A density functional method for general excited states in atoms

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Abstract

This chapter presents the development of a density functional theory (DFT)-based method for accurate, reliable treatment of various resonances in atoms. Many of these are known to be notorious for their strong correlation, proximity to more than one thresholds, degeneracy with more than one minima. Therefore these pose unusual challenges to both theoreticians and experimentalists. It is well-known that DFT has been one of the most powerful and successful tools for electronic structure calculation of atoms, molecules, solids in the past two decades. While it has witnessed diverse spectacular applications for ground states, the same for excited states, unfortunately, has come rather lately and remains somehow less conspicuous relatively. Our method uses a work-function-based exchange potential in conjunction with the popular gradient-corrected Lee-Yang-Parr correlation functional. The resulting Kohn-Sham equation, in the non-relativistic framework, is numerically solved accurately and efficiently by means of a generalized pseudospectral method through a non-uniform, optimal spatial discretization. This has been applied to a variety of excited states, such as low and high states; single, double, triple as well as multiple excitations; valence and core excitations; autoionizing states; satellites; hollow and doubly-hollow states; very high-lying Rydberg resonances; etc., of atoms and ions, with remarkable success. A thorough and systematic comparison with literature data reveals that, for all these systems, the exchange-only results are practically of Hartree-Fock quality; while with inclusion of correlation, this offers excellent agreement with available experimental data as well as those obtained from other sophisticated theoretical methods. Properties such as individual state energies, excitation energies, radial densities as well as various expectation values are studied. This helps us in predicting many states for the first time. In summary, we have presented an accurate, simple, general DFT method for description of arbitrary excited states of atoms and ions.

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I. INTRODUCTION

A central objective in modern quantum chemistry, much of materials science, condensed matter physics and various other branches in science today, is, stated simply, to understand structure, dynamics, energetics through the application of rigorous principles of quantum mechanics. While these results usually complement the information obtained from physical, chemical and biological experiments, in many cases, this could also be used to predict and unveil many hitherto unobserved phenomena. Some of the most commonly used properties are: calculating the potential energy surface (energy changes as a function of structural parameters), interaction energies (absolute as well as relative), electronic charge distribution, dipole and higher multipole moments, spectroscopic quantities such as vibrational frequencies, NMR chemical shifts, ESR \( g \) tensors, hyperfine coupling constants, chemical reactivity, mechanistic routes of a reaction, cross sections for collision with other particles, behavior of atoms/molecules under an external field, such as a strong laser field, etc. The starting point for most such quantum mechanical studies is the non-relativistic Schrödinger equation:

\[
H \Psi(r, t) = E \Psi(r, t)
\]  

(1)

\( H \) is the Hamiltonian operator including various energy components whereas the solution of this equation yields total energy \( E \), as well as the many-particle wave function, which contains all relevant informations about the system under investigation. The ultimate goal of achieving exact solution of this equation is essentially beyond our reach except for a small number of highly simplified model cases. Our systems of interest contain many atoms and electrons, where the solution easily becomes unmanageable. The main difficulty arises due to the presence of electron-electron interaction terms, and approximation methods must be invoked. This lead to the development of multitude of \textit{ab initio} methods in today’s electronic structure theory, one of the very first and successful being the Hartree-Fock (HF) method.

\textit{Every} conceivable property of a many-electron interacting system can be obtained as a functional of the ground-state electron density, \( \rho(r) \), thus replacing the complicated, intractable many-particle wave function. Stated otherwise, in principle, this scalar function of position, determines all the informations embedded in the many-body wave function of ground and all excited states. Existence of such functionals lies at the heart of density
functional theory (DFT) and as such, the electron density is defined as,

$$\rho(r_1) = N \int \cdots \int |\Psi(x_1, x_2, \cdots, x_N)|^2 \, ds_1 \, dx_2 \cdots dx_N \quad (2)$$

The multiple integration involves integral over spin coordinates of all electrons (spin integration implies summation over the possible spin states) and all but one of the spatial variables. Clearly $\rho(r)$ is a real, non-negative, visualizable function of only three spatial coordinates (in contrast to the $4N$ dimensional many-electron wave function for an $N$ electron system) with direct physical significance (can be measured experimentally unlike the complex-valued, wave function), vanishes at infinity and integrates to the total number of electrons:

$$\rho(r \to \infty) = 0$$
$$\int \rho(r) \, dr = N \quad (3)$$

Because of its transparency in dealing with the problematic inter-electronic repulsion in a rigorous quantitative way plus favorable computational cost, DFT has been the most popular and beloved of quantum mechanical methods for atoms, molecules and solids for more than three decades or so.

The first attempt to use electron density as basic variable in the context of atoms/molecules, rather than wave function is almost as old as quantum mechanics itself. In the original quantum statistical model of Thomas and Fermi [1, 2], kinetic energy of electrons is approximated as an explicit functional of density, whereas nuclear-electron attraction and electron-electron repulsion contributions are treated in a classical manner. The following simple expression of kinetic energy is derived by assuming electrons to be in the background of an idealized, non-interacting homogeneous electron gas, i.e., a fictitious model of system of constant electron density:

$$T_{TF}[\rho(r)] = \frac{3}{10} (3\pi^2)^{2/3} \int \rho(r)^{5/3} \, dr \quad (4)$$

Combining this with the classical terms, one can obtain the so-called celebrated Thomas-Fermi energy functional for electrons in an external potential $v_{ext}(r)$ as follows,

$$E_{TF}[\rho(r)] = T_{TF}[\rho(r)] + \int v_{ext}(r) \rho(r) \, dr + \frac{1}{2} \int \int \frac{\rho(r) \rho(r')}{|r - r'|} \, dr \, dr' \quad (5)$$

Here the last term represents classical electrostatic repulsion. Now, minimization of this functional $E[\rho(r)]$ for all possible $\rho(r)$ subject to the constraint on total number of electrons,

$$\int \rho(r) \, dr = N \quad (6)$$
leads to the ground-state density and energy. Since $T_{TF}[\rho]$ is only a very coarse approximation to true kinetic energy, as well as exchange and correlation effects are completely ignored, results obtained using this approach are rather crude. It misses the essential physics and chemistry, such as shell structure of atoms and molecular binding. However, this illustrates the important fact that energy of an interacting system can be written completely in terms of single-particle density alone. This was further extended by Dirac [3] to incorporate exchange effects, leading to the so-called local density approximation (LDA). This gives significant improvements over the original TF method and very much is in use, still today,

$$E_{TFD}[\rho(r)] = T_{TF}[\rho(r)] + \int v_{ext}(r)\rho(r) \, dr - \frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \int \rho(r)^{4/3} \, dr + \frac{1}{2} \int \int \frac{\rho(r)\rho(r')}{|r-r'|} \, drdr'.$$

(7)

Soon, the provocative simplicity of above density approach, compared to traditional wave-function-based methods influenced a considerably large number of calculations. However, due to the lack of a rigorous foundation (e.g., no variational principle was established as yet) combined with the fact that fairly large errors were encountered in solid-state and molecular calculations, the theory somehow lost its appeal and charm; realistic electronic structure calculation within such a deceptively simple route seemed a far cry, leading to very little practical impact on chemistry. However, the situation was about to change after the landmark paper by Hohenberg and Kohn [4], where this was put on a firm theoretical footing. This earns it the status of an exact theory of many-body system and eventually, laid the groundwork of all of modern DFT. The first HK theorem simply states that the external potential $v_{ext}(r)$ in a many-electron interacting system is uniquely determined, to within a constant, by ground-state density $\rho(r)$. Now, since $H$ is fully determined (except to a constant), it easily follows that many-body wave functions for all states (ground and excited) are also determined. Thus all properties of the system are completely determined by $\rho(r)$ only. The proof is based on reductio ad absurdum and skipped here for brevity.

Note that this is only an existence theorem and as such, completely unhelpful in providing any indication of how to predict the density of a system. The answer lies in the second theorem which states that, for any external potential $v_{ext}(r)$, one can define a functional, $E[\rho]$ in terms of $\rho(r)$, as follows,

$$E[\rho] = E_{ne}[\rho] + (T[\rho] + E_{ee}[\rho]) = \int v_{ext}(r)\rho(r) \, dr + F_{HK}[\rho]$$

(8)

Here, the energy has been separated into two parts: one that depending on the actual
system, i.e., the potential energy because of nuclear-electron attraction, and a universal term (in a sense that the form is independent of \( N, R_A, Z_A \), or in other words, \textit{same for all electrons}), consisting of the kinetic and electron repulsion energy components. For a given \( v_{\text{ext}}(\mathbf{r}) \), global minimum of this functional provides ground-state energy while, the density minimizing this functional corresponds to exact ground-state density as,

\[
E_0 = \min_{\rho \to N} \left( F[\rho] + \int \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) \, d\mathbf{r} \right); \quad F[\rho] = \min_{\Psi \to \rho} \langle \Psi | T + E_{\text{ee}} | \Psi \rangle. \tag{9}
\]

It is worth noting that, this apparently simple-looking universal or Hohenberg-Kohn functional, \( F_{\text{HK}}[\rho] \) is the holy grail of DFT. It remains absolutely silent about the explicit forms of functionals for both \( T[\rho] \) and \( E_{\text{ee}}[\rho] \). Design of their accurate forms remains one of the major challenges and lies at the forefront of modern development works in DFT. Further partitioning of energy is possible through the following realization,

\[
E_{\text{ee}}[\rho] = \frac{1}{2} \int \int \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} d\mathbf{r}' + E_{\text{nc}}[\rho] = J[\rho] + E_{\text{nc}}[\rho]. \tag{10}
\]

Here \( J[\rho] \) signifies classical Coulomb repulsion whereas the last term is associated with the non-classical contribution to electron repulsion, containing all the effects of exchange, correlation as well as self-interaction correction.

Despite the charm and simplicity of HK theorem, very little progress could be made in terms of practical applications to realistic atoms/molecules. \textit{All} this tells us is that, in principle, a unique mapping between ground-state density and energy exists. However, there is no guideline whatsoever, about the construction of this functional which delivers the ground-state energy. In so far as theoretical prediction of molecular properties are concerned through computational DFT, no conspicuous changes could be observed with the culmination of these theorems. Because one is still left with the difficult problem of solving many-body system in presence of \( v_{\text{ext}}(\mathbf{r}) \); calculations are as hard as before the HK theory. The variational principle in second theorem also calls for caution. In any real calculation, in absence of the exact functional, one is invariably left with no choice, but to use some approximate forms. The variational theorem, however, applies only to the case of \textit{exact} functionals, implying that in DFT world, energy delivered by a trial functional has absolutely no meaning. This is in sharp contrast to the conventional wave function-based, variational methods such as HF or CI, where the lower an energy \( E \), better a trial function approximates the true wave function.
A year later, in a ground breaking work, Kohn and Sham \cite{KohnSham} proposed a route to approach the hitherto unknown universal functional. The central part of their ingenious idea stems from the realization that the original many-body problem of an interacting system could be replaced by an auxiliary, fictitious non-interacting system of particles. This ansatz, then, in principle, holds the promise for exact calculations of realistic systems using only an independent-particle picture of non-interacting fermions, which are exactly soluble (in practice by numerical methods). The non-interacting reference system is constructed from a set of one-electron orbitals, facilitating the major portion of kinetic energy to be computed to a good accuracy (exact wave functions of non-interacting fermions are Slater determinants). The residual part of kinetic energy, which is usually fairly small, is then merged with the non-classical component of electron-electron repulsion, which is also unknown,

\[
F[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho]
\]

\[
E_{xc}[\rho] = (T[\rho] - T_s[\rho]) + (E_{ee}[\rho] - J[\rho]) = T_c[\rho] + E_{nc}[\rho].
\]

Here \(T_s[\rho]\) corresponds to the exact kinetic energy of a hypothetical non-interacting system having the same electron density as that of our real interacting system. The exchange-correlation (XC) functional \(E_{xc}[\rho]\) now contains everything that is unknown. Thus it includes not only the non-classical electrostatic effects of electron-electron repulsion, but also the difference of true kinetic energy \(T_c[\rho]\) and \(T_s[\rho]\). Now we are in a position to write down the celebrated Kohn-Sham (KS) equation in its standard form,

\[
\left[-\frac{1}{2}\nabla^2 + v_{\text{eff}}(r)\right] \psi_i(r) = \epsilon_i \psi_i(r)
\]

where the “effective” potential \(v_{\text{eff}}(r)\) includes the following terms,

\[
v_{\text{eff}}(r) = v_{\text{ext}}(r) + \int \frac{\rho(r')}{|r - r'|} \, dr' + v_{xc}(r).
\]

Here \(v_{\text{eff}}(r)\) and \(v_{\text{ext}}(r)\) signify the effective and external potentials respectively. Literature in DFT is very vast; many excellent books and review articles are available. Here we refer the readers to \cite{DFT_books} for a more detailed and thorough exposition on the subject.

So far, we have restricted our focus to the ground states. Now let us shift our attention to the calculation of excited states. It is well known that DFT has been one of the most powerful and successful tools in predicting numerous ground-state properties of many-electron systems such as atoms, molecules, solids, over the past four decades. However, mainly due to its
inherent weaknesses, its extension to excited-state problems has been quite difficult and rather less straightforward, so much so that DFT is often dubbed as a ground-state theory. Results on excited states remained very scarce until very recently. Although considerable progress has been made by employing several different strategies to address the problem lately, there are many crucial unresolved issues as yet, which require further attention.

