Excited-state density functional theory

Manoj K. Harbola¹, M. Hemanadhan¹, Md. Shamim¹, P. Samal²
¹Department of Physics, Indian Institute of Technology, Kanpur 208016, India
²Department of Physics, National Institute of Science Education and Research, Bhubaneswar 751005, India
E-mail: mkh@iitk.ac.in

Abstract. Starting with a brief introduction to excited-state density functional theory, we present our method of constructing modified local density approximated (MLDA) energy functionals for the excited states. We show that these functionals give accurate results for kinetic energy and exchange energy compared to the ground state LDA functionals. Further, with the inclusion of GGA correction, highly accurate total energies for excited states are obtained. We conclude with a brief discussion on the further direction of research that include the construction of correlation energy functional and exchange potential for excited states.

1. Introduction

Over the past few years, efforts to develop excited-state time-independent density functional theory have started to come to fruition. It has been shown [1, 2] that the energy for excited states can be written as a bi-functional $E[\rho, \rho_0]$ where $\rho, \rho_0$ are the corresponding excited- and ground-state densities. On the other hand, while accurate functionals for ground-states have been developed, construction of corresponding functionals for excited-states remains a challenge. An ad hoc approach has been to employ the ground-state functionals to calculate the energy for excited states [3, 4]. However this is not the correct approach both conceptually as well as from the point of view of the accuracy of results obtained.

We have been investigating various aspects of time-independent DFT over the past several years. We have studied the mapping [2, 5] of the excited-state density to the corresponding wave-function; to a non-interacting system (the Kohn-Sham system) and have developed modified local density approximate (MLDA) functionals for excited states by splitting $k$-space for the homogeneous electron gas (HEG). In the following we first describe how an excited-state density is mapped to the corresponding wave-function. We then discuss our method of constructing excited-state functional and present the corresponding results.

2. Expressing excited-state energy as a bi-functional

Since the inception of density-functional theory, it is well known that the Hohenberg-Kohn theorem [6, 7] does not apply to excited states. The first step towards developing excited-state density functional theory is therefore to establish a map from the excited-state density $\rho(\mathbf{r})$ to the corresponding wave-function $\Psi[\rho]$. This can be done by using the constrained-search approach [8], as proposed by Görling [9] and Levy-Nagy [1]. The mapping was studied in detailed by us [2]. Thus $\Psi$ is the wave-function that gives $\rho(\mathbf{r})$ and minimizes the expectation value $\left\langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \right\rangle$. Here $\hat{T}$ and $\hat{V}_{ee}$ are the kinetic energy and electron-electron interaction.
energy operators respectively. This defines the bi-functional $F[\rho, \rho_0] = \min_{\Psi} \langle \Psi | T + V_{ee} | \Psi \rangle$. Here $\rho_0$ is the ground-state density. The dependence on $\rho_0$ arises because $\Psi$ is constrained to be orthogonal to all lower state wave functions ($\Psi_0, \cdots, \Psi_{k-1}$) given by $\rho_0$. Therefore, energy $E$ for excited states becomes a bi-functional of excited state density $\rho$ and ground state density $\rho_0$, i.e.

$$E[\rho, \rho_0] = F[\rho, \rho_0] + \int \rho(r)v(r)\,dr$$

(1)

where $v(r)$ is the external potential. For further details see [2], [10] and [12]. In a similar manner, an excited-state density can also be mapped to a non-interacting system (the Kohn-Sham system). For details we refer the reader to reference [2]. In this paper our main focus is on energy functionals for excited-states.

3. Excited-state functional obtained by splitting $k$-space

When energy functionals constructed for ground states are applied to excited states, the results obtained are not accurate [11, 12, 13, 14]. To obtain functionals for excited states, we need to incorporate some more information about the excited state in addition to its density. For most of the ground-state functionals local density approximation (LDA) is the zeroth order approximation. This is based on the energy for HEG. Therefore, we begin by constructing the LDA functional for an excited-state by considering the excited state of HEG.

