Local density approximation for exchange in excited-state density functional theory

Manoj K. Harbola and Prasanjit Samal

Department of Physics, Indian Institute of Technology, Kanpur 208016, India

Abstract

Local density approximation for the exchange energy is made for treatment of excited-states in density-functional theory. It is shown that taking care of the state-dependence of the LDA exchange energy functional leads to accurate excitation energies.
Following the success of ground-state density functional theory (DFT) [1, 2], attempts have been made to develop a similar theory for the excited-states. The two directions that these investigations have taken are based on (i) time-independent theory [3, 4] that is similar to the self-consistent Kohn-Sham formalism for the ground-state, and (ii) time-dependent theory (TDDFT) [5, 6] that makes use of the fact that frequency-dependent polarizability of a system is singular at the excitation frequency. The former approach is similar to the ∆-SCF method of obtaining transition energies; Within the ground-state DFT, a similar method was proposed by Ziegler et al. [7] and von-Barth [8] to calculate the energies of the lowest-energy multiplets.

Based on the work of Levy and Nagy, we can obtain the energy \( E \) of an excited-state from its density \( \rho(r) \) from the functional

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

(1)

where \( v_{\text{ext}}(\mathbf{r}) \) is the external potential and \( F[\rho, \rho_0] \) is a functional of \( \rho \), the excited state density of a system with the ground-state density \( \rho_0 \). In general, however, the ground-state density \( \rho_0 \) can be represented by the external potential itself. Assuming non-interacting v-representability of the excited-state density, the density can be obtained by solving the excited-states Kohn-Sham equation (equations are written in atomic units)

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

(2)

as

\[
\rho(\mathbf{r}) = \sum_i n_i |\phi_i(\mathbf{r})|^2,
\]  

(3)

where \( n_i \) is the number of electrons in orbital \( \phi_i \). Here \( v_{xc}(\mathbf{r}) \) is the exchange-correlation potential for the excited-state under consideration, and is derived as the functional derivative of the excited-state exchange-correlation energy functional. The latter is obtained from the functional \( F[\rho, \rho_0] \) by subtracting from it the non-interacting kinetic energy and the Coulomb energy. For details we refer the reader to the literature [4]. Like the ground-state theory, in excited-state formalism also the exchange-correlation energy functional is
not known and has to be approximated. However, unlike the ground-state theory, the functional is not universal in that it depends on the system (through \( \rho_0 \)) and is also state-dependent. Nonetheless, calculations of excitation energies have been done \([3, 9]\) employing the regular local-density approximation (LDA) for the ground-state. These give reasonably accurate excitation energies for low lying excited-states but underestimate them when higher excitations are considered. The purpose of this paper is to lay the foundations for getting the state-dependent exchange energy functional within the local density approximation and to show that excitation energies obtained with this functional improve over those calculated by employing the ground-state functional for both the ground and the excited states.

We start by commenting upon why using the same (ground-state LDA functional) results in an underestimate of the excitation energies. As the electrons are excited in a system, the overlap between the orbitals decreases resulting in less of exchange effect compared to the ground-state. This is because now the electrons of the same spin are relatively less likely to come close. However, when we employ the ground-state functional to excited states also, this effect is ignored and consequently within the local approximation we make one more approximation. The latter gives larger magnitude of the exchange energy than what the correct local approximation for the excited-states should give, and this results in smaller excitation energies. To elaborate on this, let us take the example of a homogeneous electron gas. If it is in its ground-state, the electrons occupy wave-vectors in the k-space from \( k = 0 \) to \( k_F = (3 \pi^2 N/V)^{1/3} \), where \( N \) is the number of electrons distributed uniformly over a volume \( V \). On the other hand, in an excited-state of this system the electrons occupy the k-space from the wave-vector \( k_1 \) to \( k_2 \) so that

\[
k_2^3 - k_1^3 = 3 \pi^2 \frac{N}{V}
\]

The exchange energy in the latter case (the expression for the exchange energy is given below) is smaller in magnitude than the ground-state exchange energy. However, if we approximate it by the expression for the ground-state, its magnitude is overestimated, leading to an excited state energy more negative than its correct value.
As is clear from the discussion above, the correct local-density approximation for the inhomogeneous electron gas in an excited-state must be made by considering the electrons to be distributed over regions of k-space different from those for the ground-state. In the simplest case we can take the region to be a spherical shell of inner radius $k_1$ and outer radius $k_2$ with the two radii connected by the the relationship given in Eq. 4 above. Such a shell would represent an excited-state where the lowest energy orbitals are vacant. The expression for the exchange energy density for this distribution is easily derived and is given as

$$
\epsilon_x = \frac{E_X}{V} = -\frac{1}{8\pi^3} \left(2(k_2^3 - k_1^3)(k_2 - k_1) + (k_2^2 - k_1^2)^2\ln\left(\frac{k_2 + k_1}{k_2 - k_1}\right)\right)
$$

