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Exact inequality involving the kinetic energy functional $T_s[\rho]$ and pairs of electron densities

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Abstract

The kinetic energy functional $T_s[\rho]$ in a reference system of non-interacting electrons is a key quantity in density functional theory. Approximating it as an explicit functional of the electron density ρ is the object of continuous interest since the earliest days of quantum mechanics (Thomas–Fermi electron gas theory). A simple proof of the exact inequality $T_s[\rho_A + \rho_B] - T_s[\rho_A] - T_s[\rho_B] \geq 0$ valid for a special class of spin-compensated pairs of electron densities ρ_A and ρ_B (v^{AB} -representable pairs) is provided. The derived relation is discussed to rationalize some of the results of the past attempts to approximate $T_s[\rho]$. It is also discussed as a tool for deriving approximations to the functional $T_s[\rho]$ and/or the bi-functional $T_s^{nad}[\rho_A, \rho_B] = T_s[\rho_A + \rho_B] - T_s[\rho_A] - T_s[\rho_B]$.

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1. Introduction

One of the key functionals in density functional theory (DFT) [1] is the kinetic energy functional in a reference system of non-interacting electrons ($T_s[\rho]$) defined in the Levy ‘constrained search’ procedure [2]:

$$T_s[\rho] = \min_{\Psi_s \rightarrow \rho} \{ \langle \Psi_s | \hat{T} | \Psi_s \rangle \} \quad (1)$$

where Ψ_s denotes the trial functions of the single determinant form.

In the conventional Kohn–Sham formalism [3], evaluation of $T_s[\rho]$ as an explicit functional of electron density is avoided owing to the use of its orbital-dependent equivalent. Nevertheless, since the earliest days of quantum mechanics [4] up to now [5] many attempts have been undertaken to find a good approximation to $T_s[\rho]$ and associated with its potential $\frac{\delta T_s[\rho]}{\delta \rho}$. A good approximation to $\frac{\delta T_s[\rho]}{\delta \rho}$, would make it possible to obtain ground-state electron density from orbital-free calculations based on the direct application of Euler–Lagrange minimization of the total energy functional without the need to introduce orbitals as is done in

the Kohn–Sham formalism. Indeed, some of the developed approximations have been shown to lead to very encouraging results for various molecular systems and materials [6].

A good approximation to $T_s[\rho]$ as an explicit functional of electron density is also a key ingredient in Cortona’s formulation of DFT based on subsystems [7]. In this approach, $T_s[\rho]$ is expressed using as a basic variable not the electron density ρ but a set of electron densities $\{\rho_1, \rho_2, \dots\}$ (electron densities of atoms in ionic solids in his case) adding up to the total electron densities ρ . In a particular case of two subsystems described with ρ_A and ρ_B , $T_s[\rho]$ can be expressed in a hybrid way:

$$T_s[\rho_A + \rho_B] = T_s[\rho_A] + T_s[\rho_B] + T_s^{nad}[\rho_A, \rho_B]. \quad (2)$$

Since $T_s[\rho_A + \rho_B]$, $T_s[\rho_A]$ and $T_s[\rho_B]$ are universal functionals defined in equation (1), equation (2) can be seen as the definition of a bi-functional $T_s^{nad}[\rho_A, \rho_B]$ (referred to as the non-additive kinetic energy bi-functional in this work). Using explicit orbitals to evaluate $T_s[\rho_A]$ and $T_s[\rho_B]$ and an approximate explicit functional of the electron density to approximate $T_s^{nad}[\rho_A, \rho_B]$ leads to a computational approach which can be situated somewhere between the Kohn–Sham formalism and the orbital-free strategy.

In the model of Gordon and Kim [8], which can be seen as non-variational precursor of Cortona’s formalism, the bi-functional $T_s^{nad}[\rho_A, \rho_B]$ is used to derive the interaction energy of van der Waals complexes.