At this point, however, it may be appropriate to discuss the major difficulties in dealing with excited states within the realm of Hohenberg-Kohn-Sham (HKS) DFT. As already mentioned in the beginning, very foundation of DFT relies on a presupposition that the electron density alone is sufficient to describe all states (both ground and excited) of a desired system. Indeed, $\rho(r)$ contains all relevant informations on excited states as well besides the ground state, but the problem is that no practical way to extract this information has been found out as yet. Moreover, there is no HK theorem for excited state parallel to ground state. This is presumably due to the fact that, for a general excited state, the wave function (in general, a complex quantity) can not be bypassed through the pure state density (a real quantity). Because from a hydrodynamical point of view, phase part of the hydrodynamic function is constant for ground and some excited states (the static stationary states), but not so for a general excited state. Working completely in terms of single-particle density in contrast to the state function may be advantageous for ground states, but it is disadvantageous for excited states, because an individual excited state can not be characterized solely in terms of density. Besides, approximate functional forms of $T[\rho]$ and $E_{xc}[\rho]$, valid for both and ground states are unknown; certainly there are insurmountable difficulties in constructing exact functionals for these. Note that, there is no reason that this functional will have same general form for both ground and an arbitrary excited state. Finally one also has to deal with the nagging and tedious problem of ensuring both Hamiltonian and wave function orthogonalities, as in any standard variational calculation. Due to these reasons, excited states within DFT remains a very challenging and important area of research.

The purpose of this chapter is to present a detailed account on an excited state density functional method, which has been shown to be very promising for arbitrary excited states of atoms. This relies on a time-independent SCF procedure in contrast to the so-called time-dependent DFT (TDDFT). Its success and usefulness has been well documented in a series of papers for diverse atomic excited states [21–33]. Section II gives a brief review of some of the most prominent DFT methods for excited states currently available in the
literature. Section III presents the methodology and computational implementation used in our present work. Results from our calculation are discussed in Section IV, with reference to other theoretical methods as well as with experiments, wherever possible. Finally we conclude with a few remarks on the past, present and future of this method.

II. A BRIEF REVIEW OF EXCITED-STATE DFT

In this section we will briefly mention some of the excited state DFT methods, with emphasis on those having realistic practical applications. However, before that, a very obvious question arises: Can the original KS equation (12) be excited? To answer this, we rewrite the expression for “effective” potential in an atom in the following equivalent form,

\[ v_{\text{eff}}(r) = -\frac{Z}{r} + \int \frac{\rho(r')}{|r - r'|} \, \mathrm{d}r' + \frac{\delta E_{\text{ex}}[\rho]}{\delta \rho}. \]  

(14)

Here \( Z \) denotes nuclear charge on the atom. There is an inherent degeneracy in terms of electron spin. Moreover the other angular momentum quantum number \((l, m)\) information required to characterize an individual excited state is clearly missing. So it is not possible to select an excited state of a given space-spin symmetry corresponding to a particular electronic configuration. Next immediate question comes: can one possibly calculate an average of a set of degenerate excited states? That depends on the form of XC functional used. As mentioned before, exact forms of XC functionals are unknown as yet and almost all existing functionals are designed for ground states only. The validity of these functionals for arbitrary excited states is unknown and in fact, common sense dictates that ground and excited state functional may not have same same; in all possibility they would be different.

Introduction of spin density, \( \rho^S(r) = \rho^\alpha(r) - \rho^\beta(r) \), made it possible for the development of more flexible potentials. Here \( \rho^\alpha, \rho^\beta \) signify electron densities corresponding to the up, down spins respectively. It is easy to show that for different spin densities, \( v_{\text{eff}}^\alpha(r), v_{\text{eff}}^\beta(r) \) will be different; self-consistent solution of the spin-polarized KS equation can be obtained. A thermodynamical version of the spin-density formalism has been presented [34], which proves that standard DFT methods could be used for calculation of lowest lying state of each spatial or spin irreducible representation of a given system, since, in a sense, these represent the “ground state” in that particular symmetry. However there are inherent problems where the non-interacting case does not reduce to a single determinant. Many excited states can not be
described by a single determinant and intrinsically need a multi-configurational description. For example, consider the open-shell configuration $p^2$, as in the ground state of carbon atom, giving rise to three multiplets $^3P, ^1D, ^1S$. In accordance with the above discussion, one can obtain the energy of $^3P$ and $^1D$ terms, but not $^1S$. This can be understood from a consideration of the fact that, in absence of spin-orbit coupling, all valid states of an atom must be simultaneous eigenfunctions of not only the Hamiltonian operator $H$, but also angular momentum operators $L^2, L_z, S^2, S_z$, as well as parity operator $\Pi$, such that any given state is characterized by the following quantum numbers $L, M_L, S, M_S, \pi$, associated with these operators. In traditional wave functional methods, these informations are carried by wave functions. But in DFT, the basic variable is electron density; so, in principle, it should be $E_{xc}[\rho]$, which should contain this dependence on these above quantum numbers. On the other hand, most of the functionals in DFT depend solely in terms of charge or spin densities; therefore clearly lacking any of these mentioned quantities needed for a complete description of the state of an atom. Stated otherwise, we are facing a very important conceptual problem here: how can one describe the state of a many-electron system, which are eigenfunctions of all these operators working entirely in terms of density with no access to the correct N-electron wave function and its associated symmetry characteristics?

This problem is partially resolved by making reference to Slater’s transition state theory [35, 36]. Following this prescription, an ad-hoc approach to solve the multiplet problem was proposed, the so-called sum method [37, 38]. Here the working equations are exactly like the KS equations, but density is assumed to correspond to a fictitious transition state where one or more orbitals are fractionally occupied. These authors argue that energy of a term, not representable by a single determinant, but requires a linear combination of determinants, can not be computed by spin densities of the corresponding state functions, but can be written as a weighted sum of determinantal energies as follows:

$$E(M_j) = \sum_i A_{ji} E(D_i)$$  \hspace{1cm} (15)

Here $E(M_j), E(D_i)$ refer to the energies of different multiplets and determinants respectively. Note that the sum method has no firm theoretical justification; rather an empirical extension of the HF to the $X\alpha$ method. By using some elegant group theoretical method, a semi-automatic protocol has been developed to obtain the weights of various determinants [39, 40].

The above intuitive ideas was utilized on a rigorous foundation to formulate a scheme
in which the density is a sum of $M$ lowest-energy eigenstate densities with equal weightage [41]. Here we discuss at some length the ensemble density or fractional occupation approach to excited states [42–44]. This suggests to work with an ensemble of densities rather than a pure-state density and the subspace formulation [41] can be considered a special case of it.

The generalized eigenvalue problem for a time-independent Hamiltonian $H$ with $M$ eigenvalues $E_1 \leq E_2 \leq \cdots \leq E_M$ for its $M$ low-lying states is:

$$H \Psi_k = E_k \Psi_k \quad (k = 1, 2, \cdots, M) \quad (16)$$

Applying the Rayleigh-Ritz variational principle, one can write the ensemble energy as:

$$E = \sum_{k=1}^{M} w_k E_k, \quad 0 \leq w \leq 1, \quad 1 \leq g \leq M - 1 \quad (17)$$

where $w_1 \geq w_2 \geq \cdots \geq w_M \geq 0$ are the weighting factors chosen such that: $w_1 = w_2 = \cdots = w_{M-g} = \frac{1-w}{M-g}$, $w_{M-g+1} = w_{M-g+2} = \cdots = w_M = w$. The limit $w = 0$ corresponds to the eigenensemble of $M - g$ states ($w_1 = w_2 = \cdots = w_{M-g} = \frac{1}{M-g}$ and $w_{M-g+1} = w_{M-g+2} = \cdots = w_M = 0$), whereas $w = 1/M$ leads to the eigenensemble of $M$ states ($w_1 = w_2 = \cdots = w_M = 1/M$).

The generalized HK theorem can be established; as well as the KS equation for ensembles following the variational principle in standard manner,

$$\left[-\frac{1}{2} \nabla^2 + v_{KS}\right] u_i(r) = \epsilon_i u_i(r) \quad (18)$$

where the ensemble KS potential, given below,

$$v_{KS}(r; \rho_w) = v_{ext}(r) + \int \frac{\rho_w(r)}{|r - r'|} \, dr + v_{exc}(r; w, \rho_w) \quad (19)$$

could be defined as a functional of the ensemble density as follows,

$$\rho_w^I(r) = \frac{1 - w g_I}{M_I - 1} \sum_{m=1}^{M_I-g_I} \sum_j \lambda_{mj} |u_j(r)|^2 + w \sum_{m=M_I-g_I+1}^{M_I} \sum_j \lambda_{mj} |u_j(r)|^2. \quad (20)$$

Here $g_I$ denotes degeneracy of the $I$th multiplet, $M_I = \sum_{i=1}^{I} g_i$ defines multiplicity of the ensemble, $\lambda_{mj}$ are occupation numbers, with $0 \leq w \leq 1/M_I$. Density matrix is defined as,

$$P^{M,g}(w) = \sum_{m=1}^{M} w_m |\Psi_m\rangle \langle \Psi_m|. \quad (21)$$

The XC potential $v_{xc}$ is the functional derivative of ensemble XC energy functional $E_{xc}$,

$$v_{xc}(r; w, \rho) = \frac{\delta E_{xc}[\rho, w]}{\delta \rho(r)} \quad (22)$$
One can then express excitation energies in terms of one-electron energies $\epsilon_j$,

$$
E' = \frac{1}{g_I} \frac{d\mathcal{E}^I(w)}{dw} \bigg|_{w=w_I} + \sum_{i=2}^{I-1} \frac{1}{M_I} \frac{d\mathcal{E}^I(w)}{dw} \bigg|_{w=w_i} \tag{23}
$$

where

$$
\frac{d\mathcal{E}^I(w)}{dw} = \sum_{j=N+M_I-1}^{N-1+M_I} \epsilon_j - \frac{g_I}{M_I-1} \sum_{j=N}^{N+M_I-1} \epsilon_j + \frac{\partial E^I_{xc}}{\partial w} \bigg|_{\rho_w} \tag{24}
$$

Clearly, excitation energies cannot be calculated as a difference of the one-electron energies; there is an extra quantity (the last term) that needs to be determined.

The two-particle density matrix of the ensemble is obtained as a weighted sum of two-particle density matrices of ground and excited states as follows,

$$
\Gamma^{M,g,w}(r_1, r_2; r_1', r_2') = \sum_{m=1}^{M} w_m \Gamma^m(r_1, r_2; r_1', r_2') \tag{25}
$$

The total ensemble density takes the following form,

$$
\mathcal{E}_w^{M,g} = \text{Tr}\{P^{M,g}(w)H\} = \text{Tr}\{P^{M,g}(T + E_{ee})\} + \text{Tr}\{P^{M,g}(w)V\} = F^{M,g}(w) + \int \rho(r)v_{ext}(r)dr \tag{26}
$$

where $\rho(r)$ is the ensemble density; $V = \sum_{i=1}^{N} v_{ext}(r_i)$. The ensemble XC energy is given by,

$$
E_{xc}^{M,g}[w, \rho] = F^{M,g}[w, \rho] - T^{M,g} - J[\rho]. \tag{27}
$$

Here the last two terms denote ensemble non-interacting kinetic and Coulomb energies.

Solution of the ensemble KS equation (18) requires knowledge of the ensemble XC potential, exact form of which remains unknown and several approximations have been proposed. In [42–44], excitation energies of He were studied using the quasi-local density approximation [45]. First excitation energies of several atoms [46] as well higher excitation energies [47] have been reported using the parameter-free exchange potential of Gáspár [48], which depends explicitly on spin orbitals. Several ground-state LDA functionals have been employed for this purpose: *viz.*, Gunnarsson-Lundqvist-Wilkins [49], von Barth-Hedin [50], Ceperley-Alder [51], local density approximations parametrized by Perdew and Zunger [52] and Vosko *et al.* [53]. It is found that, in general, spin-polarized calculations provide better results compared to the non-spin-polarized ones; however, in most cases, estimated excitation energies are highly overestimated. Generally, these functionals provide results which are in close agreement with each other. These references use minimum (0) and maximum values of the weighting factor $w$. Any $w$ value satisfying the inequality in (18) is appropriate,
provided that one uses the exact XC energy. However since the latter is unknown, one has to take recourse to approximate functionals; thus different excitation energies are obtained with different \( w \). This variation is studied in detail in [47]; in some occasions the change is small, while for others considerably large variation is observed. Simple local ensemble potential has been proposed [54] for this purpose as well,

\[
v_x(\rho, w) = -3\alpha(w) \left( \frac{3\rho w}{8\pi} \right)^{1/3} \quad \text{and} \quad E_x[\rho, w] = -\frac{9}{4} \left( \frac{3}{8\pi} \right)^{1/3} \alpha(w) \int \rho^{4/3} d\mathbf{r} \quad (28)
\]

However, calculated excitation energies are still very far from the actual values. This leads us to the conclusion that like the ground-state DFT, search for accurate XC functional again remains one of the major bottlenecks in the success of ensemble or fractional occupation approach to excited-state energies and densities.