Now for a given inhomogeneous electron gas of excited-state density $\rho(r)$, the LDA is made by assigning two $r$-dependent wavevectors $k_1$ and $k_2$ related through Eq. 4 above and calculating the exchange energy per unit volume at that point from Eq. 5. For $k_1 = 0$, the expression above gives the ground-state LDA energy functional

$$
E_x[\rho] = \frac{-3}{4} \left(\frac{3}{\pi^2}\right)^{\frac{1}{3}} \int \rho^\frac{4}{3}(r)dr
$$

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

$$
T_s = \sum_i n_i < \phi_i| - \frac{1}{2}(\nabla^2|\phi_i>
$$

whereas the Thomas-Fermi kinetic energy is

$$
T_s^{TF}[\rho] = \frac{3}{10} \left(3\pi^2\right)^{\frac{2}{3}} \int \rho^\frac{5}{3}(r)dr,
$$

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

$$\tau = \frac{k_2^5 - k_1^5}{10\pi^2} \tag{9}$$

or its spin-polarized version [1, 2]. For $k_1 = 0$, this leads to the expression in Eq. 8.

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

$$k_1 = C \left(3\pi^2 \rho(r)\right)^{1/3} \tag{10}$$

where $C$ is a constant. Thus at each point in the inhomogeneous electron gas, the inner radius of the shell in k-space is determined by the density at that point with the outer radius being given via Eq. 4 as

$$k_2 = \left((1 + C^2)3\pi^2 \rho(r)\right)^{1/3} \tag{11}$$

$C = 0$ of course corresponds to the ground-state. Now with a given set of occupied and virtual orbitals for a given system, we fix $C$ for an excited-state configuration by demanding that the corresponding Thomas-Fermi kinetic energy, given by Eq. 9 with $C > 0$ for the
excited-state, have the same error as it does for the ground-state (evaluated with $C = 0$). In the example of $Be^{2+}$ given above, $C = 1.4$ gives an error of about 9.5% for the $2s3p$ configuration. Thus it is this value of $C$ that we shall use to evaluate the LDA exchange-energy and the corresponding potential in the self-consistent Kohn-Sham calculation for the $2s3p$ configuration. We note that this is one possible way of fixing the value of $C$; better ways of doing so may also exist. However, as we show below, the value of $C$ determined in this manner works quite well for the majority of excited-states investigated.

We have performed self-consistent Kohn-Sham calculations for excited-states where the electrons from the innermost orbitals are excited (as pointed out above, the simplest distribution of wavevectors that we have taken represents precisely such an excited-state) within the local-spin-density approximation (LSDA) by taking the LSDA functional as

$$E_{x}^{LSDA}[\rho^{\alpha}, \rho^{\beta}] = \frac{1}{2}E_{x}^{LDA}[2\rho^{\alpha}] + \frac{1}{2}E_{x}^{LDA}[2\rho^{\beta}]$$

(12)

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

Shown in table I are the excitation energies of helium. We show the energies for three different excited states ($2s2p \, ^3P$), ($2p \, ^3P$) and ($2s3p \, ^3P$) of the helium atom calculated with $C = 0$ (i.e. the ground-state LSDA) and with $C$ determined as described above. Since all three excited-states have only up spin electrons, $C$ shown in the table corresponds to up spin. These are all states that can be represented by a single Slater-determinant so that the LSDA is expected to work well for them. We compare our results with the exact $\Delta$-SCF results of Hartree-Fock theory. In all the excited states considered, it is seen that
whereas the error in the excitation energy obtained from the regular LSDA is about $3eV$, with the proposed functional it only a fraction of an $eV$. Thus it is clear that non-zero value of $C$ gives a better value for the excitation energy. Further, for the higher excited states the value of $C$ is larger, although it is slightly smaller when one goes from $(2s2p^3P)$ to $(2p^23P)$.

To further check the validity of our approach, we have also tested it on excited states of other systems. Shown in table II are the excitation energies of the $(2s2p^3P)$ state of the $Li^+$ ion, $(2s3p^3P)$ state of the $Be^{2+}$ ion, $(2p^34S)$ state of $Li$ atom and the $(1s^22s^22p^13P)$ state of the $Be$ atom. In the first three of these states, up spin electrons are promoted to higher energy orbitals so the $C$ given is that for the up spin. For the $Be$ atom, the down spin electrons of $1s$ state is flipped and promoted to the $2p$ level. Thus it is the down spin electron in the $2s$ state that has to be described by a shell in the k-space; thus $C$ in this system is that for the down spin. Further, since in this case both up and down spin electrons are involved, $C$ is fixed so that the error in the total Thomas-Fermi kinetic energy matches for the ground- and the excited-states. We again see that for non-zero positive values of $C$, determined with the prescription given above, excitation energies come out to be closer to the $\Delta$-SCF Hartree-Fock excitation energies than with $C = 0$.

