Testing an excited-state energy density functional and the associated potential with the ionization potential theorem

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Abstract
The modified local spin density (MLSD) functional and the related local potential for excited states is tested by employing the ionization potential theorem. The exchange functional for an excited state is constructed by splitting $k$-space. Since its functional derivative cannot be obtained easily, the corresponding exchange potential is given by an analogy to its ground-state counterpart. Further, to calculate the highest occupied orbital energy $\epsilon_{\text{max}}$ accurately, the potential is corrected for its asymptotic behaviour by employing the van Leeuwen and Baerends (LB) correction to it. $\epsilon_{\text{max}}$ so obtained is then compared with the SCF ionization energy calculated using the MLSD functional with self-interaction correction for the orbitals involved in the transition. It is shown that the two match quite accurately. The match becomes even better by tuning the LB correction with respect to a parameter in it.

Keywords: split $k$-space, exchange potential, modified local-density approximation, van Leeuwen–Baerends correction, atomic transition energies

(Some figures may appear in colour only in the online journal)

1. Introduction

Ground-state density functional theory (DFT) is the most widely used theory for electronic structure calculations [1–4]. The key to its success has been accurate exchange-correlation functionals $E_{\text{xc}}[\rho]$ developed over the past few decades [5–7]. The exchange-correlation potential $v_{\text{xc}}(r)$ required for the self-consistent (SCF) Kohn–Sham (KS) calculations is then obtained either by taking the functional derivative of $E_{\text{xc}}[\rho]$ or in some cases by using model potentials [8–10].

It is then natural to ask if the ground-state theory can be extended to perform self-consistent KS calculations for the density and total energy of excited states. Although time-dependent DFT is now routinely used for the calculations of excitation energies and the corresponding oscillator strengths, the theory has its limitations [11]. On the other hand, the progress of time-independent excited-state DFT (eDFT) has been slow. Some of the earlier investigations in this direction include the extension of ground-state theory to the lowest energy states of a given symmetry by Gunnarsson and Lundqvist [12, 13], Ziegler et al [14] and von Barth [15]. Subsequent works are the development of ensemble theory to excited states by Theophilou [16], Gross, Oliveira, Kohn [17, 18], and its application to study transition energies of atoms by Nagy [19]. Recently, the work by Görling [20] and Levy and Nagy [21, 22], both based on the constrained-search approach [23], rekindled interest in eDFT. Following this, Samal and Harbola explored DFT for excited states further [24–28]. In this paper we build on the work of [20–22, 24–28].

A crucial requirement for implementing eDFT is appropriate energy functionals for the excited states. These functionals should be as easy to use as the ground-state functionals and also provide a base for further improvement, e.g. by including gradient corrections. For the ground-states such a functional is provided by the local-density approximation (LDA), which is based on the homogeneous electron gas (HEG), and its spin-generalized version, the local spin-density (LSD) functional. Motivated by this, we have proposed an LDA-like functional for excited states [26]. This modified LDA (MLDA) functional is also obtained using the
HEG and its derivation follows exactly the same approach as that for obtaining the ground-state functionals. Thus it is an extension of the latter for excited states. The spin-generalization of the functional, the modified local spin-density (MLSD) functional with the self-interaction correction (MLSDSIC) functional for orbitals involved in transition has been shown to lead to accurate transition energies [26]. Encouraged by this, we have been subjecting our method of constructing the functional to more and more tests and find that it leads to functionals appropriate for excited states. Examples of these are: (i) the kinetic energy density functional constructed based on this method gives accurate kinetic energies for one-gap [29] and two-gap [30] systems, (ii) the split \( k \)-space based exchange functional leads to reliable excitation energies of two-gap systems [31]. In addition to these, accurate total energies are obtained with the inclusion of generalized gradient corrections to the MLSDSIC functional as discussed in the appendix. In the following, we test our method for the satisfaction of the ionization potential (IP) theorem.

According to the IP theorem for the ground states [32–35], the highest occupied KS orbital energy (\( \epsilon_{\text{max}} \)) for a system is equal to the negative of the IP of the system. Thus

\[
\epsilon_{\text{max}} = -I(N) \equiv E^0(N) - E^0(N-1)
\]

where \( E^0(N) \) and \( E^0(N-1) \) are the ground-state energies corresponding to \( N \) and \( N-1 \) electron systems. The difference of these energies for the \( N \) and \( N-1 \) electron system calculated self-consistently is referred to as \( \Delta \text{SCF} \). Equation (1) arises because the asymptotic decay of the electronic density of a system is related to its IP. On the other hand, for a KS system the asymptotic density is governed by \( \epsilon_{\text{max}} \), leading thereby to equation (1). The arguments for the ground state are equally applicable [21] to excited states and have also been formally extended [36, 37] to include these states. Thus for excited states [21, 36–41]

\[
\epsilon_{\text{max}} = E(N) - E(N-1)
\]