In another development [55, 56], KS equations were obtained by partitioning the wave function into following two components,

\[
\psi(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N) = \phi(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N) + \tilde{\psi}(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N) \quad (29)
\]

such that the two-particle density matrix becomes,

\[
\rho_2(\mathbf{r}', \mathbf{r}) = \rho_2^0(\mathbf{r}', \mathbf{r}) + \tilde{\rho}_2(\mathbf{r}', \mathbf{r}) \quad (30)
\]

where

\[
\rho_2^0(\mathbf{r}', \mathbf{r}) = N(N-1) \int |\phi(\mathbf{r}', \mathbf{r}, \mathbf{r}_3, \cdots, \mathbf{r}_N)|^2 d^4\mathbf{r}_3 d^4\mathbf{r}_4 \cdots d^4\mathbf{r}_N
\]

\[
\tilde{\rho}_2(\mathbf{r}', \mathbf{r}) = N(N-1) \int [\phi^* \tilde{\psi} + \phi \tilde{\psi}^*] d^4\mathbf{r}_3 d^4\mathbf{r}_4 \cdots d^4\mathbf{r}_N \quad (31)
\]

A factor of 2 is included in \( \rho_2^0 \) and \( \tilde{\rho}_2 \). The symbol \( \cdots \int d^4\mathbf{r}_j \) stands for real-space integration and spin summation for the jth particle. The spin-independent one-particle density \( \rho_s(\mathbf{r}) \) is,

\[
\rho_s(\mathbf{r}) = \frac{1}{N-1} \sum s' \int \rho_2^0(\mathbf{r}', \mathbf{r}) \ d\mathbf{r}' \quad (32)
\]

As a result,

\[
\sum s' \int \tilde{\rho}_2(\mathbf{r}', \mathbf{r}) \ d\mathbf{r}' = 0 \quad (33)
\]

The above properties uniquely define two components \( \phi(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N) \) and \( \tilde{\psi}(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N) \) of any eigenstate \( \psi(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N) \). Now, the variational optimization involving the N-particle Hamiltonian yields the following KS type equation,

\[
\left[ \frac{1}{2} \nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}^s(\mathbf{r}) \right] \psi_{is}(\mathbf{r}) = \epsilon_{is} \psi_{is}(\mathbf{r}) \quad (34)
\]
where the three \( v \) terms denote external, Hartree and XC potentials respectively,

\[
v_{xc}^s(r) = -\sum_{s'} \int \frac{\rho_{s'}(r')}{|r-r'|} \left[ f_{s's}(r', r) + \frac{1}{2} \sum_{s''} \frac{\delta f_{s's''}(r', r) \rho_{s''}(r)}{\delta \rho_s(r)} \right] \, dr'. \tag{35}
\]

Here \( f_{s's}(r', r) = 1 - g_{s's}(r', r) \) and \( g_{s's}(r', r) \) is the pair correlation function defined as \( \rho_{2's}^s(r', r) = \rho_{s}^s(r') \rho_s(r) g_{s's}(r', r) \). The method has produced reasonably good agreements with experimental as well as other density functional methods for total ground-state energies of free atoms, ionization and affinity energies, etc.\[56\]. However, there are significant difficulties as far as practical computations are concerned for general excited states.

A configuration-interaction scheme restricted to single excitations (CIS) has been used in the realm of DFT for electronic excitations\[57\]. HF orbital energies in the matrix elements of CIS Hamiltonian are then replaced by the corresponding eigenvalues obtained from gradient-corrected KS calculations. Additionally it requires three empirical parameters determined from a reference set to scale the Coulomb integrals and shifting the diagonal CIS matrix elements. Even though this also suffers from a lack of a solid theoretical foundation, resultant excitation energies of molecules obtained by this method show fairly good agreement. This has also been extended to multi-reference CI schemes\[58\].

Many other attempts have been made to calculate individual excited states. Some important ones are mentioned below. A time-independent quantal density functional theory (Q-DFT) of singly or multiply excited bound non-degenerate states have been proposed\[59\]. Existence of a variational KS DFT, with a minimum principle, for the self-consistent determination of an individual excited state energy and density has been established\[60\]. A perturbative approach is also suggested\[61, 62\], where the non-interacting KS Hamiltonian serves as the zeroth-order Hamiltonian. Two variants of perturbation theory (PT) were used: (a) the so-called standard DF PT, where zeroth-order Hamiltonian takes the form \( H_0 = T + V_{ext} + V_H + V_{xc} \), and the perturbation is given by \( H_1 = V_{ee} - V_H - V_{xc} \), (b) the coupling-constant PT is based on the adiabatic connection of the Hamiltonian where a link is made between KS Hamiltonian and fully interacting Hamiltonian keeping ground-state density constant, independent of \( \alpha \), such that, \( H^\alpha = T + V_{ext} + V_H + V_{xc} + \alpha (V_{ee} - V_H - V_{xc}) \). Here \( V_c^\alpha \) is second order in \( \alpha \) and equals the correlation potential when \( \alpha = 1 \). Zeroth-order Hamiltonian is again the KS Hamiltonian; the perturbing Hamiltonian contains a term \( H_1^{(1)} = \alpha (V_{ee} - V_H - V_{xc}) \), which is linear in perturbation parameter \( \alpha \) and a component \(-v_c^\alpha \), which contains second and higher order contributions. Accurate calculation of correlation
energies of excited states has been proposed via a suitable multi-reference DFT method (such as MCSCF including the complete active space). They successfully describe the non-dynamical correlation; the fraction of dynamic correlation can be taken into account by DFT [63]. Applicability of subspace DFT for atomic excited states have been studied [64]. Theories for individual excited states have been proposed elsewhere as well [65]. A localized HF-based DFT has been put forth for excitation energies of atoms, molecules [66]. This is based on separating the electron-electron interaction energy of KS wave function of a given excited state as Coulomb and exchange energy as follows [67]. The former is given as,

\[
U = \sum_{\Gamma, a, \Lambda, b} f^\Gamma_a f^\Lambda_b \times \sum_{\gamma, \lambda} \int dr' dr'' \frac{2}{|r' - r''|} \int dr'' \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Gamma, \gamma}_{a}(r') \phi^{\Lambda, \lambda}_{b}(r'') \phi^{\Lambda, \lambda}_{b}(r'') |r' - r''|
\]

The totally symmetric part \( \bar{\rho}(r) \) of electron density being given by,

\[
\bar{\rho}(r) = 2 \sum_{\Gamma, a, \gamma} \phi^{\Gamma, \gamma}_{a}(r) \phi^{\Gamma, \gamma}_{a}(r)
\]

Here \( \phi^{\Gamma, \gamma}_{a}(r) \) denotes the spatial part of orbital which belongs to the energy level \( a \) of irreducible representation \( \Gamma \) and which transforms under symmetry operations according to the symmetry partner \( \gamma \) of \( \Gamma \). Occupation number of energy level \( a \) of \( \Gamma \) is denoted by \( f^{\Gamma}_{a} \). Summation indices \( a, b \) run over all at least partially occupied, i.e., not completely unoccupied levels of \( \Gamma \). The exchange energy is then the reminder of electron-electron interaction energy of the KS wave function. The corresponding open-shell localized HF exchange potential is then expressed as \( v^{OSLHF}_{x}(r) = v^{s}_{x}(r) + v^{e}_{x}(r) \), where the two terms represent a generalized Slater potential and a correction term respectively.

Recently an optimized effective potential approach and its exchange-only implementation for excited states has been reported [68]. This uses a bifunctional DFT for excited states [60, 69] that employs a simple method of taking orthogonality constraints into account (TOCIA) [70, 71] for solving eigenvalue problems with restrictions. A \( \Delta \)SCF approach, or \( \Delta \)KS approach [72], wherein the excitation energy is simply the difference in energy between ground- and excited-state HF or KS calculation, has been employed as well, and found to be especially successful for core-excited states.

So far all the methods we have discussed lie within the purview of time-independent DFT. Now we move on to the formalisms for excitation energies within the TDDFT framework. Many excellent articles and reviews are available on the subject [73–84]; here we mention
only the essential details. Consider the unperturbed, ground-state of a many-electron system characterized by an external potential $v_0(r)$, subject to a TD perturbation $v_1(r, t)$, such that at a later time, the external potential (a functional of the TD density), is given by $v_{\text{ext}}(r, t) = v_0(r) + v_1(r, t)$. The density-density response function takes the form,

$$\chi(r, t; r', t') = \frac{\delta \rho[v_{\text{ext}}](r, t)}{\delta v_{\text{ext}}(r', t')} \bigg|_{v_0}$$  \hspace{1cm} (38)

where the functional derivative needs to be evaluated at the external potential corresponding to an unperturbed ground-state density $\rho_0$. The first-order, linear density response to the perturbation $v_1(r, t)$ is then given by,

$$\rho_1(r, t) = \int dt' \int dr' \chi(r, t; r', t') v_1(r', t')$$  \hspace{1cm} (39)

Now, realizing that the Runge-Gross theorem also holds for non-interacting particles moving in an external potential $v_s(r, t)$, one can write the KS response function of a non-interacting, unperturbed many-electron density $\rho_0$ as,

$$\chi_s(r, t; r', t') = \frac{\delta \rho[v_s](r, t)}{\delta v_s(r', t')} \bigg|_{v_s}$$  \hspace{1cm} (40)

With this definition, $\chi_s(r, t; r', t')$ is expressed in terms of static KS orbitals $\{\phi_k\}$,

$$\chi_s(r, r'; \omega) = \sum_{j,k} (f_k - f_j) \frac{\phi_k^*(r)\phi_j(r)\phi_k^*(r')\phi_j(r')}{\omega - (\epsilon_j - \epsilon_k) + i\delta}$$  \hspace{1cm} (41)

Here $f_k, f_j$ denote occupation numbers of KS orbitals; $\epsilon_j, \epsilon_k$ signify KS orbital energies; and $\omega$ is the frequency obtained after applying a Fourier transform with respect to time. Summation includes both occupied and unoccupied orbitals, plus the continuum states. Now, the first-order density change $\rho_1(r, t)$ in terms of linear response of the non-interacting system to the effective perturbation $v_{s,1}(r, t)$ can be written in terms of frequency $\omega$ as,

$$\rho_1(r, \omega) = \int \chi_s(r, r'; \omega) v_1(r', \omega) \, dr' \hspace{1cm} \int \int \chi_s(r, r'; \omega) \times \left( \frac{1}{|r' - r''|} + f_{xc}[\rho_0](r', r''; \omega) \right) \rho_1(r'', \omega) \, dr' \, dr''$$  \hspace{1cm} (42)

It is established that the frequency-dependent linear response of a finite interacting system has discrete poles at the true excitation energies $\Omega_m = E_m - E_0$ of an unperturbed system. So the idea is to calculate the shifts in KS orbital energy differences $\omega_{jk} = \epsilon_j - \epsilon_k$, which are poles of the KS response function. True excitation energies ($\Omega$) are generally not identical.
with the KS excitation energies \( \omega_{jk} \). The exact density response \( \rho_1 \), however, has poles at true excitation energies \( \omega = \Omega \). True excitation energies can then be described by those frequencies where the eigenvalues \( \lambda(\Omega) \) of the following equation,

\[
\int \mathrm{d}r \int \mathrm{d}r' \chi_s(r'', r; \omega) \left( \frac{1}{|r-r'|} + f_{xc}[\rho_0](r, r'; \omega) \right) \xi(r', \omega) = \lambda(\omega) \xi(r', \omega)
\]

(43)
satisfy \( \lambda(\Omega) = 1 \). For practical purposes, one needs to expand \( \Omega \) about one particular KS energy difference \( \omega_\nu = \omega_{jk} \):

\[
\chi_s(r'', r; \omega) = 2\alpha_\nu \frac{\Phi_\nu(r'')\Phi_\nu^*(r)}{\omega - \omega_\nu} + 2 \sum_{k \neq \nu} \alpha_k \frac{\Phi_k(r'')\Phi_k^*(r)}{\omega_\nu - \omega_k + i\delta} + \ldots
\]

\[
f_{xc}[\rho_0](r, r'; \omega) = f_{xc}[\rho_0](r, r'; \omega_\nu) \frac{\mathrm{d}f_{xc}[\rho_0](r, r'; \omega)}{\mathrm{d}\omega} \bigg|_{\omega_\nu} (\omega - \omega_\nu) + \ldots
\]

\[
\xi(r'', \omega) = \xi(r'', \omega_\nu) + \frac{\mathrm{d}\xi(r'', \omega)}{\mathrm{d}\omega} \bigg|_{\omega_\nu} (\omega - \omega_\nu) + \ldots
\]

\[
\lambda(\omega) = \frac{A(\omega_\nu)}{\omega - \omega_\nu} + B(\omega_\nu) + \ldots
\]

(44)
The index \( \nu = (j, k) \) denotes a contraction implying a single-particle transition \( k \rightarrow j \), i.e., \( \Phi_\nu(r) = \Phi_k(r)\Phi_j(r) \) and \( \alpha_\nu = n_k - n_j \). Assuming that the true excitation energy is not too far away from \( \omega_\nu \) and inserting Laurent expansions for \( \chi_s, f_{xc}, \xi, \lambda \) into the above expressions, one finds that,

\[
A(\omega_\nu) = M_{\nu\nu}(\omega_\nu)
\]

(45)

\[
B(\omega_\nu) = \left. \frac{\mathrm{d}M_{\nu\nu}}{\mathrm{d}\omega} \right|_{\omega_\nu} + \frac{1}{M_{\nu\nu}(\omega_\nu)} \sum_{k \neq \nu} \frac{M_{\nu k}(\omega_\nu)M_{k\nu}(\omega_\nu)}{\omega_\nu - \omega_k + i\delta}
\]

where the matrix elements are given by,

\[
M_{k\nu}(\omega_\nu) = 2\alpha_\nu \int \int \phi_k^*(r) \left( \frac{1}{|r-r'|} + f_{xc}(r, r'; \omega) \right) \phi_\nu(r') \mathrm{d}r \mathrm{d}r'
\]

(46)
So, the condition \( \lambda(\Omega) = 1 \) and its complex conjugate then, leads to, in lowest order,

\[
\Omega = \omega_\nu + \Re M_{\nu\nu}
\]

(47)
Just like the time-independent case, now one has to approximate the TD XC potential. The simplest construction is the adiabatic approximation, which makes use of ground-state XC potential, but replaces ground-state density \( \rho_0(r) \) with the instantaneous TD density \( \rho(r, t) \),

\[
u_{xc}^{ad}(\rho; r, t) = \left. \frac{\delta E_{xc}[\rho_0(r)]}{\delta \rho_0(r)} \right|_{\rho_0(r) = \rho(r, t)}
\]

(48)
Within the adiabatic approximation, the XC kernel can be calculated from,

\[
f_{xc}^{ad}(\mathbf{r}, t; \mathbf{r}', t') \equiv \frac{\delta v_{xc}(\rho_0; \mathbf{r})}{\delta \rho_0(\mathbf{r}')} \delta(t - t')
\]

(49)

The kernel above is local in time, but not necessarily local in space. Clearly, this approximation completely neglects the frequency dependence arising from the XC vector potential; consequently the retardation and dissipation effects are completely ignored in this picture. This has been widely used for single-particle excitation energies (see, for example, [85–88], for some recent work) with good success, although it performs rather poorly for multiple excitations and charge-transfer states. For explicit functionals of density, it is straightforward to calculate XC kernel. However, for orbital-dependent, such as meta-generalized gradient approximated (GGA) or hybrid functionals, it is not so and may be evaluated with the help of optimized effective potential or other simple, accurate approach.