The orbital occupation for an excited-state configuration and the corresponding $k$-space occupation of HEG is shown in Fig. 1. The latter has plane-wave orbitals from $k = 0$ to $k = k_1$ occupied, orbitals from $k = k_1$ to $k = k_2$ unoccupied and orbitals from $k = k_2$ to $k = k_3$ again occupied; This then is the split $k$-space for an excited state with one gap in occupation of orbitals. We utilize this information to construct LDA functionals for excited states.

![Figure 1](image.png)

Figure 1. (a) Orbital occupation of electrons (b) the corresponding $k$-space occupation of HEG, in the excited-state configuration of a one-gap system

The values of $k_1$, $k_2$ and $k_3$ are calculated from the densities of electrons in the true system using the following relations [15]:

$$k_1^3 = 3\pi^2 \rho_1$$

(2)

$$k_2^3 = 3\pi^2 \rho_2$$

(3)

$$k_3^3 = 3\pi^2 \rho_3$$

(4)

where, $\rho_1$ is the core density, $\rho_2$ the sum of the core density and the density corresponding to unoccupied orbitals in the range $k_1$ to $k_2$ and $\rho_3$ is the sum of the core, the unoccupied and the shell orbital densities between $k_2$ and $k_3$.  


We now use these wave-vectors to get the exchange and kinetic energy functionals for excited states with one set of unoccupied orbitals shown in Fig 1.

4. Excitation energy calculations

In this section we present our calculations of excited-states. In Section 4.1, we introduce the modified local density approximation (MLDA) and in Section 4.2, results of exchange only calculations using this functional are presented. In Section 4.3, we combine MLDA exchange with the LDA correlation functional to calculate the energy required to remove an electron from the inner core of the chromium, manganese and the iron atoms.

4.1. Modified local density approximation (MLDA) for excited-state exchange energy

Exact exchange energy in Hartree-Fock theory for a set of occupied orbitals is given as,

\[ E^X = -\frac{1}{2} \sum_{\sigma} \sum_{i}^{occ} \sum_{j}^{occ} \left( \phi_{i\sigma}(\mathbf{r}_1)\phi_{j\sigma}(\mathbf{r}_2) \bigg| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \bigg| \phi_{j\sigma}(\mathbf{r}_1)\phi_{i\sigma}(\mathbf{r}_2) \right) \]  

where \( \sigma \) runs over up- and down-spins, and for HEG \( \phi \)'s are plane waves,

\[ \phi = \frac{1}{\sqrt{V}} e^{i\mathbf{k} \cdot \mathbf{r}} \]  

where \( V \) is the volume over which the periodic boundary conditions are applied on the wave-function. Integrating Eq. (5) over \( k \) we get the following expression for exchange energy functional for the kind of excited states shown in Fig 1.

\[ E^{MLDA}_X = \int \rho(\mathbf{r}) [\epsilon(k_3) - \epsilon(k_2) + \epsilon(k_1)] \, d\mathbf{r} + \frac{1}{8\pi^3} \int (k_3^2 - k_1^2)^2 \ln \left( \frac{k_3 + k_1}{k_3 - k_1} \right) \, d\mathbf{r} \]

\[ - \frac{1}{8\pi^3} \int (k_2^2 - k_3^2)^2 \ln \left( \frac{k_3 + k_2}{k_3 - k_2} \right) \, d\mathbf{r} - \frac{1}{8\pi^3} \int (k_2^2 - k_1^2)^2 \ln \left( \frac{k_2 + k_1}{k_2 - k_1} \right) \, d\mathbf{r} \]  

(7)

Here \( \epsilon(k) = -\frac{3k^2}{2\pi} \) is the exchange energy per electron for the HEG in its ground-state with the Fermi wave-vector equal to \( k \). With \( k_1 = k_2 \) this functional reduces to ground state LDA approximation.