The models based on the idea of applying an ‘embedding potential’ representing the effects of the microscopic environment to the electronic structure of a molecule (or another subsystem) in condensed phase¹ provide another area of applicability of $T_s^{nad}[\rho_A, \rho_B]$. Wesolowski and Warshel noted that ‘embedding potential’ corresponds formally to freezing the electron density of the environment in the variational calculations and used $T_s^{nad}[\rho_A, \rho_B]$ to show that the embedding effective potential can be expressed *exactly* by means of universal functionals of DFT and the electron density of the microscopic environment of the system under investigation (ρ_B) [10]:

$$V_{\text{emb}}^{\text{eff}}[\rho_A, \rho_B, \mathbf{r}] = \sum_{A_B} -\frac{Z_{A_B}}{|\mathbf{r} - \mathbf{R}_{A_B}|} + \int \frac{\rho_B(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' + \frac{\delta E_{xc}[\rho_A(\mathbf{r}) + \rho_B(\mathbf{r})]}{\delta \rho_A} - \frac{\delta E_{xc}[\rho_A(\mathbf{r})]}{\delta \rho_A} + \frac{\delta T_s^{nad}[\rho_A, \rho_B]}{\delta \rho_A} \quad (3)$$

where the first term shows the explicit form of the contributions of the atomic nuclei to the effective potential and $E_{xc}[\rho]$ denotes the conventional exchange–correlation potential defined in the Kohn–Sham formalism.

Approximations to $T_s^{nad}[\rho_A, \rho_B]$ expressed as an explicit bi-functional of ρ_A and ρ_B were used also by other authors in various contexts [11].

At the first glance, development of a good approximation to $T_s^{nad}[\rho_A, \rho_B]$ is an equivalent task to the development of a good approximation to $T_s[\rho]$. It is worthwhile, however, to note that $T_s^{nad}[\rho_A, \rho_B]$ is a linear combination of $T_s[\rho]$ calculated at three different electron densities. Indeed, as pointed out earlier by Lacks and Gordon, no significant correlation was found between the accuracy of a given gradient-free and gradient-dependent approximation to $T_s[\rho]$ and the accuracy of the corresponding $T_s^{nad}[\rho_A, \rho_B]$ [12]. The above observations prompted our interest in studying, testing and developing approximations to $T_s^{nad}[\rho_A, \rho_B]$ directly. To this end, we developed a numerical procedure to test the accuracy of a given approximate to $T_s^{nad}[\rho_A, \rho_B]$ [13–16]. This procedure is based on comparison between electron densities derived from two types of minimization.

¹ There is a vast literature concerning the ‘embedded molecule approach’. For pioneering papers in chemistry and solid state physics, see [9].

- One based on the minimization of the Kohn–Sham calculations:

$$\min_{\rho \rightarrow 2N_{AB}} E_v^{\text{KS}}[\rho] \quad (4)$$

where

$$E_v^{\text{KS}}[\rho] = T_s[\rho] + \frac{1}{2} \iint \frac{\rho(\mathbf{r}')\rho(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' d\mathbf{r} + \int v(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} + E_{xc}[\rho]. \quad (5)$$

- The other based on the double minimization of the total-energy bi-functional:

$$\min_{\rho_A \rightarrow 2N_A} \min_{\rho_B \rightarrow 2N_B} E_v[\rho_A, \rho_B] \quad (6)$$

where

$$\begin{aligned} E_v[\rho_A, \rho_B] &= T_s[\rho_A] + T_s[\rho_B] + T_s^{\text{nad}}[\rho_A, \rho_B] \\ &+ \frac{1}{2} \iint \frac{(\rho_A(\mathbf{r}') + \rho_B(\mathbf{r}'))(\rho_A(\mathbf{r}) + \rho_B(\mathbf{r}))}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' d\mathbf{r} \\ &+ \int v(\mathbf{r})(\rho_A(\mathbf{r}) + \rho_B(\mathbf{r})) d\mathbf{r} + E_{xc}[\rho_A + \rho_B]. \end{aligned} \quad (7)$$

