Is size-consistency possible with density functional approximations?

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ABSTRACT

Density functional approximations do not provide size-consistent methods, contrary to what is commonly assumed in the literature. The violation is related to degeneracy. Two approaches are discussed to alleviate the problem: symmetry breaking and range separation.

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1. Introduction

It may seem that a minimal requirement for an approximation for describing an electronic system is that if it were separated into two disjoint and distant spatial regions, Ω_A and Ω_B, then the energy of the system equals the sum of the energies of the separate parts (size-consistency):

$$E(A \cdots B) = E(A) + E(B). \tag{1}$$

However, many of the approximate methods used in quantum chemistry do not satisfy this requirement. This note discusses the difficulty of satisfying this requirement in density functional theory. In the first part, density matrices are given in a second quantized form and the energy expression to which they lead is analyzed. Next, it is shown that semi-local approximations, as used in density functional calculations, do not have the structure needed to correctly describe size-consistency when degeneracy is present. Finally two ways to get around the problem are discussed. The first one exploits symmetry breaking, and is common in density functional calculations. The second one is a generalization of the Kohn–Sham scheme introducing a partial interaction between electrons. Unfortunately, in spite of some success, neither completely solves the problems related to degeneracy in density functional approximations.

The problems treated in this paper have been repeatedly addressed in the last thirty years (see, e.g., Refs. [1–6]).

2. Formulas for separated subsystems

2.1. Wave function

When treating separated subsystems, it is often assumed that the wave function of the system is given by a product of the wave functions of the subsystems:

$$\Psi(A \cdots B) = \mathscr{A} \Psi(A)\Psi(B), \tag{2}$$

where $\Psi(A)$ vanishes on Ω_B, while $\Psi(B)$ vanishes on Ω_A. $\mathscr{A}$ is the antisymmetrization operator. The ansatz of Eq. (2), is not correct when degeneracy is present in at least one of the subsystems. One should write:

$$\Psi(A \cdots B) = \mathscr{A} \sum_{i,m} c_{i,m} \Psi_i(A)\Psi_m(B), \tag{3}$$

where the indices i, m enumerate the degenerate states on the subsystems A and B, respectively. The $\Psi_i(A)$ vanish on Ω_B while the $\Psi_m(B)$ vanish on Ω_A.

For any expectation value, it is sufficient to take $\Psi_i(A)$ antisymmetric and $\Psi_m(B)$ antisymmetric; the antisymmetrization that exchanges particles between the separated subsystems does not contribute to the expectation value: a permutation of $r_1 \in \Omega_A$ and $r_2 \in \Omega_B$ in $\Psi_i(r_1, \ldots; A)\Psi_m(r_2, \ldots; B)$ produces $\Psi_i(r_2, \ldots; A)\Psi_m(r_1, \ldots; B)$ which is zero as $\Psi_i(A)$ vanishes on Ω_B and $\Psi_m(B)$ vanishes on Ω_A (see, e.g., Ref. [7]). Thus we can write

$$\Psi(A \cdots B) = \sum_{i,m} c_{im} \Psi_i(A)\Psi_m(B), \tag{4}$$

One is free to choose the basis of degenerate states, $\Psi_i(A)$, $\Psi_m(B)$, via separate unitary transformation on each of them,

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$$\Psi_i(A) = \Sigma_j U_{ij} \widetilde{\Psi}_i(A)$$
$$\Psi_m(B) = \Sigma_n V_{mn} \widetilde{\Psi}_n(B).$$

These transformations can be chosen to yield a singular value decomposition (see, e.g., Ref. [8], Eq. 2.9.1; similar to producing corresponding orbitals [9], or natural transition orbitals [10]):

$$\sum_{i,m} U_{ij} c_{im} V_{mn} = \kappa_j \delta_{jn}.$$

As only this basis will be used below, we will drop the tilde above the Ψ, in order to keep notation simple. We thus have:

$$\Psi(A \cdots B) = \sum_i \kappa_i \Psi_i(A) \Psi_i(B). \tag{5}$$

Let us consider a few simple examples. The first example is the stretched Li_2 molecule, in its singlet and triplet states, dissociating into ground states of the Li atom:

$$\begin{aligned}
\Psi_{1,2}(A) &= \Psi(Li, M_S = \pm 1/2), \\
\Psi_{1,2}(B) &= \Psi(Li, M_S = \mp 1/2), \\
\kappa_{1,2} &= \pm 1/\sqrt{2}, \quad \text{for the singlet,} \\
\kappa_{1,2} &= 1/\sqrt{2}, \quad \text{for the triplet.}
\end{aligned} \tag{6}$$

