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The approximate nonempirical kinetic-energy functional proposed by Tal and Bader is analyzed for polyatomic systems. The performance of this functional and the functionals derived from the gradient expansion approximation truncated to zeroth, second, and fourth order is investigated for a testing set of 68 neutral and charged molecules. It is shown that the Tal–Bader functional, despite the simplicity of the idea behind its construction, leads to significantly better total kinetic energies than the gradient expansion approximation functionals. The local behavior of the kinetic-energy density derived from the Tal–Bader functional is also discussed.


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Introduction of the explicit long-range nonlocality as an alternative to the gradient expansion approximation for the kinetic-energy functional

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Abstract

The approximate nonempirical kinetic-energy functional proposed by Tal and Bader is analyzed for polyatomic systems. The performance of this functional and the functionals derived from the gradient expansion approximation truncated to zeroth, second, and fourth order is investigated for a testing set of 68 neutral and charged molecules. It is shown that the Tal–Bader functional, despite the simplicity of the idea behind its construction, leads to significantly better total kinetic energies than the gradient expansion approximation functionals. The local behavior of the kinetic-energy density derived from the Tal–Bader functional is also discussed. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Following the Hohenberg–Kohn theorems, all ground-state properties of a given N-electrons system are determined by the electron density $q(r)$. In particular, the ground-state energy can be expressed as a functional of $\rho(r)$, which is conventionally written as [1,2]

$$ E[\rho] = T[\rho] + V_{\text{ee}}[\rho] + \int v(r)\rho(r)\,dr, $$

where $T[\rho]$ and $V_{\text{ee}}[\rho]$, are the kinetic and the electron–electron repulsion energy, respectively, and the last term is the energy due to the external potential $v(r)$. Except for some particular cases, the exact form of the analytic dependence of $T[\rho]$ and $V_{\text{ee}}[\rho]$ on $\rho(r)$ is unknown. To overcome the problem of the unknown form of $T[\rho]$, which is a numerically significant component of the total energy, Kohn and Sham [3] introduced an auxiliary set of orbitals $\psi_i(r)$ representing noninteracting particles. In the Kohn–Sham formalism, the total electronic energy is represented with the following functional:

$$ E[\rho] = T_s[\rho] + \frac{1}{2} \int \rho(r)\rho(r') \frac{1}{|r-r'|} \,dr \,dr' + E_{\text{xc}}[\rho] $$

where

$$ T_s[\rho] = T_s[\{\psi_i\}] = \frac{1}{2} \sum_{i=1}^{N} \int \left| \nabla \psi_i(r) \right|^2 \,dr. $$

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The success of the Kohn–Sham theory as a method to approximate the exact solution of the Schrödinger equation, originates from the fact that the only part of the total energy which needs to be approximated, the exchange–correlation energy $E_{xc} [\rho]$, is small compared to the total energy. $E_{xc} [\rho]$ collects all the energetic effects arising from the Pauli exclusion principle and the Coulomb correlation. It is also important to point out that $E_{xc} [\rho]$ includes also the component $T_c [\rho] = T [\rho] - T_s [\rho]$ originating from the effect of electron correlation on the kinetic energy. $T_c [\rho]$ is positive and small compared to the whole $T [\rho]$.

The introduction of the orbital-dependent kinetic energy $T_s [\{ \psi_i \}]$ leads, however, to a formalism in which the number of equations to solve is proportional to the number of electrons. Therefore, computer modeling of large nonperiodic systems remains still a challenging problem. One can envisage an equivalent orbital-free formalism, in which the variational principle leads to the $N$-independent Euler–Lagrange equation (see [4] for instance). Due to the lack of good approximations for the kinetic-energy functional, a practical implementation of such an orbital-free formalism remains a challenge although a significant progress has been made in this area leading to computational techniques applicable to large metal clusters [5] and in materials science [6–8].

Approximate orbital-free kinetic-energy functional is also a crucial quantity in the subsystem formulation of density functional theory introduced by Cortona [9] to study solids. This formulation is the basis of the first-principle based embedding potential introduced by Wesolowski and Warshel [10] to study embedded molecules in such a way that the molecule under investigation and its microscopic environment can be described using approximate theories of different level of accuracy (for recent applications, see [11,12]).

In the literature, various approximate functionals have been proposed. They differ in their origin, as different theoretical strategies have been applied in various groups to derive a good approximate functional (gradient expansion [13–15], Padé approximation [16], scaling properties [17], conjointness with the exchange functional [18], linear response theory [6–8]) as well as in the use of empirical parameters in their construction.