Note that, in the above formulae and throughout the text, the considered functionals and electron densities correspond to the spin-compensated case. The comparisons between the electron densities and other observables derived from the two types of minimization allowed us to detect a very serious flaw of the regular gradient expansion [17] truncated to the second order. The functional derivatives $\frac{\delta T_s^{\text{nad}}[\rho_A, \rho_B]}{\delta \rho_A}$ and $\frac{\delta T_s^{\text{nad}}[\rho_A, \rho_B]}{\delta \rho_B}$ obtained from this approximation were significantly less accurate than those derived from the zeroth order expansion [15]. Moreover, our tests showed that for a number of pairs of weakly overlapping electron densities ρ_A and ρ_B there is, indeed, no correlation between the accuracy of a given approximation to $T_s[\rho]$ and $T_s^{\text{nad}}[\rho_A, \rho_B]$ which is associated with $T_s[\rho]$ via equation (2). We found also that the numerical values of $T_s^{\text{nad}}[\rho_A, \rho_B]$ calculated using the gradient approximation truncated to the second order are negative for many considered pairs ρ_A and ρ_B .

In this paper, we show that $T_s^{\text{nad}}[\rho_A, \rho_B]$ is non-negative for a certain class of pairs of electron densities. The demonstration consists of two steps. In the first step, we define the class of pairs ρ_A and ρ_B which will be labelled v^{AB} -representable. In the second, we demonstrate that the inequality $T_s^{\text{nad}}[\rho_A, \rho_B] \geq 0$ holds for v^{AB} -representable pairs of spin-compensated electron densities. In the final analysis, we discuss the practical benefits following from the derived inequality. Throughout this paper, the functionals in the formulae are the *exact* functionals. The symbols ρ_0 and E_0 denote the *exact* ground-state electron density and energy, respectively.

2. v^{AB} -representable pairs of electron densities

Definition. A pair of spin-compensated electron densities ρ_A and ρ_B such that $\int \rho_A(\mathbf{r}) d\mathbf{r} = 2N_A$ and $\int \rho_B(\mathbf{r}) d\mathbf{r} = 2N_B$ is v^{AB} -representable if ρ_A can be obtained from N_A exact Kohn–Sham orbitals and ρ_B from the remaining N_B orbitals corresponding to some external potential $v^{AB}(\mathbf{r})$. Obviously $\rho_0 = \rho_A + \rho_B$.

We use the term ‘a v^{AB} -representable pair of electron densities ρ_A and ρ_B ’ to avoid confusion with a ‘pair of v -representable [1] electron densities’. We note also that $\frac{(N_A+N_B)!}{N_B!N_A!}$ v^{AB} -representable pairs can be generated for each particular potential v^{AB} .

According to the above definition, the construction of a v^{AB} -representable pair for a given external potential v_{ext} is quite challenging a task because it involves obtaining *exact* Kohn–Sham orbitals corresponding to $v^{AB} = v_{\text{ext}}$. However, v^{AB} -representable pairs ρ_A and ρ_B can be easily constructed from Kohn–Sham orbitals obtained using an approximate exchange–correlation potential \tilde{V}_{xc} . In such a case, v^{AB} cannot be identified with the external potential v_{ext} . The two quantities differ by more than just a constant. v^{AB} includes also the difference between the *approximate* ($V_{xc}(\rho_A + \rho_B)$) and the *exact* ($\tilde{V}_{xc}(\rho_A + \rho_B)$) exchange–correlation potentials calculated at $\rho = \rho_A + \rho_B$.

Theorem. For v^{AB} -representable pairs of electron densities ρ_A and ρ_B

$$T_s^{\text{nad}}[\rho_A, \rho_B] \geq 0. \quad (8)$$

The above theorem can be written equivalently as

$$T_s[\rho_A + \rho_B] - T_s[\rho_A] - T_s[\rho_B] \geq 0. \quad (9)$$

Proof. Let v^{AB} denote the external potential generating the electron densities ρ_A and ρ_B and $\{\phi_i^{AB}, i = 1, N_{AB}\}$ are the corresponding Kohn–Sham orbitals. The v^{AB} -representable pairs ρ_A and ρ_B can be obtained as

$$\rho_A = 2 \sum_{i=1}^{N_A} |\phi_{f_A(i)}^{AB}|^2 \quad \rho_B = 2 \sum_{j=1}^{N_B} |\phi_{f_B(j)}^{AB}|^2 \quad (10)$$

where $f_A(i)$, $i = 1, N_A$ is a pointer choosing N_A orbitals yielding ρ_A and $f_B(j)$, $j = 1, N_B$ is a pointer choosing N_B orbitals yielding ρ_B .