In practice, modern TDDFT excitation energies \(\omega\) and corresponding response functions \(X, Y\) are generally obtained by solving a non-Hermitian eigenvalue equation,

\[
\begin{bmatrix}
A & B \\
B & A
\end{bmatrix} \begin{bmatrix}
X \\
Y
\end{bmatrix} = \omega \begin{bmatrix}
1 & 0 \\
0 & -1
\end{bmatrix} \begin{bmatrix}
X \\
Y
\end{bmatrix}
\]

(50)

Here \(X, Y\) are the excitation vectors representing excitation, deexcitation components of electronic density change, whereas the elements of \(A, B\) are given by,

\[
A_{ai\sigma,bj\sigma'} = \delta_{ab}\delta_{ij}\delta_{\sigma\sigma'}(\epsilon_{a\sigma} - \epsilon_{i\sigma'}) + K_{ai\sigma,bj\sigma'}, \quad B_{ai\sigma,bj\sigma'} = K_{ai\sigma,jb\sigma'}
\]

(51)

where \(\sigma, \sigma'\) denote spin indices, \(\epsilon_{p\sigma}\) is the \(p\)th KS molecular orbital energy. Indices \(i, j, \cdots\) and \(a, b, \cdots\) correspond to occupied, virtual orbitals. Matrix element \(K_{ai\sigma,bj\sigma'}\) is given by,

\[
K_{pq\sigma,rs\sigma'} = (pq\sigma|rs\sigma') - c_x \delta_{\sigma\sigma'}(pr\sigma|qs\sigma') + f_{pq\sigma rs\sigma'}^{xc}.
\]

(52)

Here \(p, q, \cdots\) indicate general MOs and \((pq\sigma|rs\sigma')\) identifies a two-electron repulsion integral in the Mulliken notation, whereas \(c_x\) is a mixing parameter of HF exchange integral in case of hybrid functionals. The last term, \(f_{pq\sigma rs\sigma'}^{xc}\) represents a Hessian matrix element of the XC energy functional \(E_{xc}\) in terms of density, in the adiabatic approximation,

\[
f_{\sigma\sigma'}^{xc} = \frac{\delta^2 E_{xc}}{\delta \rho_\sigma(\mathbf{r}_1)\delta \rho_{\sigma'}(\mathbf{r}_2)}
\]

(53)

Finally note that, if the orbitals are assumed real, following matrices can be defined,

\[
\mathbf{F} = (\mathbf{A} - \mathbf{B})^{-1/2}(\mathbf{X} + \mathbf{Y}), \quad \Omega = (\mathbf{A} - \mathbf{B})^{1/2}(\mathbf{A} + \mathbf{B})(\mathbf{A} - \mathbf{B})^{1/2},
\]

(54)
to express the problem in compact form,

$$\Omega F = \omega^2 F$$  \hspace{1cm} (55)$$

Although, in general, the non-adiabatic correction is needed for even in low-frequency limit, it has been demonstrated that, at least for smaller systems, the largest source of error for accurate excitation energies, arises from the approximation to static XC potential. This justifies validity and wellness of adiabatic approximation for low-lying excitations in atoms, molecules. Applicability and performance of other functionals such as adiabatic, non-empirical meta-GGA as well other adiabatic hybrid functionals have been reported lately [89]. XC functionals with varying fractions of HF exchange [90, 91], self-interaction correction [92] or other combinations [93], “short-range” corrected functionals [94], methods such as CIS(D) which use exact exchange [95] have been suggested for better representation.

Numerous other variations of TDDFT for excited states have been proposed. In a resolution of identity (RI-J) approach to analytical TDDFT excited-state gradients [96], classical Coulomb energy and its derivatives are computed in an accelerated manner by expanding the density in an auxiliary basis. The Lagrangian of the excitation energy is derived, which is stationary with respect to all electronic degrees of freedom. Now the excited-state first-order properties are conveniently obtained because the Hellmann-Feynmann theorem holds. A state-specific scheme for TDDFT based on Davidson algorithm has been developed [97] to reduce the rank of response matrix and efficient memory use, without loss of accuracy. In another work [98], two-body fragment MO method (FMO2) was combined with TDDFT by dividing the system into fragments and electron density of each of these latter being determined self-consistently. In another work [99], the excitation spectrum was calculated by means of Tamm-Dancoff approximation and the spin-flip formalism [100, 101]. A double-hybrid DFT for excited states [102] is also available, where a mixing of GGA XC with HF exchange and a perturbative second-order correlation part (obtained from KS GGA orbitals and eigenvalues) is advocated. TDDFT within the Tamm-Dancoff approximation is also implemented using a pseudospectral method to evaluate the two-electron repulsion integrals [103]. On a separate work, a subspace formulation of TDDFT within the frozen-density embedding framework has been presented [104]. This allows to incorporate the couplings between electronic transitions on different subsystems which becomes very important in aggregates composed of several similar chromophores, e.g., in biological or biomimetic light-
harvesting systems. An occupation number averaging scheme \[105\] for TDDFT response theory in frequency domain has been prescribed lately, where an average of excitation energies over the occupation number is adopted; this leads to equations of non-symmetric matrix form. Another work \[106\] combines generalized orbital expansion operators (designed to generate excited states having well-defined multiplicities) and the non-collinear formulation of DFT, for treatment of excited states.

### III. THE WORK-FUNCTION ROUTE TO EXCITED STATES

In this section, we present a simple DFT method for ground and arbitrary excited states of an atom. This has been tremendously successful for many excited states of many-electron atoms. The approach is simple, computationally efficient, and has been overwhelmingly successful for an enormous number of atomic states, such as singly, doubly, triply excited states; low-, moderately high- and high-lying Rydberg states; valence as well as core excitation; autoionizing resonances and satellite states; negative atoms as well. This is within a time-independent framework and results have been presented in the references \[21–33\].

In this approach, a physical understanding of KS theory via quantum mechanical interpretation of electron-electron interaction energy functional, \(E_{ee}^{KS}[\rho]\), and its functional derivative (potential), \(v_{ee}^{KS}(r) = \delta E_{ee}^{KS}[\rho]/\delta \rho(r)\), is established in terms of fields arising from source charge distributions (quantum mechanical expectations of Hermitian operators). Further, clear provisions are made to distinguish Pauli-Coulomb correlation (due to Pauli exclusion principle and Coulomb repulsion) and kinetic energy correlation components of the energy functional and potential; each components arises from a separate field and source charge distribution \[107–110\]. It may be recalled that \(E_{ee}^{KS}[\rho]\) in KS theory represents Pauli and Coulomb correlations as well as correlation contributions to the kinetic energy. The corresponding local potential \(v_{ee}^{KS}(r)\) (obtained as a functional derivative), consists of two separate contributions: (i) a purely quantum mechanical (Pauli and Coulomb) electron-electron correlation component \(W_{ee}(r)\), and (ii) a correlation kinetic energy component \(W_{tk}(r)\).

The interaction potential, \(v_{ee}^{KS}(r)\), is defined as the work done to bring an electron from infinity to its position at \(r\) against a field \(\mathbf{F}(r)\),

\[
v_{ee}^{KS}(r) = \frac{\delta E_{ee}^{KS}[\rho]}{\delta \rho(r)} = - \int_{\infty}^{r} \mathbf{F}(r') \cdot d' = - \int_{\infty}^{r} \mathbf{F}(r') \cdot d'.
\] (56)
The field is a sum of two fields: $\mathcal{F}(\mathbf{r}) = \mathcal{E}_{ee}(\mathbf{r}) + Z_{te}(\mathbf{r})$. The first term originates from Pauli and Coulomb correlations as its quantum mechanical source-charge distribution is the pair-correlation density $g(\mathbf{r}, \mathbf{r'})$, while the second terms arises from a kinetic energy-density tensor $t_{\alpha\beta}(\mathbf{r})$. The latter accounts for the difference of the fields derived from tensor for the interacting and KS non-interacting system. The electron-electron interaction potential, $v^{KS}_{ee}(\mathbf{r})$, is expressed as a sum: $v^{KS}_{ee}(\mathbf{r}) = W_{ee}(\mathbf{r}) + W_{tc}(\mathbf{r})$, where,

$$W_{ee}(\mathbf{r}) = -\int_{\infty}^{r} \mathcal{E}_{ee}(\mathbf{r}') \cdot d\mathbf{r}', \quad W_{tc}(\mathbf{r}) = -\int_{\infty}^{r} Z_{te}(\mathbf{r}') \cdot d\mathbf{r}'. \quad (57)$$

The functional derivative in Eq. (56) can be identified as the work done due to the fact that $\nabla v^{KS}_{ee}(\mathbf{r}) = -\mathcal{F}(\mathbf{r})$, so that the sum of two works $W_{ee}(\mathbf{r})$ and $W_{tc}(\mathbf{r})$ is path-independent. The latter is rigorously valid provided the field $\mathcal{F}(\mathbf{r})$ is smooth, i.e., it is continuous, differentiable and has continuous first derivative. It is also implicit that curl of the field vanishes, i.e., $\nabla \times \mathcal{F}(\mathbf{r}) = 0$. Furthermore, for certain systems, such as closed-shell atoms, jellium metal clusters, jellium metal surfaces, open-shell atoms in central-field approximation, etc., the work done $W_{ee}(\mathbf{r})$ and $W_{tc}(\mathbf{r})$ are separately path independent, i.e., $\nabla \times \mathcal{E}_{ee}(\mathbf{r}) = \nabla \times Z_{te}(\mathbf{r}) = 0$.

Now, it is known that the pair-correlation density $g(\mathbf{r}, \mathbf{r'})$ is not a static, but rather describes a dynamical charge distribution, whose structure varies as a function of electron position. This dynamic nature is incorporated into the definition of local potential (through the force field $\mathcal{E}_{ee}(\mathbf{r})$) in which electrons move, via Coulomb’s law as,

$$\mathcal{E}_{ee}(\mathbf{r}) = \int \frac{g(\mathbf{r}, \mathbf{r'}) (\mathbf{r} - \mathbf{r'})}{|\mathbf{r} - \mathbf{r'}|^3} \, d\mathbf{r}'. \quad (58)$$

So, one can define the component $W_{ee}(\mathbf{r})$ as work done to bring an electron from infinity to its position at $\mathbf{r}$ against this force field, as given in Eq. (57). However, this can be further simplified by recognizing that pair-correlation density, $g(\mathbf{r}, \mathbf{r'})$ can be expressed as a sum of density $\rho(\mathbf{r'})$ and Fermi-Coulomb hole charge density $\rho_{xc}(\mathbf{r}, \mathbf{r'})$: $g(\mathbf{r}, \mathbf{r'}) = \rho(\mathbf{r'}) + \rho_{xc}(\mathbf{r}, \mathbf{r'})$. The field $\mathcal{E}_{ee}(\mathbf{r})$ is then constituted of two fields, namely, the Hartree ($\mathcal{E}_{H}(\mathbf{r})$) and XC ($\mathcal{E}_{xc}(\mathbf{r})$) fields as: $\mathcal{E}_{ee}(\mathbf{r}) = \mathcal{E}_{H}(\mathbf{r}) + \mathcal{E}_{xc}(\mathbf{r})$. These fields are defined again as:

$$\mathcal{E}_{H}(\mathbf{r}) = \int \frac{\rho(\mathbf{r'}) (\mathbf{r} - \mathbf{r'})}{|\mathbf{r} - \mathbf{r'}|^3} \, d\mathbf{r}', \quad \mathcal{E}_{xc}(\mathbf{r}) = \int \frac{\rho_{xc}(\mathbf{r}, \mathbf{r'}) (\mathbf{r} - \mathbf{r'})}{|\mathbf{r} - \mathbf{r'}|^3} \, d\mathbf{r}'. \quad (59)$$

The component $W_{ee}(\mathbf{r})$ is a sum of works $W_{H}(\mathbf{r})$ and $W_{xc}(\mathbf{r})$, done to move an electron in the corresponding Hartree and XC fields as $W_{ee}(\mathbf{r}) = W_{H}(\mathbf{r}) + W_{xc}(\mathbf{r})$, with,

$$W_{H}(\mathbf{r}) = -\int_{\infty}^{r} \mathcal{E}_{H}(\mathbf{r}') \cdot d\mathbf{r}', \quad W_{xc}(\mathbf{r}) = -\int_{\infty}^{r} \mathcal{E}_{xc}(\mathbf{r}') \cdot d\mathbf{r}'. \quad (60)$$
The work $W_H(r)$ is path-independent, $\nabla \times \mathcal{E}_H(r) = 0$, and also it is recognized as the Hartree potential $v_H(r)$ in DFT. The functional derivative of Coulomb self-energy functional $E_H[\rho]$ can be physically interpreted as work done in the field of electron density. The component $W_{ee}(r)$ is then given as a sum of Hartree potential and the work done to move an electron in the field of quantum mechanical Fermi-hole charge distribution: $W_{ee}(r) = v_H(r) + W_{xc}(r)$. The latter is path independent for symmetrical density systems as mentioned previously, since $\nabla \times \mathcal{E}_{xc}(r) = 0$ in all those cases. However, note that $\rho_{xc}(r, r')$ that gives rise to the field $\mathcal{E}_{xc}(r)$ need not possess the same symmetry for arbitrary electron position.

