An accurate exchange energy functional in excited-state density functional theory

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Abstract

An exchange energy functional is proposed and tested for obtaining a class of excited-state energies using density-functional formalism. The functional is the excited-state counterpart of the local-density approximation functional for the ground-state. It takes care of the state-dependence of the energy functional and leads to highly accurate excitation energies.
I. INTRODUCTION

Success of density functional theory (DFT) \[1, 2\] for the ground-state calculations had prompted search \[3, 4, 5, 6, 7, 8, 9, 10\] for similar theories for the excited-states. Over the past decade, time-dependent density-functional theory (TDDFT) \[11\] has become a standard tool \[12, 13\] for obtaining transition energies and the associated oscillator strengths. However, despite its widespread use, the theory is not without limitations. For example, calculating excitation energies for double excitation of electrons still remains \[14\] a challenge in the TDDFT approach. At the same time, the charm of getting the excitation energy as the difference between two total energies remains. This is because one can choose the excited-state at will, promoting as many electrons as one wishes to a set of chosen orbitals, calculate the total corresponding energy and find the excitation energy by subtracting the ground-state energy. Thus research in the direction of performing a Kohn-Sham like calculation for the excited-states continues.

A ground-state like DFT approach to obtain the total energy of an excited-state has been developed by Görling \[15\] and by Levy and Nagy \[16\]. The theory is based on the constrained-search approach \[17\] and proposes that the energy of an excited-state can also be written as a functional

$$E[\rho] = F[\rho, \rho_0] + \int \rho(r) v_{\text{ext}}(r) dr \quad (1)$$

of the excited-state density \(\rho(r)\). Here \(F[\rho, \rho_0]\) is a bi-density functional that depends on the ground-state density \(\rho_0\) also, and \(v_{\text{ext}}(r)\) is the external potential that the electrons are moving in. The bi-density functional for the density \(\rho\) of the \(n\)th excited-state is defined via the constrained-search formulation as

$$F[\rho, \rho_0] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{\text{ee}} | \Psi \rangle , \quad (2)$$

where \(\Psi\) is orthogonal to the lower \((n - 1)\) states of the hamiltonian, already determined by the density \(\rho_0\). Such a way of obtaining the functional \(F[\rho, \rho_0]\) makes it non-universal and also state-dependent. The exchange-correlation energy functional \(E_{xc}[\rho, \rho_0]\) for the excited-
state is then defined as the difference of $F[\rho, \rho_0]$ and the non-interacting kinetic energy $T_s[\rho, \rho_0]$ corresponding to $\rho$. The latter is defined in a manner similar to Eq. 2 by dropping the operator $\hat{V}_{ee}$ from the right hand side. Thus (for brevity, from here onwards we drop $\rho_0$ from the argument of the functional)

$$E_{xc}[\rho] = F[\rho] - T_s[\rho] .$$

(3)

With the assumption that the excited-state density is non-interacting v-representable, the density is obtained by solving the excited-states Kohn-Sham equation (atomic units are used throughout the paper)

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

(4)

as

$$\rho(r) = \sum n_i |\phi_i(r)|^2 ,$$

(5)

where $n_i$ is the occupation number of the orbital $\phi_i$. In Eq. 4, the various terms have their standard meaning with $v_{xc}(r)$ representing the exchange-correlation potential for the excited-state. It is determined by taking the functional derivative of the excited-state exchange-correlation energy functional. That a Kohn-Sham like calculation can be performed for the excited-states was first proposed by Harbola and Sahni [18] on physical grounds, and has been put [19] on a rigorous mathematical footing recently on the basis of differential virial theorem [20]. Calculations of excited-states energies based on the Harbola-Sahni work have yielded excellent results [21, 22]. The near exact exchange-correlation potential for the singlet 1$s^2\ 1S$ excited-state of helium has also been constructed [23] recently. However, we are not aware of any work where an exchange-correlation functional for the excited-states has been reported; In performing excited-state calculations [15, 16, 24], either the ground-state functionals or the orbital based-theories [18, 25] have been employed. The proposition for the construction of an excited-state exchange-correlation functional is indeed a difficult one since the functional is non-universal and also state-dependent. Thus a general functional form for it may not exist.
Against such a background, we ask if it is at all possible to obtain a simple LDA-like functional for the excited-states. To keep matters simple, we have been looking at this problem within the exchange-only approximation. In this paper we show that it is indeed possible to construct an exchange energy functional that gives transition energies comparable to the exact exchange-only theories such as Hartree-Fock \[26\], optimized potential \[25\] or the Harbola-Sahni \[27\] theory. The construction of the functional is based on the homogeneous electron-gas and in finding the final form of the functional we are guided mostly by qualitative plausibility arguments. Our work is thus exploratory in nature and represents probably the first attempt to construct an excited-state exchange-energy functional in terms of the density. The evidence of the accuracy of the functional constructed by us is given by the results of the transition energies of a large number of excited-states. We also refer the reader to ref. \[28\] for an expression for the change in the exchange energy in terms of the ground-state Kohn-Sham orbitals when an electron is promoted from a lower energy orbital to a higher one.