For the spin dependent generalization, the modified local spin density (MLSD) approximation of this functional is given by

\[ E^{MLSD}_X[\rho_{\alpha}, \rho_\beta] = \frac{1}{2} E^{MLDA}_X[2\rho_{\alpha}] + \frac{1}{2} E^{MLDA}_X[2\rho_\beta] \]  

(8)

To further improve the functional, self-interaction correction (SIC) is made to the functional above for the orbitals which are involved in transition and create a gap [13]. Then the self-interaction correction MLSD functional \( E^{MLSDSIC}_X \) is given as

\[ E^{MLSDSIC}_X = E^{MLSD}_X - E^{SIC}_X[\phi_{rem}] - E^{SIC}_X[\phi_{add}] \]  

(9)

where

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

(10)

where \( \phi_{rem} \) corresponds to the orbital from which electrons have been removed and \( \phi_{add} \) where the electrons are added and \( \rho(\phi) \) is the orbital density for the orbital \( \phi \).
4.2. Exchange-only calculations

We have used the MLSDSIC functional to calculate exchange energy of excited states with one gap. We have applied this functional to calculate excitation energy of atoms at the exchange only. Our calculation is of $\Delta SCF$ type. We do Kohn-Sham calculation with the Dirac exchange potential [16] for both the ground and excited states. The calculation are performed using the Hermann-Skillman program [17] and are therefore fully self-consistent. To calculate exchange energy for excited states we input the $k$ values calculated from the orbitals generated in excited state Kohn-Sham calculation into the functional of equation Eq. (9). The difference between the excited-state and ground-state energies then gives the excitation energies. We present in Table 1 excitation energy for a few cases where a 3s electron is transferred to a 3p level leaving a gap in 3s orbitals [11]. The numbers obtained by us are compared with those of Hartree-Fock theory. We have also given in the table results of the ground-state LDA and time-dependent density functional theory calculations [18, 19]. The accuracy of the results given in Table 1 shows that the MLSDSIC functional proposed for exchange energy shows the correctness of the physics invoked to construct this functional.

Next we apply this functional coupled with the ground-state LDA correlation energy functional to calculate energies required to remove an electron from the inner core of chromium, manganese and iron atoms.

4.3. Calculation with LDA correlation

When an electron is removed from the inner core of an atom, it leaves the resulting ion in a excited-state. Such states are formed [20] when atoms are exposed to high intensity radiation coming from synchrotron radiation sources. We now calculate the energy of such a process by using the $\Delta SCF$ method. In Table 2 we present the results of our calculations. The ground state energy is calculated by the LSD calculation including both the exchange and correlation energies as parametrized by Gunnarsson and Lundquist [21]. The excited state energy is obtained by applying MLSDSIC for the exchange energy of the excited states with the correlation energy being calculated using the ground state LSD functional for it. These results are compared with the results [22] of multi-configuration Dirac-Fock (MCDF) calculations and experimental investigations [22]. It is evident from the table that the LSD calculations underestimate the energy by about 10 % while the use of the MLSDSIC functional gives results that are close to experimental numbers.

With the success of constructing the excited state exchange energy functional, we ask ourselves whether the method of splitting $k$-space for constructing the excited state functional is general ? In the next section, we show that this is so by constructing the excited-state kinetic energy functional. The accuracy obtained with these constructed excited kinetic energy functionals for excited-states is similar to that of the ground-state functionals for the ground-
Table 2. Energy required to remove an electron from the inner core of the chromium, manganese and the iron atoms. The numbers obtained with different calculations as well as the experimental numbers are given in eV. The percentage difference from the experimental numbers is also given in the brackets.

