<i>Ni</i> ($2p^6 3p^6 4s^2 3d^{10} 4p^2$ $M_L = 2, M_S = 0$)	80.803(3.8)	84.918(1)	83.954
<i>Cu</i> ($2p^6 3p^6 4s^2 3d^{10} 4p^3$ $M_L = 0, M_S = 3/2$)	88.715(3.5)	93.118(1)	91.881
<i>Zn</i> ($2p^6 3p^6 4s^2 3d^{10} 4p^4$ $M_L = 1, M_S = 1$)	97.298(3.3)	102.002(1)	100.667
average error	5.3%	1%	

tion of individual excited states. We have employed it with inclusion of SIC to calculate transition energies of two-gap systems. Our calculation is Δ -SCF type and involves two steps. First we calculate ground state energy of the system by solving the Kohn-Sham equation with the LSD approximation. In the second step, Kohn-Sham calculation for the excited-state configuration is performed within the LSD approximation. The resulting orbitals are then used to calculate the total excited-state energy with the MLSDSIC functional for the exchange energy. Use of MLSDSIC functional for excited-state energy calculations leads to substantial improvement over the numbers obtained from LSD functional. In most of the cases studied the maximum departure of the excitation energies obtained with MLSDSIC functional from its HS value is less than 5%. As can be directly seen in the error graphs, while average percentage difference of LSD numbers for one,

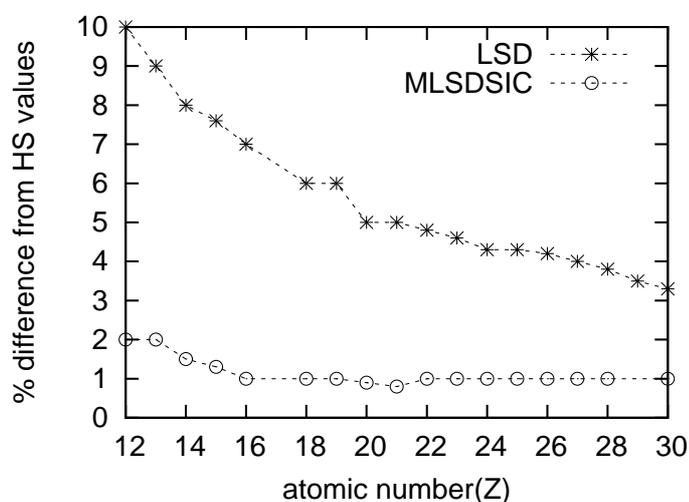


Figure 3.10: Error graph for four electron transitions.

Table 3.5: Excitation energy of states for which our results are not good. Numbers given are in atomic units.

atoms	$\Delta E(LSD)$	$\Delta E(MLSDSIC)$	$\Delta E(HS)$
$Ne(1s^2 2s^2 2p^1 3p^3 3d^2 M_L = 4, M_S = 3)$	3.435	3.418	3.331
$Na(1s^2 2s^2 2p^3 3s^1 3p^1 3d^2 M_L = 4, M_S = 1/2)$	5.314	5.193	5.372
$Mg(1s^2 2s^2 2p^3 3s^2 3p^1 3d^2 M_L = 4, M_S = 0)$	7.564	7.428	7.648

two, three, and four electrons excitations from corresponding HS values are respectively 9.5%, 11.1%, 5.7%, and 5.3% the differences for the MLSDSIC numbers are respectively 3.7%, 3.4%, 2.1% and 1% only. Therefore it is evident that the functional constructed by us is an accurate functional for calculating excitation energies within time-independent density functional formalism. Further, the accuracy obtained shows the correctness of the physics invoked in deriving the functional.

Chapter 4

Accurate exchange energy and total energy for excited states: Inclusion of gradient correction.

4.1 Introduction

Modified LSD exchange energy functional for excited states which we described in chapter 3 does give accurate excitation energy but like LSD for ground states, absolute values of total energy it leads to are not as accurate. Therefore further corrections need to be made to this functional to obtain accurate total energies of the system. In this chapter we include gradient corrections to exchange energy term. Inclusion of gradient corrections to improve the accuracy of energy functionals has been in practice since the inception of density functional theory [20,84]. Such corrections are either derived from the properties of many electrons system or constructed semi-empirically or empirically . Gradient expansion approximation(GEA) attempts to systematically develop density functionals in terms of density and its derivative. However this method has certain problems.For example the GEA first proposed by Herman but its functional derivative becomes exponentially large for exponentially decaying densities. Similarly exchange hole corresponding to GEA has non physical characteristic [22]. Therefore, a less systematic but tractable approach

is often taken to construct density functionals semi-empirically. Generalized gradient approximation(GGA) and meta-generalized gradient approximation(meta-GGA) respectively are the examples of such corrections [84, 85]. While GGA uses gradient of density and its higher power, meta-GGA includes Laplacian of the density and its higher powers. Perdew Wang [85] and Becke's [84] correction to exchange energy are the example of GGA and Perdew Burke Ernzerhof's [20] correction to exchange energy is a meta-GGA kind of correction.

In this chapter we explore how exchange energy functionals for excited states improve with the addition of Becke and PW correction.

4.2 Gradient correction for excited state exchange energy functional

Exchange energy functional reported in chapter 3 gave good excitation energies but not accurate total energy. This is because in calculation of excitation energy errors of ground and excited-states get cancelled. While the error remains there if one calculates exchange energy for excited state only. To make it more accurate now we incorporate generalized-gradient correction due to Becke and PW in the exchange energy of excited states given by MLSD. The reason for including these corrections in the same form as for the ground state is as follows. Becke's and PW's corrections to exchange energy have been constructed to satisfy certain properties which are not specific to the ground states. For example, the Becke correction is made such that the asymptotic decay of exchange energy density goes as $\frac{-1}{2r}$. The Perdew Wang correction is based on modelling the exchange hole so that it satisfies certain sum rules. Therefore, we hope that these corrections will work equally well for excited states also. With this intuition we use generalised gradient corrections for exchange energy due to Becke (equation 4.1) and Perdew-Wang(PW) (equation 4.2) to calculate exchange energy and total energy for excited states.

Exchange energy functional for excited states with the Becke's gradient correction is given as,

$$E_X^{MLSD(Becke)} = E_X^{MLSD} - \beta \sum_{\sigma} \int \rho_{\sigma}^{4/3} \frac{x_{\sigma}^2}{1 + 6\beta x_{\sigma} \sinh^{-1} x_{\sigma}} d\mathbf{r} \quad (4.1)$$

where, $x_{\sigma} = \frac{\nabla \rho_{\sigma}}{\rho_{\sigma}^{4/3}}$ and $\beta = 0.0042$. Similarly exchange energy functional for excited states with PW's gradient correction is given as

$$E_X^{MLSD(PW)} = \int \rho(\mathbf{r}) \epsilon_X^{MLSD}(\mathbf{r}) F(s) d\mathbf{r} \quad (4.2)$$

where,

$$\begin{aligned} \rho(\mathbf{r}) \epsilon_X^{MLSD} &= \rho(\mathbf{r}) [\epsilon(k_3) - \epsilon(k_2) + \epsilon(k_1)] + \frac{1}{8\pi^3} (k_3^2 - k_1^2)^2 \ln \left(\frac{k_3 + k_1}{k_3 - k_1} \right) \\ &- \frac{1}{8\pi^3} (k_3^2 - k_2^2)^2 \ln \left(\frac{k_3 + k_2}{k_3 - k_2} \right) - \frac{1}{8\pi^3} (k_2^2 - k_1^2)^2 \ln \left(\frac{k_2 + k_1}{k_2 - k_1} \right) \end{aligned} \quad (4.3)$$

and, $s = \frac{\nabla \rho}{2k_f \rho}$, $F = (1 + 0.086s^2/m + bs^4 + cs^6)^m$ with $m = 1/15, b = 14, c = 0.2$. We use these functionals to calculate energy of various excited states of atoms. Further, SIC is made for both the functionals by subtracting the self-interaction corresponding to the orbitals involved in transition of electrons. Thus,

$$E_X^{MLSDSIC(Becke)} = E_X^{MLSD(Becke)} - \sum_i^{rem} E_i^{SIC} - \sum_i^{add} E_i^{SIC} \quad (4.4)$$

and,

$$E_X^{MLSDSIC(PW)} = E_X^{MLSD(PW)} - \sum_i^{rem} E_i^{SIC} - \sum_i^{add} E_i^{SIC} \quad (4.5)$$

where,

$$E_i^{SIC}[\phi_i] = \int \int \frac{|\phi_i(\mathbf{r}_1)|^2 |\phi_i(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + E_X^{LSD}[\rho[\phi_i]] \quad (4.6)$$

4.3 Results

We have calculated total energies and excitation energies of excited states of various atoms using the gradient corrected exchange energy functionals given above. The results obtained with the use of these functionals are excellent, giving total energies for excited states which are very close to the corresponding exact exchange only values.

4.3.1 One-gap systems

In the tables 4.1 to 4.6 we present total energies and excitation energies of atomic excited states having one-gap obtained with Becke and PW functionals (with modified LSD) along with the exact exchange/Hartree-Fock(HF) values. The MLSD exchange energy functional corresponding to one-gap case which was employed here is given in equation 3.17

To calculate exchange energy and total energy we do Kohn Sham calculation with the LSD approximation for exchange potential. From the orbitals generated in this way we calculate the k wave vectors from which we get MLSD exchange energy. We add to it the gradient correction and self interaction. We use exchange energy so obtained to get total the energy for the atoms or ions. For calculation of excitation energies we calculate ground state energy with the same functional and take the difference of excited-state and ground-state energies.

Table 4.1 involves those cases where electrons are transferred from an inner s orbital to an outer p orbital. In these cases transition energy is substantial but not very large. In Table 4.2 outer most loosely bound electrons are excited to next higher orbital. Transition energies involved in these cases is quite small. In Table 4.3 electrons are transferred from an inner s orbital to an outer $3p$ orbital. Transition energy is substantial but not very large. In Table 4.4 transition of electrons from $2s$ to $3p$ orbitals have been considered. In these cases transition energy involved is large. In Table 4.5 those cases have been considered where the excited state is not the lowest energy multiplet. In these cases LSD results

Table 4.1: Total energy of excited states and excitation energy (in atomic unit) of various atoms/ions. Every transition involves one electron going from a $2s$ orbital to a $2p$ orbital. In first three columns total energies obtained by exact exchange calculation, Becke functional and perdue Wang functional are given respectively. In the last three columns corresponding excitation energies are given.

atoms/ions	$-E_{HF}^*$	$-E_{Becke}^*$	$-E_{PW}^*$	ΔE_{HF}	ΔE_{Becke}	ΔE_{PW}
$N(2s^2 2p^3 \ ^4S \rightarrow 2s^1 2p^4 \ ^4P)$	53.988	53.989	54.026	0.413	0.409	0.423
$O^+(2s^2 2p^3 \ ^4S \rightarrow 2s^1 2p^4 \ ^4P)$	73.820	73.797	73.835	0.553	0.564	0.582
$O(2s^2 2p^4 \ ^3P \rightarrow 2s^1 2p^5 \ ^3P)$	74.184	74.181	74.227	0.625	0.631	0.652
$F^+(2s^2 2p^4 \ ^3P \rightarrow 2s^1 2p^5 \ ^3P)$	98.033	98.006	98.051	0.799	0.802	0.840
$F(2s^2 2p^5 \ ^2P \rightarrow 2s^1 2p^6 \ ^2S)$	98.531	98.561	98.610	0.878	0.869	0.898
$Ne^+(2s^2 2p^5 \ ^2P \rightarrow 2s^1 2p^6 \ ^2S)$	126.861	126.745	126.791	1.083	1.074	1.111

Table 4.2: Total energy of excited states and excitation energy (in atomic unit) of some systems involving transition of one loosely bound electron.

atoms/ions	$-E_{HF}^*$	$-E_{Becke}^*$	$-E_{PW}^*$	ΔE_{HF}	ΔE_{Becke}	ΔE_{PW}
$Li(2s^1 \ ^2S \rightarrow 2p^1 \ ^2P)$	7.365	7.357	7.366	0.068	0.0702	0.075
$Na(3s^1 \ ^2S \rightarrow 3p^1 \ ^2P)$	161.786	161.804	161.890	0.073	0.0763	0.083
$Mg^+(3s^1 \ ^2S \rightarrow 3p^1 \ ^2P)$	199.214	199.210	199.297	0.158	0.171	0.182

quite close to HF results so are the results obtained with the new functional. Therefore the good thing with the proposed functional is that it uniformly improves the results for all cases. In table 4.6 two electron excitation for one-gap cases have been considered. In these cases also we find that results are quite close to the standard results.