In the present work we take a particular class of excited states in which some core orbital are filled, then there are some vacant orbitals and again there are some filled orbitals. We construct an LDA-like functional for such states in the following section.

II. CONSTRUCTION OF THE FUNCTIONAL

As stated above, we now consider such excited-states where the occupation of the orbitals is such that the electrons occupy some core orbitals and some shell orbitals, leaving the orbitals between the core and the shell region vacant. This is shown schematically in Fig. \[1\] Such an excited-state would be obtained, for example, if an electron from the filled orbitals of the ground-state is excited to just above the occupied levels. The exact exchange energy for a set of occupied orbitals is given as

\[ E_X = -\frac{1}{2} \sum_{\sigma} \sum_{i}^{\text{occ}} \sum_{j}^{\text{occ}} \left\langle \phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_2) \right| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \left| \phi_j(\mathbf{r}_1)\phi_i(\mathbf{r}_2) \right\rangle \]  \hspace{1cm} (6)
FIG. 1: Orbital occupation in an excited state configuration.

so that the excited-state exchange energy when an electron is transferred from one of the orbitals occupied in the ground-state to the lowest unoccupied level is given as

\[
E_{\text{excited}} = E_{\text{ground}} + \sum_j \left\langle \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \left| \phi_j(\mathbf{r}_1) \phi_{\text{rem}}(\mathbf{r}_2) \right| \left| \phi_{\text{add}}(\mathbf{r}_1) \phi_j(\mathbf{r}_2) \right| \rightangle 
- \frac{1}{2} \int \int \frac{|\phi_{\text{rem}}(\mathbf{r}_1)|^2 |\phi_{\text{rem}}(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2
- \frac{1}{2} \int \int \frac{|\phi_{\text{add}}(\mathbf{r}_1)|^2 |\phi_{\text{add}}(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2
\]

\[- \sum_{j(j \neq \text{add})} \left\langle \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \left| \phi_{\text{add}}(\mathbf{r}_1) \phi_j(\mathbf{r}_2) \right| \left| \phi_{\text{rem}}(\mathbf{r}_1) \phi_{\text{add}}(\mathbf{r}_2) \right| \rightangle , \tag{7}
\]

where \(\phi_{\text{rem}}\) represents the orbital from which the electron has been removed and \(\phi_{\text{add}}\) where the electron is added. The sum over the index \(j\) in the second term on the right hand side runs over all the orbitals, including \(\phi_{\text{rem}}\) and \(\phi_{\text{add}}\), up to the highest occupied orbital in the excited-state. On the other hand the sum in the fifth term runs over all the orbital except \(\phi_{\text{add}}\). We now attempt to make an LDA-like approximation for the excited-state exchange energy so that the difference (the last four terms in the equation above) between the approximate excited- and ground-state exchange energies is close to that given by the exact expression above. In making this approximation accurate, it is evident that the self-energy terms (third and fourth terms on the right hand side of Eq. 7) for the orbitals \(\phi_{\text{rem}}\) and \(\phi_{\text{add}}\) are to be treated accurately.

As the first step towards an excited-state functional, we make the correspondence between the excited-states that we are considering and similar excitations in a homogeneous electron gas (HEG). If the HEG is in it’s ground state, the electrons are filled up to the Fermi level
so that the electrons occupy wave-vectors in k-space from $k = 0$ to $k_F = (3\pi^2 \rho)^{1/3}$, where $\rho$ is the electron density. On the other hand, in an excited state of the system the electrons will occupy k-space differently compared to the ground state. For the kind of excited-states that we consider in this paper, the corresponding occupation in the k-space is as follows: The electrons occupy orbitals from $k = 0$ to $k_1$ and $k_2$ to $k_3$ with a gap in between as shown in Fig. (2). So that the excited state density is given by

$$F_{k_1 k_3 k_2 k_1}$$

FIG. 2: $k-$space occupation in the ground and the excited state configuration.