The kinetic energy $T_s[\rho_0] = T_s[\rho_A + \rho_B]$ can be derived from the Kohn–Sham orbitals ϕ_i^{AB} :

$$T_s[\rho_0] = 2 \sum_{i=1}^{N_{AB}} \left\langle \phi_i^{AB} \left| -\frac{1}{2} \nabla^2 \right| \phi_i^{AB} \right\rangle. \quad (11)$$

The summation in the above formula can be split into two components:

$$T_s[\rho_0] = 2 \sum_{i=1}^{N_A} \left\langle \phi_{f_A(i)}^{AB} \left| -\frac{1}{2} \nabla^2 \right| \phi_{f_A(i)}^{AB} \right\rangle + 2 \sum_{j=1}^{N_B} \left\langle \phi_{f_B(j)}^{AB} \left| -\frac{1}{2} \nabla^2 \right| \phi_{f_B(j)}^{AB} \right\rangle. \quad (12)$$

Following the Levy constrained search definition of $T_s[\rho]$:

$$2 \sum_{i=1}^{N_A} \left\langle \phi_{f_A(i)}^{AB} \left| -\frac{1}{2} \nabla^2 \right| \phi_{f_A(i)}^{AB} \right\rangle \geq T_s[\rho_A] \quad (13)$$

$$2 \sum_{j=1}^{N_B} \left\langle \phi_{f_B(j)}^{AB} \left| -\frac{1}{2} \nabla^2 \right| \phi_{f_B(j)}^{AB} \right\rangle \geq T_s[\rho_B]. \quad (14)$$

The above two inequalities combined with equation (12) lead to the inequality:

$$T_s[\rho_0] = T_s[\rho_A + \rho_B] \geq T_s[\rho_A] + T_s[\rho_B]. \quad (15)$$

As a result we obtain

$$T_s^{\text{nad}}[\rho_A, \rho_B] \geq 0 \quad (16)$$

which ends the proof. \square

3. Discussions and conclusions

In the final part, we underline the following practical issues relevant to the above inequality.

- Following our observation that v^{AB} -representable pairs of electron densities can be constructed from Kohn–Sham orbitals obtained *even with an approximate exchange–correlation potential*, the inequality $T_s^{nad}[\rho_A, \rho_B] \geq 0$ might be used as an easy tool to detect flaws of any given approximation to $T_s[\rho]$.
- The simplest approximation to $T_s^{nad}[\rho_A, \rho_B]$ based on the zeroth order term in the regular gradient expansion $T^{(0)}$ satisfies the derived inequality for all pairs of electron densities (for v^{AB} -representable and not v^{AB} -representable pairs alike). This follows from its explicit analytic form [10]:

$$T_s^{nad(0)}[\rho_A, \rho_B] = C_{TF} \int ((\rho_A + \rho_B)^{5/3} - \rho_A^{5/3} - \rho_B^{5/3}) \, d\mathbf{r} \geq 0 \quad (17)$$

where $C_{TF} = \frac{3}{10}(3\pi^2)^{2/3}$. This functional can be considered, therefore, as a good starting point for constructing better approximations.

