Is it possible to construct excited-state energy functionals by splitting k-space?

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Abstract

We show that our procedure of constructing excited-state energy functionals by splitting k-space, employed so far to obtain exchange energies of excited-states, is quite general. We do so by applying the same method to construct modified Thomas-Fermi kinetic energy functional and its gradient expansion up to the second order for the excited-states. We show that the resulting kinetic energy functional has the same accuracy for the excited-states as the ground-state functionals do for the ground-states.

Key-words: excited-state density-functional theory, modified Thomas-Fermi functional, gradient-expansion approximation, Gázquez-Robles functional
I. INTRODUCTION

Since the inception of ground-state density functional theory (DFT), efforts have been made to extend it to excited-states. Such attempts include the work of Ziegler et al., Gunnarsson et al., von Barth, Perdew and Levy, Pathak, Theophilou, Oliveira, Gross and Kohn, Nagy, Sen and Singh and Deb. However, a general excited-state density functional theory for individual excited-states, akin to its ground-state counterpart, has started taking shape only over the past decade or so.

In density functional theory, energy of a system is expressed as a functional of the density of the system. History of writing energy of a system in terms of its density is as old as quantum-mechanics itself. In an attempt to simplify the problem of interacting electrons, Thomas and Fermi expressed the kinetic energy of a many electron system approximately by employing the expression for the kinetic energy of the homogeneous electron gas (HEG). Similarly, Dirac gave an approximate expression for the exchange energy of a many-electron system by employing the corresponding HEG formula. With the Hohenberg-Kohn discovery of the one-to-one map between the ground-state density and the Hamiltonian of a system, it became clear that the energy of a system can indeed be expressed as a functional of its ground-state density; however, the functional is not known exactly. In the Kohn-Sham formulation of DFT, the kinetic energy component of the total energy is treated highly accurately by writing it in terms of orbitals of an auxiliary system. Thus the non-interacting kinetic energy is expressed in terms of the Kohn-Sham orbitals $|\phi_i\rangle$ as (atomic units are used throughout the paper so that we take $\hbar = m_e = |e| = 1$)

$$\sum_i f_i \langle \phi_i | - \frac{1}{2} \nabla^2 |\phi_i\rangle$$  \hspace{1cm} (1)

where $f_i$ represent the occupation of $i^{th}$ orbital. For the ground-state, $f_i = 1$ for $i^{th}$ orbital of each spin if $i \leq i_{max}$ where $i_{max}$ is the index of the uppermost occupied orbital and is 0 for all the higher orbitals. For an excited-state, the occupation is different from the ground-state; for example it could be equal to 1 for $i \leq i_1$, 0 for $i_1 < i \leq i_2$ and 1 again for $i_2 < i \leq i_3$, as shown schematically in Fig. 1. On the other hand, the exchange and correlation energies are still expressed approximately in terms of the density. Foremost among these approximations are the local-density approximation (LDA) and the local spin-density approximation (LSD).
In these approximations, the exchange and correlation energies are expressed in terms of the density by employing the corresponding expression for the HEG. Thus the LDA for the exchange energy is the same as the Dirac expression for it. Over the years, far more accurate functionals [31] for exchange and correlation energies have been constructed by going beyond the LDA and including corrections in terms of the gradient of the density. The leading term in most of these functionals is the LDA/LSD functional and in the limit of the gradient of the density vanishing, the functionals indeed reduce to the latter.

Given this background, a question that arises naturally in the development of excited-state DFT is if it would possible to construct energy functionals for these states with similar accuracy as is obtained in the ground-state functionals. In particular it is important to develop an LDA functional for the excited-states since that is the foundation on which more accurate functionals are built. We have recently constructed an exchange energy functional for excited-states within the LDA. This has been done by splitting the k-space in accordance to the occupied and unoccupied orbitals of the excited-state, as shown in Fig. 1. In the figure, we have some orbitals - the core orbitals - including the lowest energy orbitals that are occupied, then some empty orbitals and then some more orbitals - the shell orbitals - that are occupied again. The k-space, also shown in the figure, is accordingly split such that it is occupied from $k = 0$ to $k = k_1$, empty from $k_1$ to $k_2$ and then occupied again from $k_2$ to $k_3$. Here $k_1$, $k_2$ and $k_3$ are given by the equations

\begin{align*}
  k_1^3(r) &= 3\pi^2 \rho_c(r) \\
  k_2^3(r) - k_1^3(r) &= 3\pi^2 \rho_{vac}(r) \\
  k_3^3(r) - k_2^3(r) &= 3\pi^2 \rho_s(r)
\end{align*}

(2) (3) (4)

where $\rho_c$ and $\rho_s$ are the electron densities corresponding to the core and the shell orbitals. Similarly, $\rho_{vac}$ is the electron density corresponding to the set of unoccupied orbitals. Thus

\begin{align*}
  \rho_c(r) &= \sum_i |\phi_i^{core}(r)|^2 \\
  \rho_{vac}(r) &= \sum_i |\phi_i^{unocc}(r)|^2 \\
  \rho_s(r) &= \sum_i |\phi_i^{shell}(r)|^2
\end{align*}
FIG. 1: Orbital occupation of electrons (a) and the corresponding $f_i$ for each spin drawn continuously as a function of orbital energy $\epsilon_i$ (b) for the ground and an excited-state of a finite system. The corresponding k-space occupation (c), in the ground and an excited state configuration similar to that shown in (a) for a homogeneous electron gas (HEG).