where \( \epsilon_{\text{max}} \) is the highest occupied KS orbital energy of the excited state of the \( N \)-electron system, \( E(N) \) is the energy of the excited state of the \( N \) electron system and \( E(N-1) \) is the energy of \( N-1 \) electron systems; the latter need not be [36, 37] the ground-state energy of the ionic system. The theorem has been demonstrated [21, 36, 37, 39–41] numerically in the past. Thus, if the exact functionals were known, the corresponding KS calculation will give \( \epsilon_{\text{max}} \) for \( E(N) \) and \( E(N-1) \) so that equation (1) is satisfied. However, this is not the case when approximate functionals are used. For instance, when ground-state calculations are carried out using the LSD functional, the \( \Delta \text{SCF} \) values are accurate, but the \( \epsilon_{\text{max}} \) are roughly 50% of the \( \Delta \text{SCF} \) energy or the experimental values [42]. This is due to the fact that the LDA/LSD potential decays exponentially rather than correctly as \(-1/r\) in the asymptotic range \((r \rightarrow \infty)\) for charge-neutral systems. Therefore, it is less binding for the outermost electrons.

For the ground states, it is seen that if the asymptotic behaviour of the potential is improved, \( \epsilon_{\text{max}} \) becomes close to the difference \( E^0(N) - E^0(N-1) \). Two ways of making such a correction are the van Leeuwen and Baerends (LB) [8] method and the range-separated hybrid (RSH) methods [43–48]. In the LB method, a correction term is added to the LDA/LSD potential (see equations (5) and (7)) to make the effective potential go as \(-1/r\) asymptotically, while in the RSH approach the Coulomb term is split into long-range (LR) and short-range (SR) parts. Thus, \( r^{-1} \) can be written as \( r^{-1} \text{erf}(\gamma r) + r^{-1} \text{erfc}(\gamma r) \) where \( \gamma \) is a parameter [43–48]. Here the first term is LR and approaches \( 2\gamma /\sqrt{\pi} r \) as \( r \rightarrow 0 \), while the second term is close to \( \exp(-\gamma^2 r^2) \) [49] and is SR. In the RSH approach, the LR part is treated exactly and the SR part within the LDA. Recently, Stein et al [50] applied this idea to study the band gaps for a wide range of systems. In their work, \( \gamma \) is fixed by the satisfaction of the IP theorem. Motivated by their work, we have studied the IP theorem using the LB potential. The line of our investigation is as follows: we first show that the LB potential leads to the satisfaction of the IP theorem for the ground states to a high degree of accuracy. We then ask: does our approach of constructing excited-state energy functionals give the same level of accuracy for the IP theorem for excited states when applied with the LB potential? This then provides a test for our approach. The positive results of our calculations indicate that our method may be an appropriate way of extending ground-state functionals to excited states.

The LB correction to the LDA potential is given as

\[
-\beta \rho_0^{1/3}(r) \frac{x^2}{1 + 3\beta x_r \sinh^{-1}(x_r)}
\]

where the parameter \( \beta = 0.05 \); this value is obtained by fitting [8] the LB potential so that it resembles closely with the exact potential for the beryllium atom, \( \rho_0 \) is the spin density, and \( x_r \) is a dimensionless quantity given by \( x_r = \sqrt{\frac{\rho_0}{\rho_c}} \). In the present paper, the parameter \( \beta \) is chosen to satisfy the IP theorem, in a manner similar to the work of Stein et al [50]. The difference with the work of [50] is that in the present work the potential is given entirely in terms of the density whereas in the RSH functional it is written using both the wavefunction and the density. We note that recently the LB potential has also been applied [51] to calculate satisfactorily the band gaps of a wide variety of bulk systems.

In the following section, we present the results of application of the LB potential to the ground states of several atoms. It is shown that with the help of parameter \( \beta \), the LB potential can be optimized to satisfy the IP theorem to a very high degree. The results for the ground-state set up the standard against which the excited-state results are to be judged for the functional and the corresponding potential for the excited states. After this we study the IP theorem for excited states using the LB correction in conjunction with the modified LSD potential based on the idea [52] of splitting \( k \)-space for excited states. It is shown that the IP theorem is satisfied more accurately with the modified LSD potential in comparison to the ground-state LSD expression for the potential. In addition, the modified potential has proper structure at the minimum of the radial density in contrast to the ground-state LSD potential that has undesirable features at these points [53].

Before we present our results, we point out that in our calculations, the total energies are always calculated using the LSD (for ground states) or MLSDSIC (for excited states)
functions because these give reasonably accurate \( \Delta \text{SCF} \) energy differences. Furthermore when combined with the generalized gradient corrections, they also lead to accurate total energies (see the appendix). The LB potential employed, however, is not the functional derivative of these functionals and is used only for asymptotic correction of the potential. In that sense, our calculations are only partially self-consistent.