Table 4.3: Total energy of excited states and excitation energy of various atoms/ions when one electron is excited from 3s to 3p orbital.

atoms/ions	$-E_{HF}^*$	$-E_{Becke}^*$	$-E_{PW}^*$	ΔE_{HF}	ΔE_{Becke}	ΔE_{PW}
$P(3s^2 3p^3 \ ^4S \rightarrow 3s^1 3p^4 \ ^4P)$	340.417	340.400	340.507	0.302	0.307	0.324
$S(3s^2 3p^4 \ ^3P \rightarrow 3s^1 3p^5 \ ^3P)$	397.079	397.053	397.165	0.426	0.436	0.454
$Cl^+(3s^2 3p^4 \ ^3P \rightarrow 3s^1 3p^5 \ ^3P)$	458.523	458.484	458.596	0.526	0.544	0.564
$Cl(3s^2 3p^5 \ ^2P \rightarrow 3s^1 3p^6 \ ^2S)$	458.917	458.900	459.015	0.565	0.567	0.585
$Ar^+(3s^2 3p^5 \ ^2P \rightarrow 3s^1 3p^6 \ ^2S)$	525.598	525.574	525.686	0.677	0.671	0.703

Table 4.4: Total energy of excited states and excitation energy of various atoms/ions when one electron is excited from 2s to 3p orbital.

atoms/ions	$-E_{HF}^*$	$-E_{Becke}^*$	$-E_{PW}^*$	ΔE_{HF}	ΔE_{Becke}	ΔE_{PW}
$P(2s^2 3p^3 \ ^4S \rightarrow 2s^1 3p^4 \ ^4P)$	333.834	333.708	333.766	6.882	7.000	7.065
$S(2s^2 3p^4 \ ^3P \rightarrow 2s^1 3p^5 \ ^3P)$	389.257	389.116	389.174	8.246	8.373	8.445
$Cl^+(2s^2 3p^4 \ ^3P \rightarrow 2s^1 3p^5 \ ^3P)$	449.234	449.079	449.132	9.812	9.949	10.028
$Cl(2s^2 3p^5 \ ^2P \rightarrow 2s^1 3p^6 \ ^2S)$	449.768	449.602	449.659	9.714	9.864	9.941
$Ar^+(2s^2 3p^5 \ ^2P \rightarrow 2s^1 3p^6 \ ^2S)$	514.882	514.699	514.751	11.393	11.566	11.638

Table 4.5: Total energy of excited states and excitation energy of various atoms/ions excited state is not the lowest energy multiplet.

atoms/ions	$-E_{HF}^*$	$-E_{Becke}^*$	$-E_{PW}^*$	ΔE_{HF}	ΔE_{Becke}	ΔE_{PW}
$B(2s^2 2p^1 \ ^2P \rightarrow 2s^1 2p^2 \ ^2D)$	24.312	24.304	24.330	0.217	0.211	0.220
$C^+(2s^2 2p^1 \ ^2P \rightarrow 2s^1 2p^2 \ ^2D)$	36.963	36.945	36.975	0.329	0.328	0.342
$C(2s^2 2p^2 \ ^3P \rightarrow 2s^1 2p^3 \ ^3D)$	37.395	37.376	37.409	0.294	0.303	0.315
$N^+(2s^2 2p^2 \ ^3P \rightarrow 2s^1 2p^3 \ ^3D)$	53.917	53.434	53.471	0.414	0.439	0.454
$Si^+(3s^2 3p^1 \ ^2P \rightarrow 3s^1 3p^2 \ ^2D)$	288.299	288.289	288.394	0.274	0.282	0.297
$Si(3s^2 3p^2 \ ^3P \rightarrow 3s^1 3p^3 \ ^3D)$	288.62	288.606	288.711	0.234	0.246	0.260

Table 4.6: Total energy of excited states and excitation energy of various atoms/ions when two electrons are involved in transition.

atoms/ions	$-E_{HF}^*$	$-E_{Becke}^*$	$-E_{PW}^*$	ΔE_{HF}	ΔE_{Becke}	ΔE_{PW}
$Be(2s^2\ ^1S \rightarrow 2p^2\ ^1D)$	14.301	14.291	14.300	0.272	0.264	0.288
$B(2s^2 2p^1\ ^2P \rightarrow 2p^3\ ^2D)$	24.059	24.023	24.037	0.470	0.491	0.513
$C^+(2s^2 2p^1\ ^2P \rightarrow 2p^3\ ^2D)$	36.595	36.540	36.552	0.697	0.733	0.765
$C(2s^2 2p^2\ ^3P \rightarrow 2p^4\ ^3P)$	36.946	36.934	36.948	0.743	0.746	0.776
$N^+(2s^2 2p^2\ ^3P \rightarrow 2p^4\ ^3P)$	52.865	52.841	52.892	1.023	1.032	1.173
$N(2s^2 2p^3\ ^4S \rightarrow 2p^5\ ^2P)$	53.222	53.202	53.224	1.179	1.196	1.225
$O^+(2s^2 2p^3\ ^4S \rightarrow 2p^5\ ^2P)$	72.829	72.795	72.811	1.544	1.566	1.606
$O(2s^2 2p^4\ ^3P \rightarrow 2p^6\ ^1S)$	73.306	73.319	73.339	1.5032	1.494	1.540
$F^+(2s^2 2p^4\ ^3P \rightarrow 2p^6\ ^1S)$	96.934	96.935	96.947	1.898	1.883	1.944
$Mg(3s^2\ ^1S \rightarrow 3p^2\ ^1D)$	199.357	199.362	199.480	0.258	0.257	0.255
$S(3s^2 3p^4\ ^3P \rightarrow 3p^6\ ^1S)$	396.478	396.455	396.552	1.027	1.034	1.067
$P(3s^2 3p^3\ ^4S \rightarrow 3p^5\ ^2P)$	339.865	339.834	339.930	0.854	0.874	0.901
$Si^+(3s^2 3p^1\ ^2P \rightarrow 3p^3\ ^2D)$	287.987	287.944	288.034	0.586	0.627	0.657
$Si(3s^2 3p^2\ ^3P \rightarrow 3p^4\ ^3P)$	288.268	288.250	288.342	0.586	0.602	0.629
$Cl^+(3s^2 3p^2\ ^3P \rightarrow 3p^4\ ^3P)$	457.795	457.767	457.860	1.254	1.261	1.300

4.3.2 Two gap systems

In table 4.7 we present total energies and excitation energies of atomic excited states having two-gaps. The MLSD exchange energy functional corresponding to two-gap case which was employed here is given by spin dependent generalization of equation 3.35 The steps involved in the calculation are exactly same as that of one-gap cases. The results calculated for total energy and excitation energies match very well with standard results given in the table. This corroborates the generality of the idea invoked in the construction of exchange energy functionals.

Table 4.7: Total energy and excitation energy of various atoms/ions having two gaps.

atoms/ions	$-E_{HF}^*$	$-E_{Becke}^*$	$-E_{PW}^*$	ΔE_{HF}	ΔE_{Becke}	ΔE_{PW}
$B(2p^1 3p^2 M_L = 3, M_S = 1/2)$	23.516	23.441	23.442	1.010	1.064	1.108
$N(2p^4 3p^1 M_L = 2, M_S = 3/2)$	52.958	52.874	52.884	1.438	1.524	1.565
$F(2p^6 3p^1 M_L = 1, M_S = 1/2)$	97.034	96.959	96.971	2.371	2.471	2.527
$Ne(2p^6 3p^2 M_L = 1, M_S = 1)$	124.594	124.420	124.424	3.948	4.167	4.248
$Na(2s^1 2p^6 3p^2 M_L = 1, M_S = 1/2)$	159.236	159.159	159.203	2.615	2.722	2.770
$Al(2s^1 2p^6 3s^1 3p^3 M_L = 0, M_S = 1/2)$	237.16	237.064	237.115	4.702	4.816	4.879
$Ar(2p^6 3s^0 3p^6 4p^2 M_L = 2, M_S = 0)$	524.215	524.074	524.156	2.589	2.722	2.776
$K(2p^6 3s^1 3p^6 4p^2 M_L = 1, M_S = 1/2)$	597.523	597.436	597.542	1.626	1.850	2.169

4.4 Concluding remarks and future prospects

We have added generalized-gradient correction to exchange energy functional to obtain better approximation for exchange energy. The correction terms used here have been taken from the ground state DFT on the basis of argument that these functionals satisfy some general properties satisfied by both the ground as well as excited states. Therefore these should be applicable to excited states too. Use of gradient corrected functional for excited is found to lead to the results in right direction. Becke and PW corrections which we have employed here are found to consistently improve the results for excited states total energy and excitation energy. The results obtained from such calculation compare very closely with Hartree Fock results.

Chapter 5

Exchange potential for excited states

5.1 Introduction

This is an exploratory chapter that presents various attempts to obtain exchange potential for split-k cases. In the previous chapter we have constructed exchange energy functional for excited states. To use this functional for excited states, we first do Kohn-Sham calculation for excited states so that from the resulting orbitals we can construct the desired densities. In doing so we have used the LDA exchange potential which has been constructed for ground states. From the orbitals thus obtained we calculate the total energy. However an important aspect of these calculations is the quality of orbitals and corresponding orbital energies. If we want to improve orbitals and the orbital energies, then we need to incorporate a better potential [41, 80, 86, 87]. Ideally the functional derivative of the MLSD functional. However, taking functional derivative of the MLSD functional has proven to be impossible; it is for this reason that we have been performing our calculations with the LSD potential itself.

In this chapter we construct exchange potential for excited states using the idea of split k-space and apply it to calculate excitation energies of various excited states of different atoms. Our aim is to construct an exchange potential which has no orbital

dependence for a given type of excited state so that it qualifies to be the Kohn-Sham potential.

There have been some intermittent attempts to construct accurate exchange potential for excited states. Gaspar's [89] and Nagy's [54, 90] investigations in this direction are a few to mention. They have given an ensemble averaged exchange potential for the excited states and have used the resulting potential to calculate excitation energy for single excitations. However, in such calculations the beauty of ground-state like density functional calculation for an individual excited state is always missing.

Exchange-correlation potential ($v_{xc}(\mathbf{r})$) is defined as functional derivative given by equation 1.32. Thus;

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho}$$

Usually the exchange-correlation potential is split into exchange and correlation potential. i.e. $v_{xc}([\rho]; \mathbf{r}) = v_x([\rho]; \mathbf{r}) + v_c([\rho]; \mathbf{r})$. The mapping from an interacting system to a non-interacting system is exact but neither of the v_x and v_c is known exactly in a form that can be used in the calculations for the practical purposes. As has been discussed in chapter 1, we therefore use approximate potential in our calculations. The widely used approximation for ground state in DFT is the local density approximation(LDA) for the exchange and correlation part. But LDA counterpart for excited states does not exist. For finite systems contribution from exchange part is much larger than that from the correlation part, Therefore in this work we have dealt with the exchange part first.

As deliberated upon in chapter 1, exchange potential is obtained by taking functional derivative of exchange energy functional.

$$v_x(\mathbf{r}) = \frac{\delta E_x[\rho]}{\delta \rho} \quad (5.1)$$

Therefore, for excited states the exchange potential could be obtained by taking functional derivative with respect to total density of the exchange energy functional developed in

the previous chapter. As mentioned earlier, the functional derivative cannot be obtained due to this reason we resort to a different approach. Our idea is that we can construct exchange potential first, by using some physical arguments and to calculate corresponding exchange energy we can use the Levy-Perdew relation for the exchange energy. Although this relation gives origin dependent energy [27, 97–99] for atoms it is perfectly al-right with the origin of the nucleus.

To come up with an exchange potential, let us have a re-look at the exchange for ground state. The LDA exchange potential for ground state is the Dirac exchange potential which is equal to the Hartree-Fock exchange potential for the highest occupied orbital(HOMO). This happens to be same as the Functional derivative of exchange energy with respect to density. i.e..

$$v_i^{HF}(\mathbf{r})|_{i=HOMO} = \frac{\delta E_x^{LDA}(\rho)}{\delta \rho(\mathbf{r})} \quad (5.2)$$

Therefore, for excited states we do the same. We calculate the Hartree-Fock exchange potential which is orbital dependent and take the potential for each electron to be equal to the potential corresponding to the upper most occupied orbital(HOMO). In the following we show that this is also equal to the functional derivative of modified exchange energy functional reported in the previous chapter [70] for excited states with respect to the density corresponding to the largest wave-vector in the k-space. We have been pursuing the idea of constructing the energy functionals for excited-states by using split k-space for the past few years with significant success. We have shown that accurate exchange energy and kinetic energy functional can be constructed in this manner [70, 100]. In the present work we have employed the same idea to construct the exchange potential for excited states.