$$k_3^3 = 3\pi^2 \rho_c ,$$  \hspace{1cm} (8)

$$k_3^3 - k_2^3 = 3\pi^2 \rho_s ,$$  \hspace{1cm} (9)

and

$$k_3^3 - k_2^3 + k_1^3 = 3\pi^2 \rho$$  \hspace{1cm} (10)

where

$$\rho = \rho_c + \rho_s .$$  \hspace{1cm} (11)

In Eq. (8) $\rho_c$ and $\rho_s$ are the core (corresponding to the electrons occupying $k-$space from zero to $k_1$) and the shell (corresponding to the electrons occupying $k-$space from $k_2$ to $k_3$) density, respectively, and $\rho$ is the total density.

The exchange energy for the HEG that occupies the k-space as described above can be obtained exactly and is given as (MLDA stands for modified local density approximation)

$$E_X^{MLDA} = E_X^{core} + E_X^{shell} + E_X^{core-shell}$$  \hspace{1cm} (12)
where

\[ E_{\text{core}}^X = V \left[ -\frac{k_1^4}{4\pi^3} \right] \]  

(13)

is the exchange energy of the core electrons,

\[ E_{\text{shell}}^X = -\frac{V}{8\pi^3} \left[ 2(k_3^3 - k_2^3)(k_3 - k_2) + (k_3^2 - k_2^2)^2 \ln \left( \frac{k_3 + k_2}{k_3 - k_2} \right) \right] \]  

(14)

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

\[ E_{\text{core-shell}}^X = -\frac{V}{8\pi^3} \left[ 2(k_3^3 - k_2^3)k_1^3 + 2(k_3^3 - k_2^3)k_1 + (k_2^2 - k_1^2)^2 \ln \left( \frac{k_2 + k_1}{k_2 - k_1} \right) \right] \]

\[ - \left( k_3^2 - k_1^2 \right)^2 \ln \left( \frac{k_3 + k_1}{k_3 - k_1} \right) \]  

(15)

represents the exchange energy of interaction between the core and the shell electrons. Here \( V \) is the volume of the HEG. After adding the three terms, the exchange-energy can also be written in the form

\[ E_{\text{MLDA}}^X = \int \rho [\epsilon(k_3) - \epsilon(k_2) + \epsilon(k_1)] \, dr + \log \text{terms} \]  

(16)

where \( \epsilon(k) \) represents the exchange-energy per particle when the HEG is in its ground-state with the Fermi momentum equal to \( k \). The equation above has a nice interpretation: The integral on the right-hand side represents the exchange energy of the system of electrons with density \( \rho \) when per electron energy is written as \( [\epsilon(k_3) - \epsilon(k_2) + \epsilon(k_1)] \), i.e. the per electron energy is given according to the occupation in the k-space (compare with Eq. 10).

The log terms, on the other hand, have no such simple interpretation. They have the kinetic energy density in them but we have not been able to write the terms in as easy a form as the first term. That the functional above has all the right limits if we take \( k_1 = k_2 \) or \( k_2 = k_3 \) is easily verified. Finally, the modified local spin density (LSD) functional \( E_{\text{X MLSD}}^X[\rho_\alpha, \rho_\beta] \) in terms of the spin densities \( \rho_\alpha \) and \( \rho_\beta \) is easily obtained from the functional above as

\[ E_{\text{X MLSD}}^X[\rho_\alpha, \rho_\beta] = \frac{1}{2} E_{\text{X MLDA}}^X[2\rho^\alpha] + \frac{1}{2} E_{\text{X MLDA}}^X[2\rho^\beta] \]  

(17)

Having derived the exchange functional for the HEG, we now apply it to the excited-states of various atoms to check if the functional above gives exchange energy differences...
accurately. The excited-states chosen are such that they can be represented by a single Slater determinant so that the LDA is a good approximation\textsuperscript{3, 5} for them. The different radii in the k-space, $k_1$, $k_2$ and $k_3$, needed to evaluate the exchange energy are found by Eqs.\textsuperscript{8, 9} and\textsuperscript{10}. For each state (ground and excited), the same set of orbitals\textsuperscript{29} is employed to get the Hartree-Fock and the LSD exchange energies. We calculate the LSD and MLSD exchange energies using spherical spin densities since the effect of non-sphericity on the total exchange energy is small\textsuperscript{30}.