Finally, the KS electron-interaction energy $E_{ee}^{KS}[\rho]$ can also be expressed in terms of above fields (and hence source charge distribution) as follows. The quantum mechanical electron-interaction energy is,

$$E_{ee}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \mathbf{r} \cdot \mathcal{E}_{ee}(\mathbf{r}),$$

which can be further reduced to its Coulomb self-energy and XC components,

$$E_H[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \mathbf{r} \cdot \mathcal{E}_H(\mathbf{r}), \quad E_{xc}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \mathbf{r} \cdot \mathcal{E}_{xc}(\mathbf{r}),$$

and the correlation-kinetic energy component is,

$$T_c[\rho] = \frac{1}{2} \int d\mathbf{r} \rho(\mathbf{r}) \mathbf{r} \cdot Z_{t_{c}}(\mathbf{r}).$$

Such a description for XC potential in terms of the source charge distribution, gives a hope of writing KS equation of an interacting many-electron system which could, in principle, be applicable for both ground and excited states. Because, this procedure leads to a universal prescription, independent of any state, as it does not have a definite functional form; it is completely and uniquely determined by the electronic configuration of a particular state in question. Hence the applicability for ground as well as excited states; the same equation gives it all. Although the present method falls within the spirit of exchange energy as defined in Slater’s theory via Fermi-hole charge distribution, it is expected to offer improvement over the Hartree-Fock-Slater (equivalent to LDA method in DFT) theory, because current scheme accounts for the dynamic nature of charge distribution. This definition gives the expected falling off $(1/r)$ of exchange potential at large $r$. Since at $r \to \infty$, the Coulomb-hole contributions to the interaction in Eq. (62) is already zero, this implies that current method should give almost exact results in the asymptotic region.
Now, we proceed to some details of the actual numerical implementation. Note that the work $v_x(r)$ against the force field due to a Fermi-hole charge can be determined exactly since the latter is known explicitly in terms of orbitals as,

$$\rho_x(r, r') = -\frac{|\gamma(r, r')|^2}{2\rho(r)}, \quad \gamma(r, r') = \sum_i \phi^*_{i}(r) \phi_{i}(r'). \quad (64)$$

Here the terms have following meaning. $\gamma(r, r')$ refers to the single-particle density matrix spherically averaged over electronic coordinates for a given orbital angular quantum number, $\phi_i(r) = R_{nl}(r) Y_{lm}(\Omega)$ signifies the single-particle orbital, and $\rho(r)$ is the total electron density expressed in terms of occupied orbitals, $\rho(r) = \sum_i |\phi_i(r)|^2$. For spherically symmetric systems, exchange part in Eq. (59) can be simplified as,

$$E_{x,r}(r) = -\frac{1}{4\pi} \int \rho_x(r, r') \frac{\partial}{\partial r} \frac{1}{|r - r'|} dr'd\Omega_r. \quad (65)$$

Now one can use the well-known expansion,

$$\frac{1}{|r - r'|} = 4\pi \sum_{\nu', m', l'} \frac{1}{2l' + 1} Y_{\nu' m'}(\Omega) Y_{\nu' m'}(\Omega') \frac{r_{\nu'}^<}{r_{\nu'}^>}, \quad (66)$$

to obtain

$$E_{x,r}(r) = \frac{1}{2\pi \rho(r)} \int \frac{1}{\rho(r)} \sum_{n,l,m,n',l',m'} R_{nl}(r) R_{nl'}(r') \left[ \frac{\partial}{\partial r} \frac{r_{\nu'}^<}{r_{\nu'}^> + 1} \right] r^2 dr' \frac{(2l + 1)}{(2l' + 1)} \times C^2(l \nu' l'; m, m' - m, m') C^2(l \nu' l'; 000), \quad (67)$$

where $R_{nl}(r)$ denotes radial part of the single-particle orbitals and $C$’s are the Clebsch-Gordan coefficients \[111\]. Now the exchange integral in Eq. (60) can be written as an integral over radial coordinates only,

$$v_x(r) = -\int_0^r E_{x,r}(r') \ dr'.$$ \quad (68)

While the exchange potential $v_x(r)$ can be accurately calculated through the procedure as delineated above, the correlation potential $v_c(r)$ remains unknown and must be approximated for practical calculations. In the present work, two correlation functionals are used, (i) a simple, local, parametrized Wigner-type potential \[112\] (ii) a slightly more complicated, generalized gradient-corrected correlation energy functional of Lee-Yang-Parr (LYP) \[113\].
With this choice of $v_x(r)$ and $v_c(r)$, the following KS-type differential equation is solved self-consistently to produce a self-consistent set of orbitals, from which $\rho(r)$ is constructed,

$$\left[ -\frac{1}{2} \nabla^2 + v_{es}(r) + v_{xc}(r) \right] \phi_i(r) = \varepsilon_i \phi_i(r), \quad (69)$$

where $v_{es}(r)$ represents the usual Hartree electrostatic potential including electron-nuclear attraction and inter-electronic Coulomb repulsion, whereas $v_{xc}(r) = v_x(r) + v_c(r)$. Total energy is then obtained as a sum of following terms in the usual manner,

$$T = -\frac{1}{2} \sum_i \int \phi_i^*(r) \nabla^2 \phi_i(r) \, dr, \quad E_{es} = -Z \int \frac{\rho(r)}{r} \, dr + \frac{1}{2} \int \int \frac{\rho(r)\rho(r')}{|r-r'|} \, dr \, dr'. \quad (70)$$

Two-electron Hartree and exchange energies can be simplified further,

$$E_H = \frac{1}{2} \sum \int \int R_{nl}^2(r) R_{n'l'}^2(r') \frac{r'^{l'}}{r^{l'+1}} \frac{r^{l}}{r'^{l'+1}} \, dr \, dr' \times C(l''l'; m0m0) C(l''l'; 000) C(l''l'; m'0m') C(l''l'; 000)$$

$$E_x = \sum (\text{pairs with parallel spin}) \int \int R_{nl}(r) R_{n'l'}(r) R_{n'l'}(r') R_{n'l'}(r') \frac{r'^{l'}}{r^{l'+1}} \frac{r^{l}}{r'^{l'+1}} \, dr \, dr' \times C^2(l''l'; m, m - m', m') C^2(l''l'; 000) \times \left( \frac{2l + 1}{2l' + 1} \right) \quad (71)$$

Now a few words should be mentioned regarding numerical solution of the KS equation for orbitals. In earlier stages of the development of this method \cite{21-29}, a Numerov-type finite difference (FD) scheme was adopted for the discretization of spatial coordinates. It is, however, well-known that, due to existence of Coulomb singularity at the origin and presence of long-range nature of the Coulomb potential, FD methods require a large number of grid points to achieve decent accuracy even for ground-state calculations. Certainly excited (especially those higher-lying Rydberg ones) would need much more grid points to properly describe their long tail. Here, we describe the extension of the generalized pseudospectral (GPS) method for nonuniform and optimal spatial discretization and solution of KS equation, Eq. (69). This procedure has been demonstrated to be capable of providing high precision solution of eigenvalues and wave functions for a variety of singular as well as non-singular potentials, like Hulthen, Yukawa, Spiked harmonic oscillators, logarithmic, Hellmann potentials; very accurate results have also been obtained for static and dynamic calculation in Coulomb singular systems (like atoms, molecules) such as electronic structure, multi-photon processes in strong fields, Rydberg atom spectroscopy and dynamics, etc. \cite{30-33,114-123}. In addition, the GPS method is computationally orders of magnitude faster.
than the equal-spacing FD methods. In what follows, we briefly outline the GPS procedure appropriate for our present DFT study. General discussion on the approach could be found in additional references [124, 125].

The most important feature of this method is to approximate an *exact* function \( f(x) \) defined on the interval \([-1, 1]\) by an \( N \)th-order polynomial \( f_N(x) \),

\[
f(x) \approx f_N(x) = \sum_{j=0}^{N} f(x_j) g_j(x), \tag{72}\]

such that the approximation be *exact at collocation points* \( x_j \),

\[
f_N(x_j) = f(x_j). \tag{73}\]

We chose to employ the Legendre pseudospectral method where \( x_0 = -1, x_N = 1, \) and \( x_j (j = 1, \ldots, N - 1) \) are determined by roots of first derivative of the Legendre polynomial \( P_N(x) \) with respect to \( x \), i.e., \( P'_N(x_j) = 0 \). In Eq. (72), \( g_j(x) \) are the cardinal functions satisfying a unique property \( g_j(x_j') = \delta_j j' \), and defined by,

\[
g_j(x) = -\frac{1}{N(N + 1)P_N(x_j)} \frac{(1 - x^2) P'_N(x)}{x - x_j}, \tag{74}\]

The general eigenvalue problem for our radial KS-type equation can now be written as,

\[
\hat{H}(r)\psi(r) = E\psi(r), \tag{75}\]

with

\[
\hat{H}(r) = -\frac{1}{2} \frac{d^2}{dr^2} + V(r), \tag{76}\]

For structure and dynamics calculations this involves Coulomb potential, which typically has a singularity problem at \( r = 0 \), as well as the long-range \(-1/r\) behavior. This usually requires a large number of grid points in the *equal-spacing* finite-difference methods, which are not feasible to extend to Rydberg state calculations. This can be overcome by first mapping the semi-infinite domain \( r \in [0, \infty] \) into a finite domain \( x \in [-1, 1] \) by a mapping transformation \( r = r(x) \) and then using the Legendre pseudospectral discretization technique. At this stage, following algebraic nonlinear mapping [126, 127] is used,

\[
r = r(x) = L \frac{1 + x}{1 - x + \alpha}, \tag{77}\]

where \( L \) and \( \alpha = 2L/r_{\text{max}} \) are the mapping parameters. Further, introducing,

\[
\psi(r(x)) = \sqrt{r'(x)} f(x) \tag{78}\]
and following a symmetrization procedure, a transformed Hamiltonian is obtained as,

$$\hat{H}(x) = -\frac{1}{2} \frac{1}{r'(x)} \frac{d^2}{dx^2} \frac{1}{r'(x)} + V(r(x)) + V_m(x),$$  \hspace{1cm} (79)

where

$$V_m(x) = \frac{3(r'')^2 - 2r''r'}{8(r')^4}. \hspace{1cm} (80)$$

The advantage of this mapping scheme is that this leads to a symmetric matrix eigenvalue problem. Note that for the mapping used here, $V_m(x) = 0$. Therefore, discretizing our Hamiltonian by GPS method leads to the following set of coupled equations,

$$\sum_{j=0}^{N} \left[ -\frac{1}{2} D^{(2)}_{j,j} + \delta_{j,j'} V(r(x_j)) + \delta_{j,j'} V_m(r(x_j)) \right] A_j = E A_{j'}, \hspace{1cm} j = 1, \ldots, N - 1, \hspace{1cm} (81)$$

$$A_j = r'(x_j) f(x_j) \left[ P_N(x_j) \right]^{-1} = \left[ r'(x_j) \right]^{1/2} \psi(r(x_j)) \left[ P_N(x_j) \right]^{-1}. \hspace{1cm} (82)$$

Here $D^{(2)}_{j,j}$ represents symmetrized second derivative of the cardinal function in respect to $r$,

$$D^{(2)}_{j,j} = \left[ r'(x_{j'}) \right]^{-1} d^{(2)}_{j,j} \left[ r'(x_j) \right]^{-1}, \hspace{1cm} (83)$$

and

$$d^{(2)}_{j,j} = \frac{1}{r'(x_j)} \frac{(N + 1)(N + 2)}{6(1 - x_j)^2} \frac{1}{r'(x)}, \hspace{1cm} j = j', \hspace{1cm} (84)$$

$$= \frac{1}{r'(x_{j'})} \frac{1}{(x_j - x_{j'})^2} \frac{1}{r'(x_j)}, \hspace{1cm} j \neq j'. \hspace{1cm} (84)$$

The orbitals {$\phi_i(r)$} obtained from self-consistent solution of KS equation (69) are used to construct various determinants for a given electronic configuration of an atom, which, in turn, could be employed to calculate the associated multiplets related to this configuration. Here we use Slater’s diagonal sum rule for the multiplet energies [128]. Similar strategy for multiplets has been adopted earlier [37, 40, 129, 132].