The total electron density $\rho(r)$ is given as

$$\rho(r) = \rho_c(r) + \rho_s(r)$$

For detailed derivation of these equations, we refer the reader to the next section. Employing the exchange energy functional developed by us, we have been performing accurate calculations of excited-state energies of a variety of systems including the band gaps of a wide variety of semiconductors in the recent past.

Although the results obtained by us with the excited-state exchange energy functional are impressive, the question that we have been asking ourselves is if the method employed by us - that of splitting the k-space - to construct the functional is general. If the answer is in the affirmative, the same method should also lead to reasonably accurate functionals for other components, viz. the kinetic and the correlation energies, of the total energy. Further, we should be able to build on the LDA to include higher order corrections in terms of the gradient of the density. In this paper we address this question in connection with the non-interacting kinetic energy of a system of electrons. Our aim in these investigations is to explore if a kinetic energy functional for excited states, constructed by splitting the
k-space, gives similar accuracy for exact kinetic energy of these states as the well known Thomas-Fermi or the gradient-expansion approximation (GEA) functionals\[3, 4\] do for the ground states. We show in this paper that it does. Thus our present results demonstrate the robustness of our procedure of constructing energy functionals for the excited-states of a many-electron system.

We note that besides the GEA functional, there is another approach to constructing kinetic-energy functionals \[33\] for the ground-state, which employs two exact asymptotic forms: Thomas-Fermi for the HEG and the von-Weizsacker term \[34\] for one-orbital systems. If our approach has universality, it should also work for functional such as the Gázquez-Robles functional proposed in reference \[33\]. We show in this paper that it does.

We start in the next section with a description of the Thomas-Fermi approximation for the non-interacting kinetic energy for the ground-state. This approximation is the LDA for the kinetic energy. We then discuss the gradient expansion approximation (GEA) for the kinetic energy up to the second-order in the density gradient. Results for a few atomic systems and the key features of these results are then discussed. This forms the background against which the kinetic energy functional for the excited-state is then constructed and tested in the section after the next one. We end the paper with some concluding remarks.

We point out that our aim in this paper is to explore conceptually if our approach yields kinetic energy functionals that have accuracy similar to their ground-state counterparts. Our work shows that it does. Question arises: Can these functionals be applied to obtain average excited-state energies. This possibility is being explored. However, density-based functionals cannot be expected to reproduce the exact answer for the kinetic energy, as given by equation 1. Therefore the operational utility of the kinetic energy density-functionals for excited-states is similar to that of traditional Thomas-Fermi functional or its extensions for the ground-state.

II. LDA AND GEA UP TO THE SECOND ORDER FOR THE NON-INTERACTING KINETIC ENERGY OF THE GROUND-STATE

The basis of the LDA is the homogeneous electron gas for which the kinetic and the exchange energies can be expressed in a rather simple form involving the density of the system. For the non-interacting kinetic energy we consider a gas of non-interacting electrons
that fill the k-space from \( k = 0 \) to \( k = k_F \) because of the Pauli exclusion principle. The wavefunction for an electron in a state specified by wavevector \( \mathbf{k} \) is

\[
\psi_k(\mathbf{r}) = \frac{1}{\sqrt{V}} \exp(i\mathbf{k} \cdot \mathbf{r}),
\]

where \( V \) is the volume over which the periodic boundary conditions are applied on the wavefunction. Assuming the volume to be a large cube of side \( L \), the wavevectors \( \mathbf{k} \) take the values

\[
\mathbf{k} = \frac{2\pi}{L}(n_1 \hat{x} + n_2 \hat{y} + n_3 \hat{z})
\]

where \( n_i = 1, 2, 3 \ldots \) with the maximum value such that the magnitude of the largest \( \mathbf{k} \) is \( k_F \). The density of k-points in the k-space is therefore \( \frac{V}{4\pi^3} \) and the density of states including the spin of the electrons is \( \frac{V}{4\pi^3} \). Equating the total number of electrons \( N \) within the volume \( V \) to the number of states within a sphere of radius \( k_F \), referred to as the Fermi sphere, leads to

\[
k_F = (3\pi^2 \rho)^{\frac{1}{3}}
\]

where \( \rho = \frac{N}{V} \) is the number density of the homogeneous electron gas. Similarly the total kinetic energy is calculated by summing the kinetic energy \( \frac{k^2}{2} \) of a state specified by the wavevector \( \mathbf{k} \) over the Fermi sphere. It gives the kinetic energy density or the kinetic energy \( t_s \) per unit volume to be

\[
t_s = \frac{k_F^2}{10\pi^2} = \frac{3}{10} (3\pi^2 \rho)^{\frac{2}{3}}
\]