In Table I we show the difference between the excited-state exchange energy and the ground-state exchange energy for some atoms and ions. In the first column we give the difference as obtained by the Hartree-Fock expression for the exchange energy. In the second column, the numbers are given for both the excited-state and the ground-state exchange energies obtained by employing the ground-state LSD functional. The third column gives the energy difference when the excited-state exchange energy is calculated using the functional of Eq.\textsuperscript{12}. It is clearly seen that the ground-state LSD approximation underestimates this energy difference. This is not surprising since the ground-state functional would give a larger exchange energy for the excited-state than what a proper excited-state functional should give. However, when the functional of Eq.\textsuperscript{12} is employed to calculate the exchange energy for the excited-states we find, to our surprise, that for the majority of the atoms the functional overestimates the differences by a large amount, whereas we expected to find the error to be about 10% which is the general LDA exchange energy error. We note that this large difference cannot come because we have spherical densities. If non-spherical densities are used, the difference may increase even further. For example, for the fluorine atom, the ground-state exchange energy will become more negative for non-spherical densities. On the other hand, the excited-state exchange energy will remain unchanged since the density is already spherical. This will result in an even larger difference in the exchange energies of the two states.

We now look for possible sources of error in the exchange-energy differences when the functional of Eq.\textsuperscript{12} is employed to get the exchange energy for the excited-states. For this
we examine Eq. 7 in which the last four terms on the right hand side represent the exchange energy difference. Thus

\[ \Delta E_X = \sum_j \left( \phi_{\text{rem}}(\mathbf{r}_1)\phi_j(\mathbf{r}_2) \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \phi_j(\mathbf{r}_1)\phi_{\text{rem}}(\mathbf{r}_2) \right) 
- \frac{1}{2} \int \int \left| \phi_{\text{rem}}(\mathbf{r}_1) \right|^2 \left| \phi_{\text{rem}}(\mathbf{r}_2) \right|^2 d\mathbf{r}_1 d\mathbf{r}_2 
- \frac{1}{2} \int \int \left| \phi_{\text{add}}(\mathbf{r}_1) \right|^2 \left| \phi_{\text{add}}(\mathbf{r}_2) \right|^2 d\mathbf{r}_1 d\mathbf{r}_2 
- \sum_{j(j \neq \text{add})} \left( \phi_{\text{add}}(\mathbf{r}_1)\phi_j(\mathbf{r}_2) \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \phi_j(\mathbf{r}_1)\phi_{\text{add}}(\mathbf{r}_2) \right) \right). \]  

(18)

It is the LDA values to this term that are given in Table I. The sources of error in this term we suspect are the self-exchange energies of the orbitals \( \phi_{\text{rem}} \) and \( \phi_{\text{add}} \) involved in the electron transfer. We now argue that the self-energy correction for both the terms should be in the same direction. Thus for both the orbitals the self-interaction correction (SIC) is made by subtracting

\[ E_X^{\text{SIC}}[\phi] = \frac{1}{2} \int \int \left| \phi(\mathbf{r}_1) \right|^2 \left| \phi(\mathbf{r}_2) \right|^2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 - E_X^{\text{LSD}}[\rho(\phi)], \]  

(19)

where \( \rho(\phi) \) is the orbital density for the orbital \( \phi \). The argument goes as follows. The LDA should be reasonably accurate when the integral over \( k \) is continuous. This makes the first term in the energy difference accurate. We do have a choice of writing the first and the second terms as

\[ \sum_{j\neq\text{rem}} \left( \phi_{\text{rem}}(\mathbf{r}_1)\phi_j(\mathbf{r}_2) \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \phi_j(\mathbf{r}_1)\phi_{\text{rem}}(\mathbf{r}_2) \right) + \frac{1}{2} \int \int \left| \phi_{\text{rem}}(\mathbf{r}_1) \right|^2 \left| \phi_{\text{rem}}(\mathbf{r}_2) \right|^2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \]  

(20)

but then the first term above will not be accurate as the LDA to it would involve integration in \( k \)-space with a break from \( k_1 \) to \( k_2 \). Therefore to keep the LDA accurate, we keep the summation continuous and write the self-interaction energy of the electron removed with a negative sign in front. By including the self-interaction correction for the removed electron only, we find that the error in the exchange energy difference reduces to about 10% of the corresponding HF value. To make the difference even more accurate, we now consider the term for the orbital \( \phi_{\text{add}} \) where the electron is added. There the electron comes in with its self-interaction so for the added orbital too \( E_X^{\text{SIC}} \) should be subtracted to make the results
for the energy difference comparable to the Hartree-Fock results. Thus the final expression for the exchange-energy that we have is