The outline of this chapter is as follows. In the sub-section 5.2.1 we describe the construction of potential as derived from the idea taken from the ground state that HF potential for HOMO is the Kohn-Sham exchange potential for all the electrons of the system and in sub-section 5.2.2 construction of exchange potential from the functional

derivative of the exchange energy functional is described for the excited states. In this section we also describe how we change the exchange potential to make it better. In section 5.5 we present results and conclude in section 5.7.

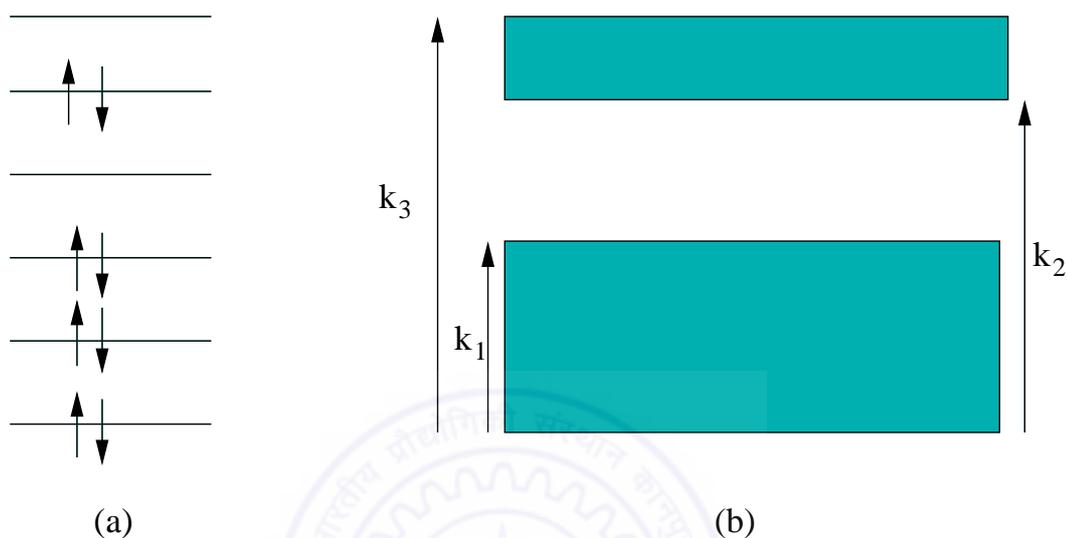


Figure 5.1: Orbital and the corresponding k – space occupation in the excited state configuration of a homogeneous electron gas(HEG).

5.2 Construction of Exchange potential for excited-states

To construct an LDA exchange potential for excited states we map the excited state density to the corresponding k -space for homogeneous electron gas(HEG) as shown in figure 5.1 . Unlike the ground state, now k -space has a gap corresponding to the missing orbitals. The exchange potential for an excited state of HEG can be obtained in two ways.(i) From the Hartree-Fock expression for exchange potential and (ii) From the functional derivative of exchange energy of the electrons taken with respect to the density including the occupied and unoccupied orbitals. In the following we describe the two methods one by one.

5.2.1 LDA Exchange potential from the Hartree-Fock exchange potential

The Hartree-Fock exchange potential for a system of fermions is given by

$$v_x^i = v_x(\phi_i) = - \sum_j \int \frac{\phi_j^*(\mathbf{r}')\phi_i(\mathbf{r}')\phi_j(\mathbf{r})}{\phi_i(\mathbf{r})|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (5.3)$$

where ϕ_i are the Hartree-Fock orbitals and the summation goes over all the occupied orbitals. Note that the potential is orbital dependent. For homogeneous electron gas,

$$\phi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}} \quad (5.4)$$

Using this form of wave function in equation 5.3 we get an exchange potential for one-gap systems shown in figure 5.1 to be given by,

$$v_x^k = \frac{1}{\pi} \left[-k_1 + k_2 - k_3 - \frac{k_1^2 - k^2}{2k} \ln \left| \frac{k + k_1}{k - k_1} \right| + \frac{k_2^2 - k^2}{2k} \ln \left| \frac{k + k_2}{k - k_2} \right| - \frac{k_3^2 - k^2}{2k} \ln \left| \frac{k + k_3}{k - k_3} \right| \right] \quad (5.5)$$

which is an orbital dependent potential. To make this potential an orbital independent potential we draw the analogy from the ground state exchange potential, where the exact LDA potential is equal to the HF potential for the HOMO. Therefore we take the potential seen by the electron in HOMO as the exchange potential for all the electrons. For this we put $k = k_3$. With this the Hartree-Fock exchange potential of eqn 5.5 for the excited state reduces to the following expression for exchange potential .

$$v_x^{MLDA} = \frac{k_3}{\pi} \left[-1 + x_2 - x_1 + \frac{1}{2}(1 - x_1^2) \ln \left| \frac{1 + x_1}{1 - x_1} \right| - \frac{1}{2}(1 - x_2^2) \ln \left| \frac{1 + x_2}{1 - x_2} \right| \right] \quad (5.6)$$

where,

$$x_1 = \frac{k_1}{k_3}, x_2 = \frac{k_2}{k_3} \quad (5.7)$$

5.2.2 LDA Exchange potential from functional derivative

In chapter 3 we have given [70] that for all systems having configuration same as that shown in figure 5.1, the LDA approximation to the exchange energy functional is given by

$$\begin{aligned}
 E_X^{MLDA} &= \int \rho(\mathbf{r}) [\epsilon(k_3) - \epsilon(k_2) + \epsilon(k_1)] d\mathbf{r} + \frac{1}{8\pi^3} \int (k_3^2 - k_1^2)^2 \ln \left(\frac{k_3 + k_1}{k_3 - k_1} \right) d\mathbf{r} \\
 &- \frac{1}{8\pi^3} \int (k_3^2 - k_2^2)^2 \ln \left(\frac{k_3 + k_2}{k_3 - k_2} \right) d\mathbf{r} - \frac{1}{8\pi^3} \int (k_2^2 - k_1^2)^2 \ln \left(\frac{k_2 + k_1}{k_2 - k_1} \right) d\mathbf{r}
 \end{aligned} \tag{5.8}$$

Here $\epsilon(k) = -\frac{3k}{4\pi}$ is the exchange energy per electron for the HEG in its ground-state with the Fermi wave-vector equal to k . These are shown in figure 5.1 and are related to the density of core electrons, missing electrons and shell electrons as give below

$$k_1^3 = 3\pi^2 \rho_{core} \tag{5.9}$$

$$k_2^3 - k_1^3 = 3\pi^2 \rho_{missing} \tag{5.10}$$

$$k_3^3 - k_2^3 = 3\pi^2 \rho_{shell} \tag{5.11}$$

The exchange energy functional given by equation 5.8 is a highly accurate approximation for excited states . This has been demonstrated by calculation of accurate excitation energies employing it [70] also by band gap calculations [73] . Therefore if we take functional derivative of this functional with respect to density we should get an accurate modified LDA exchange potential for this class of excited states. i.e.

$$v_x^{MLDA}(\mathbf{r}) = \frac{\delta \mathbf{E}_x^{MLDA}(\rho)}{\delta \rho(\mathbf{r})} \quad (5.12)$$

However, it is not possible to get a workable analytical expression for $v_x^{MLDA}(\mathbf{r})$ out of eqn 5.12. Therefore on the basis physical argument that the chemical potential of the system corresponds to the highest occupied orbital, we instead take the functional derivative of exchange energy functional with respect to ρ_3 , which is the density corresponding to the highest wave vector k_3 . Therefore we now approximate the exchange potential to be,

$$v_x^{MLDA}(\mathbf{r}) = \frac{\delta \mathbf{E}_x^{MLDA}(\rho)}{\delta \rho_3(\mathbf{r})} \quad (5.13)$$

where,

$$\rho_3(\mathbf{r}) = \frac{k_3^3}{3\pi^2} \quad (5.14)$$

The potential obtained in this manner is exactly equal to that given by equation 5.6. In the above, We have reached the same results from two different arguments. This is reassuring about the correctness of the approach taken. Therefore we expect this potential to work well.

We have employed the exchange potential given by equation 5.6 in a self consistent calculation and then have used the Levy-Perdew relation to obtain exchange energy of the atoms studied. We note that although recently it has been pointed out that Levy-Perdew relation gives origin dependent energy, for atoms it gives no problem with nucleus taken as the origin [21]. The results for excitation thus obtained are quite accurate for many cases, yielding significant improvement over the ground state LSD potential but there are cases where the potential does not seem to make much difference; in fact in some cases result obtained are deviating from exact values more than that of LSD values. We studied various cases and based on our analysis we suggest a change in the potential of equation 5.6. We propose the new form of the potential to have an orbital dependent exponent so that it will work well for all types of excitation. Here mention that it is

on the basis of excitation energy calculation that we are modifying the potential. If we calculate just difference in exchange energy to see if satisfies LP theorem then it appears to working fine. Reason is that exchange energy is much larger than excitation energy therefore small discrepancy in exchange energy calculation does not appear to be making much difference. However the same does in calculation of excitation energy. With the changes incorporated, the potential takes the following form.

$$v_x^{MLSD} = \frac{k_3}{\pi} \left[-1 + x_2 - x_1 + \frac{1}{2}(1 - x_1^{a^\sigma}) \ln \left| \frac{1+x_1}{1-x_1} \right| - \frac{1}{2}(1 - x_2^{a^\sigma}) \ln \left| \frac{1+x_2}{1-x_2} \right| \right] \quad (5.15)$$

where the exponent a^σ depends upon the number of electrons missing from an orbital and on the degeneracy of that orbital and its value is determined by using the formula

$$a^\sigma = \frac{2N_m^\sigma}{d^\sigma + 1} \quad (5.16)$$

where, N_m^σ and d^σ are, respectively, the number of missing electron from the orbital and degeneracy of the orbital from which the electron is missing respectively and σ is the spin index of the electrons.

The new modified exchange potential for excited states as given by equation 5.15 improves the LDA results uniformly for almost all cases to which it was applied. This potential has similar behaviour as the LDA potential, but overall the potential reduces the LDA error for excited states substantially.

Further, the exchange potential given by equation 5.15 is independent of orbitals for one gap system. The calculation using the exchange potential proposed above are performed as follows: (i) Solve Kohn-Sham equation with the exchange potential given by equation 5.15 (ii) Calculate the exchange energy from the potential using the Levy-Perdew relation as follows;

$$E_X^{MLSDSIC} = E_X^{MLSD} - \sum_i^{rem} E_i^{SIC} - \sum_i^{add} E_i^{SIC} \quad (5.17)$$

where,

$$E_i^{SIC}[\phi_i] = \int \int \frac{|\phi_i(\mathbf{r}_1)|^2 |\phi_i(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + E_X^{LSD}[\rho[\phi_i]] \quad (5.18)$$

with

$$E_x^{MLSD} = - \int \rho(\mathbf{r}) \mathbf{r} \cdot \nabla v_x^{MLSD} d\mathbf{r} \quad (5.19)$$

5.3 Test for the Exchange potential

The potential we are reporting here is an approximation to the exact functional derivative of the exchange energy functional. Therefore, two questions arise: (i) How close this potential is to the functional derivative, and (ii) Is it better than the ground state LDA potential for excited states? To answer these two questions we test whether this potential satisfies the following two theorems;

a) Levy-Perdew theorem with respect to E_x^{MLSD} functional proposed in previous chapter.

$$E_X = - \int \rho(\mathbf{r}) \mathbf{r} \cdot \nabla v_x d\mathbf{r} \quad (5.20)$$

where $\rho(\mathbf{r})$ is the total density and in place of v_x we use potential of equation 5.15. To test the accuracy, we calculate the left hand side with equation 3.17 and right hand side with the potential of equation 5.15

b) Janak Theorem

$$\frac{\partial E}{\partial n_i} = \epsilon_i \quad (5.21)$$

where ϵ_i is the orbital energy and n_i is the occupation of that orbital and E is the total energy, where ϵ_i is obtained from the solution of Kohn-Sham equation with the proposed exchange potential and total energy is calculated using the MLSDSIC functional of previous chapter.

set of orbitals are missing (two-gap systems). This kind of systems were studied earlier in chapter 3

The excited states of this kind are shown in figure 5.2. Study of such excited states is necessary to confirm that the exchange potential reported here has quite general applicability. As we see the k-space of such excited states has two gaps corresponding to the two set of un-occupied orbitals. The LDA exchange potential which ignores the gap in k-space doesn't work well for these cases. Whereas the exchange potential we are reporting here explicitly takes into account the missing orbitals therefore works better than the LDA exchange potential.

The construction of exchange potential for two-gap system goes exactly in the same line as that for the one gap case.