2. Results for the ground-state IP theorem using the LB potential

In this section, we first present the ground-state exchange-only \( \epsilon_{\text{max}} \) and \( \text{SCF} \) energies obtained with the LSD and the LB potential for a few atoms. Following that, we also present the results with correlation functional included. Our calculations are performed using the central-field approximation [54] whereby the potential is taken to be spherically symmetric. The results for the ground states are not entirely new in light of some previous work [55] but it is necessary to give them here to put the new results of excited states in proper perspective.

The LDA exchange-energy functional \( E_x \) [56] for ground-state density \( \rho(\mathbf{r}) \) is given by

\[
E_x^{\text{LDA}}[\rho(\mathbf{r})] = -\frac{3}{4} \frac{\beta}{\pi} \left( \frac{2}{3} \right)^{1/3} \int \rho^{4/3}(\mathbf{r}) \, d\mathbf{r}
\]

(4)

and the corresponding potential \( v_x^{\text{LDA}} \) required for self-consistency calculations is

\[
v_x^{\text{LDA}} = - \left( \frac{3\rho(\mathbf{r})}{\pi} \right)^{1/3}.
\]

Spin generalization of the expression of equation (4), the LSD approximation, is obtained by using

\[
E_x^{\text{LSD}}[\rho_{\uparrow}, \rho_{\downarrow}] = \frac{1}{2} v_x^{\text{LDA}}[\rho_{\uparrow}] + \frac{1}{2} v_x^{\text{LDA}}[\rho_{\downarrow}],
\]

(6)

where \( \rho_{\uparrow} \) and \( \rho_{\downarrow} \) are the spin-densities corresponding to up- and down-spin electrons. The corresponding LSD potential is

\[
v_x^{\text{LSD}} = \frac{\delta E_x^{\text{LSD}}}{\delta \rho_{\uparrow}} = - \left( \frac{6\rho_{\uparrow}(\mathbf{r})}{\pi} \right)^{1/3}.
\]

(7)

In table 1, the \( \epsilon_{\text{max}} \) and \( \Delta \text{SCF} \) obtained using the LSD exchange functional equation (6) and its potential equation (7) are shown for several atoms. As is well-known and noted earlier, the LSD underestimates the highest occupied orbital energy (HO) roughly by 50%, due to incorrect asymptotic exponential behaviour of the LSD exchange potential of equation (7). The \( \Delta \text{SCF} \) energies, however, are close to the Hartree–Fock (HF) values. As stated in the previous section, \( \epsilon_{\text{max}} \) and \( \Delta \text{SCF} \) energies become consistent with each other if asymptotically the potential goes correctly as \(-1/r\). The LB potential does that.

The LB potential \( v_{x,\beta}^{\text{LB}}(\mathbf{r}) \) [8], is calculated by including the LB correction of equation (3) to the LSD potential and is given as

\[
v_{x,\beta}^{\text{LB}}(\mathbf{r}) = v_{x,\beta}^{\text{LSD}} - \beta \rho(\mathbf{r})^{1/3} \frac{\beta_x^2}{1 + 3\beta_x \sinh^{-1}(\beta_x)}.
\]

(8)

In the original LB potential, parameter \( \beta = 0.05 \). In the present work, in addition to using this value of \( \beta \), we also optimize it by the satisfaction of the IP theorem. In the latter calculation, \( \beta \) is varied until \( \epsilon_{\text{max}} \) and \( \Delta \text{SCF} \) energies match, i.e.

\[
\epsilon_{\text{max}}^\beta = E(N, \beta) - E(N - 1, \beta) = \Delta \text{SCF}.
\]

(9)

Here, \( \epsilon_{\text{max}}^\beta \) is the highest occupied eigenvalue for a specific choice of \( \beta \). The price for employing the asymptotically corrected model exchange potential is that the corresponding exchange functional is not known. Although in the past the Levy–Perdew relation [57] has been used to get the corresponding exchange-energies from the potential [55], this may not always be correct [58]. This difficulty can be circumvented by using the method of [59]. However the resulting energies are not accurate. For this reason, we use the potential above in the KS calculations but employ the LSD exchange functional for calculating the total energies and their differences. We note that the energies \( E(N, \beta) \), \( E(N - 1, \beta) \) depend on \( \beta \) implicitly via the spin-densities.