IV. RESULTS AND DISCUSSION

At first, we give some sample results for singly excited $1s^2ns^2S$, $1s^2np^2P$ states of Li, as well $1s^22sns^3S$ Be, $1s^22snp^3P$ states of Be, in Table I. Note that in this and all other following tables, we present only non-relativistic results; state energies are in atomic units,
TABLE I: Comparison of singly excited-state energies of Li and Be (in a.u.) with literature data. Numbers in parentheses denote absolute percentage deviations with respect to reference values. Taken from ref. [30].

| State  | −E(X)   | −E(XC)   | −E(Literature) |
|--------|---------|----------|----------------|
| Li     |         |          |                |
| 1s^23s^2S | 7.30966 | 7.35773 (0.05) | 7.35394^b  |
|        | 7.31021a|          |                |
| 1s^25s^2S | 7.25996 | 7.30466 (0.01) | 7.30339^b  |
| 1s^22p^2P | 7.36486 | 7.41204 (0.03) | 7.41016^c  |
|        | 7.36507a|          |                |
| 1s^24p^2P | 7.26859 | 7.31262 (0.01) | 7.31190^c  |
| Be     |         |          |                |
| 1s^22s3s^3S | 14.37798 | 14.42917 (0.20) | 14.42629^e |
|        | 14.48311d|          |                |
| 1s^22s5s^3S | 14.30562 | 14.34996  |                |
| 1s^22s2p^3P | 14.51068 | 14.56660 (0.03) | 14.56223^e |
|        | 14.51150d|          |                |
| 1s^22s4p^3P | 14.31462 | 14.35910  |                |
|        | 14.31464d|          |                |

^a HF result, ref. [133].    ^b Ref. [134].    ^c Ref. [135].    ^d HF result, ref. [136].    ^e Ref. [137].

while excitation energies in eV. For all these calculations, a convergence criteria of 10^{−5} and 10^{−6}, as well a radial grid of 500 points have been used. In the literature generally excitation energies are reported, while individual state energies are given seldom. However, in a DFT study of low-lying singly excited states of some open-shell atoms (B, C, O, F, Na, Mg, Al, Si, P, Cl) [27], excitation energies from X-only and numerical HF methods are found to be in good agreement with each other. Surprisingly, however, the two correlation energy functionals (Wigner and LYP) did not show any considerable improvements in excitation energies although excited-state energies were dramatically improved. Therefore, in this work, we consider both the state energies and excitation energies. In this table, two sets of calculations are performed; solution of Eq. (69) with (i) \( v_{xc} = v_x \) (exchange-only or E(X)) and (ii) \( v_x + v_c \) (exchange plus correlation or E(XC)). These states as well the other ones in proceeding tables are of great significance in atomic physics; thus have been studied by both experimentalists and theoreticians by employing a multitude of techniques and formalisms. Some prominent reference values are quoted for comparison, wherever possible. The X-only results are fairly close to the HF values [133, 136], errors ranging from 0.0057% to as low as 0.0001% for Be 1s^22s4p^3P, indicating the accuracy in our calculation. The doublet S states of Li are compared with the full-core-plus-correlation method with multi-configuration interaction wave functions [134], while doublet P states with a combined configuration-interaction-Hylleraas method [135]. For Be, literature is quite scanty and present density


TABLE II: Calculated doubly excited-state (\(n_s^2 \ 1S\), \(n_p^2 \ 1D\)) energies of He (in a.u.) along with literature data for comparison. Numbers in parentheses denote absolute percentage errors with respect to literature data. Adopted from ref. [30].

| State       | \(-E(\text{XC})\) | \(-E(\text{Literature})\) | State       | \(-E(\text{XC})\) | \(-E(\text{Literature})\) |
|-------------|---------------------|-----------------------------|-------------|---------------------|-----------------------------|
| 2s\(^2\) 1S | 0.76637 (1.48)      | 0.77787\(^a\)              | 2p\(^2\) 1D | 0.69272 (1.31)      | 0.70195\(^c\)              |
| 3s\(^2\) 1S | 0.34578 (2.19)      | 0.35354\(^a\)              | 3p\(^2\) 1D | 0.31540 (0.04)      | 0.31554\(^c\)              |
| 4s\(^2\) 1S | 0.19659 (2.19)      | 0.20099\(^a\)              | 4p\(^2\) 1D | 0.18095             |                             |
| 5s\(^2\) 1S | 0.12754 (2.12)      | 0.13030\(^b\)              | 5p\(^2\) 1D | 0.11610             |                             |
| 6s\(^2\) 1S | 0.08808 (3.05)      | 0.09085\(^b\)              | 6p\(^2\) 1D | 0.08115             |                             |
| 7s\(^2\) 1S | 0.06524 (3.35)      | 0.0675\(^b\)               | 7p\(^2\) 1D | 0.05980             |                             |
| 9s\(^2\) 1S | 0.03889             |                             | 9p\(^2\) 1D | 0.03604             |                             |
| 11s\(^2\) 1S | 0.02503             |                             | 11p\(^2\) 1D | 0.02414             |                             |
| 13s\(^2\) 1S | 0.01811             |                             | 13p\(^2\) 1D | 0.01728             |                             |
| 15s\(^2\) 1S | 0.01348             |                             | 15p\(^2\) 1D | 0.01297             |                             |
| 17s\(^2\) 1S | 0.01132             |                             | 17p\(^2\) 1D | 0.01010             |                             |

\(^a\) Ref. [138]. \(^b\) Ref. [137]. \(^c\) Ref. [139].

Functional results match very closely with the multi-configuration calculations [137]. One finds some overestimation in total energy caused by the LYP correlation functional employed here; errors ranging from 0.052%–0.003%. For a more detailed discussion, see [30].

Next, in Table II, some even-parity doubly excited states (\(n_s^2 \ 1S\), \(n_p^2 \ 1D\), \(n=2–17\)) of He are presented. Many of these have been identified to be autoionizing in nature, e.g., \(n_s^2 \ 1S\). It is seen that the calculated energy values have never fallen below the quoted results. In the former case, DFT results are comparable to literature data for smaller \(n\) and tends to increase gradually with an increasing \(n\), as evident from the absolute per cent deviations given in the parentheses. This could occur either because of the inadequate description of long-range nature of correlation potential employed or some deficiencies in the work-function formalism itself. Finally we see that while accuracy of doubly excited state calculation is not as good as that of singly excited state, error in the former still remains well within 3.6%. More details on these could be found in ref. [30].

Now, single and double excitation energies of selected states of He, Be, are displayed in Table III, along with some reference values. These are estimated with respect to our calculated, non-relativistic ground-state energies of He, Be, i.e., \(-2.90384\) and \(-14.66749\) a.u. (as obtained from the same KS equation (69)). No experimental results could be
found for doubly excited resonances. In some occasions, our calculated excitation energies have fallen below the experimental results. This is not surprising keeping in mind that the present methodology is non-variational. As a consequence, the variational restriction on a particular excited state being the lowest of a given space-spin symmetry does not hold good. Here we also report the single-particle KS energies (obtained from the difference of KS eigenvalues) for single excitations in He, Be [140], which, of course, do not show the multiplet separation. The excitation energies from true KS potential for He, Be are clearly quite good. However, those from some other commonly used approximate exchange energy functionals (such as LDA) produce large errors in excitation energy [140]. Also, it may be

| State                | Present Work | $\Delta \epsilon_{KS}$ | Other theory | Experiment |
|----------------------|--------------|-------------------------|--------------|------------|
| **Single excitation of He and Be** |              |                         |              |            |
| He 1s2s $^3S$        | 0.72839 (0.02) | 0.7460$^a$              | 0.72850$^b$  | 0.72833$^c$|
| He 1s2s $^1S$        | 0.75759 (0.02) | 0.75775$^b$             | 0.75759$^c$  |            |
| He 1s2p $^3P$        | 0.77041 (0.02) | 0.7772$^a$              | 0.77056$^b$  | 0.77039$^c$|
| He 1s2p $^1P$        | 0.77971 (0.02) | 0.77988$^b$             | 0.77972$^c$  |            |
| He 1s3s $^3S$        | 0.83494 (0.01) | 0.8392$^a$              | 0.83504$^b$  | 0.83486$^c$|
| He 1s3s $^1S$        | 0.84231 (0.02) | 0.84245$^b$             | 0.84228$^c$  |            |
| He 1s3p $^3P$        | 0.84548 (0.02) | 0.8476$^a$              | 0.84564$^b$  | 0.84547$^c$|
| He 1s3p $^1P$        | 0.84841 (0.02) | 0.84858$^b$             | 0.84841$^c$  |            |
| Be 1s2s2p $^3P$      | 0.10089       | 0.1327$^a$              | 0.100153$^c$ |           |
| Be 1s2s2s $^3S$      | 0.23832(0.63) | 0.2444$^a$              | 0.236823$^d$ | 0.237304$^c$|
| Be 1s2s4p $^3P$      | 0.30839       | 0.3046$^a$              | 0.300487$^c$ |            |
| Be 1s2s5s $^3S$      | 0.31753       | 0.3153$^a$              | 0.314429$^c$ |            |
| **Double excitation of He** |              |                         |              |            |
| He 2s$^2$ $^1S$      | 2.13747(0.54) | 2.1259$^e$, 2.1285$^f$  | 2.1259$^e$, 2.1285$^f$ |   |
| He 3s$^2$ $^1S$      | 2.55836(0.61) | 2.5425$^g$, 2.5496$^h$  | 2.5425$^g$, 2.5496$^h$ |   |
| He 4s$^2$ $^1S$      | 2.70725(0.48) | 2.6942$^g$, 2.7017$^i$  | 2.6942$^g$, 2.7017$^i$ |   |
| He 5s$^2$ $^1S$      | 2.77630(0.10) | 2.7735$^j$              | 2.7735$^j$  |            |
| He 6s$^2$ $^1S$      | 2.81576(0.10) | 2.8129$^j$              | 2.8129$^j$  |            |
| He 7s$^2$ $^1S$      | 2.83860(0.09) | 2.8302$^h$              | 2.8302$^h$  |            |
| He 2p$^2$ $^1D$      | 2.21120(0.68) | 2.1961$^b$, 2.2082$^f$  | 2.1961$^b$, 2.2082$^f$ |   |
| He 3p$^2$ $^1D$      | 2.58844(1.60) | 2.5477$^k$, 2.5995$^l$  | 2.5477$^k$, 2.5995$^l$ |   |
| He 4p$^2$ $^1D$      | 2.72289(1.08) | 2.6938$^b$              | 2.6938$^b$  |            |

$^a$ Ref. [140]. $^b$ Ref. [141, 142]. $^c$ Ref. [143]. $^d$ Ref. [144]. $^e$ Ref. [145]. $^f$ Ref. [146]. $^g$ Ref. [137]. $^h$ Ref. [147].

TABLE III: Single and double excitation energies of He and Be (in a.u.) compared with literature data. Numbers in parentheses denote absolute percentage errors with respect to the best theoretical data available. Adopted from ref. [30].
mentioned here that, for excitation energies in Ne satellites \[26\], both LDA and one of the most commonly used gradient-corrected exchange functional \[148\] have been found to be absolutely unsuitable for such studies, producing very large errors. Besides, present results are not corrected for relativistic effects, which is included in the experimental values. Single excitations in He show reasonably good agreement with both theory and experiment, while for Be the corresponding discrepancy is somehow larger. Nevertheless, the overall agreement between current results and literature data is quite satisfactory. Apart from the errors in XC potentials as discussed earlier, another possible source could be rooted in the \textit{single-determinantal} nature of our method. Assumption of spherical symmetry in dealing with the exchange potential could also bring some inaccuracies. Stated differently, the solenoidal component of the electric field $\mathcal{E}_x(r)$ may not be negligible compared to the irrotational component for these states, although this usually holds quite well for atoms \[110\]. As a further check, some representative radial expectation values for singly and doubly excited states of He as well as singly excited states of Li, Be have also been studied \[30\]. These match quite well with the HF values \[149\], once again reassuring the accuracy in our calculation.

Now we move on to the triple excitations. For this purpose, we compare our DFT excitation energies for all the eight $2l^2l^2l''$ ($n = 2$ intrashell) triply excited states, \textit{viz.}, $2s^22p^2 \, 2P^o$; $2s2p^2 \, 2D^e, 4P^e, 2P^e, 2S^e$; and $2p^3 \, 2D^o, 2P^o, 4S^o$ of selected members of Li-isoelectronic series, i.e., $B^{2+}$, $N^{4+}$ and $F^{6+}$ in Table IV. At this stage, it may be appropriate to illustrate the details of a multiplet calculation from individual determinants by an example. For this, we consider all the four multiplets $^2D, ^4P, ^2P, ^2S$ associated with a $2s2p^2$ configuration. This gives rise to 30 determinants which satisfy following relations (left and right correspond to the multiplet and determinantal energies),

\[
\begin{align*}
^2D &= (0^+1^+1^-) \\
^4P &= (0^+1^+0^+) \\
^2D + ^4P + ^2P &= (0^+1^+0^-) + (0^+1^-0^+) + (0^-1^+0^+) \\
^2D + ^4P + ^2P + ^2S &= (0^+1^+ - 1^-) + (0^+1^- - 1^+) + (0^-1^+ - 1^-) + (0^+0^+0^-) 
\end{align*}
\]

where the numbers denote $m_l$ values while $(+, -)$ $m_s$ values. For more details, see \[24\].