The exchange energy functional for the two-gap system is given by [91]

$$\begin{aligned}
E_X^{MLDA} &= \int \rho(\mathbf{r}) [\epsilon(k_5) - \epsilon(k_4) + \epsilon(k_3) - \epsilon(k_2) + \epsilon(k_1)] d\mathbf{r} \\
&- \frac{1}{8\pi^3} \int \left[(k_3^2 - k_2^2)^2 \ln \left(\frac{k_3 + k_2}{k_3 - k_2} \right) \right] d\mathbf{r} - \frac{1}{8\pi^3} \int \left[(k_5^2 - k_4^2)^2 \ln \left(\frac{k_5 + k_4}{k_5 - k_4} \right) \right] d\mathbf{r} \\
&- \frac{1}{8\pi^3} \int \left[(k_2^2 - k_1^2)^2 \ln \left(\frac{k_2 + k_1}{k_2 - k_1} \right) \right] d\mathbf{r} + \frac{1}{8\pi^3} \int \left[(k_3^2 - k_1^2)^2 \ln \left(\frac{k_3 + k_1}{k_3 - k_1} \right) \right] d\mathbf{r} \\
&- \frac{1}{8\pi^3} \int \left[(k_4^2 - k_1^2)^2 \ln \left(\frac{k_4 + k_1}{k_4 - k_1} \right) \right] d\mathbf{r} + \frac{1}{8\pi^3} \int \left[(k_5^2 - k_1^2)^2 \ln \left(\frac{k_5 + k_1}{k_5 - k_1} \right) \right] d\mathbf{r} \\
&+ \frac{1}{8\pi^3} \int \left[(k_5^2 - k_3^2)^2 \ln \left(\frac{k_5 + k_3}{k_5 - k_3} \right) \right] d\mathbf{r} - \frac{1}{8\pi^3} \int \left[(k_4^2 - k_3^2)^2 \ln \left(\frac{k_4 + k_3}{k_4 - k_3} \right) \right] d\mathbf{r} \\
&- \frac{1}{8\pi^3} \int \left[(k_5^2 - k_2^2)^2 \ln \left(\frac{k_5 + k_2}{k_5 - k_2} \right) \right] d\mathbf{r} + \frac{1}{8\pi^3} \int \left[(k_4^2 - k_2^2)^2 \ln \left(\frac{k_4 + k_2}{k_4 - k_2} \right) \right] d\mathbf{r}
\end{aligned} \tag{5.22}$$

We take functional derivative of the above exchange energy functional with respect to density corresponding to the highest wave-vector, here k_5 . The expression for the exchange potential we get is

$$\begin{aligned}
v_x^{MLDA} &= \frac{k_5}{\pi} \left[-1 + x_4 - x_3 + x_2 - x_1 + \frac{1}{2}(1 - x_1^2) \ln \left| \frac{1 + x_1}{1 - x_1} \right| \right] \\
&- \frac{k_5}{\pi} \left[\frac{1}{2}(1 - x_2^2) \ln \left| \frac{1 + x_2}{1 - x_2} \right| + \frac{1}{2}(1 - x_3^2) \ln \left| \frac{1 + x_3}{1 - x_3} \right| \right] \\
&- \frac{k_5}{\pi} \left[\frac{1}{2}(1 - x_4^2) \ln \left| \frac{1 + x_4}{1 - x_4} \right| \right]
\end{aligned} \tag{5.23}$$

The same expression is obtained by calculating the Hartree-Fock potential corresponding the highest occupied orbital.

As in the case of one gap we modify the exchange potential to make it better. The final expression for the exchange potential for two-gap system after modification is given by

$$\begin{aligned}
v_x^{MLSD} &= \frac{k_5}{\pi} \left[-1 + x_4 - x_3 + x_2 - x_1 + \frac{1}{2}(1 - x_1^{a^\sigma}) \ln \left| \frac{1 + x_1}{1 - x_1} \right| \right] \\
&- \frac{k_5}{\pi} \left[\frac{1}{2}(1 - x_2^{a^\sigma}) \ln \left| \frac{1 + x_2}{1 - x_2} \right| + \frac{1}{2}(1 - x_3^{a^\sigma}) \ln \left| \frac{1 + x_3}{1 - x_3} \right| \right] \\
&- \frac{k_5}{\pi} \left[\frac{1}{2}(1 - x_4^{a^\sigma}) \ln \left| \frac{1 + x_4}{1 - x_4} \right| \right]
\end{aligned} \tag{5.24}$$

Where, in this case a^σ is given by,

$$a^\sigma = \frac{2(N_{m1}^\sigma + N_{m2}^\sigma)}{d_1^\sigma + d_2^\sigma + 1} \tag{5.25}$$

Here, $N_{m1}^\sigma, N_{m2}^\sigma$ are number of electrons missing in the first and second gaps respectively and d_1^σ, d_2^σ are the degeneracies of the corresponding orbitals from where electrons are missing.

In two-gap cases also, we use Levy-Perdew theorem to calculate exchange energy corresponding to the potential of equation 5.24.

5.5 Results

In this section we report the results obtained with the exchange potential constructed in the section-II and V. We use Hermann Skillman program for our calculations with some changes to incorporate the new potential for excited states. All the calculations are fully self-consistent and as simple as the ground state calculations . Since LDA as well all its modified forms are good for the states which can be represented by single determinants, therefore we do calculation for a particular configuration rather than a state. Further all our calculations are done in central field approximation, that is we take density to be spherical . This approximation is justified because the non-spherical of density does not make much difference [102].

The results presented here are for the class of the systems which have one gap in the occupation of orbitals and also for the systems having two gaps. To clearly show the advantage of constructing exchange potential for excited states we compare all our results with the corresponding results obtained with ground state LSD exchange potential and for excitation energies we have compared our results with standard results also wherever we could do.

We first present the results for the test of Levy-Perdew theorem and Janak theorem in the subsections 5.5.1 and 5.5.2 respectively. The results presented in these two sections are for one gap cases. In subsections 5.5.3 and 5.5.4 we discuss the calculation of excitation energies for one-gap and two-gap systems.

5.5.1 Test for the Levy-Perdew theorem

We first calculate exchange energy using Levy-Perdew relation 5.20 and then we calculate the exchange energy using functional 3.17 of previous chapter. In calculation of exchange energy with Levy-Perdew relation we use the proposed MLSD potential. If the proposed MLSD potential is a good potential then difference in exchange energy calculated by two

methods should come out to be small. We repeat the above calculation with LSD potential and compare the difference in exchange energy obtained with proposed MLSD potential and LSD potential. We find that for most of the cases this difference is smaller for the MLSD potential as compared to the LSD exchange potential. This shows that for excited states MLSD exchange potential is closer to the exact exchange potential than the LSD potential is. The results for the configurations of atoms and ions given in table 5.1 and table 5.3 are displayed in figure 5.3 and figure 5.4 respectively. In the figures MLSDSC stands for self consistent calculation with MLSD potential of equation 5.15.

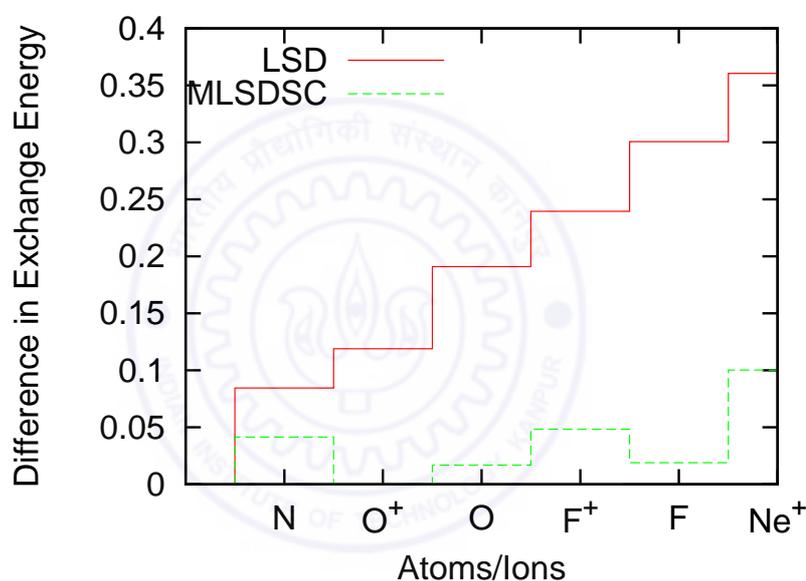


Figure 5.3: Difference in exchange energies as calculated from Levy-Perdew relation using the MLSD and LSD exchange potential and that calculated with the Exchange energy functional for the atoms/ions shown on the horizontal axis. In the figures MLSDSC stands for self consistent calculation with MLSD potential of equation 5.15. Energy is in a.u.

5.5.2 Test for Janak Theorem

Change in total energy is sensitive to the nature of exchange potential. Therefore, if the modified exchange potential reported here is accurate one, it should satisfy Janak

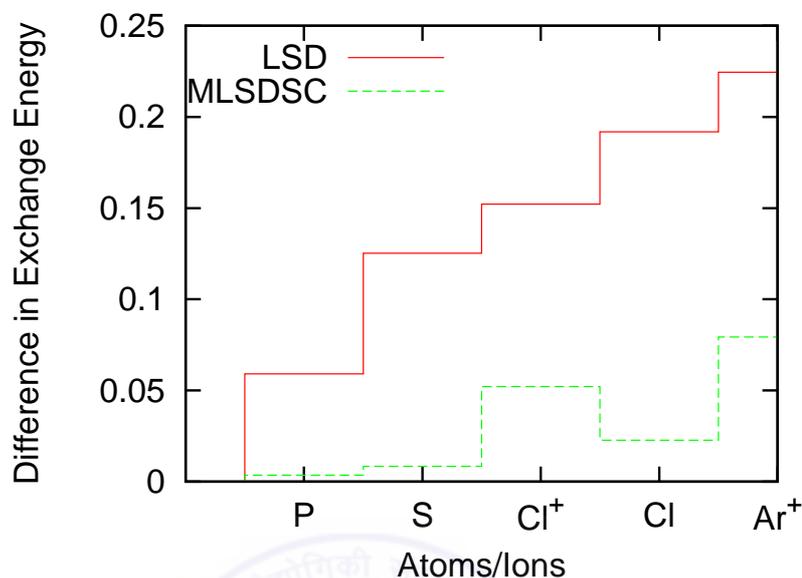


Figure 5.4: Difference in exchange energies as calculated with Levy-Perdew relation using the MLSD and LSD exchange potential and that calculated with the Exchange energy functional for the atoms/ions shown on the horizontal axis. In the figures MLSDSC stands for self consistent calculation with MLSD potential of equation 5.15. Energy is in a.u.

Theorem [102] . To test this we take a configuration of an atom with one gap and vary the occupation of a particular orbital. As the occupation is changed from given value to a value less by one the corresponding total energy and the orbital energy of that orbital is noted for each intermediate occupations. From the table generated in this way we calculate the slope of energy with respect to the occupation of the orbital. Then we plot the slope against the orbital energy . If Janak theorem is satisfied the curve obtained in this way should coincide with a line having slope equal to one. The result for Cl atom having configuration $1s^2 2s^2 2p^6 3s^1 3p^6$; $M_l = 0, M_s = 1/2$ is shown in figure 5.5. Here orbital considered is the up spin $2p$ orbital.

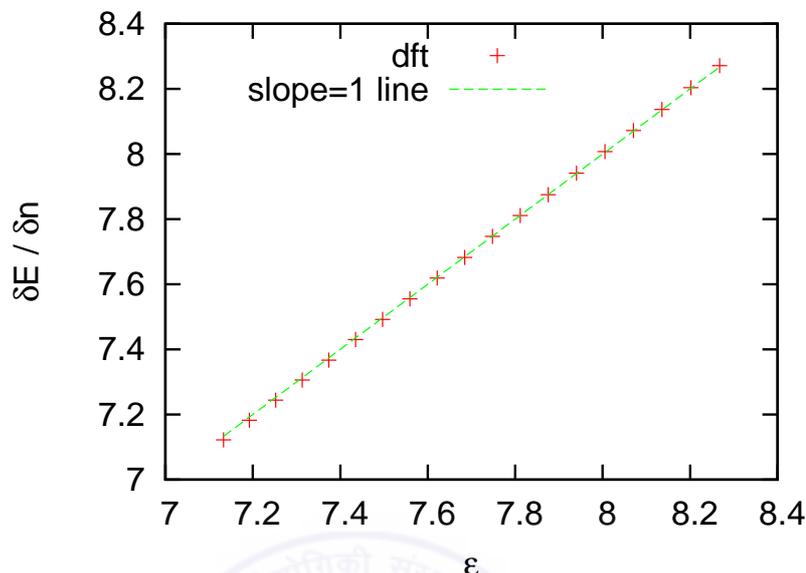


Figure 5.5: Derivative of energy with respect to the orbital occupation versus the orbital energy and slope equals one line.