Shown in table III are the numbers for the fluorine atom and neon positive ion excited-states. One of the excited-states $(1s^12s^22p^62S)$ in each system corresponds to a shell in the k-space, whereas the other one $(1s^22s^12p^62S)$ does not. As pointed out earlier, a shell in k-space represents well an excited-state in which the lowest lying orbitals are vacant. Thus we see that for the $(1s^12s^22p^62S)$ state of both the systems, the error in the excitation energy as given by the proposed functional is smaller by a factor of about two in comparison to the corresponding error in the LSDA excitation energy. The relative error in the case of LSDA is about 1.2% whereas our functional gives an error of 0.6%. Since the excitation in these cases involve single-electron being transferred, TDDFT calculation can also be performed to determine the excitation energy. For the fluorine atom, TDDFT gives the excitation energy from the ground to the $(1s^12s^22p^62S)$ to be 23.7848 a.u. which is in error by 29.94 eV. Similarly for the neon ion, the excitation energy comes out to be 29.9615 a.u. which is in
error by 33.48 eV.

The other excited-states\((1s^22s^12p^6 \, 2S)\) shown in table III are those in which the lowest lying orbitals are not vacant, since one of the 2s electrons has been excited to the 2p orbital in fluorine or in a mono-positive ion of neon. In these cases, the corresponding wavevectors will not form a shell but will be distributed in some other manner; one possibility is an occupied sphere (of radius \(k_1\)) representing the core states, then a vacant shell (from radius \(k_1\) to \(k_2\)) for the unoccupied states followed again by an occupied shell (from \(k_2\) to \(k_3\)) representing the outer electrons. Thus the functional of Eq. 5 above is not expected to be as accurate for such excited-states as it is for those with empty lowest states; although it should still be better than the ground-state LSDA. This is clear from numbers in table III: we see that although the error in the excitation energy does become smaller, but not as much as in the cases discussed earlier. Also the relative error in these case is quite large.

Work on functionals with a different k-space occupation, which is more appropriate for such excited-states, is in progress. TDDFT calculations in these cases give quite accurate energies.

We have shown above that the correct local-density approximation for the kinetic energy and exchange energy in excited-state density-functional theory \([4]\) is made by taking the electrons to be occupying wavevectors differently than for the ground-state, and gives results that are superior to those obtained by applying the same approximation for the ground as well as the excited states. As an example of this, we took the simplest case in which the occupied wave-vectors form a spherical shell. Through this we have demonstrated that if consistency is maintained in making the LDA for different states, the resulting excitation energies are much better than those obtained by employing the same LDA for the ground- and the excited-state. Although our method of finding the inner and out radii is an \textit{ad hoc} one, some justification for it exists on the basis of conjointness \([11]\) of the kinetic and exchange energy.

To understand the functional proposed by us better, we have also looked at the spherical average \([10]\) of the Fermi-hole when the k-space is occupied differently than for the ground-
state. We find that the spherical averaged hole corresponding to the functional proposed is closer to the spherically-averaged exact hole than that corresponding to the ground-state functional. These results will be presented in the future.

Next question that we address is if the excited-state LDA proposed by us can be generalised to include the gradient corrections. The answer is in the affirmative. As the first step, we assume that the LDA functional is changed but the gradient corrections are the same for both the ground- and excited-state functionals. Further, in this paper we have focussed on kinetic and exchange energy. The correlation energy could also be better approximated using a similar approach. Work in these directions has already been started.

The motivation for the present work stems from the requirement of excited-state density-functional theory that functionals for excited states be state-dependent. The result of making the functionals state-dependent is that the errors in the total energy for both the ground- and excited-states are roughly the same and hence the difference of energies comes out to be accurate in comparison to the results of Hartree-Fock theory, exact-exchange calculations \[4\] using the optimized potential method \[13\] or the near exact exchange calculations \[12\] using the Harbola-Shani potential \[14\]. We note that in the latter three theories, the state-dependence of the exchange functional is automatically accounted for by the use of exchange-energy functional that depends on orbitals rather than the density.

**Acknowledgement:** We thank Professor K.D. Sen for providing data on different excited-states of atoms. We also thank Professor R. Prasad for fruitful discussion.

---

[1] R.M. Dreizler and E.K.U. Gross, *Density Functional Theory*, (Springer-Verlag, Berlin, 1990)
[2] R.G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules*, (Oxford University Press, Oxford, 1999).
[3] A. Görling, Phys. Rev. A **59**, 3359 (1999).
[4] M. Levy and Á. Nagy, Phys. Rev. Lett. **83**, 4361 (1999).
[5] M.E. Casida in *Recent Advances in Density Functional Methods, Part 1*, edited by D.P. Chong (World Scientific, Singapore, 1995).
[6] M. Petersilka and E.K.U. Gross, Phys. Rev. Lett. 76, 1212 (1996).