The local density approximation to the kinetic energy \( \sum_i f_i \langle \phi_i | -\frac{1}{2} \nabla^2 | \phi_i \rangle \) for the ground-state of an inhomogeneous electron gas, such as that in an atom or a molecule, of space-dependent density \( \rho(\mathbf{r}) = \sum_i f_i |\phi_i(\mathbf{r})|^2 \) corresponds to approximating the kinetic energy density at each point by the formula above and integrating it over the entire volume. This leads to the Thomas-Fermi kinetic energy functional

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

where \( k_F(\mathbf{r}) \) and \( \rho(\mathbf{r}) \) at each point in space are related by equation 8. In equation 10 the superscript (0) indicates that this is the zeroth-order approximation to the exact kinetic
energy for an inhomogeneous electron gas. It is well known to underestimate the exact kinetic energy. If the number of up and down spin electrons is different, the functional given above can be written in terms of the spin densities $\rho \uparrow$ and $\rho \downarrow$ as

$$T[\rho \uparrow, \rho \downarrow] = \frac{1}{2}(T_s^{(0)}[2\rho \uparrow] + T_s^{(0)}[2\rho \downarrow])$$  \hspace{1cm} (11)$$

Exact kinetic energy for some closed-shell hydrogen-like atoms and the Thomas Fermi approximation to it for the same atoms is given in Table I. Table II gives the exact kinetic energy for atoms from H to Ne for the density obtained by solving the Kohn-Sham equation for it within the Gunnarsson-Lundquist parametrization of the LDA for the exchange-correlation energy. As is evident from the Tables, Thomas-Fermi functional underestimates the exact kinetic energy by about 5% to 10%.

The first correction to the Thomas-Fermi functional in terms of the density gradient is proportional to the square of the gradient of the density and is given as

$$T_s^{(2)}[\rho] = \frac{1}{72} \int |\nabla \rho(\mathbf{r})|^2 \rho(\mathbf{r}) d\mathbf{r}$$  \hspace{1cm} (12)$$

This is easily derived from the expansion of the response function of a non-interacting electron gas. The correction term is also generalized in terms of the spin densities as given by equation (11). Equation (12) represents the lowest-order gradient correction to the Thomas-Fermi functional. The gradient-corrected kinetic energy $T^{(0)} + T^{(2)}$ is also given in Tables I and II for the atomic systems given there. It is seen that the inclusion of the second-order correction brings the approximate kinetic energy closer to the exact one, with the difference being less than 1%. The question that we now address is if kinetic energy functionals can also be written for excited states using ideas employed to generate functionals for the ground-state.

### III. LDA AND GEA UP TO THE SECOND ORDER FOR THE NON-INTERACTING KINETIC ENERGY OF EXCITED-STATES

One straightforward choice for the functionals to be employed for excited-states is to use the ground-state functionals described in the section above. However, the way k-space is occupied to construct the ground-state functionals does not reflect proper occupation of orbitals that are occupied in an excited-state. While for the excited-states of a given
number of electrons in a homogeneous electron gas we expect orbitals with relatively larger magnitude of wavevectors to be occupied, this does not happen if we use the ground-state functional to approximate the kinetic energy of excited-states; as such the ground-state functional would underestimate the kinetic energy of excited-states by a much larger amount than the proper excited-state functional should. This is shown in Table III where we have shown the approximate kinetic-energy, calculated using the ground-state LSD and GEA functionals of the section above, of some excited-states of a few hydrogen-like atoms and have compared them to the exact kinetic energy. It is seen from the Tables that the ground-state functionals indeed underestimate the exact kinetic energy of excited states by significantly larger amount than they do for the ground-states. In Table IV, the approximate kinetic energies are compared to the exact kinetic energies for excited-state densities obtained by solving the Kohn-Sham equation with the Gunnarsson-Lundquister parametrization. Here also the error in numbers obtained by applying the ground-state functionals is quite large.