5.5.3 Excitation energy for one-gap systems.

Now we employ the potential constructed in section-II to calculate transition energies for various configurations of atomic systems. Our calculation is ΔSCF type. For ground states our potential reduces to regular ground state LSD exchange potential, Therefore we do two self-consistent calculations one for ground state and one for the excited state, and from the difference of the two we get the transition energies.

In tables 5.1 to 5.8 we present transition energies for one-gap systems. The results given in the table 5.1-5.7 are for excitations of one electron for different cases and in table-5.8 transition energies for excitation of two electrons are given. In the tables $(MLSDSIC)^{sc}$ stands for self-consistent calculation with the MLSD version exchange potential given in equation 5.6 and $(MLSDSIC)^{scx}$ stands for self-consistent calculation with the MLSD version exchange potential given in equation 5.15. Different tables give

Table 5.1: Transition energies, in atomic units, of an electron being excited from the $2s$ orbital of some atoms to their $2p$ 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. Third column gives transition obtained with potential of equation 5.6 and in the fourth column are the numbers obtained with potential of equation 5.15. The last column gives the transition energies obtained by employing TDDFT.

atoms/ions	ΔE_{HF}	ΔE_{LSD}	$\Delta E(MLSDSIC)^{sc}$	$\Delta E(MLSDSIC)^{scx}$	ΔE_{TDDFT}
$N(2s^2 2p^3 \ ^4S \rightarrow 2s^1 2p^4 \ ^4P)$	0.4127	0.3905	0.4954	0.4549	0.4153
$O^+(2s^2 2p^3 \ ^4S \rightarrow 2s^1 2p^4 \ ^4P)$	0.5530	0.5397	0.6452	0.5581	0.5694
$O(2s^2 2p^4 \ ^3P \rightarrow 2s^1 2p^5 \ ^3P)$	0.6255	0.5243	0.6821	0.6460	0.5912
$F^+(2s^2 2p^4 \ ^3P \rightarrow 2s^1 2p^5 \ ^3P)$	0.7988	0.6789	0.8399	0.7540	0.7651
$F(2s^2 2p^5 \ ^2P \rightarrow 2s^1 2p^6 \ ^2S)$	0.8781	0.6671	0.8651	0.8445	0.7659
$Ne^+(2s^2 2p^5 \ ^2P \rightarrow 2s^1 2p^6 \ ^2S)$	1.0830	0.8334	1.0348	0.9620	0.9546
Average error		14.30%	9.45%	5.70%	

Table 5.2: The caption is the same as that for Table 2 except that we are now considering transitions from the outermost orbital to an upper orbital for weakly bound systems.

atoms/ions	ΔE_{HF}	ΔE_{LSD}	$\Delta E(MLSDSIC)^{sc}$	$\Delta E(MLSDSIC)^{scx}$	ΔE_{TDDFT}
$Li(2s^1 \ ^2S \rightarrow 2p^1 \ ^2P)$	0.0677	0.0646	0.0973	0.09217	0.0724
$Na(3s^1 \ ^2S \rightarrow 3p^1 \ ^2P)$	0.0725	0.0751	0.0669	0.0774	0.0791
$Mg^+(3s^1 \ ^2S \rightarrow 3p^1 \ ^2P)$	0.1578	0.1585	0.1800	0.1580	0.1734
Average error		2.80%	21.60%	14.30%	

transition energies in different types of transition. In some cases tightly bound electrons have been excited while in some cases loosely bound electrons have been excited. The results are compared with LSD , HF and TDDFT results, wherever possible. we see that with the potential reported here the results obtained are far better than that obtained by employing ground state LDA potential for most of the cases studied here except few cases where our results are as good as the LDA numbers.

5.5.4 Excitation energy for two-gap systems.

In tables 5.9 to 5.12 transition energies for two-gap systems are given. Here we have considered excitation of one to four electrons. As is evident from the tables the excited state exchange potential reported here gives substantial improvement over the LSD results.

Table 5.3: Electron transition energy from the 3s to the 3p orbital in some atoms.

atoms/ions	ΔE_{HF}	ΔE_{LSD}	$\Delta E(MLSDSIC)^{sc}$	$\Delta E(MLSDSIC)^{scx}$	ΔE_{TDDFT}
$P(3s^2 3p^3 \ ^4S \rightarrow 3s^1 3p^4 \ ^4P)$	0.3023	0.2934	0.3380	0.3027	0.3183
$S(3s^2 3p^4 \ ^3P \rightarrow 3s^1 3p^5 \ ^3P)$	0.4264	0.3615	0.4877	0.4246	0.4122
$Cl^+(3s^2 3p^4 \ ^3P \rightarrow 3s^1 3p^5 \ ^3P)$	0.5264	0.4482	0.5983	0.5419	0.5113
$Cl(3s^2 3p^5 \ ^2P \rightarrow 3s^1 3p^6 \ ^2S)$	0.5653	0.4301	0.6181	0.5400	0.4996
$Ar^+(3s^2 3p^5 \ ^2P \rightarrow 3s^1 3p^6 \ ^2S)$	0.6769	0.5174	0.7264	0.5965	0.6007
Average error		15.8%	11.28%	3.92%	

Table 5.4: Electron transition energy from the 2s to the 3p orbital in the same atoms as in Table 4.

atoms/ions	ΔE_{HF}	ΔE_{LSD}	$\Delta E(MLSDSIC)^{sc}$	$\Delta E(MLSDSIC)^{scx}$	ΔE_{TDDFT}
$P(2s^2 3p^3 \ ^4S \rightarrow 2s^1 3p^4 \ ^4P)$	6.8820	6.4188	6.8165	6.6290	6.1573
$S(2s^2 3p^4 \ ^3P \rightarrow 2s^1 3p^5 \ ^3P)$	8.2456	7.7337	8.1723	8.0045	7.4533
$Cl^+(2s^2 3p^4 \ ^3P \rightarrow 2s^1 3p^5 \ ^3P)$	9.8117	9.2551	9.7273	9.6933	8.9618
$Cl(2s^2 3p^5 \ ^2P \rightarrow 2s^1 3p^6 \ ^2S)$	9.7143	9.1653	9.6484	9.5153	8.8686
$Ar^+(2s^2 3p^5 \ ^2P \rightarrow 2s^1 3p^6 \ ^2S)$	11.3926	10.8009	11.3214	11.1982	10.4901
Average error		5.86%	0.81%	2.28%	

Table 5.5: Electron transition energy when the upper state is not the lowest energy multiplet.

atoms/ions	ΔE_{HF}	ΔE_{LSD}	$\Delta E_{MLSDSIC}^{sc}$	$\Delta E(MLSDSIC)^{scx}$	ΔE_{TDDFT}
$B(2s^2 2p^1 \ ^2P \rightarrow 2s^1 2p^2 \ ^2D)$	0.2172	0.1993	0.2696	0.2458	0.2168
$C^+(2s^2 2p^1 \ ^2P \rightarrow 2s^1 2p^2 \ ^2D)$	0.3290	0.3078	0.3889	0.3225	0.3325
$C(2s^2 2p^2 \ ^3P \rightarrow 2s^1 2p^3 \ ^3D)$	0.2942	0.2878	0.3755	0.2967	0.3090
$N^+(2s^2 2p^2 \ ^3P \rightarrow 2s^1 2p^3 \ ^3D)$	0.4140	0.4149	0.5093	0.4377	0.4433
$Si^+(3s^2 3p^1 \ ^2P \rightarrow 3s^1 3p^2 \ ^2D)$	0.2743	0.2632	0.3098	0.2607	0.2864
$Si(3s^2 3p^2 \ ^3P \rightarrow 3s^1 3p^3 \ ^3D)$	0.2343	0.2356	0.2661	0.2445	0.2567
Average error		3.86%	19.67%	7.20%	

Table 5.6: Electron transition energy when an 's' electron is transferred to a 'd' orbital.

atoms/ions	ΔE_{HF}	ΔE_{LSD}	$\Delta E(MLSDSIC)^{sc}$	$\Delta E(MLSDSIC)^{scx}$	ΔE_{TDDFT}
$Sc(3s^2 3d^1 \ ^2D \rightarrow 3s^1 3d^2 \ ^2G)$	2.1562	1.8584	2.1800	2.0185	1.8649
$Ti(3s^2 3d^2 \ ^3F \rightarrow 3s^1 3d^3 \ ^5F)$	2.2453	1.9740	2.2963	2.0242	—
$Ti(3s^2 3d^2 \ ^3F \rightarrow 3s^1 3d^3 \ ^3H)$	2.3861	2.0827	2.4190	2.2331	2.0951
$V(3s^2 3d^3 \ ^4F \rightarrow 3s^1 3d^4 \ ^4H)$	2.6098	2.3107	2.6611	2.4524	2.3266
$Mn(3s^2 3d^5 \ ^6S \rightarrow 3s^1 3d^6 \ ^6D)$	3.1331	2.7860	3.1637	2.9137	2.8062
$Fe(3s^2 3d^6 \ ^5D \rightarrow 3s^1 3d^7 \ ^5F)$	3.4187	3.0483	3.4792	3.2326	3.0755
$Co(3s^2 3d^7 \ ^4F \rightarrow 3s^1 3d^8 \ ^4F)$	3.7623	3.3178	3.7952	3.5489	3.3516
$Ni(3s^2 3d^8 \ ^3F \rightarrow 3s^1 3d^9 \ ^3D)$	4.1204	3.5949	4.1135	3.8639	3.6351
Average error		12.05%	1.33%	6.60%	

Table 5.7: Electron transition energy when a ‘p’ electron is transferred to a ‘d’ orbital.

atoms/ions	ΔE_{HF}	ΔE_{LSD}	$\Delta E(MLSDSIC)^{sc}$	$\Delta E(MLSDSIC)^{scx}$	ΔE_{TDDFT}
<i>Sc</i> ($3p^6 3d^1 \ ^2D \rightarrow 3p^5 3d^2 \ ^2H$)	1.1295	1.1018	1.4925	1.1366	1.2128
<i>Ti</i> ($3p^6 3d^2 \ ^3F \rightarrow 3p^5 3d^3 \ ^3I$)	1.2698	1.2478	1.6617	1.2811	1.3586
<i>V</i> ($3p^6 3d^3 \ ^4F \rightarrow 3p^5 3d^4 \ ^4I$)	1.4153	1.3959	1.8318	1.4297	1.5042
<i>Mn</i> ($3p^6 3d^5 \ ^6S \rightarrow 3p^5 3d^6 \ ^6F$)	1.7270	1.6431	2.1824	1.7405	1.8073
<i>Fe</i> ($3p^6 3d^6 \ ^5D \rightarrow 3p^5 3d^7 \ ^5G$)	1.8785	1.8784	2.4249	2.0030	1.9898
<i>Co</i> ($3p^6 3d^7 \ ^4F \rightarrow 3p^5 3d^8 \ ^4G$)	2.1178	2.0568	2.6522	2.2910	2.1755
<i>Ni</i> ($3p^6 3d^8 \ ^3F \rightarrow 3p^5 3d^9 \ ^3F$)	2.4232	2.2402	2.8756	2.5923	2.3656
Average error		2.95%	24.33%	3.59%	

Table 5.8: Excitation energies of some atoms when two electrons are excited.

atoms/ions	ΔE_{HF}	ΔE_{LSD}	$\Delta E(MLSDSIC)^{sc}$	$\Delta E(MLSDSIC)^{scx}$
<i>Be</i> ($2s^2 \ ^1S \rightarrow 2p^2 \ ^1D$)	0.2718	0.2538	0.3598	0.3108
<i>B</i> ($2s^2 2p^1 \ ^2P \rightarrow 2p^3 \ ^2D$)	0.4698	0.4117	0.5779	0.5166
<i>C</i> ⁺ ($2s^2 2p^1 \ ^2P \rightarrow 2p^3 \ ^2D$)	0.6966	0.6211	0.8122	0.6836
<i>C</i> ($2s^2 2p^2 \ ^3P \rightarrow 2p^4 \ ^3P$)	0.7427	0.5950	0.8131	0.7503
<i>N</i> ⁺ ($2s^2 2p^2 \ ^3P \rightarrow 2p^4 \ ^3P$)	1.0234	0.8369	1.0754	0.9414
<i>N</i> ($2s^2 2p^3 \ ^4S \rightarrow 2p^5 \ ^2P$)	1.1789	0.9440	1.2371	1.1668
<i>O</i> ⁺ ($2s^2 2p^3 \ ^4S \rightarrow 2p^5 \ ^2P$)	1.5444	1.2552	1.5621	1.4178
<i>O</i> ($2s^2 2p^4 \ ^3P \rightarrow 2p^6 \ ^1S$)	1.5032	1.1333	1.4180	1.3690
<i>F</i> ⁺ ($2s^2 2p^4 \ ^3P \rightarrow 2p^6 \ ^1S$)	1.8983	1.4381	1.8129	1.6715
<i>Mg</i> ($3s^2 \ ^1S \rightarrow 3p^2 \ ^1D$)	0.2578	0.2555	0.2774	0.2612
<i>S</i> ($3s^2 3p^4 \ ^3P \rightarrow 3p^6 \ ^1S$)	1.0273	0.7807	1.1306	0.9783
<i>P</i> ($3s^2 3p^3 \ ^4S \rightarrow 3p^5 \ ^2P$)	0.8539	0.6927	0.9661	0.8477
<i>Si</i> ⁺ ($3s^2 3p^1 \ ^2P \rightarrow 3p^3 \ ^2D$)	0.5856	0.5377	0.6979	0.5750
<i>Si</i> ($3s^2 3p^2 \ ^3P \rightarrow 3p^4 \ ^3P$)	0.5860	0.4928	0.6703	0.5706
<i>Cl</i> ⁺ ($3s^2 3p^2 \ ^3P \rightarrow 3p^4 \ ^3P$)	1.2535	0.9551	1.3493	1.1067
Average error		16.4%	11.64%	6.18%