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

(21)

where \( E^{\text{MLSD}}_X \) is the energy functional given by Eq. 12 and \( E^{\text{SIC}}_X[\phi] \) is given by Eq. 19. We now compute the exchange energy differences given by the functional in Eq. 21 and show them in Table I. As is evident from the numbers displayed there, the functional of Eq. 21 gives highly accurate exchange-energy differences for all the systems considered. When the exchange-energy difference between the ground- and the excited-state is small, the HF, LSD and the functionals derived above, all give roughly the same results. However, when this difference is large, the LDA underestimates the magnitude of the difference by a large amount whereas the functional of Eq. 12 overestimates it. Only when the latter is corrected for the self-interaction is the difference almost the same as the Hartree-Fock difference.

Having obtained the functional to obtain accurate exchange energy difference, we now apply it to a large number of excited-states of the class considered here and find that we get the transition energies very close to those given by the Hartree-Fock theory.

III. RESULTS

We now employ the exchange functional \( E^{\text{MLSDSIC}}_X \) proposed above to obtain the transition energies for a variety of excitations in different atoms. We find that for all the systems the transition energies obtained by us are very close to the corresponding Hartree-Fock energies [32]. Our calculations proceed as follows: We get the ground-state energy by solving the Kohn-Sham equation with the effective exchange potential calculated using the Dirac formula [33]. We then solve the Kohn-Sham equation with the same (corresponding to the ground-state) functional for the excited-state configuration. This gives us the excited-state energy \( E_{\text{LSD}} \). The difference between \( E_{\text{LSD}} \) and the ground-state energy gives us the transition energy \( \Delta E_{\text{LSD}} \). We then employ the Kohn-Sham orbitals from this calculation to get the modified LDA exchange energy including SIC by employing the functional
Making appropriate corrections we then get the total excited-state energy corresponding to this functional, and its difference with the ground-state energy gives us $\Delta E_{MLSDSIC}$. Although we have not performed self-consistent calculations with the new functional, self-consistency is not expected to affect the results significantly. This is because, as we shall see in the results, the major difference in the transition energies given by different functionals arises from the difference in the value of the exchange energy itself.

Shown in Table II are the transition energies $\Delta E_{HF}$, $\Delta E_{LSD}$ and $\Delta E_{MLSDSIC}$ for some light atoms and ions when one of their inner electrons is excited to the lowest available orbital. The excitation energy in these systems is such that for some of them $\Delta E_{LSD}$ is close to $\Delta E_{HF}$ but for others it is not. However, $\Delta E_{MLSDSIC}$ is uniformly accurate for all the systems. We note that the error in $\Delta E_{LSD}$ is almost fully from the error in the corresponding exchange energy difference. This is evident from a comparison of the numbers in Table I (for the exchange energy differences) and in Table II.

In Table III we look at the excitation energies of the alkali atoms and $Mg^{+}$ by exciting an electron from the uppermost orbital to an outer orbital. These are weakly bound systems and as such their excitation energies are relatively smaller. Thus they provide a good testing ground for the proposed functional. An interesting point about these systems is that the LSD itself gives excitation energies close to the HF excitation energies. It is therefore quite gratifying to see that the transition energies obtained by the new functional also are of very good quality, although the present method tends to slightly overestimate the transition energies.

Next we consider some bigger atoms where we can excite the electron from more than one inner orbital. Shown in Tables IV and V are the excitation energies for the atoms in the third row of the periodic table. In Table IV we consider an electron being excited from the 3s orbital to the 3p orbital. In all these case $\Delta E_{LSD}$ is smaller than the true energy difference whereas the present functional gives highly accurate estimates of the transition energy. Notice again that the error in the value of $\Delta E_{LSD}$ arises mainly from the error in the exchange energy.
In Table V, we show the transition energies for the same set of atoms and ions as in Table IV, but for the electron now being excited from the 2s orbital to the 3p orbital. Consequently the energy of excitation is much larger in this case. The LSD in all these cases underestimates the excitation energy, whereas the present functional gives accurate results although slightly overestimating them. However, the error with respect to the LSD is reduced by a factor of 5 or more.

Shown in Table VI are the excitation energies for a group of atoms for which the LSD gives transition energies very close to the HF excitation energies. In all the cases we find that the functional proposed here is able to give accurate excitation energies. Thus we find that when the LSD results are accurate, so are the results given by the new functional. What is significant, however, is that when the LSD results are poor, the new functional properly corrects the error in LSD.