Presented in table 1 are also the results for \( \epsilon_{\text{max}} \) and \( \Delta \text{SCF} \) energies using the LB potential with \( \beta = 0.05 \) and the LB potential with optimized \( \beta \). As mentioned above, the total energies and \( \Delta \text{SCF} \) energies are calculated using the LSD functional in all the calculations. Also shown in table 1 are the \( \epsilon_{\text{max}} \) and \( \Delta \text{SCF} \) energies obtained from HF calculations [60]. Comparing the results of the LSD and LB calculations with the corresponding numbers in Hartree–Fock theory, it is evident that (i) the \( \Delta \text{SCF} \) values given by the LSD functional are reasonably close to the corresponding HF values, and (ii) using

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**Table 1. Comparison of the highest occupied eigenvalue \( \epsilon_{\text{max}} \) and the \( \Delta \text{SCF} \) energies for atoms in their ground-state calculated using different exchange-only potentials.**

| Atoms/ion         | \( \epsilon_{\text{max}} \) | \( \Delta \text{SCF} \) | \( \epsilon_{\text{max}} \) | \( \Delta \text{SCF} \) | \( \epsilon_{\text{max}} \) | \( \Delta \text{SCF} \) |
|-------------------|-----------------------------|--------------------------|-----------------------------|--------------------------|-----------------------------|--------------------------|
| He(1\(^2\) S)    | 0.517                       | 0.811                    | 0.794                       | 0.810                    | 0.064                       | 0.809                    |
| Li(2\(^1\) S)    | 0.100                       | 0.185                    | 0.175                       | 0.182                    | 0.073                       | 0.182                    |
| Be(2\(^1\) S)    | 0.170                       | 0.281                    | 0.282                       | 0.278                    | 0.043                       | 0.278                    |
| B(2\(^2\) 2\(^1\) P) | 0.120                      | 0.278                    | 0.263                       | 0.274                    | 0.075                       | 0.273                    |
| C(2\(^2\) 2\(^1\) P) | 0.196                      | 0.396                    | 0.366                       | 0.394                    | 0.104                       | 0.392                    |
| N(2\(^2\) 2\(^1\) S) | 0.276                      | 0.515                    | 0.476                       | 0.513                    | 0.112                       | 0.511                    |
| O(2\(^2\) 2\(^1\) P) | 0.210                      | 0.436                    | 0.448                       | 0.431                    | 0.035                       | 0.432                    |
| F(2\(^2\) 2\(^1\) P) | 0.326                      | 0.597                    | 0.585                       | 0.594                    | 0.060                       | 0.594                    |
| Ne(2\(^2\) 2\(^1\) S) | 0.443                      | 0.754                    | 0.724                       | 0.751                    | 0.077                       | 0.749                    |

(All the energies are in au.)
Figure 1. Plot of $\epsilon_{\text{max}}$ versus $\Delta\text{SCF}$ energies using different exchange-only potentials for various atoms in their ground-state. The parameter $\beta$ in the LB potential is set to 0.05 in this calculation.

Next, motivated by the work of [50], we tune the parameter $\beta$ in the LB potential so that $\epsilon_{\text{max}}$ matches with the $\Delta\text{SCF}$ energies. The optimized $\beta$ and the corresponding energies are also shown in table 1. As is evident, the highest orbital energy $\epsilon_{\text{max}}$ can be made to match with $\Delta\text{SCF}$ energies by choosing $\beta$ through the IP theorem.

Having presented our results for the exchange-only calculations, we next include correlation using the LSD approximation. The correlation functional we use is that parametrized by Vosko et al [61]. The orbital energies $\epsilon_{\text{max}}$ and the $\Delta\text{SCF}$ energies for the LB and $\beta$-optimized LB are presented in table 2 in comparison with the experimental results [42]. From these results, we see that with the asymptotically corrected LB potential, the IP theorem is satisfied remarkably well. Further, the match between $\epsilon_{\text{max}}$, $\Delta\text{SCF}$ and experimental results is much better when $\beta$ is tuned rather than being kept fixed.

The radial density and the exchange potential for the up-spin electron of Li ground-state obtained using the LSD approximation and the LB potentials are shown in figure 2. Also shown in figure 2 is the KLI potential [62], which is essentially the exchange potential, for comparison. It is seen that from about $r = 0.2$ au onwards, the LB potentials with both $\beta = 0.05$ and the optimized $\beta$ are quite close to the KLI potential. On the other hand, the LB potential for $r < 0.2$ au is deeper than the KLI potential. Furthermore, all three potentials go as $-1/r$ in the asymptotic regions. In contrast, the LSD potential underestimates the magnitude of...
the exact potential all over. The bump in the potential for Li is at the minimum in the radial densities [63].

Having given the results for the ground states, we now turn our attention to excited states and show that the exchange functional and potential constructed for these states by splitting the k-space for HEG give results with accuracy similar to the ground states.

3. Split k-space method for constructing excited-state energy functionals and excited-state potential

3.1. The MLSDSIC functional for excited states

In eDFT, we have proposed that excited-state energies be calculated using the MLSD functional that is developed [26, 29–31] by extending the LSD functional for the ground states. To make calculations of transition energies more accurate, the MLSD functional is combined with SIC for orbitals involved in excitations, as discussed below. We call this functional the MLSDSIC functional.