Table 5.9: Excitation energy of two-gap systems(one electron excitation). Numbers given are in atomic units. The first column gives the atom and the excited-state to which the system is excited from the ground-state. In the second column are given the transition energies obtained by doing ground state LSD calculation for both ground state and the excited-state. The third column gives transition energies obtained by employing potential of equation 5.23. Fourth column gives number obtained with the potential of equation 5.24. The HS values are given in the last column

atoms	$\Delta E(LSD)$	$\Delta E(MLSDSIC)^{sc}$	$\Delta E(MLSDSIC)^{scx}$	$\Delta E(HS)$
$B(2s^1 2p^1 3s^1 M_L = 1, M_S = 1/2)$	0.380	0.517	0.460	0.406
$C(2s^1 2p^2 3s^1 M_L = 1, M_S = 1)$	0.575	0.854	0.752	0.658
$O(2s^1 2p^4 3p^1 M_L = 2, M_S = 1)$	1.044	1.277	1.246	1.230
$F(2s^1 2p^5 3p^1 M_L = 2, M_S = 1/2)$	1.259	1.515	1.482	1.463
$Ne(2s^1 2p^6 4s^1 M_L = 0, M_S = 0)$	1.538	1.815	1.796	1.796
$Mg(2s^1 2p^6 3s^2 4s^1 M_L = 0, M_S = 0)$	3.170	3.545	3.506	3.490
$Si(2s^1 2p^6 3s^2 3p^2 4s^1 M_L = 1, M_S = 1)$	5.385	5.845	5.778	5.785
$P(2s^1 2p^6 3s^2 3p^3 4s^1 M_L = 0, M_S = 3/2)$	6.656	7.162	7.080	7.095
$S(2s^1 2p^6 3p^4 4s^1 M_L = 1, M_S = 1)$	8.069	8.693	8.596	8.547
$Cl(2s^1 2p^6 3s^2 3p^5 4s^1 M_L = 1, M_S = 1/2)$	9.548	10.256	10.166	10.114
average error	9.5%	8.1%	3.1%	

The configurations of the excited taken here are exactly same as that in [70] for one-gap and the configurations of two gap systems are same as that in [91]. Therefore more details about these can be found there.

5.6 Exchange potential from work function formalism

In work function formalism as described in Harbola and Sahni's works [61, 62], exchange potential is defined as work done in bringing a unit charge from infinity to a given point in the field of exchange hole. Thus

$$v_x = - \int_{\infty}^r \mathbf{E}_X \cdot d\mathbf{l} \quad (5.26)$$

where \mathbf{E}_X is the electric field due to Fermi hole and is given by,

$$\mathbf{E}_X = \int \frac{\rho_X}{|\mathbf{r} - \mathbf{r}'|^3} (\mathbf{r} - \mathbf{r}') d\mathbf{r}' \quad (5.27)$$

Table 5.10: Excitation energy of two-gap systems (two electron excitation). Numbers given are in atomic units.

atoms	$\Delta E(LSD)$	$\Delta E(MLSDSIC)^{sc}$	$\Delta E(MLSDSIC)^{scx}$	$\Delta E(HS)$
$B(2p^1 3p^2 M_L = 3, M_S = 1/2)$	0.966	1.098	1.051	1.010
$C(2p^2 3p^2 M_L = 2, M_S = 2)$	1.286	1.537	1.429	1.409
$N(2p^4 3p^1 M_L = 2, M_S = 3/2)$	1.257	1.559	1.453	1.438
$F(2p^6 3p^1 M_L = 1, M_S = 1/2)$	1.945	2.385	2.281	2.371
$Ne(2p^6 3p^2 M_L = 1, M_S = 1)$	3.438	4.037	3.874	3.948
$Na(2s^1 2p^6 3p^2 M_L = 1, M_S = 1/2)$	2.318	2.653	2.599	2.615
$Al(2s^1 2p^6 3s^1 3p^3 M_L = 0, M_S = 1/2)$	4.254	4.707	4.623	4.702
$Ar(2p^6 3s^0 3p^6 4p^2 M_L = 2, M_S = 0)$	2.216	2.201	2.190	2.589
$K(2p^6 3s^1 3p^6 4p^2 M_L = 1, M_S = 1/2)$	1.407	1.471	1.461	1.626
$Cu(2p^6 3s^1 3p^3 3d^{10} 4s^2 4p^1 M_L = 1, M_S = 1/2)$	6.825	8.012	7.261	7.404
average error	11.1%	6.3%	4.2%	

Table 5.11: Excitation energy of two-gap systems (three electron excitation). Numbers given are in atomic units.

atoms	$\Delta E(LSD)$	$\Delta E(MLSDSIC)^{sc}$	$\Delta E(MLSDSIC)^{scx}$	$\Delta E(HS)$
$O(2s^1 2p^2 3p^3 M_L = 1, M_S = 2)$	2.868	3.217	3.070	3.070
$Ne(2s^1 2p^4 3p^3 M_L = 1, M_S = 2)$	4.047	4.406	4.344	4.354
$Na(2s^1 2p^5 3p^3 M_L = 1, M_S = 1/2)$	4.046	4.416	4.370	4.399
$Mg(2s^1 2p^4 3s^2 3p^3 M_L = 1, M_S = 0)$	8.160	8.342	8.292	8.256
$P(2s^2 2p^6 3s^1 4p^3 4s^1 M_L = 1, M_S = 3/2)$	1.751	1.792	1.669	1.635
$Ar(2s^2 2p^6 3s^1 3p^4 4p^3 M_L = 1, M_S = 0)$	2.590	2.646	2.528	2.491
$Ca(2s^2 2p^6 3s^1 3p^6 4p^3 M_L = 0, M_S = 1)$	1.914	1.996	1.974	2.190
$Zn(3s^1 3p^4 3d^{10} 4s^2 4p^3 M_L = 1, M_S = 0)$	11.633	13.203	12.555	12.407
average error	5.7%	4.8%	2%	

Table 5.12: Excitation energy of two-gap systems (four electron excitation). Numbers given are in atomic units.

atoms	$\Delta E(LSD)$	$\Delta E(MLSDSIC)^{sc}$	$\Delta E(MLSDSIC)^{scx}$	$\Delta E(HS)$
<i>Mg</i> ($2p^6 3p^4$ $M_L = 1, M_S = 1$)	7.053	7.825	7.619	7.805
<i>Al</i> ($2p^6 3p^5$ $M_L = 1, M_S = 1/2$)	9.219	10.127	9.885	10.116
<i>Si</i> ($2p^6 3p^6$ $M_L = 0, M_S = 0$)	11.609	12.644	12.382	12.666
<i>P</i> ($2p^6 3p^6 4s^1$ $M_L = 0, M_S = 1/2$)	14.595	15.747	15.445	15.799
<i>S</i> ($2p^6 3p^6 4s^2$ $M_L = 0, M_S = 0$)	18.031	19.309	18.980	19.387
<i>Ar</i> ($2p^6 3p^6 4s^2 3d^2$ $M_L = 4, M_S = 0$)	26.346	27.949	27.661	28.026
<i>K</i> ($2p^6 3p^6 4s^2 3d^3$ $M_L = 5, M_S = 1/2$)	30.748	32.493	32.246	32.555
<i>Ca</i> ($2p^6 3p^6 4s^2 3d^4$ $M_L = 6, M_S = 0$)	35.280	37.172	36.977	37.220
<i>Sc</i> ($2p^6 3p^6 4s^2 3d^5$ $M_L = 0, M_S = 5/2$)	39.672	41.693	41.570	41.783
<i>Ti</i> ($2p^6 3p^6 4s^2 3d^6$ $M_L = 2, M_S = 2$)	44.658	46.894	46.839	46.931
<i>V</i> ($2p^6 3p^6 4s^2 3d^7$ $M_L = 3, M_S = 3/2$)	49.892	52.315	52.370	52.294
<i>Cr</i> ($2p^6 3p^6 4s^2 3d^8$ $M_L = 3, M_S = 1$)	55.477	58.0865	58.263	57.985
<i>Mn</i> ($2p^6 3p^6 4s^2 3d^9$ $M_L = 2, M_S = 1/2$)	61.128	64.143	64.233	63.887
<i>Fe</i> ($2p^6 3p^6 4s^2 3d^{10}$ $M_L = 0, M_S = 0$)	66.944	70.035	70.378	69.862
<i>Co</i> ($2p^6 3p^6 4s^2 3d^{10} 4p^1$ $M_L = 1, M_S = 1/2$)	73.557	76.864	77.269	76.594
<i>Ni</i> ($2p^6 3p^6 4s^2 3d^{10} 4p^2$ $M_L = 2, M_S = 0$)	80.803	84.337	84.805	83.954
<i>Cu</i> ($2p^6 3p^6 4s^2 3d^{10} 4p^3$ $M_L = 0, M_S = 3/2$)	88.715	92.555	93.087	91.881
<i>Zn</i> ($2p^6 3p^6 4s^2 3d^{10} 4p^4$ $M_L = 1, M_S = 1$)	97.298	101.322	101.926	100.667
average error	5.3%	0.4%	1.2%	

The above equation can be re-written as,

$$\mathbf{E}_X = -\nabla \int \frac{\rho_X}{|\mathbf{r} - \mathbf{r}'|} (\mathbf{r} - \mathbf{r}') d\mathbf{r}' + \int \frac{\nabla \rho_X}{|\mathbf{r} - \mathbf{r}'|} (\mathbf{r} - \mathbf{r}') d\mathbf{r}' \quad (5.28)$$

the first term after ∇ on the right hand side of the above equation represents the Slater's potential (V_s) and it's written as $V_s = -\frac{2\varepsilon_x}{\rho}$, where ε_x represents exchange energy per unit volume and ρ is electron density. This is true for both ground state as well as for the excited states. The second term on the right hand side is actually what brings difference between Slater's potential and Dirac's potential in local density approximation for v_x in ground states. Therefore, its value must be equal to $-\nabla \frac{k_f}{2\pi}$ in local density approximation, where, $k_f = (3\pi^2 \rho)^{1/3}$. Thus for ground states we have,

$$v_x = \frac{2\varepsilon_x}{\rho} + \frac{k_f}{2\pi} \quad (5.29)$$

Since the first term on the right hand side retains its form for the excited states also, the only thing that changes for excited states is the second term. However let us make a crude approximation and keep the second term also unchanged for excited states. Therefore for excited state also we have the same potential as given by equation 5.29 with ε_x for one

Table 5.13: Excitation energy obtained with new exchange potential given in equation 5.29 and comparison with standard results.

atoms/ions	ΔE_{HF}	ΔE_{LSD}	$\Delta E(new)$	$\Delta E(MLSDSIC)^{scx}$	ΔE_{TDDFT}
$O^+(2s^2 2p^3 \ ^4S \rightarrow 2s^1 2p^4 \ ^4P)$	0.5530	0.5397	0.6426	0.5581	0.5694
$O(2s^2 2p^4 \ ^3P \rightarrow 2s^1 2p^5 \ ^3P)$	0.6255	0.5243	0.5296	0.6460	0.5912
$F^+(2s^2 2p^4 \ ^3P \rightarrow 2s^1 2p^5 \ ^3P)$	0.7988	0.6789	0.7365	0.7540	0.7651
$F(2s^2 2p^5 \ ^2P \rightarrow 2s^1 2p^6 \ ^2S)$	0.8781	0.6671	0.8099	0.8445	0.7659
$Ne^+(2s^2 2p^5 \ ^2P \rightarrow 2s^1 2p^6 \ ^2S)$	1.0830	0.8334	0.9169	0.9620	0.9546
Average error		14.30%	8.32%	5.70%	

gap given by,

$$\begin{aligned} \epsilon_x = & [\epsilon(k_3) - \epsilon(k_2) + \epsilon(k_1)] + \frac{1}{8\pi^3} \int (k_3^2 - k_1^2)^2 \ln \left(\frac{k_3 + k_1}{k_3 - k_1} \right) \\ & - \frac{1}{8\pi^3} \int (k_3^2 - k_2^2)^2 \ln \left(\frac{k_3 + k_2}{k_3 - k_2} \right) - \frac{1}{8\pi^3} \int (k_2^2 - k_1^2)^2 \ln \left(\frac{k_2 + k_1}{k_2 - k_1} \right) \end{aligned} \quad (5.30)$$

and a similar looking form for higher excited states. Here $\epsilon(k_i)$ are the exchange energy per particle corresponding to Fermi wave vector k_i . Exchange potential given by Eq. 5.29 become much better if the second term in it is replaced by $\frac{2k_3+k_1-k_f}{4\pi}$. In the table 5.13 we give calculation of excitation energy for one gap systems obtained with this potential.