In this work, we analyze the performance of the functional introduced by Tal and Bader [19]. The test of this functional on atomic systems reported in the original paper of Tal and Bader showed that this functional performs rather well although no empirical parameters have been used in its construction. We apply the Tal–Bader functional to the case of polyatomic systems and compare its numerical performance with that of other ‘empirical-parameters-free’ functionals derived from the gradient expansion approximation (GEA). The Tal–Bader functional incorporates the long-range nonlocality as the kinetic-energy density at a given point $r$ depends not only on the electron density at $r$ (and in its infinitesimal vicinity as in the case of gradient-dependent functionals) but also on the electron density at the position of the nuclei.

2. Kinetic-energy functionals

There are several possible theoretical roads leading to approximate kinetic-energy functionals $T_s [\rho]$ of various level of accuracy. The most relevant to the main issue of this work is the gradient expansion approximation [13–15]. For slowly varying densities, the kinetic energy can be developed in a series involving the density $\rho(r)$ and its derivatives:

$$T_{GEA} [\rho] = \sum_{n=0}^{\infty} T_{2n} [\rho]$$

$$= \sum_{n=0}^{\infty} \int t_{2n} (\rho(r), \nabla \rho(r), \ldots) dr,$$

(4)

$$t_0 = \frac{3}{10} (3 \pi^2)^{2/3} \rho^{5/3},$$

(5)

$$t_2 = \frac{1}{72} \frac{\| \nabla \rho \|^2}{\rho},$$

(6)

$$t_4 = \frac{(3 \pi^2)^{-1/3} \rho^{1/3}}{540} \rho \left( \frac{\nabla^2 \rho}{\rho} \right)^2 - \frac{9}{8} \frac{\nabla^2 \rho}{\rho} \left( \frac{\nabla \rho}{\rho} \right)^2 + \frac{1}{3} \left( \frac{\nabla \rho}{\rho} \right)^4,$$

(7)
As shown by Thomas and Fermi (TF) [20,21] the term $T_1[\rho]$ is the exact kinetic-energy functional for the uniform electron gas, but represents a rather poor approximation for atomic and molecular densities, leading to an underestimation of 5–10% of the total kinetic energy. Adding to $T_1[\rho]$ the second term, $T_2[\rho]$, leads to the second order gradient expansion which is known to underestimate the kinetic energy by about 0.5–1%, whereas adding $T_3[\rho] + T_4[\rho]$ results in an overestimation of the kinetic energy of a similar magnitude. The analytic form of $T_6[\rho]$ is known [15] but is divergent for exponentially decaying densities as those of atoms and molecules. The term appearing in the second order of GEA (but with another coefficient) was first derived by von Weizsäcker [22]:

$$T_W[\rho] = 9T_2[\rho] = \frac{1}{8} \int \frac{|\nabla \rho(r)|^2}{\rho(r)} \, dr. \quad (8)$$

$T_W[\rho]$ yields the exact kinetic energy for one-electron systems and systems with two electrons occupying the same orbital, and the density $(1/8)|\nabla \rho|^2/\rho$ behaves correctly both at the nuclear cusps and at the long distance from the nuclei [19]. For these reasons, several functionals with $T_W[\rho]$ as the leading term were proposed in the literature (see for example [23,24]).

Due to the limited accuracy of the GEA kinetic-energy functionals various approximate functionals have then been developed. Among them, there is the group of the semi-local ones belonging to the generalized gradient approximation (GGA) which can be cast into the form

$$T_{\text{GGA}}[\rho] = \frac{3}{10} \frac{3s \rho^{5/3}}{ho^{2/3}} \int F(s(r)) \rho(r)^{2/3} \, dr, \quad (9)$$

where $s = |\nabla \rho|/(2k_F \rho)$ is the scaled density gradient with $k_F = (3\pi^2 \rho)^{1/3}$ the local Fermi vector and $F(s)$ the enhancement factor which determines the gradient-dependency of the functional. Different analytical forms for $F(s)$ have appeared in the literature, such as the Padé approximation of DePristo and Kress [16] or the two approximate functionals proposed by Ou-Yang and Levy [17] derived from nonuniform scaling properties considerations. Yet another route to derive $F(s)$ was proposed by Lee et al. [18] who conjectured the conjointness between the kinetic- and exchange-energy functionals. This conjecture opened new possibilities in constructing approximate gradient-dependent kinetic-energy functionals profiting from the progress in the development of approximating the exchange-energy functional [18,25–28]. For the exchange–correlation energy, GGA is a very successful approximation, but the kinetic-energy functionals of the GGA form seem to have several flaws which prevents us to reach desired level of accuracy and especially in formalisms where a good functional derivative of the kinetic energy is required. For recent studies on GGA kinetic-energy functionals, see [29–31].