Next, we consider the state of the stretched Li_2 molecule, dissociating into the ground state ionic forms:

$$\begin{aligned}
&Li^+ \cdots Li^- \leftrightarrow Li^- \cdots Li^+: \\
&\Psi_{1,2}(A) = \Psi(Li^\pm), \\
&\Psi_{1,2}(B) = \Psi(Li^\mp), \\
&\kappa_{1,2} = 1/\sqrt{2}.
\end{aligned} \tag{7}$$

For the stretched ground state of Li_2^+ we take

$$\begin{aligned}
\Psi_1(A) &= \Psi(Li, M_S = 1/2), \\
\Psi_1(B) &= \Psi(Li^+), \\
\Psi_2(A) &= \Psi(Li^+), \\
\Psi_2(B) &= \Psi(Li, M_S = 1/2), \\
\kappa_{1,2} &= 1/\sqrt{2}.
\end{aligned} \tag{8}$$

Please notice that while in the lowest singlet or triplet state of the stretched Li_2 molecule all $\Psi_i(A)$ had the same number of electrons, this was not the case in the last two examples.

2.2. Reduced density matrices

In order to avoid problems with particle number, and to deal with separation in space, we will use field operators, $\psi_\sigma(r)$, where $\sigma = \uparrow$ or $\downarrow$ (a closely related formalism is also used in a similar context in Ref. [5]). The first-order density matrix is given by the expectation value of the operator:

$$\hat{\gamma}(r, r') = \sum_\sigma \psi_\sigma^\dagger(r) \psi_\sigma(r'). \tag{9}$$

By choosing in the equation above $r = r'$ we have the density operator,

$$\hat{\rho}(r) = \sum_\sigma \psi_\sigma^\dagger(r) \psi_\sigma(r). \tag{10}$$

For the two-particle density, we have

$$\begin{aligned}
\hat{P}(r_1, r_2) &= \sum_{\sigma_1, \sigma_2} \psi_{\sigma_1}^\dagger(r_1) \psi_{\sigma_2}^\dagger(r_2) \psi_{\sigma_2}(r_2) \psi_{\sigma_1}(r_1) \\
&= \hat{\rho}(r_1) \hat{\rho}(r_2) - \delta(r_1 - r_2) \hat{\rho}(r_1).
\end{aligned} \tag{11}$$

Using now the expression for $\Psi(A \dots B)$, Eq. (5), we get for the density of the dissociated system:

$$\begin{aligned}
\rho(r) &= \langle \Psi(A \dots B) | \hat{\rho}(r) | \Psi(A \cdots B) \rangle \\
&= \sum_{i,j} \kappa_i^* \kappa_j \langle \Psi_i(A) \Psi_i(B) | \hat{\rho}(r) | \Psi_j(A) \Psi_j(B) \rangle.
\end{aligned}$$

We have to consider two situations: r is either in Ω_A, or in Ω_B. For example, when r is in Ω_A, we have:

$$\rho(r) = \sum_{i,j} \kappa_i^* \kappa_j \langle \Psi_i(A) | \hat{\rho}(r) | \Psi_j(A) \rangle \langle \Psi_i(B) | \Psi_j(B) \rangle$$

With

$$|\kappa_i|^2 = \omega_i \tag{12}$$

and using the orthonormality of the wave functions, we obtain

$$\rho(r) = \sum_i \omega_i \langle \Psi_i(X) | \hat{\rho}(r) | \Psi_i(X) \rangle = \sum_i \omega_i \rho_i(r; X), \quad r \in \Omega_X,$$
$$X : A \text{ or } B, \tag{13}$$

where we have identified on the right hand side subsystem quantities,

$$\rho_i(r; X) = \langle \Psi_i(X) | \hat{\rho}(r) | \Psi_i(X) \rangle, \quad r \in \Omega_X, \ X : A \text{ or } B \tag{14}$$

As, by construction, Eqs. (5) and (12),

$$\begin{aligned}
&\omega_i \in [0, 1], \\
&\sum_i \omega_i = 1.
\end{aligned} \tag{15}$$

the ω_i can be seen as weights of an ensemble.