Finally, we consider the cases where two electrons are excited to the higher orbitals. As already pointed out, double excitations are difficult to deal with in the TDDFT approach to finding excitation energies. Results for different excitations for a variety of atomic systems are shown in Table VII. As is evident from the table, for all the systems, our method gives excellent results whereas the LSD underestimates the energies.

IV. DISCUSSION AND CONCLUDING REMARKS

In the above we have presented a new LDA-like functional for obtaining the excitation energies. It has been employed to investigate over 40 excited states. The results show that our procedure gives accurate excitation energies for all of them, whereas for most of the systems the LSD underestimates the energy difference. We have worked within the exchange-only approximation and have chosen a particular class of excited-states. What we have learnt through the study reported here is that a simple extension of the LDA to the excited-states overestimates the energy differences. This is due to the self-interaction of the electron inherent in the LDA. When corrected for the self-interaction through a careful
analysis, the resulting functional gives highly accurate answers for the excited-states. Thus if more accurate functionals than the LDA are employed, our method of developing excited-state functionals should give good excited-state functionals.

In the present work, we have developed a functional for a particular class of excited states and demonstrated that it is possible to construct excited-state energy functionals that are capable of giving transition energies close to the exact theory. We are now working on functionals for states other than considered in this paper. As pointed out in the introduction, excited-state functionals are not universal and therefore have to be dealt with separately for different kinds of excited-states.

In this work, we have also not looked at the correlation energy functionals. Can correlation energy functionals be developed along similar lines? We trust that it should be possible and are working on this problem.

Finally, we also wish to look at the ultimate excitation i.e. the ionization of the system. If the electron is removed from the uppermost orbital, the LDA is known to give good ionization energies when calculated through the total energy difference. In these cases too our functional would give results the same as those obtained from the LDA: If we go through the arguments presented earlier, we find that in these cases our functional reduces to the LDA functional for the core electrons. This is because in calculating the exchange energy, the summation over the occupied orbitals is continuous and therefore we do not have to make any self-interaction correction for the removed electron. Further the shell electron density vanishes so the contribution from the added electron is zero. Interestingly, we find that if we ionize the atom by removing an electron from the inner orbitals, we obtain accurate removal energies if we think of the process in two steps - first removing an electron from the top level and then exciting the resulting ion by exciting an electron from the inner orbital to the top of filled orbitals. More work on such different kinds of excitation is in progress and will be reported in the future.

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TABLE I: Difference in the exchange energies of the ground- and excited-states of some atoms and ions. The First column gives the atom/ion and the transition, the second column the difference $\Delta E_X^{HF}$ as obtained in Hartree-Fock theory, the third column the difference $\Delta E_X^{LSD}$ given by the ground-state energy functional. The fourth and the fifth column describe the difference as obtained with the functional proposed in this paper. The fourth column gives the exchange-energy difference $\Delta E_X^{MLSD}$ obtained by employing the functional of Eq. [20] whereas the fifth column gives that given by the functional of Eq. [20] $\Delta E_X^{MLSDSIC}$. Numbers given are in atomic units.

| atoms/ions                  | $\Delta E_X^{HF}$ | $\Delta E_X^{LSD}$ | $\Delta E_X^{MLSD}$ | $\Delta E_X^{MLSDSIC}$ |
|-----------------------------|-------------------|--------------------|--------------------|-----------------------|
| $Li(2s^1 2S \rightarrow 2p^1 2P)$ | 0.0278            | 0.0264             | 0.0587             | 0.0282                |
| $B(2s^2 2p^1 2P \rightarrow 2s^1 2p^2 2D)$ | 0.0353            | 0.0319             | 0.0998             | 0.0412                |
| $C(2s^2 2p^2 3P \rightarrow 2s^1 2p^3 3D)$ | 0.0372            | 0.0332             | 0.1188             | 0.0454                |
| $N(2s^2 2p^3 4S \rightarrow 2s^1 2p^4 4P)$ | 0.0399            | 0.0353             | 0.1381             | 0.0503                |
| $O(2s^2 2p^4 3P \rightarrow 2s^1 2p^5 3P)$ | 0.1582            | 0.0585             | 0.2634             | 0.1624                |
| $F(2s^2 2p^5 2P \rightarrow 2s^1 2p^6 2S)$ | 0.3021            | 0.0891             | 0.3908             | 0.2765                |
| $Ne^+ (2s^2 2p^5 2P \rightarrow 2s^1 2p^6 2S)$ | 0.3339            | 0.0722             | 0.4397             | 0.3037                |
| $S(3s^2 3p^4 3P \rightarrow 3s^1 3p^5 3P)$ | 0.1106            | 0.0475             | 0.1798             | 0.1252                |
| $Cl^+ (3s^2 3p^4 3P \rightarrow 3s^1 3p^5 3P)$ | 0.1257            | 0.0483             | 0.2050             | 0.1441                |
| $Cl(3s^2 3p^5 2P \rightarrow 3s^1 3p^6 2S)$ | 0.2010            | 0.0603             | 0.2567             | 0.1969                |
### Table II: Transition Energies, in Atomic Units, of an Electron Being Excited from the 2s Orbital of Some Atoms to Their 2p Orbital