To develop a kinetic energy functional corresponding to excited-states, we have proposed \cite{22} in the context of exchange energy that the k-space be split in accordance to the occupation of orbitals in the excited-state of a system. This is shown in Fig. 1 for an excited-state where some lowest lying orbitals - the core orbitals - are occupied, then there are some vacant orbitals and then some more orbitals - the shell orbitals - are occupied. According to our method of constructing excited-state functionals for such a system, the k-space is also occupied correspondingly with orbitals up to \( k_1 \) being occupied with \( k_1 \) given by equation 2, orbitals between \( k_1 \) and \( k_2 \) being vacant with \( k_2 \) given by equation 3 and again orbitals from \( k_2 \) to \( k_3 \) being occupied with \( k_3 \) given by equation 4. Now steps leading to equation 10 are taken to derive the kinetic energy for such a system. The corresponding LDA functional \( T^*(0) \) for the excited-state is then given as

\[
T^*(0)(k_1, k_2, k_3) = \frac{1}{10\pi^2} \int \left( k_1^5(r) + k_2^5(r) - k_3^5(r) \right) dr \tag{13}
\]

The spin-density generalization of equation 13 is given by equation 11. We call the functional given by equation 13 the modified Thomas-Fermi functional. In the functional above the term \( \frac{1}{10\pi^2} \int (k_1^5(r)) dr \) represents the kinetic energy of the core orbitals whereas \( \frac{1}{10\pi^2} \int (k_3^5(r) - k_2^5(r)) dr \) that of the shell orbitals. Thus \( \sum_i \langle \phi_i^{\text{core}} \mid -\frac{1}{2} \nabla^2 \mid \phi_i^{\text{core}} \rangle \) is approximated by the former while \( \sum_i \langle \phi_i^{\text{shell}} \mid -\frac{1}{2} \nabla^2 \mid \phi_i^{\text{shell}} \rangle \) by the latter.

We now test the functional of equation 13 for excited-states of hydrogen-like and real
atoms. Shown in Table III are the approximate kinetic energies calculated using the functional of equation 13 for excited-states of hydrogen-like atoms. The numbers shown are for excited-states in which orbitals up to principal quantum number \( n_1 \) are occupied, those from \( n_1 + 1 \) to \( n_2 \) are vacant and then \( n_2 + 1 \) to \( n_3 \) are again occupied. It is seen that the energies calculated with the functional of equation 13 are better approximation to the exact kinetic energy in comparison to the ground-state functional of equation 10. Thus while the ground-state kinetic energy functional \( T^{(0)} \) given by equation 10 underestimates the excited-state kinetic energy by a substantial amount, the excited-state functional \( T^{*{(0)}} \) given by equation 13 has the same accuracy for the excited-states as the ground-state functional does for the ground-state. In Table IV the numbers for approximate kinetic energy as obtained by applying the Thomas-Fermi functional and the modified Thomas-Fermi functional of equation 13 for the density of Kohn-Sham are given. These densities have been obtained by solving the Kohn-Sham equation within the local-spin density approximation for the exchange-correlation energy. The numbers are compared with the exact kinetic energy \( \sum_i f_i \langle \phi_i | -\frac{1}{2} \nabla^2 | \phi_i \rangle \) with \( f_i \) representing the number of electrons in the \( i^{th} \) orbital, obtained from the Kohn-Sham orbitals \( |\phi_i\rangle \). Similar to the case of hydrogen-like atoms, here too the functional of equation 13 gives kinetic energies that are better than those obtained from the ground-state functional and has similar accuracy as the ground-state functional does for the ground-state densities. We thus conclude that the modified Thomas-Fermi functional of equation 13 is the correct zeroth-order approximation for the kinetic energies of excited-states. More importantly, this indicates that the idea of constructing excited-state energy functionals by splitting the \( k \)-space is a sound one.

We next discuss the gradient expansion approximation for the excited-states kinetic energy. Since the kinetic energy is a sum of kinetic energy of individual orbitals, the second order correction to the kinetic energy for an excited-state can also be written exactly in the same manner as the zeroth order approximation given by equation 13. Thus the second-order gradient correction to the excited-state kinetic energy is given as

\[
T^{*(2)}(k_1, k_2, k_3) = \frac{1}{72} \int \frac{|\nabla \rho(r; k_1)|^2}{\rho(r; k_1)} dr + \frac{1}{72} \int \frac{|\nabla \rho(r; k_3)|^2}{\rho(r; k_3)} dr - \frac{1}{72} \int \frac{|\nabla \rho(r; k_2)|^2}{\rho(r; k_2)} dr \tag{14}
\]

Like in the functional of equation 13 the term \( \frac{1}{72} \int \frac{\nabla^2 \rho(r; k_1)}{\rho(r; k_1)} dr \) gives the gradient correction to the core-orbitals kinetic energy while the last two terms give it for the shell orbitals. Here \( \rho(r; k) = \frac{k^3}{3\pi} \) is the ground-state density corresponding to Fermi wavevector \( k \). The
spin-density generalization of equation 14 is given by equation 11. In Tables III and IV we also show the second-order corrected kinetic energy \( T^s(0) + T^s(2) \) for excited-states of hydrogen-like and real atoms, respectively, and compare it to the exact kinetic energies. It is again seen that the second order-correction calculated by using equation 14 leads to improved kinetic energies for the excited-states.