In the simple examples given above, (Eqs. (6)–(8)) the $\omega_i = |\kappa_i|^2$ were restricted to 1/2, to the equi-ensemble situation. In general, this must not be the case. For example, in Eq. (8), a weak perturbation competing with that of the interaction between atoms may destroy symmetry and progressively displace the density between them.

In the same way as for obtaining Eq. (13), we obtain for the first-order density matrix, when r and r' are in the same region,

$$\begin{aligned}
\gamma(r, r') &= \sum_i \omega_i \langle \Psi_i(X) | \hat{\gamma}(r, r') | \Psi_i(X) \rangle \\
&= \sum_i \omega_i \gamma_i(r, r'; X), \quad r, r' \in \Omega_X, \ X : A \text{ or } B. \tag{16}
\end{aligned}$$

As for the density, we identify subsystem density matrices,

$$\gamma_i(r, r'; X) = \langle \Psi_i(X) | \hat{\gamma}(r, r') | \Psi_i(X) \rangle, \quad r, r' \in \Omega_X, \ X : A \text{ or } B. \tag{17}$$

When r and r' are in different regions, the formula is different:

$$\gamma(r, r') = \sum_{i,j} \kappa_i^* \kappa_j \sum_\sigma \langle \Psi_i(A) | \psi_\sigma^\dagger(r) | \Psi_j(A) \rangle \langle \Psi_i(B) | \psi_\sigma(r') | \Psi_j(B) \rangle$$
$$r \in \Omega_A, \quad r' \in \Omega_B \tag{18}$$

and a similar expression when r is in Ω_B and r' in Ω_A. We notice that products of subsystem quantities show up.

The r.h.s. of Eq. (18) is not necessarily zero: although it is zero in cases like those described by Eq. (6) because $\langle \Psi_i(B) | \psi_\sigma(r') | \Psi_j(B) \rangle = 0$, this term is non-zero in situations like those given by Eq. (8) where Ψ_i and Ψ_j have different particle number.

A similar expression is obtained for the two-particle density

$$
P(r_1, r_2) = \begin{cases} \sum_i \omega_i \langle \Psi_i(X)|\hat{P}(r_1, r_2)|\Psi_i(X)\rangle = \sum_i \omega_i P_i(r_1, r_2; X) & r_1, r_2 \in \Omega_X, \quad X : A, \text{ or } B \\ \sum_{ij} \kappa_i^* \kappa_j \langle \Psi_i(A)|\hat{P}(r_1)|\Psi_j(A)\rangle \Psi_j(B)\rangle|\hat{\rho}(r_2)|\Psi_j(B) & r_1 \in \Omega_A, \quad r_2 \in \Omega_B \\ \sum_{ij} \kappa_i^* \kappa_j \langle \Psi_i(A)|\hat{P}(r_2)|\Psi_j(A)\rangle \Psi_j(B)\rangle|\hat{\rho}(r_1)|\Psi_j(B) & r_1 \in \Omega_B, \quad r_2 \in \Omega_A \end{cases}
\tag{19}
$$

where

$$
P_i(r_1, r_2; X) = \langle \Psi_i(X)|\hat{P}(r_1, r_2')|\Psi_i(X)\rangle, \quad r_1, r_2 \in \Omega_X, \ X : A \text{ or } B.
\tag{20}
$$

Sometimes $\langle \Psi_i(A)|\hat{\rho}(r)|\Psi_j(A)\rangle$ is zero for $i \neq j$. This is the case, for instance, for the examples given above (Eqs. (6)–(8)) which yield zero either because they differ by M_s, or by particle number. However, this is not always the case. For example when $\Psi_i(A)$ are p_x, p_y functions: $\langle \Psi_1|\hat{\rho}|\Psi_1\rangle = p_x^2, \langle \Psi_2|\hat{\rho}|\Psi_2\rangle = p_y^2$ and $\langle \Psi_1|\hat{\rho}|\Psi_2\rangle = p_x p_y$.