The first column gives this energy as obtained in Hartree-Fock theory. The numbers in the second column are obtained by employing the ground-state LDA for both the ground- and the excited-state. The last column gives the energies given by employing the ground-state LDA for the ground-state and the functional of Eq. 20 for the excited-state.

| Atoms/Ions | $\Delta E_{HF}$ | $\Delta E_{(LSD)}$ | $\Delta E_{(MLSDSIC)}$ |
|------------|-----------------|--------------------|------------------------|
| $N(2s^22p^3\,4S \rightarrow 2s^12p^4\,4P)$ | 0.4127 | 0.3905 | 0.4014 |
| $O^+(2s^22p^3\,4S \rightarrow 2s^12p^4\,4P)$ | 0.5530 | 0.5397 | 0.5571 |
| $O(2s^22p^4\,3P \rightarrow 2s^12p^5\,3P)$ | 0.6255 | 0.5243 | 0.6214 |
| $F^+(2s^22p^4\,3P \rightarrow 2s^12p^5\,3P)$ | 0.7988 | 0.6789 | 0.8005 |
| $F(2s^22p^5\,2P \rightarrow 2s^12p^6\,2S)$ | 0.8781 | 0.6671 | 0.8573 |
| $Ne^+(2s^22p^5\,2P \rightarrow 2s^12p^6\,2S)$ | 1.0830 | 0.8334 | 1.0607 |

### Table III: The Caption is the Same as That for Table I Except That We Are Now Considering Transitions from the Outermost Orbital to an Upper Orbital for Weakly Bound Systems

| Atoms/Ions | $\Delta E_{HF}$ | $\Delta E_{(LSD)}$ | $\Delta E_{(MLSDSIC)}$ |
|------------|-----------------|--------------------|------------------------|
| $Li(2s^1\,2S \rightarrow 2p^1\,2P)$ | 0.0677 | 0.0646 | 0.0672 |
| $Na(3s^1\,2S \rightarrow 3p^1\,2P)$ | 0.0725 | 0.0751 | 0.0753 |
| $Mg^+(3s^1\,2S \rightarrow 3p^1\,2P)$ | 0.1578 | 0.1585 | 0.1696 |
| $K(4s^1\,2S \rightarrow 4p^1\,2P)$ | 0.0516 | 0.0556 | 0.0580 |

### Table IV: Electron Transition Energy from the 3s to the 3p Orbital in Some Atoms

| Atoms/Ions | $\Delta E_{HF}$ | $\Delta E_{(LSD)}$ | $\Delta E_{(MLSDSIC)}$ |
|------------|-----------------|--------------------|------------------------|
| $P(3s^23p^3\,4S \rightarrow 3s^13p^4\,4P)$ | 0.3023 | 0.2934 | 0.3055 |
| $S(3s^23p^4\,3P \rightarrow 3s^13p^5\,3P)$ | 0.4264 | 0.3615 | 0.4334 |
| $Cl^+(3s^23p^4\,3P \rightarrow 3s^13p^5\,3P)$ | 0.5264 | 0.4482 | 0.5403 |
| $Cl(3s^23p^5\,2P \rightarrow 3s^13p^6\,2S)$ | 0.5653 | 0.4301 | 0.5630 |
| $Ar^+(3s^23p^5\,2P \rightarrow 3s^13p^6\,2S)$ | 0.6769 | 0.5174 | 0.6766 |
TABLE V: Electron transition energy from the 2s to the 3p orbital in the same atoms as in Table IV.