As an extreme test for the functional of equations 13 and 14, we apply them to excited-states where there are no core electrons, i.e. all the electrons have been excited. The exact and approximate kinetic energies for such states are given in Table V for the Kohn-Sham densities. Comparison of the numbers given shows the following: while the ground-state functional of equations 10 and 12 underestimate the exact kinetic energy by very large amount, the excited-state functionals of equations 13 and 14 bring the error down significantly. This again points to the soundness of the idea - that of splitting the k-space - behind the construction of these functionals.

IV. GÁZQUEZ-ROBLES FUNCTIONAL FOR EXCITED-STATES

As mentioned in the introduction, there are other forms of the kinetic energy functional for the ground-state that are based on considerations other than the LDA and it gradient expansion. One of these approaches constructs a functional by combining the von-Weizsacker functional

\[
T^W[\rho] = \frac{1}{8} \int \frac{\nabla \rho^2}{\rho} dr,
\]

which is exact for one-orbital systems and the Thomas-Fermi (equation 10) functional with a correction factor

\[
C(N) = \left(1 - \frac{2}{N}\right) \left(1 - \frac{A_1}{N^\frac{2}{3}} + \frac{A_2}{N^\frac{4}{3}}\right),
\]

where \( N \) is the number of electrons in the system. Thus the final functional is

\[
T^{(0)g}[\rho] = T^W(\rho) + C(N)T^{s(0)}(\rho)
\]

The constants \( A_1 = 1.314 \) and \( A_2 = 0.0021 \) for spin-compensated case. It is easily generalized to the spin dependent case through equation 11. In the functional above, the von-Weizsacker term gives accurate kinetic energy for the lowest orbital and the contribution from the rest of the orbitals is accounted for by the second term. Thus the factor \( (1 - \frac{2}{N}) \) in
the second term plays an important role of subtracting from the Thomas-Fermi functional
the kinetic energy contribution of the lowest orbital, treated exactly by the first term.

Applying the same arguments that were used to derive equation 13 and 12 - that the kinetic energy for an excited-state is written as a combination of the ground-state kinetic energy functionals corresponding to the wavevectors \( k_1, k_2 \) and \( k_3 \) - we write the excited-state Gámez-Robles functional as

\[
T^*g(k_1, k_2, k_3) = T^{(0)g}(\rho(\mathbf{r}; k_1)) + T^{(0)g}(\rho(\mathbf{r}; k_3)) - T^{(0)g}(\rho(\mathbf{r}; k_2)) 
\] (18)

We have also tested the ground-state Gámez-Robles functional (equation 17) and its excited-state generalization (equation 18) for the excited-states studied in Tables IV and V. The results are shown in Tables VI and VII. It is evident from the numbers presented that with the Gámez-Robles functional also, our approach leads to an excited-state functional that estimates the kinetic energy of an excited-state better than its ground-state counterpart. We note, however, that unlike the GEA functional the Gámez-Robles functional is not uniformly accurate for all the excited-states studied. This could be because the parameters of the functional have been optimized using the ground-state kinetic energies of atoms within the Hartree-Fock theory. Nonetheless, by applying our approach to two kinetic-energy functionals, which are derived by two different methods, we have shown that our method leads to improved functionals for excited states.

V. CONCLUDING REMARKS

In this work we have tested the idea of constructing the LDA to excited-state energy functionals of time-independent density functional theory by splitting the k-space in the context of non-interacting kinetic energy functionals. Our results show that the functionals obtained by such a method have the same accuracy for the excited-states as the ground-state functionals do for the ground-states. Further, we have shown that gradient correction can also be made on such functionals. The general nature of our proposal is evident from the fact that applying it to a different kinetic-energy functional also leads to an improved functional for the excited-states. In the future we would like to derive the gradient correction given by equation 14 in a manner similar to that 35 for the ground-state, i.e. from the response function of the excited HEG. Further, it would also be interesting to see if excited-state
functional derived here can be used to approximately calculate excited-state energies by employing a variational form for the excited-state densities.

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TABLE I: Closed Shell : Exact and Thomas Fermi (Equation 10 of the text ) $T^{(0)}$ and Gradient corrected kinetic energy $T^{(0)} + T^{(2)}$ (Equation 12 of the text ) for closed shell hydrogen like atoms. Numbers given are in atomic units. Percentage errors as shown in brackets under each number.