The basis of the MLSD exchange-energy functional is the split k-space method [52]. In this method, the k-space for HEG is occupied in accordance to the orbital occupation of a given excited state. In figure 3, we show an excited state, where some orbitals (core) are occupied, followed by vacant (unocc) orbitals and then again some more orbitals are occupied (shell). To construct excited-state energy functionals for such a state, the density for each point is mapped onto the k-space, also shown in figure 3, in terms of \( \rho_s, \rho_c \) and \( \rho_l \) corresponding to the electron densities of core, vacant (unocc) and the shell orbitals. Further,

\[
\rho_s(r) = \sum_{i=1}^{n_1} |\phi_i^{\text{core}}(r)|^2
\]

(13)

\[
\rho_c(r) = \sum_{i=n_1+1}^{n_2} |\phi_i^{\text{unocc}}(r)|^2
\]

(14)

\[
\rho_l(r) = \sum_{i=n_2+1}^{n_3} |\phi_i^{\text{shell}}(r)|^2
\]

(15)

where the first \( n_1 \) orbitals are occupied, \( n_1 + 1 \) to \( n_2 \) are vacant followed by occupied orbitals from \( n_2 + 1 \) to \( n_3 \). The total electron density \( \rho(r) \) is given as

\[
\rho(r) = \rho_s(r) + \rho_c(r)
\]

(16)

or

\[
\rho(r) = \rho_1(r) - \rho_2(r) + \rho_3(r)
\]

(17)

with \( \rho_1 = \rho_s, \rho_2 = \rho_c + \rho_l \) and \( \rho_3 = \rho_l + \rho_c + \rho_l \). Using this, we have constructed the kinetic [29] and exchange-energy functionals [26] for excited states that give accurate kinetic, exchange, and transition energies. In the following we describe the MLSDSIC exchange functional and its application to excited states.

We consider the class of excited-systems shown in figure 3 for which the MLDA functional is given by [26]

\[
E_{\chi}^{\text{MLDA}}[\rho] = \int \rho(r)[\epsilon(k_3) - \epsilon(k_2) + \epsilon(k_1)]dr
\]

\[
+ \frac{1}{8\pi^3} \int (k_3^2 - k_1^2)^2 \ln \left(\frac{k_3 + k_1}{k_3 - k_1}\right)dr
\]

\[
- \frac{1}{8\pi^3} \int (k_3^2 - k_2^2)^2 \ln \left(\frac{k_3 + k_2}{k_3 - k_2}\right)dr
\]

\[
+ \frac{1}{8\pi^3} \int (k_2^2 - k_1^2)^2 \ln \left(\frac{k_2 + k_1}{k_2 - k_1}\right)dr
\]

(18)
where $\epsilon(k_i) = \frac{2k_i^2}{\hbar^2}$ is the exchange-energy per particle for the ground state of HEG with Fermi wavector $k_i$. Like the ground-state functional the MLSD functional is given as

$$ E_{X}^{\text{MLSD}}[\rho] = \frac{1}{2} E_{\text{X}}^{\text{MLDA}}[2\rho_1] + \frac{1}{2} E_{\text{X}}^{\text{MLDA}}[2\rho_2]. $$ (19)

For calculation of excited-state energies, the functional above is further improved by including SIC for orbitals involved in the transition. This gives the MLSDSIC functional [26]

$$ E_{X}^{\text{MLSDSIC}} = E_{X}^{\text{MLSD}} - \sum_{i} E_{i}^{\text{SIC}} - \sum_{i} E_{i}^{\text{add}} $$ (20)

where,

$$ E_{i}^{\text{SIC}}[\phi_i] = \int \int \frac{|\phi_i(r_1)|^2|\phi_i(r_2)|^2}{|r_1 - r_2|^2} \, dr_1 \, dr_2 + E_{i}^{\text{LSD}}[\rho(\phi_i)] $$ (21)

with the summation index $i$ in equation (20) running over the orbitals from which the electrons are removed and create a gap, and the orbitals to which the electrons are added. $E_{X}^{\text{MLSD}}[\rho(\phi_i)]$ in equation (21) is the exchange energy corresponding to the $\phi_i$ orbital in the LSD approximation.

The $E_{X}^{\text{MLSD}}$ functional of equation (20) can be made more accurate by including the generalized gradient corrections in it. When this is done, not only the transition energies but also the total energies for excited states become quite close to their Hartree–Fock counterparts. This is discussed in detail in the appendix, where the Becke [5] and Perdew-Wang [64] generalized gradient-correction are added to the MLSDSIC functionals to get total energies.

The potential $v_{i}^{\text{MLSD}}$ associated with the MLSD functional of equation (19) is given as

$$ v_{i}^{\text{MLSD}}(r) = \frac{\delta E_{X}^{\text{MLSD}}[\rho]}{\delta \rho_{\phi_i}(r)}. $$ (22)

However, it has not been possible to get a workable analytical expression for $v_{i}^{\text{MLSD}}(r)$ from equations (19) and (22). Therefore on the basis of arguments based on ground-state theory, in the next subsection, we model the potential. For completeness we note the earlier attempts to construct accurate excited-state potentials by Gaspar [65] and Nagy [66]. They have given an ensemble averaged exchange potential for excited states and using this potential, they calculate excitation energy for single electron excitations. In the next subsection we propose an excited-state LSD-like exchange potential based on split $k$-space. This potential is similar to its ground-state LSD counterpart. We refer to this as the MLSD potential. We further correct the potential for its asymptotic behaviour with the LB correction. With the asymptotically corrected MLSD potential, we show that the IP theorem for excited states is satisfied to a good accuracy.