In this case, we no more report individual state energies as these are very difficult to compare directly; instead only excitation energies are reported. To put our results in proper perspective, all triple excitation energies in this table are computed with respect to the
TABLE IV: Comparison of calculated excitation energies (in eV) of the n=2 intrashell triply excited states of B\(^{2+}\), N\(^{4+}\) and F\(^{6+}\) relative to the non-relativistic ground states of \([150]\). GPS signifies present work. See ref. \([32]\) for details.

| State         | B\(^{2+}\)          | N\(^{4+}\)        | F\(^{6+}\)        |
|---------------|---------------------|--------------------|--------------------|
|               | GPS     | Ref.    | GPS     | Ref.    | GPS     | Ref.    |
| 2s\(^2\)2p\(^2\) P\(^o\) | 436.588 |         | 894.541 |         | 1514.229 |         |
| 2s2p\(^2\) 3P\(^c\) | 436.917 |         | 894.876 |         | 1514.474 |         |
| 2s2p\(^2\) 2D\(^e\) | 441.893 |         | 902.655 |         | 1524.898 |         |
| 2p\(^3\) 4S\(^o\)   | 443.852 | 443.86\(\pm\)444.15 \(\pm\) | 905.329 | 905.15\(\pm\)905.15 \(\pm\) | 1528.187 | 1530.42\(\pm\)1529.35 \(\pm\) |
| 2p\(^3\) 2S\(^c\)   | 445.387 | 445.11\(\pm\)445.75 \(\pm\) | 907.930 | 907.41\(\pm\)907.87 \(\pm\) | 1531.822 | 1533.61\(\pm\)1533.18 \(\pm\) |
| 2p\(^2\) 2P\(^e\)   | 445.814 | 445.35\(\pm\)446.21 \(\pm\) | 908.455 | 907.99\(\pm\)908.59 \(\pm\) | 1532.717 | 1534.55\(\pm\)1534.17 \(\pm\) |
| 2p\(^3\) 2D\(^o\)   | 446.173 | 446.02\(\pm\)446.58 \(\pm\) | 909.089 | 909.02\(\pm\)909.37 \(\pm\) | 1533.816 | 1536.01\(\pm\)1535.35 \(\pm\) |
| 2p\(^3\) 2P\(^o\)   | 450.088 | 450.04\(\pm\)450.65 \(\pm\) | 915.023 | 915.00\(\pm\)915.47 \(\pm\) | 1541.946 | 1543.95\(\pm\)1543.46 \(\pm\) |

\(a\) Ref. \[151\]. \(b\) Ref. \[152\]. \(c\) Ref. \[153\]. \(d\) Ref. \[154\].

Accurate non-relativistic ground state of \([150]\). No experimental results have been reported as yet in the literature and appropriate theoretical results are quoted here. All these states are autoionizing except the 2p\(^3\) 4S\(^o\), which is bound, metastable against auto-ionization by conservation of parity and angular momentum. These are studied through a multi-configuration-interaction type formalism within a Rayleigh-Ritz variational principle \[154\]. Recently a perturbation theory method (1/Z expansion) \[151\] as well a truncated diagonalization method \[152, 153\] have been employed to determine the position of all these states. It is gratifying that our current positions for all these 8 states for these 3 ions follow the same orderings as in \[151–153\], which clearly demonstrates the reliability in our calculation. All these excitation energies show excellent agreement with the literature data, with a maximum discrepancy of 0.125%; for the three ions the deviation ranges are 0.0005–0.125%, 0.007–0.049% and 0.044–0.099% respectively. Both underestimation and over-estimation is observed in excitation energies.

Now we present results for triply excited hollow resonances, 2l\(l^\prime\)nl\(n^\prime\) (n \(\geq\) 2) in Li. In \[31\], 12 such resonance series, viz., 2s\(^2\)ns\(^2\)S\(^e\), 2s\(^2\)np\(^2\)P\(^o\), 2s\(^2\)nd\(^2\)D\(^e\), 2p\(^2\)ns\(^2\)D\(^e\),4P\(^e\), 2s2pns\(^4\)P\(^o\), 2s2pnp\(^4\)D\(^e\), 2p\(^2\)np\(^2\)F\(^o\),4D\(^o\), 2p\(^2\)nd\(^2\)G\(^e\), 4F\(^e\) and 2s2pnd\(^4\)F\(^o\), covering a total of about 270 low-, moderately high- and high-lying states (with n as high as 25) were studied in some detail. These represent the model case of a highly correlated, multi-excited three
TABLE V: 2s^2ns^2S^e and 2s^2np^2P^o resonances of Li. State energies and excitation energies, relative to the ground state of Li. GPS signifies present work. See [31] for details.

| n | (A,ns) 2s^2S | Excitation energy(eV) | (A,np) 2P^o | Excitation energy(eV) |
|---|-------------|----------------------|-------------|----------------------|
|   | GPS | Ref. | GPS | Ref. | GPS | Ref. | GPS | Ref. |
| 2 | 1.9871 | 2.0048 | 149.396 | 148.632 | 148.822 | 2.0102 | 148.788 | 148.914 | 2.2428 |
|   | 1.9740 | 1.9935 | 1.991 | 1.9879 | 1.9075 | 1.9214 | 1.9145 | 1.8996 | 1.9068 |
| 3 | 1.9094 | 1.9165 | 151.510 | 150.855 | 151.317 | 151.025 | 151.755 | 150.902 | 151.570 | 151.263 |
| 6 | 1.9004 | 1.9072 | 151.755 | 151.092 | 151.570 | 151.263 | 151.861 | 151.190 | 151.665 |
| 8 | 1.8965 | 1.9037 | 151.918 | 151.247 | 151.717 | 1.8943 | 1.9034 | 1.8961 | 1.9034 |
| 10 | 1.8944 | 1.9018 | 151.970 | 151.296 | 1.8925 | 1.8918 | 1.8917 | 1.8918 | 1.8918 |
| 12 | 1.8925 | | 151.992 | 151.318 | 1.8916 | 1.8916 | 1.8914 | 152.000 | 151.325 |
| 16 | 1.8917 | | | | | 151.994 |
| 20 | | | | | | |
| 22 | | | | | | |

a Ref. [156], b Ref. [157], c Ref. [152], d Ref. [158], e Ref. [159], f Ref. [160], g Ref. [162], h Ref. [163], i Ref. [164], j Ref. [164], k Ref. [164], l Ref. [164].

The electron system in presence of a nucleus, and hence a four-body Coulombic problem. These are often termed as hollow states, as all three electrons reside in higher shells leaving the K shell empty. They have many fascinating properties, as well are very difficult for both theory and experiments. For example, these are difficult to produce from ground state by single photon absorption or electron impact excitation; also they have proximity to more than one thresholds; moreover there are infinite open channels associated with these resonance. Table V gives some representative state energies and excitation energies of even-parity 2s^2ns^2S^e and odd-parity 2s^2np^2P^o resonances in Li (n=2–22). The latter is calculated relative to the accurate ground state of Li, using full core plus correlation within a multi-configuration interaction wave function [155]. The reference energy value −7.47805953 a.u. is to be compared with our present value of −7.4782839 a.u. In literature, these states are conveniently classified using our independent particle model classification [152, 170] where the six core Li+ n=2 intrashell doubly excited states, viz., 2s^2 1S^e, 2s2p^3P^o, 2p^2 3P^e, 2p^2 1D^e, 2s2p 1P^o and 2p^2 1S^e are denoted by A, B, C, D, E and F respectively. For the former, no experimental results are available as yet. Lower members of the former series
TABLE VI: Selected $3l^3l'n''$ term energies (in a.u.) and excitation energies (in eV) of Li, relative to the ground state of $1s^2$. Adopted from ref. [31].

| State       | $-E$    | Exc. energy | State       | $-E$    | Exc. energy | State       | $-E$    | Exc. energy |
|-------------|---------|-------------|-------------|---------|-------------|-------------|---------|-------------|
| $3s^24s$ $^2S^o$ | 0.90054 | 178.959     | $3p^3$ $4S^o$ | 1.00055 | 176.238     | $3p^24s$ $4P^o$ | 0.89860 | 179.012     |
| $3s^26s$ $^2S^o$ | 0.85729 | 180.136     | $3s3p$ $4P^o$ | 0.93313 | 178.972     | $3p^6$ $4P^o$ | 0.85744 | 180.132     |
| $3s^23p$ $^2P^o$ | 1.01210$^a$ | 175.924$^{b,c}$ | $3s3p$ $5P^o$ | 0.90193 | 178.921     | $3p^24s$ $2D^e$ | 0.87282 | 179.713     |
| $3s^26p$ $^2P^o$ | 0.85558 | 180.182     | $3s3p$ $5P^o$ | 0.89924 | 179.994     | $3p^24p$ $4D^o$ | 0.89642 | 179.071     |
| $3s^23d$ $^2D^e$ | 0.97108 | 177.040     | $3s3p$ $5P^o$ | 0.88767 | 179.309     | $3p^25p$ $2F^o$ | 0.83433 | 180.513     |
| $3s^26d$ $^2D^e$ | 0.85352 | 180.238     | $3s3p$ $5d$ $^4F^o$ | 0.89400 | 179.137     | $3p^25p$ $2F^o$ | 0.83225 | 180.817     |
| $3s3p^2$ $^4P^o$ | 1.02288$^d$ | 175.630     | $3s3p$ $6d$ $^4F^o$ | 0.88517 | 179.377     | $3p^26p$ $2F^o$ | 0.82921 | 180.513     |

$^a$Reference theoretical values are: 1.043414 a.u. [167], 1.043 a.u. [157] and 1.040985 a.u. [168].

$^b$Reference experimental results are: 175.25 eV [169] and 175.165 ± 0.050 eV [167].

$^c$Reference theoretical values are: 174.11 eV [167], 174.14 eV [169] and 175.15 eV [168].

$^d$Reference theoretical value is: 1.0393859 a.u. [168].

have been studied in considerable detail by a variety of techniques, such as a hyper-spherical coordinate method [162], a combination of saddle point and complex coordinate rotation [166]. Of late, an eigenphase derivative technique in conjunction with a quantum defect theory [163] reported the low and high resonances up to $n = 22$, whereas the same up to $n = 12$ were done by a truncated diagonalization method [152]. Our DFT results are in good agreement with these references; state energies lie about 0.36–0.88% above [152], whereas the excitation energies are higher by 0.41–0.51% from those of [163]. The $(A,ns)^2P^o$ resonances are the most widely studied series in Li, both theoretically and experimentally. Position of the lowest in this series has been experimentally measured at 142.33 eV [161], 142.35 eV [160]. These are generally supported by theoretical calculations, e.g., combined saddle-point and complex coordinate rotation approach [156], a complex scaling method having correlated basis functions constructed from B-splines [157], an R-matrix theory [159], etc. Present excitation energy is only 0.02% above the experimental results. Other members of the series with $n = 3–7$ are in reasonably good agreement with complex coordinate rotation calculations [164]. Our state energies are underestimated by 0.24–0.98% with respect to those of [156, 164], leading to higher excitation energies (deviations with respect to [159, 165] being only 0.05–0.32% and 0.43–0.46% for $n = 2–9$ and $n = 3–10$ respectively). For further discussion on these and other hollow resonances see [31].