Accuracy of exchange potential can also be tested by ionization energy theorem. Which states that ionization energy is equal to negative of highest occupied energy for Kohn Sham system. Use of accurate potential leads to accurate orbital energies. Therefore, by comparing energy difference of a system and its positive ion with highest occupied orbital energy we can check accuracy of the potential employed for calculation. This work is being pursued by our group.

5.7 Discussion and concluding remarks

We have constructed exchange potential for excited states in local density approximation. Since calculating functional derivative of exchange energy functional constructed by us is difficult, we have resorted to an approximation in calculating functional derivative.

Further, We have derived the same potential by using an arguments which is used in ground state case for obtaining Dirac exchange potential from Hartree Fock exchange potential. On the basis of our studies of various excited state we have introduced an exponent into the exchange potential to make it better. This exponent adjusts its value depending on the total number of electrons and number of missing electrons. The potential is of great significance, since it does not vary with different electrons in a given state and has correct ground state limit. It can be used for excited states of any type, only thing one has to do is to extend the potential accordingly which is not a difficult task. To subject it to real test for accuracy, we have used virial relation to calculate exchange energy, instead of calculating the exchange energy from the functional.

We have shown that the exchange potential reported here satisfies Levy-Perdew theorem and Janak theorem very well and it also gives reasonably good excitation energies for most of the cases studied here, reducing the average error by a factor or 2 or more. Although it is orbital dependent, for particular classes of excited it becomes same for all electrons, therefore ground state like K-S calculation can be performed. We have employed this potential to one-gap as well as to two gap systems with encouraging success.

Chapter 6

Summary and future prospects

The work contained in the thesis is concerned with the application of density functional theory(DFT) to excited states of interacting systems. It spells out a method for construction of exchange energy functional for excited states. The same method has been used to construct exchange potential for excited states. Further, we have discussed inclusion of gradient correction to these functionals to improve their accuracy. To test the functionality of these functionals, we have done extensive calculation of excitation energy and total energy of various atomic systems and have compared the results with available standard data. To test the accuracy of exchange potential we do exchange energy calculation through virial relation of Levy and Perdew and use the same to calculate excitation energy of various classes of excited states of different atoms and ions. We have also subjected the potential to a test to see if it satisfies Jank theorem. In the following paragraphs we give chapter wise outline of the work presented in this thesis.

Density functional theory(DFT) has emerged (in Walter Kohn's words) out of despair to surmount the exponential wall. In principle solution of Schrödinger's equation gives all the information about a given system but, extracting information through its solution is the real pest. Solution of Schrödinger equation becomes increasingly difficult as number of interacting particles increases. In such difficult cases DFT provides

an alternative. It maps the real interacting many particle system to a non-interacting many particle system. Thus in place of Schroedinger's equation now we have Kohn-Sham equation. This simplification comes at the cost of introducing a demon called exchange correlation term. Its presence acts as if now electrons do not interact with each other. DFT is in principal an exact theory but approximation creeps in as soon as we look at the exchange and correlation term. Since we do not have exact form for these. The great advantage one has is that exchange correlation terms can be built step by step with LDA ,GGA and meta-GGA approximation. With these approximation DFT does very well in ground state level studies. How do we go about doing excited state studies with DFT? Extension of DFT to excited states is greeted with some serious issues. I have discussed the non-existence of Hohenberg Kohn theorem for excited states. i.e no one to one mapping between excited state density and external potential. This is a big issue and has been addressed by Gorling,Levy and Nagy, Samal and Harbola. Based on Harbola and Samal's work we conclude that a Kohn Sham system corresponding to a given excited state is identified by comparison of K.E of the virtual Kohn Sham system and the real system.

In the second chapter a very fundamental point about excited state density has been discussed. It is shown that density of even an auto ionizing state has exponential decay in asymptotic limit and this decay is dictated by lowest ionization energy of the system. And the same is true for all other excited state densities. We have supported our argument with numerical calculation on excited state densities.

In the third chapter we have constructed an accurate exchange energy functional for excited states. Need for such functional arises because existing LDA functionals do not work well when applied to excited states. The reason for this failure being lack of information contained in density about the excited states. What it means is that density of the system does not uniquely and explicitly specifies a particular excited states. Had this not been the case LDA functional would have been as successful for the excited states as it is for the ground states. In despair all we can do is to design functional and potential for

excited states which themselves contain the information about the excited states. That is what we have done here. To construct the exchange energy functional we map the electron density onto k -space. For an excited state k -space looks similar to orbital configuration of the system. Thus, for an excited state we have fill spaces for occupied orbitals and gaps corresponding to electrons missing from orbitals. Expression for exchange energy is first developed for the homogeneous electron gas by simply integrating the Hartree Fock exchange energy term, and then the same is used for systems having non-uniform density by applying local density approximation. To make it better its local spin density approximation (LSD) generalization is done. As it is apparent, the functional derived in this manner is written in terms of wave vectors k 's which depict the occupation and vacancy in k -space. However, these k ' do implicitly depend on the densities of ground state and excited state. Thus, energy functionals for excited states are bi-functional of the two densities. These functionals lead to accurate calculation of excitation energies for various excited states.

In the fourth chapter we have shown that inclusion of gradient correction to excited state functional developed by us leads to very accurate total energy in exchange only calculation. We have used Becke's and PW's generalized gradient correction to exchange energy functional for our calculation of excited states. Use of above mentioned gradient correction for excited state is justified because these functionals have been constructed on physical grounds which are not specific to ground states only. It would be interesting if we systematically develop gradient correction for excited states systematically. A similar work has been done by our group for kinetic energy functional where gradient correction excited state energy functional has been reported. In future we hope to extend our work on exchange energy functional.

In the fifth chapter construction of exchange potential has been discussed. This is done either by taking functional derivative of exchange energy functional developed in chapter with respect to density or from the HF exchange potential itself. The potential works well for excited states but has some scope for further development. In the following

chapter accurate exchange energies, total energies and excitation energies are calculate using gradient corrected exchange energy functional for excited states.

In the appendix-A attempts have been made to calculate correlation energy for excited states. However there is not much success. Therefore, this also remains open for further developments.



Bibliography

- [1] L.H. Thomas, Proc. Cambridge Phil. Soc. **23**, 542 (1926).
- [2] E. Fermi, Z. Phys. **48**, 73 (1928).
- [3] P. Hohenberg and W. Kohn, Phys. Rev **136**, B864, (1964)
- [4] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133, (1965)
- [5] *Recent Developments and Applications of Modern Density Functional Theory*, edited by J.M. Seminario (Elsevier 1996)
- [6] R. Singh and B. M. Deb, Phys. Rep. **311**, 47 (1999) and references therein.
- [7] E. G. Parr and W. Yang, 1989 *Density-Functional Theory of Atoms and Molecules* (New York: Oxford University Press)
- [8] W. Kohn, Rev. Mod. Phys. **71**, 1253 (1999)
- [9] N.H March, *Self-Consistent Fields in Atoms* (Pergamon Press 1975)
- [10] J. C. Slater in *The self-consistent field for molecules and solids* (McGraw Hill, New York, 1974), vol. 4.
- [11] J. C. Slater, Phys. Rev. **81**, 385 (1953)
- [12] *Recent Developments and Applications of Modern Density Functional Theory*, edited by J.M. Seminario(Elsevier 1996)

- [13] R. M. Dreizler and E. K. U. Gross, 1990 *Density Functional Theory* (Berlin: Springer-Verlag)
- [14] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
- [15] *A Primer in Density Functional Theory*, edited by C. Fiolhais, F. Nogueira and M. Marques (Springer, Berlin, 2003)
- [16] M. Levy, J.P. Perdew, Phys. Rev. A **32**, 2010 (1985).
- [17] M. Shamim and M. K. Harbola, Chem. Phys. Letter **464**, 135 (2008)
- [18] C.O. Almbladh, U. von Barth, Phys. Rev. B **31**, 3231 (1985).
- [19] F. Herman, J. P. Van Dyke and I. B. Ortenburger, Phys. Rev. Lett. **22**, 807 (1969).
- [20] J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996); *ibid* 78, 1396(E) (1997). See also V. Staroverov et al., Phys. Rev. A **74**, 044501 (2006).
- [21] K. Burke, F. G. Cruz and Kin-Chung Lam, J. Chem. Phys. **109**, 8161 (1998)
- [22] J. P. Perdew, Phys. Rev. Lett. **55**, 1665 (1985).
- [23] J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, Phys. Rev. Lett **91**, 146401 (2003).
- [24] A. D. Becke, Phys. Rev. A **38** , 3098 (1988)
- [25] C. F. Weizsacker, Z. Phys. **96**, 431 (1935)
- [26] Larry Spruch, Rev. Mod. Phys. **63**, 151 (1991)
- [27] R. v. Leeuwen and E.J. Baerends, Phys. Rev. A **49**, 2421, (1994)
- [28] N. Umezawa, Phys. Rev. A **74** , 032505 (2006)
- [29] E. Fermi and E. Amaldi, Accad. Ital. Roma **6** , 119 (1934).

- [30] A. D. Becke, E. R. Johnson, J. Chem. Phys. **124**, 221101 (2006)
- [31] R. G. Parr, M. Levy, J. L. Balduz Jr. , Phys. Rev. Lett **49**, 1691 (1982).
- [32] U. von Barth, Phys. Rev. A **20** 1693, (1979).
- [33] O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13** 4274, (1976).
- [34] T. Ziegler ,A. Rauk and E. J. Baerends , Theor. Chim. Acta **43**, 261 (1997).
- [35] R. K. Pathak, Phys. Rev. A **29**, 978 (1984)
- [36] J. P. Perdew and M. Levy, Phys. Rev. B **31**, 6264 (1985)
- [37] E. K. U. Gross, L. N. Oliviera and W. Kohn, Phys. Rev. A **37**, 2809 (1988)
- [38] A. K. Theophilou, J. Phys. C **12**, 5419 (1979)
- [39] L. N. Oliviera , E. K. U. Gross and W. Kohn, Phys. Rev. A **37** 2821 , (1998)
- [40] M. K. Harbola, Phys. Rev. A **69**, 042512 (2004)
- [41] K. D. Sen, Chem. Phys. Lett. **188**, 510 (1992)
- [42] Á. Nagy, Adv. Quantum Chem. **42**, 363 (2002)
- [43] Á. Nagy, Phys. Rep. **298**, 1 (1998)
- [44] M.M. Morrell, R.G. Parr, M. Levy, J. Chem. Phys. **62**, 549 (1975)
- [45] J. Katriel, E.R. Davidson, Proc. Natl. Acad. Sci. USA **77** 4403 (1980)
- [46] M. Levy, J.P. Perdew, V. Sahni, Phys. Rev. A **30** 2745 (1984)
- [47] Y. Tal, Phys. Rev. A **18**, 1781 (1978)
- [48] B. L. Hammond, W.A. Lester, Jr. and P.J.Reynolds, *Monte Carlo Ab initio quantum chemistry*(Wrold Scientific, Singapore, 1994).