| atoms                | $T^{Exact}$ | $T^{(0)}$ | $T^{(0)} + T^{(2)}$ |
|----------------------|-------------|-----------|---------------------|
| $He(1s^2)$           | 3.672       | 4.134     | (8.2) (3.4)         |
| $Be([He]2s^2)$       | 17.719      | 19.785    | (11.4) (1.1)        |
| $Ne([Be]2p^6)$       | 188.849     | 202.869   | (5.6) (1.4)         |
| $Mg([Ne]3s^2)$       | 284.712     | 305.978   | (6.3) (0.6)         |
| $Ar([Mg]3p^6)$       | 737.963     | 790.652   | (6.8) (0.2)         |
TABLE II: Exact Kinetic Energy of ground state of some atoms as obtained by solving the Kohn-Sham equation with the Gunnarsson-Lundquist parametrization of the LSD for exchange and correlation energy. Numbers given are in atomic units. The exact kinetic energy is compared with the Thomas-Fermi (Equation 10) and gradient corrected functional (Equation 13)

| atoms          | KS  | $T^{(0)}$ | $T^{(0)} + T^{(2)}$ |
|----------------|-----|-----------|---------------------|
| $H(1s^1)$      | 0.430 | 0.390     | 0.438               |
|                |      |           | (9.3) (1.8)         |
| $He(1s^2)$     | 2.780 | 2.468     | 2.777               |
|                |      |           | (11.2) (1.1)        |
| $Li([He]2s^1)$ | 7.269 | 6.521     | 7.305               |
|                |      |           | (10.3) (0.5)        |
| $Be([He]2s^2)$ | 14.331| 12.860    | 14.347              |
|                |      |           | (10.3) (0.1)        |
| $B([Be]2p^1)$  | 24.201| 21.649    | 24.040              |
|                |      |           | (10.5) (0.7)        |
| $C([Be]2p^2)$  | 37.277| 33.476    | 36.980              |
|                |      |           | (10.2) (0.8)        |
| $N([Be]2p^3)$  | 53.899| 48.946    | 53.778              |
|                |      |           | (9.2) (0.2)         |
| $O([Be]2p^4)$  | 74.223| 67.084    | 73.406              |
|                |      |           | (9.6) (1.1)         |
| $F([Be]2p^5)$  | 98.742| 89.450    | 97.472              |
|                |      |           | (9.4) (1.3)         |
| $Ne([Be]2p^6)$ | 127.794| 116.838   | 126.778             |
|                |      |           | (8.6) (0.8)         |
TABLE III: Kinetic energies (in atomic units) of excited states of hydrogen like atoms. Z gives the atomic number of the atom and the excited state is such that the orbitals are occupied upto $n_1$, vacant from $n_1 + 1$ to $n_2$ and occupied again from $n_2 + 1$ to $n_3$ and the corresponding approximate kinetic energies. The latter are calculated by applying ground-state functionals $T^{(0)}$ and $T^{(0)} + T^{(2)}$ of Equations 10 and 12 and the excited state functionals of Equations 13 and 14. The corresponding errors are given below each number.

| Z  | $n_1$ | $n_2$ | $n_3$ | $T^{(Exact)}$ | $T^{(0)}$ | $T^{(0)} + T^{(2)}$ | $T^{(0)} + T^{(2)}$ | $T^{*^{(0)}}$ | $T^{*^{(0)} + T^{*^{(2)}}}$ |
|----|------|------|------|---------------|----------|-------------------|-------------------|-------------|------------------|
| 10 | 1    | 2    | 5    | 400           | 331.315  | 345.737           | 389.390          | 403.006     |
|    |      |      |      |               | (17.17) | (13.57)           | (2.65)           | (0.75)      |
| 15 | 2    | 4    | 6    | 900           | 700.795 | 737.727           | 873.249          | 907.667     |
|    |      |      |      |               | (22.13) | (18.03)           | (2.97)           | (0.85)      |
| 20 | 2    | 5    | 7    | 1600          | 1177.696| 1249.214          | 1553.078         | 1620.010    |
|    |      |      |      |               | (26.39) | (21.92)           | (2.93)           | (1.25)      |
| 20 | 2    | 5    | 8    | 2000          | 1486.889| 1558.398          | 1952.452         | 2019.384    |
|    |      |      |      |               | (25.66) | (22.08)           | (2.38)           | (0.97)      |
| 25 | 3    | 4    | 7    | 3750          | 3316.238| 3437.872          | 3665.147         | 3779.984    |
|    |      |      |      |               | (11.57) | (8.32)            | (2.26)           | (0.80)      |
| 30 | 3    | 4    | 7    | 5400          | 4773.266| 4960.075          | 5275.695         | 5456.973    |
|    |      |      |      |               | (11.61) | (8.15)            | (2.30)           | (1.06)      |
| 30 | 5    | 8    | 10   | 6300          | 5410.076| 5597.432          | 6171.908         | 6353.568    |
|    |      |      |      |               | (14.13) | (11.15)           | (2.03)           | (0.85)      |
| 35 | 2    | 4    | 6    | 4900          | 3806.116| 4071.146          | 4745.025         | 5017.298    |
|    |      |      |      |               | (22.32) | (16.91)           | (3.16)           | (2.39)      |
| 40 | 7    | 9    | 12   | 16000         | 14534.00| 14904.93          | 15748.793        | 16139.184   |
|    |      |      |      |               | (9.16)  | (6.84)            | (1.57)           | (0.87)      |
| 45 | 3    | 4    | 9    | 16200         | 14521.834| 15010.222         | 15880.574        | 16426.318   |
|    |      |      |      |               | (10.36) | (7.34)            | (1.97)           | (1.40)      |
TABLE IV: Exact kinetic energies (in atomic units) of excited states of some atoms as obtained by solving the the Kohn-Sham equation with Gunnarsson-Lundquist parametrization of the LSD for exchange and correlation energy and the corresponding approximate kinetic energies. The latter are calculated by applying ground-state functionals $T^{(0)}$ and $T^{(0)} + T^{(2)}$ of Equations 10 and 12 and the excited state functionals of Equations 13 and 14. The corresponding errors are given below each number.