| ion(state)          | $\Delta E_{LSD}$ [13] | $\Delta E_{MLSDSIC}$ [13] | $\Delta E_{MCDF}$ [22] | $\Delta E_{EXPT}$ [22] |
|---------------------|-----------------------|-----------------------------|-------------------------|------------------------|
| $Cr^+(3s3p^33d^5(7S)4s^8S)$ | 74.6( 4.6)            | 81.6(4.3)                   | 79.4(1.5)               | 78.2                   |
| $Cr^+(3s3p^33d^5(7S)4s^6S)$ | 76.1( 9.2)            | 84.2(0.5)                   | 81.4(2.9)               | 83.8                   |
| $Cr^+(3s3p^33d^5(5S)4s^6S)$ | 79.5(17.0)            | 88.0(8.5)                   | 92.1(4.3)               | 96.2                   |
| $Mn^+(3s3p^63d^44s^27S)$ | 87.5( 5.7)            | 95.0(2.3)                   | 93.4(0.6)               | 92.8                   |
| $Mn^+(3s3p^63d^54s^25S)$ | 92.7( 6.6)            | 101.9(2.6)                  | 99.9(0.0)               | 99.3                   |
| $Mn^+(3s^23p^53d^6(6S)4s^25P)$ | 63.4(15.5)           | 73.0(2.7)                   | 75.3(0.0)               | 75.0                   |
| $Fe^+(3s3p^63d^44s^26D)$ | 96.3( 6.4)            | 106.1(3.1)                  | 101.3(0.2)              | 102.9                  |
| $Fe^+(3s3p^63d^54s^24D)$ | 100.7( 7.3)           | 112.0(3.0)                  | 110.9(2.0)              | 108.7                  |

state kinetic energies.

5. Kinetic energy functional
The non-interacting kinetic energy for the excited states in terms of Kohn-Sham orbitals is given as $\sum_i f_i \langle \phi_i | -\frac{1}{2} \nabla^2 | \phi_i \rangle$ where $f_i$ represents the occupation of $i$th orbital

The ground-state kinetic energy functional up to second-order in the gradient $\nabla \rho$ of the density $\rho$ is given as

$$T[\rho] = T_s^{(0)}[\rho] + T_s^{(2)}[\rho]$$ (11)

where

$$\rho = \rho_1 - \rho_2 + \rho_3$$ (12)

$$T_s^{(0)}[\rho] = \frac{1}{10\pi^2} \int k_F^5(r) dr$$
$$= \frac{3}{10} (3\pi^2)^{\frac{5}{3}} \int \rho^{\frac{5}{3}}(r) dr$$ (13)

is the Thomas-Fermi kinetic energy functional with $k_F(r) = (3\pi^2 \rho(r))^{1/3}$ and

$$T_s^{(2)}[\rho] = \frac{1}{72} \int \frac{|\nabla \rho(r)|^2}{\rho(r)} dr$$ (14)

is the second-order gradient correction.

The split $k$-space based kinetic energy functional for the one-gap systems up to the second order in density gradient $|\nabla \rho|$ is [23]

$$T = \sum_{i,\text{core}} \langle \phi_i | -\frac{1}{2} \nabla^2 | \phi_i \rangle + \sum_{i,\text{shell}} \langle \phi_i | -\frac{1}{2} \nabla^2 | \phi_i \rangle$$
$$\approx T^{* (0)} + T^{* (2)}$$ (15)
Table 3. Exact kinetic energies (in atomic units) of excited states of some atoms compared
with the corresponding approximate kinetic energies [14] calculated by applying ground-state
functionals of Eqs. (13) and (14) and the excited state functionals of Eqs. (16), (17) and (18).