In Eq. (19), as well as in Eq. (18), one can substitute $\kappa_i \kappa_j$ by $\text{sign}(\kappa_i \kappa_j)\sqrt{\omega_i \omega_j}$, but cannot eliminate κ_i due to the sign function. For example, in Eq. (6), $\text{sign}(\kappa_1 \kappa_2) = -1$ for the singlet, but $\text{sign}(\kappa_1 \kappa_2) = +1$ for the triplet.

2.3. Energy

To compute the energy, we now use:

$$
E = \frac{1}{2} \int \nabla_{r'}^2 \gamma(r, r')|_{r'=r} + \int v_{ne}(r)\rho(r) + \frac{1}{2} \int \int P(r_1, r_2)/|r_1 - r_2|,
\tag{21}
$$

which yields with Eqs. given above for the density, density matrix, and two-particle density, after separating into integration domains:

$$
E = \sum_i \omega_i \sum_{X=A,B} \left(\frac{1}{2} \int_{\Omega_X} \nabla r'^2 \gamma(r, r'; X)|_{r'=r} + \int_{\Omega_X} v_{ne}(r)\rho(r; X) \right.
$$
$$
\left. + \frac{1}{2} \int_{\Omega_X} \int_{\Omega_X} P(r_1, r_2; X)/|r_1 - r_2| \right).
\tag{22}
$$

As we consider subsystems that are infinitely separated, the terms containing r in one spatial domain, and r' in the other do not contribute to the energy expression:

- To obtain the kinetic energy, r' is set to r after taking the derivative with respect to r'.
- The term in the pair density where r and r' are in different regions is multiplied by the inverse distance of the two subsystems, and vanishes when the separation becomes infinite.

We can group together the terms in Eq. (22) that are integrated over the same domain to get

$$
E(A \cdots B) + \sum_i \omega_i(E(\Psi_i(A)) + E(\Psi_i(B))).
\tag{23}
$$

Notice that we cannot always use $E(\Psi_i(A)) = E(A)$, as we have not assumed that the number of electrons on system A has to be the same for all Ψ_i (cf. example in Eq. (7) or (8)). In such a case degeneracy is produced by having the same $E(\Psi_i(A)) + E(\Psi_i(B))$ for all i.

The energy of one of the subsystems can be defined as

$$
E(X) = \sum_i \omega_i E(\Psi_i(X)), \quad X : A \text{ or } B,
\tag{24}
$$

which is also the formula given in Ref. [1] as the energy of a system with non-integer particle number. Its failure with approximate density functionals, already mentioned by Slater [11], generalized in Ref. [1], has aroused renewed interest recently [12,13]. Of course, Eq. (24) can also be trivially applied when all $E(\Psi_i(X))$ are equal.

It should be stressed here that as soon as the distance becomes finite, there will be terms like

$$
\frac{1}{2} \int_{\Omega_A} \int_{\Omega_B} P_i(r_1, r_2; X)/|r_1 - r_2|
$$
$$
= \sum_{ij} k_i^* k_j \frac{1}{2} \int_{\Omega_A} \int_{\Omega_B} \langle \Psi_i(A)|\hat{\rho}(r_1)|\Psi_j(A)\rangle \langle \Psi_i(B)|\hat{\rho}(r_2)|\Psi_j(B)\rangle/|r_1 - r_2|
\tag{25}
$$

showing up. Notice that these are not expressed in terms of ρ_i, and ω_i only. Such a situation is also interesting when the subsystems are well-separated, in the sense that $\Psi_i(X)$ is ≈ 0 outside Ω_X, but not infinitely far apart. For example biradicals can provide such situations (see, e.g., Ref. [14]).