Table VI extends the method for some higher lying triply excited hollow resonances of Li having both K and L shells empty, the so-called doubly hollow states, viz., $3l^3l'n''(3\leq n\leq6)$.
(2S⁰, 2P⁰, 2D⁰, 2F⁰, 4S⁰, 4P⁰, 4D²⁰, 4F²⁰). For 2l/2l′nl″ resonances, several accurate, reliable experimental and theoretical results are available; however, the same for 3l/3l′nl″ resonances, are very limited mainly because of the greater challenges encountered. These have very distinctive features: (a) they are weak (by about an order of magnitude compared to the lower hollow states), broad and having much larger widths [169]. The principal difficulties with these higher hollow states at larger photon energies are mainly due to a very rapid increase in the density of possible triply excited and other lower states of same symmetry, as well as of the number of open channels available, giving rise to very strong and quite complicated electron correlation effects. Nevertheless some attempts have been made, which are quoted here. The energies and decay rates of N⁴⁺ and N²⁺ 3l3l′3l″ have been studied using a CI approach [171]. Positions and widths of N⁴⁺ (3,3,3) 2S²⁰ states are investigated by a space partition as well as a stabilization procedure both of which use the L² discretization [172]. A large scale state specific theory calculations for 11 n=3 resonances of He⁻ has been suggested [173]. Critical issues in the theory and computation of the lowest three n=3 intrashell states, viz., 3s3p² 2P⁰, 3s3p² 4P⁰ and 3s3p² 2D⁰ of Z=2–7 in the light of state specific theory, has been published [168]. Energies, widths and Auger branching ratios for eight He⁻ 3l3l′3l″ states are calculated by complex rotation method [168]. A semi-quantitative analysis of the angular correlation of 64 n=3 intrashell states of a model three-electron atom confined on the surface of a sphere were presented recently [174]. The only result available for such triply photo-excited (3,3,3) KL hollow state for Li are the 3s3p² 2P⁰ and 3s3p² 4P⁰, both theoretically, whereas only the former experimentally. The former’s position has been measured at 175.25 and 175.165 eV by synchrotron radiation measurement [169] and photo-ion spectroscopy [167]. In a saddle-point calculation with R-matrix approximation [167], a 570-term 25 angular component wave function gives an energy of −1.043414 a.u., and position at 174.11 eV. This is in reasonable agreement with the complex rotation calculation of −1.043 a.u., [157], and the state specific result [168] of −1.0409856 a.u., as well as, with the multi-configuration Dirac-Fock [169] excitation energy of 174.14 eV. DFT energy value of −1.01210 a.u., gives its position at 175.940 eV, (about 0.67 eV above the experimental value of [169]) and matches well with the state specific result of 175.15 eV [168]. Calculated 3s3p² 4P⁰ state energy of −1.02288 a.u., matches closely with the state specific result of −1.0393859 a.u. [168]. Leaving aside a few of those as mentioned above, most of these can not be compared directly due to lack of any reference values and we expect that these
results may be useful in future studies of these resonances. Note that our result gives 3s3p^2^4P^e as the lowest n=3 resonance rather than the 3s^23p^2^2P^o, the former lying 0.0108 a.u., below the latter which coincides with the ordering found in other calculation such as complex rotation for He^−[175] and CI calculation for N^4+[171]. However this disagrees with the state specific calculation of [168], where the ordering is reversed and separation for Li being about 0.0016 a.u. Clearly, more accurate calculation with better correlation functionals would be required to achieve such smaller separations (of the order of 1×10^{-3} a.u.) within this DFT formalism to reach a more authentic conclusion. Now Fig. 1 depicts the radial densities for some representative (a) 2l2′l′n′l′′ and (b) 3l3′l′n′l′′ hollow states; as expected, they show the characteristic shell structures (superpositions of orbital radial densities).

Now Table VII reports DFT energies for ground and excited states of some negative atoms, namely, Li− and Be−. For the former, 4 states are considered, viz., [He]2s^2 1S^e, 1s2s2p^2 5P^e, [He]2p^3 5S^o, 1s2s2p3p 5P^e; while for the latter 3 states, i.e, [He]2s2p^2 4P^e, [He]2p^3 4S^o, 1s2s2p^3 6S^o. Two sets of energies are reported viz., X-only (non-correlated) and XC (correlated, with LYP functional). Excepting the core-excited even-parity 1s2s2p3p 5P^e of Li− (reported lately), the rest 4 states have been investigated quite extensively. Comparisons with literature data are made, wherever possible. Per cent deviations are given in parentheses; for X-only case these are relative to the lone literature results in

FIG. 1: The radial densities (a.u.) of 2s^23s 2S^e states for (a) B^2+, C^3+, N^4+ and (b) O^5+, F^6+, Ne^7+ respectively. Taken from ref. [32].
column 4; for XC case, these are with respect to the recent variational Monte Carlo (VMC) [176] values except for the 4th state of Li$^-$, where such a result is unavailable; and this is given in reference to the saddle-point calculation of [177]. Our X-only ground state of Li$^-$ is higher from the accurate HF calculation of [178] by a marginal 0.0004 a.u. The XC energy shows fairly good agreement (slightly above) with the accurate correlated MCHF-$n$ expansion considering all expansions [178], as well as VMC method [176]. These seem to be in considerable disagreement with the earlier result of [179]. X-only results for the core-excited high-spin even-parity $^5P_e$ and odd-parity $^5S_o$ states of Li$^-$ also show excellent agreement with the HF energy [176], while XC energies match well with literature values, such as VMC [176], CI [180], variational multi-configuration calculation [181], saddle-point [177], MCHF [182], etc. Note that XC energies for these two states are lower than all of these reference results by 0.171 and 0.137%, respectively giving maximum deviations in our calculation. As already verified, the X-only results are practically of HF quality; hence this overestimation is probably caused by the approximate correlation potential used. Note that while ours is a single determinantal method, some of these correlated calculations are highly elaborate and extensive; for example, in [181], a 45 angular component 1004-term wave function was used, [180] used a 320-term CI and [177] used 7-50 angular spin components with 541–1298 linear parameters for the former. Nevertheless, as clearly seen, our results exhibit a rather small discrepancy from these references. Even-parity $^5P_e$ state has been considered rather lately [177]. Current energy value shows very good matching with the reference, where the authors used a saddle-point restricted variational method with accurate multi-configurational wave functions built from STO basis sets. Be$^-$ does not have a [He]2s$^2$2p $^2P$ ground state; three metastable bound states found in the discrete spectrum are given here. [He]2s2p$^2$ $^4P_e$, [He]2p$^3$ $^4S_o$ and 1s2s2p$^3$ $^6S_o$ states lie below the Be 1s$^2$2s2p $^3P$, 1s$^2$2p$^2$ $^3P$ and 1s2s2p$^2$ $^5P$ excited states. X-only energies are again in excellent agreement with the HF results [183]. A decent number of sophisticated accurate theoretical results are found in literature for the correlated case. Notable amongst them are the CI calculation of [183] including single, double, triple, quadrupole sub-shell excitations. First two states have also been studied through a method of full core plus correlation and restricted variation approach [184]. XC energies, in this case, show better agreements with literature results than those for Li$^-$; however, as in Li$^-$ again falling below the reference values for all three states. Also a combined Rayleigh-Ritz and a method of restricted variation exists for the $^6S_o$ state [185].
TABLE VII: Calculated ground and excited states of Li$^-$, Be$^-$ along with literature data. Numbers in the parentheses denote absolute per cent deviations. Adopted from [33].

| Ion     | State                  | X-only | −E(a.u.) | X-only | −E(a.u.) |
|---------|------------------------|--------|----------|--------|----------|
|         |                        | This work | Ref. | This work | Ref. |
| Li$^-$  | [He]2s$^2$ 1S\textsuperscript{e} | 7.4278(0.005) | 7.4282\textsuperscript{a} | 7.4984(0.009) | 7.4553\textsuperscript{b},7.5008\textsuperscript{c}, 7.4991\textsuperscript{d} |
|         | 1s2s2p$^2$ 5P\textsuperscript{e} | 5.3640(0.006) | 5.3643\textsuperscript{c} | 5.3925(0.171) | 5.3866\textsuperscript{d,e}, 5.3833\textsuperscript{f}, 5.3865\textsuperscript{f}, 5.3863\textsuperscript{k} |
|         | 1s2p$^3$ 5S\textsuperscript{o} | 5.2223(0.004) | 5.2225\textsuperscript{c} | 5.2608(0.137) | 5.2561\textsuperscript{d,e}, 5.2536\textsuperscript{f}, 5.2560\textsuperscript{f}, 5.2558\textsuperscript{k} |
| Be$^-$  | [He]2s2p$^2$ 4P\textsuperscript{e} | 14.5078(0.008) | 14.5090\textsuperscript{g} | 14.5806(0.062) | 14.5779\textsuperscript{h}, 14.5716\textsuperscript{i}, 14.5708\textsuperscript{j}, 14.5769\textsuperscript{k} |
|         | [He]2p$^3$ 4S\textsuperscript{o} | 14.3272(0.002) | 14.3275\textsuperscript{g} | 14.4081(0.049) | 14.4063\textsuperscript{h}, 14.4010\textsuperscript{i}, 14.4002\textsuperscript{j} |
|         | 1s2s2p$^3$ 6S\textsuperscript{o} | 10.4279(0.009) | 10.4288\textsuperscript{g} | 10.4758(0.092) | 10.4662\textsuperscript{h}, 10.4615\textsuperscript{i}, 10.4711\textsuperscript{j} |

\textsuperscript{a}Ref. \[178\].  \textsuperscript{b}Ref. \[179\].  \textsuperscript{c}Ref. \[176\].  \textsuperscript{d}Ref. \[181\].  \textsuperscript{e}Ref. \[177\].  \textsuperscript{f}Ref. \[180\].  \textsuperscript{g}Ref. \[183\].  \textsuperscript{h}Ref. \[184\].  \textsuperscript{i}Ref. \[185\].  \textsuperscript{j}Ref. \[186\].  \textsuperscript{k}Ref. \[182\].

The transition wavelengths of Li$^-$ 1s2s2p$^2$ 5P\textsuperscript{e} → 1s2p$^3$ 5S\textsuperscript{o} and Be$^-$ [He]2s2p$^2$ 4P\textsuperscript{e} → [He] 2p$^3$ 4S\textsuperscript{o} have also been found to be in good agreement with literature results [33].

Before passing, a few remarks should be made on the present approach. Although DFT has enjoyed remarkable success for studying properties of atoms, molecules, solids, clusters in ground states, the same for excited states has been less conspicuous, partly because of complete abandoning of the state-function concept. Other major problems are cumbersome wave function and Hamiltonian orthogonality requirements between a given excited state and other lower states of same space-spin symmetry, as well as the unavailability of universal XC energy density functional. Despite all these difficulties, numerous attractive and elegant attempts have been made over the years to tackle these issues. However, until only very recently, most of the proposed methods have been either found to be computationally rather difficult to implement or producing large errors in excitation energies, except TDDFT where decent excitation energies are obtained. Moreover, it is not a straightforward task to extract the radial density. Also, most of these methods have dealt with lower and singly excited states; multiple and higher excitations, especially the Rydberg series as studied here, have not been reported so far by any other DFT approach except the current method. Also note that while the recently popular TDDFT route provides accurate excitation energies efficiently, extraction of individual state energies as well as densities, expectation values are not easy. The present scheme however, offers a simple, attractive way to produce energies,
excitation energies as well as densities and expectation values with very good accuracy. In 
the current approach, all the well-known problems of DFT have essentially been bypassed 
by bringing the traditional wave function concept within DFT, so that the atomic orbital 
and electronic configuration pictures are retained. Fermi-hole charge distribution and hence 
local exchange potential is precisely in terms of orbitals, which will be different for ground 
and excited states. Not being explicitly dependent on any functional form, the exchange 
potential is universal; it is fixed by the given electronic configuration of a particular state. 
Thus the same KS equation is now valid for both ground and excited states, obviating the 
necessity for obtaining the exchange potential as a functional derivative of exchange energy 
density functional. Instead it is now directly obtained from Fermi hole charge distribution. 
Due to the locality of XC potential, SCF solution of KS equation is computationally much 
easier than the HF equations, which involve a nonlocal integral operator. Yet, as demon-
strated above, our X-only results are practically of HF quality and with correlation included, 
results go much beyond the HF level. Unlike many other sophisticated quantum mechanical 
methods, the present methodology does not involve basis set dependence, continuum mixing 
or explicit $r_{12}$ dependence; it works essentially in the single determinantal framework.

In the HKS DFT, all many-body effects are incorporated into a local multiplicative poten-
tial, obtained as a functional derivative $\delta E_{xc}[\rho]/\delta \rho$ within the variational principle. Although 
the exact form of this $E_{xc}[\rho]$ is unknown, good approximations exist; however, with these 
approximations, bounds of total energy are no longer rigorous. Therefore the work-function 
prescription is not derived from the variational principle for energy, in the sense that it is not 
expressible as $\delta E_{xc}[\rho]/\delta \rho$, but is based on a physical interpretation for the local many body 
potential that an electron moves in an electrostatic potential arising from the Fermi-hole 
charge distribution. So even though a KS-type equation is solved with the work-function 
potential, this procedure is not subject to a variational bound. Thus the variational re-
striction on the excited state being the lowest state of a particular space-spin symmetry 
is not applicable here. Furthermore, although the existence of a local effective potential 
is guaranteed in KS DFT, no mathematical proof for the existence of such a potential for 
excited states has been known. Therefore, a key assumption is that excited states can also 
be described by a local potential. This is based on the fact that the physical argument used 
for the construction of ground state potential, can also be equally applied for excited states. 
Further discussion on the method and its application could be found in [21–33].
V. CONCLUSION

A simple DFT methodology has been presented for accurate, reliable, efficient calculation of ground and excited states of neutral, positive, negative atoms. Nonrelativistic energies, excitation energies, radial densities, radial expectation values, transition wave lengths are reported and compared with the best theoretical and experimental results available till date. The work-function exchange in conjunction with a GPS scheme for the solution of resulting KS equation makes it a simple and computationally efficient route for these important challenging systems. The accuracy achieved within this single determinantal framework is quite comparable to those from more elaborate and extensive calculations available in the literature. Success and usefulness of the method has been clearly demonstrated for a wide variety of excitations from single to multiple and low to very high Rydberg resonances as well as the satellite states, hollow, doubly hollow states etc. Computed quantities show excellent agreement with literature results. Almost all of these systems are highly correlated. Since the exchange potential is treated quite accurately (almost as good as HF), a major source of error in the present work is certainly due to the inefficiency of LYP potential in incorporating the delicate and intricate correlation effects, which could be further improved or replaced by more accurate energy density functionals for better accuracy. The assumption of spherical symmetry in calculating the exchange potential could also account for partial errors as well. In other words, the rotational component of electric field may not have insignificant contribution compared to the irrotational component for these states, in general, although this usually holds true. To summarize, this work presented a current account of a simple general and efficient DFT-based method for accurate and faithful description of multiply excited atomic systems.

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