| Atom          | ZEROTH ORDER | SECOND ORDER |
|---------------|--------------|--------------|
|               | $T^{(0)}$    | $T^{(0)} + T^{(2)}$ | $T^{(0)} + T^{(2)}$ |
| $Be(1s^22s^02p^33s^2)$ | 12.278 12.459 13.768 13.945 13.768 | |
| $O(1s^22s^02p^6)$       | 64.154 67.545 73.094 73.704 70.068 | |
| $Ne(1s^22s^02p^63s^2)$  | 109.521 116.152 124.508 125.947 118.891 | |
| $Mg(1s^22s^02p^63s^23p^2)$ | 169.083 180.095 191.942 194.392 182.740 | |
| $Ar(1s^22s^02p^63s^23p^64s^2)$ | 443.200 474.671 501.507 507.648 474.770 | |

where,

$$T^{*\text{unpol}}[k_1,k_2,k_3] = \frac{1}{10\pi^2} \int \left( k_1^5(r) - k_2^5(r) + k_3^5(r) \right) dr$$

(16)

and,

$$T^{*\text{unpol}}^{(2)} = \frac{1}{72} \int \frac{\left| \nabla \rho_1(r) \right|^2}{\rho_1(r)} dr - \frac{1}{72} \int \frac{\left| \nabla \rho_2(r) \right|^2}{\rho_2(r)} dr + \frac{1}{72} \int \frac{\left| \nabla \rho_3(r) \right|^2}{\rho_3(r)} dr$$

(17)

where the subscript ‘unpol’ refers to a system with equal number of spin up and spin down
electrons. For unequal spin densities the functional is given as,

$$T^*[\rho_\alpha, \rho_\beta] = \frac{1}{2} (T^*[2\rho_\alpha] + T^*[2\rho_\beta])$$

(18)

where $\rho_\alpha$ and $\rho_\beta$ denote the density of the up and the down spin electrons, respectively.

Results obtained with this kinetic energy functional for some excited states [14] with one gap
are presented in Table 3, where we compare the kinetic energies for excited states calculated
using Eqs. (16), (17) and (18) with the exact Kohn-Sham kinetic energies obtained by solving the
Kohn-Sham equation with Gunnarsson-Lundquist parametrization [21] of the LSD for exchange
correlation energy. The densities used in Eqs. (16), (17) and (18) above are the ones obtained
from the Kohn-Sham calculations done for the exact kinetic energy. Also shown in Table 3 are
the corresponding energies calculated from the ground state kinetic energy functional $T^{(0)}$ of
Eq. (13) and its gradient correction $T^{(2)}$ of Eq. (14) using the same densities. As is evident from
the Table 3, the ground state based functionals underestimate the exact kinetic energies by a
large amount whereas the proposed functional reduces the error significantly. This points to the
correctness of physics invoked to construct the functionals.

The functional for the exchange and the kinetic energies discussed above are for excited states
with one gap. They are easily extended to excited states with more than one gap leading to
equally accurate results for these states. For further details the readers may refer to [13, 23].

6. Response function analysis

The exchange and kinetic energy functionals are accurately constructed based on split $k$-space as
mentioned above in Section 4.1 and 5, where excited energy $E$ is written in terms of $\rho_1, \rho_2, \rho_3$ i.e
$E[\rho_1, \rho_2, \rho_3]$. Now we ask ourselves if it is necessary to write energy in terms of $\rho_1, \rho_2, \rho_3$ or it can
be written in terms of density $\rho = \rho_1 - \rho_2 + \rho_3$ only. In this section, we show through response
function analysis [23] that writing excited-state energy in terms of $\rho$ is not as easy as it is for
the ground-state energy. To show this, we first write the response function for non-interacting
HEG under a perturbation \( v(\mathbf{r}) \) and expand it to calculate the changes in the kinetic energy functional. The response function for excited system of Fig. 1 is given by

\[
\chi_G^{(0)}(k_1, k_2, k_3; \mathbf{q}) = \chi_G^{(0)}(k_1; \mathbf{q}) - \chi_G^{(0)}(k_2; \mathbf{q}) + \chi_G^{(0)}(k_3; \mathbf{q})
\]  