2.4. Density functional theory

In exact density functional theory, one obtains the ground state energy

$$
E = F[\rho] + \int \rho(r) v_{ne}(r)
\tag{26}
$$

by using the 'external' potential v_{ne} (of interaction between nuclei and electrons) and the ('universal') functional of the density F for any ground state density, ρ.

In the case we consider, disjointness is produced by infinite separation of subsystems, and we have, using Eq. (13), $(\rho(r) = \rho(r; A) + \rho(r; B))$, introducing the notation $\rho_i(A)$ for the density produced by $\psi_i(A)$

$$
\rho = \sum_i \omega_i(\rho_i(A) + \rho_i(B))
\tag{27}
$$

and by using Eq. (23),

$$
F\left[\sum_i \omega_i(\rho_i(A) + \rho_i(B)) \right] + \sum_i \omega_i \int (\rho_i(A) + \rho_i(B)) v_{ne}
$$
$$
= \sum_i \omega_i \left(F[\rho_i(A)] + \int \rho_i(A) v_{ne} + F[\rho_i(B)] + \int \rho_i(B) v_{ne} \right)
\tag{28}
$$

yielding

$$
F\left[\sum_i \omega_i(\rho_i(A) + \rho_i(B)) \right] = \sum_i \omega_i(F[\rho_i(A)] + F[\rho_i(B)])
$$
$$
= \sum_i \omega_i F[\rho_i(A)] + \sum_i \omega_i F[\rho_i(B)]
\tag{29}
$$

Here, too, one can define a contribution of a subsystem

$$
F(X) = \sum_i \omega_i F[\rho_i(X)].
\tag{30}
$$

Notice that all the $F[\rho_i(X)]$ are equal when symmetry produces degeneracy in subsystem X: all $E(\Psi_i(X))$ are equal due to degeneracy, $\int \rho_i v_{ne}$ are equal (as one is transformed into another by symmetry operations), and the differences between the former and the latter (yielding F) are equal, too. Finally as $\sum_i \omega_i = 1$, they are all equal to $F(X)$.

2.5. Density functional approximations

In the literature it is often stated that 'the exact functional is unfortunately unknown'. This statement is wrong, as the exact functional is known (see, e.g., Ref. [15]), and even accessible by numerical calculations (see, e.g., Ref. [16]). However, it is significantly more difficult to obtain the ground state energy after constructing the exact density functional and using it in Eq. (26) than to use the same level of approximation in directly solving the Schrödinger equation. However, approximations can be made which have proven to yield very good results, in spite of their astonishing simplicity.

Density functional approximations are constructed

- decomposing the universal density functional
- making approximations requiring the knowledge of ρ over small regions of space.

Decomposing the universal density functional is dictated by the wish to introduce physical knowledge. For example, Hohenberg and Kohn [17] split

$$F[\rho] = G[\rho] + U[\rho] \tag{31}$$

by defining the Coulomb term

$$U[\rho] = \frac{1}{2} \int \int \rho(r_1)\rho(r_2)/|\rho(r_1) - \rho(r_2)| \tag{32}$$

and Kohn and Sham [18] split further

$$G[\rho] = T_s[\rho] + E_{xc}[\rho] \tag{33}$$

by defining the kinetic energy of the system of non-interacting fermions, $T_s[\rho]$; E_{xc} is the exchange and correlation energy.

The advantage of introducing $U[\rho]$ is the correct treatment of the electrostatic interaction: on one hand, by Eq. (26), the interaction between electrons and nuclei is treated exactly, as is the interaction between nuclei. Approximations for $U[\rho]$ would destroy the balance, and generate serious problems, e.g., for Madelung forces in crystals. Recall also the problems which existed in the sixties when designing semi-empirical methods when the nuclear attraction was not properly compensated by the electron repulsion [19]. $T_s[\rho]$ was introduced to take into account the effects of the Pauli repulsion, which is mainly manifest in the kinetic energy.