| atoms/ions | $\Delta E_{HF}$ | $\Delta E$(LSD) | $\Delta E$(MLSDSIC) |
|------------|-----------------|-----------------|---------------------|
| $P(2s^23p^3 \ 4S \rightarrow 2s^13p^4 \ 4P)$ | 6.8820 | 6.4188 | 6.9564 |
| $S(2s^23p^4 \ 3P \rightarrow 2s^13p^5 \ 3P)$ | 8.2456 | 7.7337 | 8.3271 |
| $Cl^+(2s^23p^4 \ 3P \rightarrow 2s^13p^5 \ 3P)$ | 9.8117 | 9.2551 | 9.8997 |
| $Cl(2s^23p^5 \ 2P \rightarrow 2s^13p^6 \ 2S)$ | 9.7143 | 9.1653 | 9.8171 |
| $Ar^+(2s^23p^5 \ 2P \rightarrow 2s^13p^6 \ 2S)$ | 11.3926 | 10.8009 | 11.5061 |

TABLE VI: Electron transition energies for atoms where LSD transition energies are accurate

| atoms/ions | $\Delta E_{HF}$ | $\Delta E$(LSD) | $\Delta E$(MLSDSIC) |
|------------|-----------------|-----------------|---------------------|
| $B(2s^22p^1 \ 2P \rightarrow 2s^12p^2 \ 2D)$ | 0.2172 | 0.1993 | 0.2061 |
| $C^+(2s^22p^1 \ 2P \rightarrow 2s^12p^2 \ 2D)$ | 0.3290 | 0.3078 | 0.3216 |
| $C(2s^22p^2 \ 3P \rightarrow 2s^12p^3 \ 3D)$ | 0.2942 | 0.2878 | 0.2967 |
| $N^+(2s^22p^2 \ 3P \rightarrow 2s^12p^3 \ 3D)$ | 0.4140 | 0.4149 | 0.4305 |
| $Si^+(3s^22p^1 \ 2P \rightarrow 3s^13p^2 \ 2D)$ | 0.2743 | 0.2632 | 0.2799 |
| $Si(3s^22p^2 \ 3P \rightarrow 3s^13p^3 \ 3D)$ | 0.2343 | 0.2356 | 0.2442 |
TABLE VII: Excitation energies of some atoms when two electrons are excited.

| atoms/ions                     | $\Delta E_{HF}$ | $\Delta E$(LSD) | $\Delta E$(MLSDSIC) |
|-------------------------------|-----------------|-----------------|---------------------|
| $Be(2s^2 1S \rightarrow 2p^2 1D)$ | 0.2718          | 0.2538          | 0.2655              |
| $B(2s^22p^1 2P \rightarrow 2p^3 2D)$ | 0.4698          | 0.4117          | 0.4798              |
| $C^+(2s^22p^1 2P \rightarrow 2p^3 2D)$ | 0.6966          | 0.6211          | 0.7180              |
| $C(2s^22p^2 3P \rightarrow 2p^4 3P)$ | 0.7427          | 0.5950          | 0.7312              |
| $N^+(2s^22p^2 3P \rightarrow 2p^4 3P)$ | 1.0234          | 0.8369          | 1.0143              |
| $N(2s^22p^3 4S \rightarrow 2p^5 2P)$ | 1.1789          | 0.9440          | 1.1785              |
| $O^+(2s^22p^3 4P \rightarrow 2p^5 2P)$ | 1.5444          | 1.2552          | 1.5480              |
| $O(2s^22p^4 3P \rightarrow 2p^6 1S)$ | 1.5032          | 1.1333          | 1.4736              |
| $F^+(2s^22p^4 3P \rightarrow 2p^6 1S)$ | 1.8983          | 1.4381          | 1.8494              |
| $Mg(3s^2 1S \rightarrow 3p^2 1D)$ | 0.2578          | 0.2555          | 0.2651              |
| $S(3s^23p^4 3P \rightarrow 3p^6 1S)$ | 1.0273          | 0.7807          | 1.0266              |
| $P(3s^23p^4 3S \rightarrow 3p^5 2P)$ | 0.8539          | 0.6927          | 0.8680              |
| $Si^+(3s^23p^1 2P \rightarrow 3p^3 2D)$ | 0.5856          | 0.5377          | 0.6230              |
| $Si(3s^23p^2 3P \rightarrow 3p^4 3P)$ | 0.5860          | 0.4928          | 0.5986              |
| $Cl^+(3s^23p^2 3P \rightarrow 3p^4 3P)$ | 1.2535          | 0.9551          | 1.2516              |