- The contribution of the second-order term in the regular gradient expansion $T^{(2)}$ is non-positive for all pairs of electron densities (for v^{AB} -representable and not v^{AB} -representable pairs alike). This follows from its explicit analytic form [10]:

$$T_s^{nad(2)}[\rho_A, \rho_B] = -\frac{1}{72} \int \frac{|\rho_A \nabla \rho_B + \rho_B \nabla \rho_A|^2}{\rho_A \rho_B (\rho_A + \rho_B)} \, d\mathbf{r} \leq 0. \quad (18)$$

The violation of the $T_s^{nad}[\rho_A, \rho_B] \geq 0$ inequality explains the very poor performance of this functional detected in our earlier studies [15]. We recall now that $T_s^{(2)}[\rho]$ is closely related to the von Weizsaecker functional $T_s^W[\rho]$ [18] ($T_s^W[\rho] = 9T_s^{(2)}[\rho]$), which is the *exact* kinetic energy functional for one- and two-spin-compensated electron systems. Using $T_s^W[\rho]$ to approximate $T_s^{nad}[\rho_A, \rho_B]$ leads, therefore, to a gross violation of the derived inequality. $T_s^W[\rho]$ has been used by many authors as the starting point for development of better approximations of the general form [19]:

$$T_s[\rho] \approx T_s^W[\rho] + \text{small correction}. \quad (19)$$

Our result suggests that the contribution of the ‘small correction’ to $T_s^{nad}[\rho_A, \rho_B]$ must be non-negative and must outweigh the negative contribution due to T_s^W .

- The inequality $T_s^{nad}[\rho_A, \rho_B] \geq 0$ provides a formal justification for a good performance of our generalized gradient approximation type of $T_s^{nad}[\rho_A, \rho_B]$ [16] for small overlaps between ρ_A and ρ_B . The gradient-dependence of this functional is such that at small electron densities, i.e. where negative contributions to $T_s^{nad}[\rho_A, \rho_B]$ due to the second-order term might prevail, they are smoothly cut out.

For practical reasons, we limited the scope of this work to pairs of spin-compensated pairs of v^{AB} -representable electron densities. Construction of a similar inequality for other cases is not straightforward. The condition that each component ρ_A and ρ_B contains an integer number of electrons cannot be dropped because this is one of the conditions of v -representability a key element in our proof. Dropping the condition $\int \rho_A \, d\mathbf{r} = 2N_A$ and $\int \rho_B \, d\mathbf{r} = 2N_B$ and replacing it by a weaker one $\int \rho_A \, d\mathbf{r} = K_A$ and $\int \rho_B \, d\mathbf{r} = K_B$ (where K can be either odd or even) could be useful. To derive an analogue of the inequality $T_s^{nad}[\rho_A, \rho_B] \geq 0$ valid for *two* v^{AB} -representable pairs of spin densities, an extension of the kinetic energy functional to the spin densities must be added to our previous considerations. The Olivier–Perdew construction

[20] allows one to derive the spin-density functional from a given density functional of the kinetic energy

$$T_s[\rho^{\text{up}}, \rho^{\text{down}}] = \frac{1}{2}(T_s[2\rho^{\text{up}}] + T_s[2\rho^{\text{down}}]). \quad (20)$$

Below, we discuss only a particular case of such a generalization. Applying the Oliver–Perdew construction to such a system partitioned as that $\rho^{\text{up}} = \frac{1}{2}\rho$ and $\rho^{\text{down}} = \rho^{\text{up}}$ provides a tempting case because the *exact* analytic form of all relevant functionals i.e. $T_s[\rho] = T_s[\rho^{\text{up}}, \rho^{\text{down}}]$, $T_s[\rho^{\text{up}}, 0]$, and $T_s[0, \rho^{\text{down}}]$ is known: $T_s[\rho^{2e}] = T_s^{\text{W}}[\rho^{2e}]$, $T_s[\rho^{\text{up}(1e)}, 0] = T_s^{\text{W}}[\rho^{\text{up}(1e)}]$ and $T_s[\rho^{\text{down}(1e)}, 0] = T_s^{\text{W}}[\rho^{\text{down}(1e)}]$. Unfortunately, inspecting the analytic form of $T_s^{\text{W}}[\rho]$ shows that the analogue of the inequality $T_s^{\text{nad}}[\rho_A, \rho_B] \geq 0$ takes a trivial form in this case: $T_s[\rho^{(2e)}] - T_s[\rho^{\text{up},(1e)}, 0] - T_s[0, \rho^{\text{down},(1e)}] = 0$ which does not lead to any new physical insights.

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