(19)

where \( \chi_G^{(0)}(k; \mathbf{q}) \) is the response function for the ground state with Fermi wave vector \( k \) and is given as

\[
\chi_G^{(0)}(k; \mathbf{q}) = -\frac{1}{\pi^2 q} \left[ \frac{q k}{2} + \left( \frac{k^2}{2} - \frac{q^2}{8} \right) \ln \left| \frac{q + 2k}{q - 2k} \right| \right]
\]  

(20)

The corresponding excited-state kinetic energy functional up to the second-order in \( \nabla \rho \) is obtained by expanding the response function in Eq. (19) up to order \( q^2 \) and gives:

\[
T[\rho(\mathbf{r})] = T^{(0)}[\rho] + \frac{\pi^2}{2} \int \frac{\Delta \rho(\mathbf{r})^2}{(k_1 - k_2 + k_3)} d\mathbf{r} + \frac{\pi^2}{24} \int \frac{\nabla \rho(\mathbf{r})^2}{(k_1 - k_2 + k_3)^2} \left[ \frac{1}{k_1} - \frac{1}{k_2} + \frac{1}{k_3} \right] d\mathbf{r}
\]  

(21)

where \( \Delta \rho(\mathbf{r}) \) is the change in the density due to \( v(\mathbf{r}) \) and \( \nabla \rho(\mathbf{r}) \) is the gradient of the density.

The second term in the expression above \( \frac{\delta T^{(0)}[\rho]}{\delta \rho(\mathbf{r})} \delta \rho(\mathbf{r}) \) is identified as the second-derivative of functional \( T^{(0)} \) of Eq. 16. It is clear from Eq. 21 that this derivative cannot be written in terms of \( \rho = \rho_1 - \rho_2 + \rho_3 \) alone. The third term above is identified as the gradient correction to the kinetic energy up to the second order in \( \nabla \rho \). In the asymptotic limit \( (r \to \infty) \)

\[
k_3 \sim \exp \left( -\frac{2}{3} (2\varepsilon_{max})^{1/2} r \right)
\]

where \( \varepsilon_{max} \) is the highest occupied orbital energy [24]. For excited states \( k_1 < k_2 < k_3 \) so the gradient term in asymptotic limit is proportional to \( \frac{\nabla \rho_3(\mathbf{r})^2}{k_1 k_3} \sim \frac{k_3}{k_1} \). In terms of orbital energies \( \varepsilon_1, \varepsilon_2, \varepsilon_3 \) corresponding to \( k_1, k_2 \) and \( k_3 \), this is given by \( \exp \left[ \frac{2}{3} \sqrt{\varepsilon_1 - 4\varepsilon_2} r \right] \). Since, \( |\varepsilon_1| > |\varepsilon_2| > |\varepsilon_3| \), the lowest-order gradient term diverges in the asymptotic limit for \( |\varepsilon_1| > 16 |\varepsilon_3| \) if we insist on expanding the kinetic energy functional in terms of the density.

The above analysis shows that it may not be easy to expand the kinetic energy functional for excited-states beyond the zeroth-order in terms of the total excited-state density. This difficulty is easily circumvented if we employ \( \rho_1, \rho_2 \) and \( \rho_3 \), as mentioned above in Section 3, 4.1 and 5.

7. Accurate total energy for excited states

Exchange energy functional reported in the Section 4.1 gives accurate energy differences. To make the functional more accurate we now incorporate [25] gradient corrections into MLSDSIC exchange energy functional. For this we use gradient corrections for exchange energy due to Becke [26] and Perdew Wang (PW) [27]. In doing so we are guided by the fact that these functionals are constructed to satisfy certain exact properties, such as the exchange energy density in the asymptotic region, that are common to both the ground as well as the excited states. Thus, with the inclusion of Becke and Perdew Wang gradient corrections the exchange energy functionals are written respectively as,

\[
E_X^{\text{MLSDSIC(Becke)}} = E_X^{\text{MLSDSIC}} - \beta \sum_{\sigma} \int \frac{x_\sigma^2}{1 + 6\beta x_\sigma \sinh^{-1} x_\sigma} d\mathbf{r}
\]  