In this work, we explore an alternative route to approximate the kinetic-energy functional which can potentially overcome the shortcomings of truncated GEA or other semi-local functionals. We use the functional proposed by Tal and Bader (TB) [19] which takes the form

$$T_{\text{TB}}[\rho] = T_{\text{TB}}[\rho_a] + T_W[\rho_s] + \sum_{z=1}^{N_{\text{nuc}}} T_{W}[\rho_{rz}], \quad (10)$$

with $\rho_{rz}(r)$ and $\rho_s(r)$ being defined by

$$\rho_{rz}(r) = \rho(r) e^{-Z_z |r - R_z|} \quad (11)$$

and

$$\rho_s(r) = \rho(r) - \rho_s(r) = \rho(r) - \sum_{z=1}^{N_{\text{nuc}}} \rho_{rz}(r), \quad (12)$$

respectively, where $R_z$ and $Z_z$ are the position and the nuclear charge of the nucleus $z$ in the molecule. $\rho_s(r)$ and $\rho_s(r)$ denote the slowly and rapidly varying components of the total electron density.

It is worthwhile to point out that application of the Tal–Bader functional to polyatomic systems is not straightforward. Due to the infinite range of the exponential function, the $\rho_s(r)$ component defined in Eqs. (11) and (12) cannot be assumed to be always positive (particularly at the position of the nuclei). To avoid using unphysical quantities, we applied an alternative partitioning of $\rho(r)$ into $\rho_s(r)$ and $\rho_r(r)$:

$$\rho_s(r) = \max \left( 0, \rho(r) - \sum_{z=1}^{N_{\text{nuc}}} \rho_{rz}(r) \right). \quad (13)$$
and consequently

\[ \rho_i(r) = \rho(r) - \rho_\epsilon(r). \] (14)

This new partitioning makes it possible to apply Eq. (10) not only for atoms but also for polyatomic systems as both components \( \rho_i(r) \) and \( \rho_\epsilon(r) \) are always positive.

To our knowledge, the only systematic test of the Tal–Bader functional was made by its original authors [19] for atomic systems. Hernández and Gáezquez [32] applied the functional in the framework of variational calculations with minimal-basis-set-type electron densities.

3. Results

68 neutral and charged molecules (see Table 1) consisting of second, third, and fourth period atoms in their experimental geometries were chosen to compare the performance of the Tal–Bader functional with that derived from GEA. The ref-

Table 1

<table>
<thead>
<tr>
<th>The 68 molecules of the testing set</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be₂, B₂, C₂, N₂, O₂, F₂, Na₂, Al₂, Si₂, P₂, S₂, Cl₂, K₂, Cr₂, Cu₂,</td>
</tr>
<tr>
<td>BeF, BeS, BO, BF, BCl, CN, CO, CF, CP, CS, NO, NF, NS, NBr, NaF, NaCl, MgO, SiO, SiF,</td>
</tr>
<tr>
<td>SiS, PN, PO, PS, SO, ClO, CIF, KF, KC,</td>
</tr>
<tr>
<td>BF₃, BCl₃, CO₂, CS₂, N₂O, NO₂, NCO, O₃, OCS, F₂O, SiF₂, SO₃, CINO, ClO₂,</td>
</tr>
<tr>
<td>C⁺₂, C₂⁺, N⁺₂, O⁺₂, O₂⁺, P⁺₂, S⁺₂, Cl⁺₂, NO⁺, PO⁺, CO⁺₂</td>
</tr>
</tbody>
</table>

Fig. 1. Exact and Tal–Bader kinetic-energy density plotted along the internuclear axis of the CO molecule with the C atom at \( r = 0 \) and the O atom at \( r = 2.13 \) a.u.
erence electron densities and Kohn–Sham orbitals of each molecule in the testing set were derived using the PW91 [33] exchange–correlation energy functional. The Kohn–Sham orbitals were used to evaluate the exact value of the noninteracting kinetic energy $T^\text{exact}_s = T_s[\{\psi_i\}]$ (Eq. (3)), and the densities to evaluate the value of the different approximate orbital-free expressions $T_s[\rho]$. For spin-polarized densities, a standard Ansatz was used [34]:

$$T_s[\rho_{\uparrow}, \rho_{\downarrow}] = \frac{1}{2}(T_s[2\rho_{\uparrow}] + T_s[2\rho_{\downarrow}]). \quad (15)$$

For each molecule and each considered approximate functional, the percentage of error $\Delta = 100(T_s[\rho] - T^\text{exact}_s)/T^\text{exact}_s$ was calculated, and then the mean percentage of error $\bar{\Delta}$, the mean percentage of absolute error $\bar{\Delta}_{abs}$, and the standard deviation $\Delta_{std}$ were calculated.