[7] T. Ziegler, A. Rauk and E.J. Baerends, Theor. Chim. Acta 43, 261 (1977).

[8] U. von Barth, Phys. Rev. A 20, 1693 (1979).

[9] M.K. Harbola, Phys. Rev. A 65, 052504 (2002).

[10] O. Gunnarsson, M. Johnson and B.I. Lundquist, Phys. Rev. B 20, 3136 (1979).

[11] N.H. March and R. Santamaria, Int. J. Quantum Chem. 39, 585 (1991).

[12] R. Singh and B.M. Deb, Phys. Rep. 311, 47 (1999); K.D. Sen, Chem. Phys. Lett. 188, 510 (1992).

[13] R.T. Sharp and G.K. Horton, Phys. Rev. 90, 3876 (1953); J.D. Talman and W.F. Shadwick, Phys. Rev. A 14, 36 (1976).

[14] M.K. Harbola and V. Sahni, Phys. Rev. Lett. 62, 489 (1989).
TABLE I: Total energies and the excitation energies (in atomic units) of three different excited-states of helium atom for $C = 0$ (ground-state functional) and the value of $C$ determined by comparison of exact and Thomas-Fermi kinetic energies for up spin. The corresponding Hartree-Fock (HF) excitation energies determined by $\Delta$-SCF method are given in the last line of each set. The last column gives in eV the magnitude of the difference between the HF and the DFT transition energies.

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


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

| State     | C  | Total Energy (a.u.) | Excitation Energy (a.u.) | Error (eV) |
|-----------|----|---------------------|--------------------------|------------|
| $Li^+$ ion |    |                     |                          |            |
| $1s^2(^1S)$ | -  | -7.0086             | -                        | -          |
| $2s2p(^3P)$ | 0.0 | -1.8228             | 5.1858                   | 4.89       |
|           | 1.06 | -1.6361             | 5.3725                   | 0.19       |
|           |      | $\Delta E_{HF} = 5.3655$ |               |            |
| $Be^{2+}$ ion |   |                     |                          |            |
| $1s^2(^1S)$ | -  | -13.2943            | -                        | -          |
| $2s3p(^3P)$ | 0.0 | -2.5488             | 10.7455                  | 8.28       |
|           | 1.421 | -2.3253             | 10.9691                  | 2.19       |
|           |      | $\Delta E_{HF} = 11.0499$ |               |            |
| Li atom   |    |                     |                          |            |
| $1s^22s(^2S)$ | -  | -7.1934             | -                        | -          |
| $2p(^4S)$  | 0.0 | -2.1061             | 5.0873                   | 7.32       |
|           | 0.777 | -1.9262             | 5.2672                   | 2.43       |
|           |      | $\Delta E_{HF} = 5.3565$ |               |            |
| Be atom   |    |                     |                          |            |
| $1s^22s(^1S)$ | -  | -14.2233            | -                        | -          |
| $1s^12s^2p(^3P)$ | 0.0 | -10.1470            | 4.0863                   | 3.07       |
|           | 1.062 | -10.0582            | 4.1646                   | 0.94       |
|           |      | $\Delta E_{HF} = 4.1991$ |               |            |
TABLE III: The table caption is the same as that for Table II except that the numbers are for fluorine atom and neon ion.

| State | C | Total Energy (a.u.) | Excitation Energy (a.u.) | Error (eV) |
|-------|---|---------------------|--------------------------|------------|
| **F atom** | | | | |
| $1s^22s^22p^5(2P)$ | - | -98.4740 | - | - |
| $1s^12s^22p^6(2S)$ | 0.0 | -73.9002 | 24.5738 | 8.47 |
| | 0.685 | -73.4263 | 25.0477 | 4.42 |
| $\Delta E_{HF} = 24.8852$ | | | | |
| $1s^22s^12p^6(2S)$ | 0.0 | -97.8069 | 0.6671 | 5.74 |
| | 0.238 | -97.7492 | 0.7248 | 4.17 |
| $\Delta E_{HF} = 0.8781$ | | | | |
| **Ne**$^+$ ion | | | | |
| $1s^22s^22p^5(2P)$ | - | -126.7371 | - | - |
| $1s^12s^22p^6(2S)$ | 0.0 | -95.8931 | 30.8440 | 9.47 |
| | 0.670 | -95.3537 | 31.3834 | 5.20 |
| $\Delta E_{HF} = 31.1921$ | | | | |
| $1s^22s^12p^6(2S)$ | 0.0 | -125.9027 | 0.8344 | 6.76 |
| | 0.244 | -125.8311 | 0.9060 | 4.81 |
| $\Delta E_{HF} = 1.0829$ | | | | |