- [49] N.C. Handy, M.T. Marron, H.J. Silverstone, Phys. Rev. **180**, 45 (1969)
- [50] F.J. Galvez, E.J. Buendia, A. Sarsa, J. Chem. Phys. **118**, 6858 (2003)
- [51] F.J. Galvez, E.J. Buendia, A. Sarsa, J. Chem. Phys. **123**, 034302 (2005)
- [52] P.O. Lowdin, Phys. Rev. **97**, 1474 (1955)
- [53] B.C. Carlson, M.K. Joseph, Phys. Rev. **121**, 659 (1961)
- [54] Á. Nagy, J. Phys. B **29**, 389 (1996)
- [55] M. Levy and Á. Nagy, Phys. Rev. Lett. **83**, 4361 (1999)
Nagy Á and M. Levy, Phys. Rev. A **63**, 052502 (1999)
- [56] P. W. Ayers and M. Levy, Phys. Rev. A **80**, 012508 (2009)
- [57] M. K. Harbola, Phys. Rev. A **65**, 052504 (2002)
- [58] I. Lindgren and S. Salomonson, Phys. Rev. A **70**, 032509 (2004)
I. Lindgren, S. Salomonson and Möller, Int. J. Quant. Chem. **102**, 1010 (2005)
- [59] S.H Vosko, L. Wilk and M. Nusair, Can. J. Phys. **58**(8), 1200 (1980)
- [60] J. D. Talman and W. F. Shadwick, Phys. Rev. A **14**, 36 (1976)
- [61] M. K. Harbola and V. Sahni, Phys. Rev. Lett. **62**, 489 (1989)
- [62] M. K. Harbola 2008 *Chemical Reactivity Theory, A Density Functional View*, Ch-7, Page-83, edited by P.K. Chattaraj (CRC Press, USA,)
- [63] A. Savin, C. J. Umrigar and X. Gonze, Chem. Phys. Lett. **288**, 391 (1998)
- [64] A. K. Roy and S. I. Chu, Phys. Rev. A **65**, 052508 (2002) ; A. K. Roy and A. F. Jalbout, Chem. Phys. Lett. **445**, 355 (2007)
- [65] P. Samal and M. K. Harbola, J. Phys. B **39**, 4065 (2006)

- [66] T. L. Gilbert, Phys. Rev. B **12**, 2111 (1975).
- [67] P. W. Ayers, S. Liu, Phys. Rev. A **75**, 022514 (2007)
- [68] M. Levy, Proc. Natl. Acad. Sci. UDA **76**, 6062 (1979)
- [69] E. H. Lieb and S. Oxford, Int. J. Quantum Chem. **19**, 427 (1981)
- [70] P. Samal , M. K. Harbola, J.Phys.B At.Mol.Opt.Phys.**38**, 3765 (2005)
- [71] M. K. Harbola , P. Samal, J.Phys.B:At.Mol.Opt.Phys.**42**, 015003 (2009)
- [72] M. K. Harbola, M. Shamim, P. Samal,M. Rahaman , S. Ganguly and A. Mookerjee, AIP conf. proceed.**1108**, 54 (2009)
- [73] M. Rahaman, S. Ganguly, P. Samal, M. K. Harbola, T. Saha-Dasgupta, A. Mookerjee, Physica B **404**, 1137 (2006)
- [74] P. Samal 2006 Ph.D Thesis, IIT Kanpur
- [75] P. Samal ,M. K. Harbola and A. Holas, Chem. Phys. Lett. **419**, 217 (2006)
- [76] Cheng Chia-Lun, Q. Wu and T. V. Voorhis, J. Chem. Phys. **129**, 124112 (2008)
- [77] U. I. Safronova , A. S. Safronova and Beiersdorfer, J. Phys. B: At. Mol. Opt. Phys. **42** 165010, (2009)
- [78] C. F. Fischer, 1977 *The Hartree-Fock method for atoms* (Wiley, New York)
- [79] V. Sahni , Y. Li and M. K. Harbola, 1992 Phys. Rev. A **45**, 1434 (1992)
- [80] Y. Wang , J. P. Perdew , J. A. Chevary , L. D. Macdinald and S. H. Vosko, Phys. Rev. A **41**, 78 (1990)
- [81] P. A. M. Dirac, Proc. Cambridge Phil. Roy. Soc. **26**(3), 376 (1930)
- [82] C. Kamal and C. J. Aparna, Phys. Chem. **131**, 164708 (2009)

- [83] C. Kamal, T. K. Ghanty, Arup Banerjee, and Aparna Chakrabarti, *J. Chem. Phys.* **131**, 164708 (2009)
- [84] A. D. Becke *et al* *J. Chem. Phys.* **124**, 221101 (2006).
- [85] J.P. Perdew, Y. Wang, *Phys. Rev. B* **33**, 8800 (1986)
- [86] R. T. Sharp and G. K. Horton, *Phys. Rev* **90**, 317 (1953)
- [87] J. D. Talman and W. F. Shadwick, *Phys. Rev. A* **14**, 36 (1976)
- [88] U. von Barth, *Phys. Rev. A* **20**, 1693 (1979)
- [89] Gaspar, *Acta Phys. Hung.* **35**, 213 (1974)
- [90] Á. Nagy, *Phys. Rev. A* **37**, 2821 (1990)
- [91] M. Shamim and M. K. Harbola, *J. Phys. B* **43**, 215002 (2010)
- [92] M. Levy and Á. Nagy, *Phys. Rev. Lett.* **83**, 4361 (1999)
Á. Nagy and M. Levy, *Phys. Rev. A* **63**, 052502 (2001)
- [93] A. Görling, *Phys. Rev. A* **59**, 3359 , (1999)
- [94] M. Petersilka , U. J. Gossmann and E. K. U. Gross, *Phys. Rev. Lett.* **76**, 1212 (1996)
- [95] M. E. Casida in *Recent Advances in Density Functional Methods, Part 1* edited by D. P. Chong (Singapore: World Scientific, 1995)
- [96] M.J. Frisch et al. 2001 Gaussian 98; Revision A.11.1, Gaussian Inc.,
- [97] D. J. Tozer and N. C. Handy, *Phys. Chem. Chem. Phys.* **2**, 2117 (2000)
- [98] Y. Kurzwil and M. Head-Gordon, *Phys. Rev. A* **80**, 012509 (2009)
- [99] K. Burke, F. G. Cruz, K.C. Lam, *J. Chem. Phys.* **109**, 8161 (1998)

- [100] M. Hemanadhan and M. K. Harbola, *J. Mol Struct:Theochem* **943**, 152 (2009)
- [101] J. P. Perdew and A. Zunger, *Phys.Rev. B* **23**, 5048 (1981)
- [102] J. F. Janak and A. R. Williams, *Phys. Rev. B* **23**, 6301 (1981)
- [103] R. Colle, O. Salvetti, *Theoret. Chim. Acta (Berl.)* **37**, 329 (1975)
- [104] C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988)



Appendix A

Correlation Energy for Excited States: Preliminary Calculations.

In this appendix we try to apply our method of constructing functionals for excited states, to obtain correlation energy functionals. Using our approach modify Lee Yang Parr version of correlation energy functional to obtain a functional for excited states.

Correlation energy (E_c) is defined as the difference between exact non-relativistic energy and Hartree Fock energy. Since Hartree fock calculation is an approximate calculation, energy obtained is always above the exact non-relativistic energy. Therefore, correlation is always negative. Although E_c is a small number as compared to the other contribution to total energy, it plays important role in formation of negative ions, in deciding geometry of molecules and in electric and magnetic proprieties of solids.

Estimation of correlation is not as simple as estimation of exchange energy. In one approach this is done by calculating energy of system by using multi-configuration integration calculation. However as the number of Slater determinants increase the computation cost becomes exorbitant. Therefore this is not a feasible approach. Analytically, correlation energy has been calculated in low and high density limit. To obtain correlation energy for intermediate densities interpolation between the two density limits is done.

Density functional method has been employed to calculate correlation energy for ground states of atoms and molecules. However there is no complete analytical formula for correlation energy. This is because we do not know the exact form of the wave function that carries the effect of Coulomb correlation. In the absence of such functional one has to do with those obtained by parametrization of Monte-Carlo results.

Colle Salvetti formula for correlation energy [103] and its extension to density functional form by Lee, Yang and Parr (LYP) [104] give reasonable good estimation of correlation energy for ground states of atoms and molecules. The aim of work in this appendix is to extend LYP functional for correlation energy to excited states. For this we follow the idea of splitting the k - space in accordance with the occupation of orbitals in excited state.

The LYP formula for correlation energy of atoms in ground state is given by,

$$E_c = -a \int \frac{\rho(\mathbf{r}) + 2b\rho(\mathbf{r})^{-5/3} \left[\rho_\alpha(\mathbf{r})t_{HF}^\alpha + \rho_\beta(\mathbf{r})t_{HF}^\beta - \rho(\mathbf{r})t_w(\mathbf{r}) \right] e^{-c\rho(\mathbf{r})^{1/3}}}{1 + d\rho(\mathbf{r})^{-1/2}} \gamma(\mathbf{r}) d\mathbf{r} \quad (\text{A.1})$$

where,

$$\gamma(\mathbf{r}) = 2 \left[1 - \frac{\rho_\alpha^2(\mathbf{r}) + \rho_\beta^2(\mathbf{r})}{\rho(\mathbf{r})^2} \right] \quad (\text{A.2})$$

$$t_{HF}^\alpha = \frac{1}{2} t_{HF}(2\rho_\alpha(\mathbf{r}), \mathbf{r}) \quad (\text{A.3})$$

is Hartree Fock kinetic energy density for spin up.

$$t_{HF}^\beta = \frac{1}{2} t_{HF}(2\rho_\beta(\mathbf{r}), \mathbf{r}) \quad (\text{A.4})$$

is Hartree Fock kinetic energy density for spin down.

$$t_{HF} = t_{TF} + \frac{1}{9} t_W(\mathbf{r}) + \frac{1}{18} \nabla^2 \rho \quad (\text{A.5})$$

is total Hartree-Fock energy density.

$$t_{TF} = \frac{3}{10} (3\pi^2)^{2/3} \rho^{5/3} \quad (\text{A.6})$$

is Thomas-Fermi Kinetic energy density.

$$t_w = \frac{1}{8} \frac{|\nabla\rho|^2}{\rho} - \frac{1}{8} \nabla^2\rho \quad (\text{A.7})$$

is Weizsacker correction [25] to kinetic energy density.

For an excited state with one-gap Thomas Fermi kinetic energy term is given by,

$$t_{TF}^{excited} = \frac{3}{10} (3\pi^2)^{2/3} \left[\rho_3^{5/3} - \rho_2^{5/3} + \rho_1^{5/3} \right] \quad (\text{A.8})$$

and Weizsacker correction term becomes,

$$t_w^{excited} = \frac{1}{8} \left[\frac{|\nabla\rho_3|^2}{\rho_3} - \frac{|\nabla\rho_2|^2}{\rho_2} + \frac{|\nabla\rho_1|^2}{\rho_1} \right] - \frac{1}{8} [\nabla^2\rho_3 - \nabla^2\rho_2 + \nabla^2\rho_1] \quad (\text{A.9})$$

Since the derivation of Colle-Salvetti and LYP formulae are quite general, therefore the should be applicable to excited states also. For excited states we use modified expressions for kinetic energy term and Weizsacker term in Eq.A.1 and expect to get reasonable correlation energy for excited states. However as shown in the table A.1, such modification does not lead to appreciable change in correlation energy and we get same energy for excited states as corresponding values for the ground states. calculation for excited stated states of atoms does not give desired results. We find that this modification does not lead to significant improvement over the correlation energy obtained with ground state functional.

Since the above mentioned approach does not seem to work, we look for another simple method to achieve the goal. Coll-Salvetti formulation for correlation energy has been obtained by choosing such values for parameters a, b, c and d so as to get correct correlation energy for ground state of He atom. Therefore, these parameters might be different for excited states. We did fitting for a particular excited state of He and tried to calculate correlation energy of excited states of other atoms. Again the method does not seem to work. We conclude that for excited states, parameters a, b, c and d are state

Table A.1: Correlation energy of some atoms and ions. In second column ground state correlation energies (E_c°) are give and in third column correlation energies (E_c^*) for corresponding excited states are given.

atom/ion(state)	$-E_c^\circ$	$-E_c^*$
$N(2s^22p^3\ ^4S \rightarrow 2s^12p^4\ ^4P)$	0.2073	0.2081
$O^+(2s^22p^3\ ^4S \rightarrow 2s^12p^4\ ^4P)$	0.2332	0.2338
$F(2s^22p^5\ ^2P \rightarrow 2s^12p^6\ ^2S)$	0.3718	0.3723
$Ne^+(2s^22p^5\ ^2P \rightarrow 2s^12p^6\ ^2S)$	0.3889	0.3891
$Na(3s^1\ ^2S \rightarrow 3p^1\ ^2P)$	0.4558	0.4562

dependent therefore one particular values of these parameters may not work for all types of excited states.

A.1 Discussion and concluding remarks

In this Appendix we tried to extend our idea of constructing functional for excited states, to the correlation regime. However, our attempt to construct correlation energy functional for excited states by modifying the LYP expression did not lead us to similar success as we have seen previously for exchange energy. Reason for this failure is perhaps presence of strongly state dependent parameters a, b, c and d in the expression. In our future work we hope to improve upon this.

To get better results with this approach one will have to first fix the values of parameters a, b, c and d . Correlation energy functional for excited states can be developed systematically through response function analysis. We plan to take this approach in our future work.