(22)

where, \( x_\sigma = \frac{\nabla \rho_\sigma}{\rho_\sigma} \) and \( \beta = 0.0042 \)

\[
E_X^{\text{MLSD(PW)}} = \int \epsilon_X^{\text{MLSD}} F(s) d\mathbf{r} - E_X^{\text{SIC}}[\phi_{\text{rem}}] - E_X^{\text{SIC}}[\phi_{\text{add}}]
\]  

(23)
Table 4. Total energy of an excited state $|E\rangle$ and excitation energy of various atoms/ions. $|0\rangle$ denotes the ground state. (Numbers given are in atomic units)

| atoms/ions $(|0\rangle \rightarrow |E\rangle)$ | $-E_{HF}^s$ | $-E_{Becke}^s$ | $-E_{PW}^s$ | $\Delta E_{HF}$ | $\Delta E_{Becke}$ | $\Delta E_{PW}$ |
|----------------------------------------|----------|-------------|-----------|-------------|-------------|-----------|
| $N(2s^22p^3^4S \rightarrow 2s^12p^1^4P)$ | 53.988 | 53.898 | 54.026 | 0.413 | 0.409 | 0.423 |
| $O^+(2s^22p^3^4S \rightarrow 2s^12p^1^4P)$ | 73.820 | 73.797 | 73.835 | 0.553 | 0.564 | 0.582 |
| $O(2s^22p^3^3P \rightarrow 2s^12p^5^3P)$ | 74.184 | 74.181 | 74.227 | 0.625 | 0.631 | 0.652 |
| $F^+(2s^22p^4^3P \rightarrow 2s^12p^5^3P)$ | 98.033 | 98.006 | 98.051 | 0.799 | 0.802 | 0.840 |
| $F(2s^22p^5^2P \rightarrow 2s^12p^5^2S)$ | 98.531 | 98.561 | 98.610 | 0.878 | 0.869 | 0.898 |
| $Ne^+(2s^22p^6^2P \rightarrow 2s^12p^5^2S)$ | 126.861 | 126.745 | 126.791 | 1.083 | 1.074 | 1.111 |

where,

$$
e^{MLSD}_X = \rho(\mathbf{r}) \left[ \epsilon(k_3) - \epsilon(k_2) + \epsilon(k_1) \right] + \frac{1}{8\pi^3} (k_3^2 - k_2^2)^2 \ln \left( \frac{k_3 + k_1}{k_3 - k_1} \right) - \frac{1}{8\pi^3} (k_3^2 - k_2^2)^2 \ln \left( \frac{k_3 + k_2}{k_3 - k_2} \right) - \frac{1}{8\pi^3} (k_2^2 - k_1^2)^2 \ln \left( \frac{k_2 + k_1}{k_2 - k_1} \right)$$

and,

$$s = \frac{\nabla \rho}{2\rho}, \quad F = (1 + 0.086 s^2/m + bs^4 + cs^6)^m$$

with $m = 1/15, b = 14, c = 0.2$.

We have calculated the total energies of excited states of various atoms using these gradient corrections. The results obtained in this manner are shown in Table 4. It is evident from the results that the GGA correction added to $E^{MLSD}\!$ leads to total energy for excited states which is very close to the corresponding exact exchange only values.

8. Conclusion

From the discussion presented in this article it is clear that the idea of splitting the $k$-space to construct functional for excited states is quite general and is consistent with formulation of excited state density functional theory. We have tried to extend Colle-Salvetti correlation energy functional to excited states and have also obtained exchange potential for excited states using the same idea of splitting the $k$-space. Results obtained with exchange potential are encouraging. Thus the method may pave way for further development of energy functionals for excited states.

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