| Atom           | $T^{(Exact)}$ | $T^{(0)}$  | $T^{(0)} + T^{(2)}$ | $T^{*(0)}$ | $T^{*(0)} + T^{*(2)}$ |
|----------------|---------------|------------|---------------------|------------|------------------------|
| $Be(1s^22s^02p^03s^2)$ | 13.768        | 12.278     | 13.768              | 12.459     | 13.945                 |
|                | (10.82)       | (0.0)      | (9.51)              | (1.29)     |                        |
| $O(1s^22s^02p^6)$ | 73.094        | 64.154     | 70.068              | 67.545     | 73.704                 |
|                | (12.23)       | (4.14)     | (7.59)              | (0.83)     |                        |
| $O(1s^22s^02p^03s^23p^4)$ | 65.764    | 56.967     | 63.516              | 59.834     | 66.291                 |
|                | (13.38)       | (3.42)     | (9.02)              | (0.80)     |                        |
| $O(1s^22s^02p^03s^03p^6)$ | 65.506    | 56.344     | 62.815              | 59.885     | 66.313                 |
|                | (13.99)       | (4.11)     | (8.58)              | (1.23)     |                        |
| $Ne(1s^22s^02p^63s^2)$ | 124.508      | 109.521    | 118.891             | 116.152    | 125.947                |
|                | (12.04)       | (4.51)     | (6.71)              | (1.16)     |                        |
| $Ne(1s^22s^02p^03s^23p^6)$ | 109.241    | 93.430     | 103.889             | 99.675     | 109.920                |
|                | (14.47)       | (4.90)     | (8.76)              | (0.62)     |                        |
| $Mg(1s^22s^02p^63s^23p^2)$ | 191.942      | 169.083    | 182.740             | 180.095    | 194.392                |
|                | (11.91)       | (4.79)     | (6.17)              | (1.28)     |                        |
| $Ar(1s^22s^02p^63s^23p^04s^2)$ | 501.507    | 443.200    | 474.770             | 474.671    | 507.648                |
|                | (11.63)       | (5.33)     | (5.35)              | (1.22)     |                        |
TABLE V: Exact kinetic energies (in atomic units) of pure excited states of some atoms (i.e. all the electrons have been excited) as obtained by solving the the Kohn-Sham equation with Gunnarsson-Lundquist parametrization of the LSD for exchange and correlation energy and the corresponding approximate kinetic energies. The latter are calculated by applying ground-state functionals $T^{(0)}$ and $T^{(0)} + T^{(2)}$ of Equations 10 and 12 and the excited state functionals of Equations 13 and 14. The corresponding errors are given below each number.