### 3.2. Generalization of Dirac exchange potential for excited states using split k-space

The Hartree–Fock exchange potential for the $i$th occupied orbital $\phi_i(r)$ for a system of electrons is given by

$$ v_{i,j}^{\text{HF}} = v_i(\phi_i) = - \sum_j \int \frac{\phi_j^*(r') \phi_j(r') \phi_i(r)}{\phi_i(r')|r-r'|} \, dr'. $$ (23)

where summation $j$ is over all the occupied orbitals $\phi_j$. For the HEG, the wavefunction is given by

$$ \phi_k(r) = \frac{1}{\sqrt{V}} e^{i(k \cdot r)}. $$ (24)

where $V$ is the volume of the system. Using this form of the wavefunction in equation (23) we get the exchange potential (for $k > k_2$)

$$ v_{i}(k) = - \frac{1}{\pi} \left[ k_1 - k_2 + k - \frac{k_1^2 - k_2^2}{2k} \ln \frac{k + k_1}{k - k_1} \right] $$

$$ - \frac{k_1^2 - k_2^2}{2k} \ln \frac{k + k_2}{k - k_2} + \frac{k_2^2 - k_1^2}{2k} \ln \frac{k + k_1}{k - k_1} $$ (25)

for $\phi_k(r)$ in the one-gap systems shown in figure 3, where $k_1, k_2$ and $k_3$ are given by equations (10)–(12).

This potential is orbital dependent. To make it an orbital-independent potential of KS theory for excited states, we draw the analogy from the ground-state exchange potential in the LDA. The LDA potential of equation (5) is the Hartree–Fock exchange potential corresponding to the highest occupied orbital (HOMO) of the HEG of density $\rho(r)$. Thus in excited states too, we take the potential for the electron in HOMO of HEG in excited state (figure 3(b)) as the exchange potential for all the electrons. For this we put $k = k_3$ in equation (25) and get the following expression for the MLDA potential

$$ v_{i}^{\text{MLDA}} = - \frac{k_3}{\pi} \left[ 1 - x_2 - \frac{1}{2} \left( 1 - x_1^2 \right) \ln \frac{1 + x_1}{1 - x_1} \right] $$

$$ + \frac{1}{2} \left( 1 - x_1^2 \right) \ln \left| \frac{1 + x_1}{1 - x_1} \right| $$ (26)

where, $x_1 = \frac{k_1}{k_3}, x_2 = \frac{k_2}{k_3}$. To get the MLSD potential $v_{i}^{\text{MLSD}}$ for spin-densities $\rho_1, \rho_2$ and $\rho_3$ in equation (26) are calculated with the spin-densities $2\rho_{1,\sigma}, 2\rho_{2,\sigma}, 2\rho_{3,\sigma}, \rho_{1,\sigma}, \rho_{2,\sigma}$ and $\rho_{3,\sigma}$ are related to the core-, vacant- and shell-orbitals (see equations (13)–(15)).

The MLSD potential corresponding to equation (26) is also obtained by taking the functional derivative of the exchange functional $E_{X}^{\text{MLSD}}$ of equation (19) with respect to $\rho_\sigma(r)$, corresponding to the largest wave-vector in the $k$-space. Thus, we reach the same result from two different paths; this in some sense assures us about the adequacy of the approach taken. When this potential is corrected for its asymptotic behaviour by adding the LB gradient term of equation (3) corresponding to largest wave-vector $k_3$, we obtain the modified LB (MLB) potential

$$ v_{i}^{\text{MLB}} = v_{i}^{\text{MLSD}} - \beta \rho^{1/3}(r) \frac{x_{1,\sigma}^2}{1 + \frac{1}{3} \beta x_{1,\sigma} \sinh^{-1}(x_{1,\sigma})}. $$ (27)

In the following section, we test the MLB potential using the IP theorem for excited states and show that it satisfies the IP theorem as accurately as the LB potential does for the ground states. On the other hand, the LB potential of equation (8) does not satisfy the IP theorem that well. This indicates that the potential derived on the basis of splitting $k$-space is more appropriate for excited-state calculations.
4. Results for excited states

In performing self-consistent calculations for atoms, the MLB potential of equation (27) is employed as the exchange potential in the excited-state KS equations. Like the ground states, calculations for excited states are also performed using the central-field approximation [54]. Having obtained the orbitals and the corresponding densities, we calculate the total energy for an excited state as has been described in section 3.1.