Table 2 shows that the TF functional provides, as expected, a very poor approximation leading to
total kinetic energy underestimated by about 8%. Taking into account the following terms in the gradient expansion significantly reduces the error: GEA in second order underestimates the kinetic energy by about 0.7%, while GEA in fourth order overestimates it by 0.7%. Employing the Tal–Bader functional reduces the value of $\Delta_{\text{abs}}$ to about 0.4%, while $\overline{\Delta}$ is reduced to the small value of $-0.08\%$, indicating that the Tal–Bader functional is not showing a particular trend to underestimate or overestimate the total kinetic energy. The value of 0.6 for $\Delta_{\text{std}}$ indicates a larger dispersion around $\overline{\Delta}$ than for GEA (second and fourth order).

Turning back to the Tal–Bader functional, its authors noted that the kinetic-energy density $(1/2) \sum_{\nu} |\nabla \psi_{\nu}(\mathbf{r})|^{2}$ (this choice for the definition of the kinetic-energy density implies it to be everywhere positive and finite) is represented exactly by the von Weizsäcker term (Eq. (8)) on top of a nucleus and in the asymptotic regions far from the nuclei. This correct local behavior of the von Weizsäcker term, motivated Tal and Bader to propose their functional in which the von Weizsäcker term plays a key role. The local behavior of the exact and Tal–Bader kinetic-energy density ($t(\mathbf{r})$) of CO and N$_{2}$ molecules is shown in Figs. 1 and 2, respectively. For the CO molecule, $t(\mathbf{r})$ is plotted along the internuclear axis with the C atom at $r = 0$ and the O atom at $r = 2.13$ a.u. The Tal–Bader kinetic-energy density reproduces well the exact one in the regions close to the nuclei whereas it slightly overestimates the exact quantity in the mid-bond region. Fig. 2 shows similar trends for the N$_{2}$ molecule and provides also a good example of the correct local behavior of the Tal–Bader functional in the asymptotic region far from nuclei ($r \rightarrow -\infty$).

The good performance of the Tal–Bader functional prompted us to explore its applicability for such cases where considerations underlying the

![Fig. 3. The density $\rho$ and its rapidly $\rho_{r}$ and slowly $\rho_{s}$ varying components in the BH molecule with the B atom at $r = 0$ and the H atom at $r = 2.33$ a.u.](image-url)
separation of $\rho(r)$ into $\rho_s(r)$ and $\rho_r(r)$ are less applicable. For one- and two-electron atoms, the Tal–Bader construction is not an adequate scheme as the von Weizsäcker term provides the exact functional. For such cases, the Tal–Bader construction leads obviously to a worse approximation as indicated by the fact that in their original work Tal and Bader showed that their functional performs not as good for the helium atom as it does for heavier atoms. Moreover, the separation into rapidly and slowly varying densities correlates with the fact that the former is determined by the core electrons in the case of heavier atoms. The Tal–Bader functional can be expected, therefore, to be less applicable for hydrogen-containing molecules (not considered in our testing set), which is in fact, what we found. This originates from the qualitative differences in partitioning of $\rho(r)$ into $\rho_s(r)$ and $\rho_r(r)$. As indicated before, for hydrogen-free molecules, Eqs. (11) and (12) lead to a negative and very small value of $\rho_s(r)$ only at atomic nuclei, resulting in negligible numerical significance of our modification of the partitioning scheme (Eqs. (13) and (14)) which enforces non-negativity of $\rho_s(r)$. For hydrogen-containing molecules, Eqs. (11) and (12) can lead to negative values of $\rho_s(r)$ in extended regions. Fig. 3 shows the Tal–Bader partitioning scheme of $\rho(r)$ for the BH molecule, where we can see negative values for $\rho_s(r)$ occurring in the vicinity of the H atom (at $r = 2.33$ a.u.) in the direction opposite to the B atom (at $r = 0$). This leads in practice to a very strong dependence of the accuracy of the Tal–Bader functional on the way the nonnegativity of $\rho_s(r)$ is enforced.

4. Conclusions

The numerical results presented in this work show that the Tal–Bader functional applied to polyatomic systems has proven to be an interesting alternative to the gradient expansion approximation. It is based on the separation between the rapidly varying component of the electron density determined by the inner core electrons and the remaining part which is smoother. The overall accuracy of the Tal–Bader functional for the total kinetic energy is better than the ones obtained with the GEA functionals. Formally, the functional considered in this work can be seen as a simple step towards introduction of long-range nonlocality: the kinetic-energy density at a given point, obtained using such a functional, is determined not only by the electron density at this point (and possibly in its infinitesimal vicinity) but also by the value of the electron density at several distant points. Missing true nonlocality is an important flaw of local and semi-local approximate functionals (see for example Herring [35] who pointed out the highly nonlocal behavior of the kinetic energy or the recent paper by Wang et al. [30] exposing flaws of GGA kinetic-energy functionals).

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