| Atom          | $T^{(Exact)}$ | $T^{(0)}$ | $T^{(0)} + T^{(2)}$ | $T^{*(0)}$ | $T^{*(0)} + T^{*(2)}$ |
|---------------|---------------|-----------|---------------------|------------|------------------------|
| $He(2s^2)$    | 0.736         | 0.181     | 0.263               | 0.575      | 0.595                  |
|               | (75.41)       | (64.27)   | (21.88)             | (19.16)    |                        |
| $He(2s^02p^2)$| 0.676         | 0.292     | 0.315               | 0.614      | 0.606                  |
|               | (56.86)       | (53.43)   | (9.18)              | (10.34)    |                        |
| $Be(2s^22p^2)$| 4.815         | 2.160     | 2.409               | 4.066      | 4.079                  |
|               | (55.14)       | (49.97)   | (15.57)             | (15.30)    |                        |
| $Be(2p^4)$    | 4.565         | 2.219     | 2.370               | 4.337      | 4.277                  |
|               | (51.39)       | (48.09)   | (5.01)              | (6.32)     |                        |
| $Be(3s^23p^2)$| 2.253         | 0.475     | 0.611               | 1.935      | 1.943                  |
|               | (78.94)       | (72.89)   | (14.11)             | (13.78)    |                        |
| $O(2s^22p^6)$ | 33.286        | 20.073    | 21.139              | 30.953     | 30.781                 |
|               | (39.70)       | (36.49)   | (7.01)              | (7.53)     |                        |
| $O(3s^23p^6)$ | 15.655        | 4.504     | 5.207               | 14.106     | 14.077                 |
|               | (71.23)       | (66.74)   | (9.89)              | (10.08)    |                        |
| $Ne(2s^22p^63s^2)$ | 60.842    | 37.673    | 39.607              | 57.398     | 57.256                 |
|               | (38.08)       | (34.90)   | (5.66)              | (5.89)     |                        |
| $Mg(2s^22p^63s^23p^2)$ | 98.521    | 61.973    | 65.046              | 93.451     | 93.380                 |
|               | (37.10)       | (33.98)   | (5.15)              | (5.22)     |                        |
| $Mg(2p^63s^23p^4)$ | 88.796     | 51.142    | 53.748              | 89.023     | 88.477                 |
|               | (42.40)       | (39.47)   | (0.25)              | (0.36)     |                        |
| $Ar(2s^22p^63s^23p^64s^2)$ | 283.517  | 184.194   | 192.359             | 270.299    | 270.662                |
|               | (35.03)       | (32.15)   | (4.66)              | (4.53)     |                        |
TABLE VI: Exact kinetic energies (in atomic units) of excited states of some atoms as obtained by solving the Kohn-Sham equation with Gunnarsson-Lundquist parametrization of the LSD for exchange and correlation energy and the corresponding approximate kinetic energies obtained by applying the ground-state Gáquez functional $T^{(0)g}$ of Equation 17 and the excited state functional $T^{*g}$ of Equation 18. The corresponding errors are given below each number.

| Atom         | $T^{(Exact)}$ | $T^{(0)g}$  | $T^{*g}$  |
|--------------|---------------|-------------|-----------|
| Be$(1s^22s^02p^03s^2)$ | 13.768        | 14.472      | 14.282    |
|              | (5.11)        | (3.73)      |           |
| O$(1s^22s^02p^6)$        | 73.094        | 69.760      | 73.151    |
|              | (4.56)        | (0.08)      |           |
| O$(1s^22s^02p^03s^23p^4)$ | 65.764        | 73.210      | 70.675    |
|              | (11.32)       | (7.45)      |           |
| O$(1s^22s^02p^03s^03p^6)$ | 65.506        | 72.756      | 69.242    |
|              | (11.07)       | (5.70)      |           |
| Ne$(1s^22s^02p^63s^2)$  | 124.508       | 118.552     | 124.722   |
|              | (4.78)        | (0.17)      |           |
| Ne$(1s^22s^02p^03s^23p^6)$ | 109.241       | 123.323     | 118.816   |
|              | (12.89)       | (8.77)      |           |
| Mg$(1s^22s^02p^63s^23p^2)$ | 191.942       | 182.374     | 192.450   |
|              | (4.98)        | (0.26)      |           |
| Ar$(1s^22s^02p^63s^23p^04s^2)$ | 501.507       | 480.681     | 508.486   |
|              | (4.15)        | (1.39)      |           |
TABLE VII: Exact kinetic energies (in atomic units) of pure excited states of some atoms (i.e. all the electrons have been excited) as obtained by solving the the Kohn-Sham equation with Gunnarsson-Lundquist parametrization of the LSD for exchange and correlation energy and the corresponding approximate kinetic energies obtained by applying the ground-state Gámez functional $T^{(0)g}$ of Equation 17 and the excited state functional $T^{*g}$ of Equation 18. The corresponding errors are given below each number.

| Atom          | $T^{(Exact)}$ | $T^{(0)g}$  | $T^{*g}$  |
|---------------|---------------|-------------|-----------|
| Be($2s^22p^2$) | 4.815         | 2.596       | 3.560     |
|               | (46.08)       | (26.07)     |           |
| Be($2p^4$)    | 4.565         | 1.721       | 3.303     |
|               | (62.29)       | (27.65)     |           |
| Be($3s^23p^2$) | 2.253         | 1.304       | 3.133     |
|               | (42.12)       | (39.07)     |           |
| O($2s^22p^6$) | 33.286        | 14.769      | 26.284    |
|               | (55.63)       | (21.04)     |           |
| O($3s^23p^6$) | 15.655        | 7.489       | 21.615    |
|               | (52.16)       | (38.07)     |           |
| Ne($2s^22p^63s^2$) | 60.842 | 29.171      | 51.372 |
|               | (52.05)       | (15.57)     |           |
| Mg($2s^22p^63s^23p^2$) | 98.521 | 49.498      | 86.222 |
|               | (49.76)       | (12.48)     |           |
| Mg($2p^63s^23p^4$) | 88.796 | 41.533      | 81.642 |
|               | (53.23)       | (8.06)      |           |
| Ar($2s^22p^63s^23p^64s^2$) | 283.517 | 155.167     | 265.599 |
|               | (45.27)       | (6.32)      |           |