We have considered systems for which both the atomic excited states and its ionic states can be represented by a single Slater determinant; this is done because LSD/MLSDSIC excited states and its ionic states can be represented by a single Slater determinant; this is done because LSD/MLSDSIC exchange-only potentials of LB, MLB and HF for various atoms in table 3 for comparison. We first note that the MLB potential gives \( \varepsilon_{\text{max}} \) which are smaller in magnitude in comparison to those given by LB and for majority of cases are closer to the \( \Delta \text{SCF} \) values. This indicates that the MLB potential is better than the LB potential in this respect. Furthermore, it is evident that the \( \Delta \text{SCF} \) values and \( \varepsilon_{\text{max}} \) energies obtained from the MLB potential are reasonably close to the corresponding \( \Delta \text{SCF} \) values given by HF theory. The results of table 3 are shown graphically in figure 4. The figure shows that the MLB potential satisfies the IP theorem accurately while the LB and HF both deviate from it. Thus accounting for the occupation of orbitals in the \( k \)-space gives better results for the theorem. The satisfaction of the IP theorem can be made more accurate by tuning \( \beta \). This is also shown in table 3. Finally, it is noted that \( \varepsilon_{\text{max}} \) and \( \Delta \text{SCF} \) of HF theory match with each other quite well when the \( (N-1) \) electron state is the ionic ground-state but not in other cases.

![Figure 4](image-url)
the KLI potential for the ground-states. The LB potential for the excited states, on the other hand, is not close to the exact potential and has an unphysical negative spike at the minimum of radial density which is not present in the MLB potential. Similar unsmooth behaviour of the potential is observed [53] in the LSD potential. This behaviour is due to the excited-state density being very small in the intershell regions. Thus it is clear that the exchange potentials obtained on the basis of split $k$-space give a much better description of an excited-state than the ground-state LB potential. Finally we note that for the ground-states the LDA potential fails to improve substantially. Hence the excited-state functionals and potentials derived by splitting $k$-space functional are close to the experimental values [68]. Also shown in table are energies calculated by tuning $\beta$ to satisfy the IP theorem. Like in the exchange-only case ($B(4p^{1}2P)$) here also $\beta$ cannot be found to satisfy the IP theorem.

We now include correlation and compare our results with experiments [68]. The lack of correlation potential for excited-states forces us to rely on the ground-state potential. In table 4 are the results of calculations performed using the ground-state VWN potential added to the MLB potential. It is seen that similar to the ground-state, the $\Delta$SCF energies obtained with the split $k$-space functional are close to the experimental values [68].

5. Concluding remarks

The ground-state density functional theory is a well established theory with accurate functionals for exchange and correlation energies. Excited-state DFT, on the other hand, is being explored over the past decade or so. A question that we have been addressing in this connection is if ground-state functionals can be easily generalized to excited states. Our investigations indicate that the simplest ground-state functional, the LDA functional, can be extended to excited states by splitting the $k$-space according to the orbital occupation in a system. The functional thus generated, when combined with self-interaction correction for the orbitals involved in transition, leads to accurate transition energies. However, for the ground-states the LDA potential fails to give proper eigenenergies for the highest occupied orbitals because of its incorrect asymptotic structure. When the latter is improved by including the van LB correction, the eigenvalues improve substantially. Hence the excited-state functionals and potentials derived by splitting $k$-space is a possible way of extending ground-state functionals to excited states. In this paper we have demonstrated that this is indeed the case by showing that (i) inclusion of generalized gradient correction

Table 4. Comparison of the highest occupied eigenvalue $\epsilon_{\text{max}}$ and the $\Delta$SCF energies for atoms in various excited states calculated using MLB exchange-only potential with VWN correlation potential with the experimental values. The numbers in the second and third column are obtained with $\beta = 0.05$ in equation (27) while those in column 5 are obtained by optimizing $\beta$. The corresponding $\beta$ values are given in column 4. (All the energies are in au.)

| Atom                | $-\epsilon_{\text{max}}$ | $\Delta$SCF | $-\epsilon_{\text{max}}$ (= $\Delta$SCF) | Expt [68] |
|---------------------|---------------------------|-------------|------------------------------------------|-----------|
| Li(2p$^{1}$3s$^{1}2P$) | 0.110 0.128               | 0.230 0.127  | 0.230 0.127                               | 0.130     |
| B(2s$^{2}$2p$^{5}2D$) | 0.214 0.252               | 0.600 0.247  | 0.257                                     |           |
| C(2s$^{2}$2p$^{5}2D$) | 0.262 0.300               | 0.500 0.295  | 0.318                                     |           |
| N(2s$^{1}$2p$^{4}$4P) | 0.308 0.344               | 0.350 0.339  | 0.348                                     |           |
| O(2s$^{2}$2p$^{6}$3P) | 0.453 0.441               | 0.040 0.442  | 0.471                                     |           |
| F(2s$^{2}$2p$^{5}$2S) | 0.594 0.604               | 0.056 0.600  | 0.623                                     |           |
| Ne$(^{2}S^{1}2p^{6}2S)$ | 1.409 1.444               | 0.080 1.443  | 1.442                                     |           |
| Li(3s$^{1}$3p$^{1}$2S) | 0.079 0.081               | 0.060 0.081  | 0.074                                     |           |
| Li(4s$^{1}$3s$^{1}2S$) | 0.042 0.046               | 0.122 0.046  | 0.039                                     |           |
| B(3s$^{1}$3p$^{1}$2S) | 0.123 0.136               | 0.200 0.136  | 0.122                                     |           |
| B(4p$^{1}$3P)       | 0.079 0.099               | – –         | 0.083                                     |           |
| Be(2s$^{1}$3s$^{1}$3S) | 0.107 0.112               | 0.082 0.112  | 0.105                                     |           |
to MLSDSIC functional gives accurate total energies for excited states, and (ii) improvement of the asymptotic structure of the MLSD potential for excited states gives eigenvalues for the highest occupied orbitals that satisfy the ionization potential theorem well. We therefore conclude that the method of splitting $k$-space may be the way forward to construct functionals for excited states.

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Appendix. Generalized gradient-corrected exchange-energy functionals

The MLSDSIC exchange-energy functional for excited states with Becke’s gradient correction [5] is given as,

$$
e_{\text{MLSDSIC(Becke)}}(\mathbf{r}) = \epsilon_{\text{MLSD}}(\mathbf{r}) - \epsilon_{\text{SIC}}(\mathbf{r})$$

where $\epsilon_{\text{MLSD}}(\mathbf{r})$ is the MLSD exchange-energy functional as given by equation (19), and $\epsilon_{\text{SIC}}(\mathbf{r})$ is the self-interaction correction for orbitals involved in transition given by equation (21). Here the parameter $\gamma = 0.0042$. Similarly the exchange-energy functional for excited states with Perdew–Wang’s (PW) gradient correction [64] is given as

$$
e_{\text{MLSDSIC(PW)}}(\mathbf{r}) = \int \epsilon_{\text{MLSD}}(s) \, d\mathbf{r} - E_{\text{SIC}}$$

References

[1] Parr R G and Yang W 1989 Density-Functional Theory of Atoms and Molecules (International Series of Monographs on Chemistry vol 16) (New York: Oxford University Press)
[2] Dreizler R M and Gross E K U 1990 Density-Functional Theory: an Approach to the Quantum Many-Body Problem (New York: Springer)
[3] March N H 1992 Electron Density Theory of Atoms and Molecules (Theoretical Chemistry Series) (London: Academic)
[4] Engel E and Dreizler R M 2011 Density Functional Theory: an Advanced Course (Theoretical and Mathematical Physics) (Berlin: Springer)
[5] Becke A D 1988 Phys. Rev. A 38 3098
[6] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[7] Perdew J P, Burke K and Ernzerhof M 1997 Phys. Rev. Lett. 78 1396 (erratum)
[8] van Leeuwen R and Baerends E J 1994 Phys. Rev. A 49 2421
[9] Umezawa N 2006 Phys. Rev. A 74 032505
[10] Becke A D and Johnson E R 2006 J. Chem. Phys. 124 21101
[11] Ullrich C A 2012 Time-Dependent Density-Functional Theory: Concepts and Applications (Oxford Graduate Texts) (New York: Oxford University Press)
[12] Gunnarsson O and Lundqvist B I 1976 Phys. Rev. B 13 4274
[13] Gunnarsson O and Lundqvist B I 1977 Phys. Rev. B 15 6006
[14] Ziegler T, Rauk A and Baerends E J 1979 Theor. Chim. Acta 43 261
[15] von Barth U 1979 Phys. Rev. A 20 1693
[16] Theophiloou A K 1979 J. Phys. C: Solid State Phys. 12 5419
[17] Gross E K U, Oliveira L N and Kohn W 1988 Phys. Rev. A 37 2809
[18] Oliveira L N, Gross E K U and Kohn W 1988 Phys. Rev. A 37 2821
[19] Nagy Á 1996 Phys. Rev. A 53 3660
[20] Görling A 1999 Phys. Rev. A 59 3359

Table A1. Total energy and excitation energy of various atoms/ions using the generalized gradient-corrected MLSDSIC functionals of equations (A.1), (A.2).

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

For the total energy calculations, either the LSD or MLSD potential is used for solving the excited-state KS equations and the total energies are obtained using the exchange-energy functionals (equations (A.1), (A.2)) above. The total energies thus obtained are shown in table A1 along with their HF counterparts. It is clear from the table that the total energies obtained with these functionals are close to their HF values. Also shown in the table are the $\Delta$SCF energies obtained using these functionals. The $\Delta$SCF energies are comparable to the exact HF results. Thus, using the MLSDSIC functional with the generalized gradient-corrected functionals gives not only accurate transition energies but also equally accurate total energies.