Making approximations requiring the knowledge of ρ over small regions of space means using for density functionals approximations of the type

$$\int f(\rho, |\nabla\rho|, \ldots) \tag{34}$$

(called semi-local) as they need only information on ρ in a small region of space (at r, and around r, to obtain ρ's derivatives). This has the computational advantage of producing linear scaling of the computational time with respect to the size of the system.

Semi-local approximations (Eq. (34)) seem also to be justified by another statement often found in literature, namely 'density functional theory is size-consistent'. Exact density functional theory, by being exact, satisfies, of course, the requirement of size-consistency. However, the statement is not always valid when speaking about density functional approximations.

Let us first consider the argument of size-consistency (see, e.g., Ref. [22]).

$$\int f(\rho, \ldots) = \sum_X \int_{\Omega_X} \int f(\rho, \ldots) \overset{?}{=} \sum_X \int_{\Omega_X} \int f(\rho(X), \ldots). \tag{35}$$

Usually, one assumes that the density is an 'intensive' quantity, that its value in point $r \in \Omega_A$ is not affected by anything happening elsewhere, i.e., $\rho(r) = \rho(r;X)$, for $r \in \Omega_x$, and thus the second equal-

ity would be true. However, when degeneracy is present, we have to use Eq. (13), which yields

$$\int f(\rho, \ldots) = \sum_X \int_{\omega_x} f\left(\sum_i \omega_i \rho_i, \ldots\right) \overset{?}{=} \sum_X \sum_i \omega_i \int_{\omega_x} f(\rho_i(X), \ldots). \tag{36}$$

A form of f which would satisfy the second equality is $f \propto \rho$, but this is, of course, not interesting, as the integration simply yields a constant times the number of electrons in a system, and thus no contribution to reaction energies. Taking $f \propto \rho^{4/3}$, as is done for the dominating term in almost all $E_{xc}[\rho]$ approximations, brings in – even when the ρ_i are spatially separated – a prefactor $\omega_i^{4/3}$ which immediately shows that size-consistency is not satisfied.

Maybe the most important degeneracy-related difficulty is that in Eq. (29) one needs to obtain the same result for all ω_i. The values of ω_i are determined by the way the system is 'prepared', but the energy must not be affected by it. Let us first consider the case when the degeneracy does not modify the number of electrons on a subsystem. In this case, as stated below Eq. (30), the same value is obtained for the exact F, for all degenerate densities ρ_i. This is very difficult to achieve with approximations, as they are constructed to give changes in energies related to small changes in the density (by bond formation), while in the presence of degeneracy it is required that no change in the energy occurs for significant density changes [3]. None of the known approximations is able to reproduce this feature.

When the number of electrons is not kept constant within one of the subsystems, like in the example of Eq. (8), the situation is also complicated. The approximate functional by its semi-local character, cannot see the other subsystem. We have to construct functionals which are linear, as required by Eq. (30). This is more difficult to do than it may seem at first sight. The problem can be illustrated by noticing that already the separation given in Eqs. (31), (32) introduces a term which is non-linear (in the weights ω_i):

$$U\left[\sum_i \omega_i \rho_i\right] = \sum_{ij} \omega_i \omega_j \frac{1}{2} \int \int \rho_i(r_1)\rho_j(r_2)/|r_1 - r_2|$$
$$= \sum_i \omega_i U[\rho_i] - \sum_{i<j} \omega_i \omega_j U[\rho_i - \rho_j]. \tag{37}$$

Even if the ρ_i are on different subsystems, the last term on the r.h.s. in Eq. (37) does not vanish; it only reduces to terms $\omega_i^2 U[\rho_i]$ that are not small in magnitude compared to the linear terms.

As F is linear, cf. Eq. (30), using the separation given in Eq. (31) implies compensating the non-linear term above by an identical term in $G[\rho]$. Thus, approximations made on $G[\rho]$ get more complicated. Please notice that the non-linear term in Eq. (37) has similitude with the self-interaction term as it describes some spurious interaction (here between members of an ensemble).

For a one- and a two-electron system, T_s can be explicitly written down in terms of the density ρ (as $N\varphi^2 = \rho$; φ is the orbital yielding ρ and minimizing $\frac{1}{2} \int |\nabla\varphi|^2$):

$$T_s[\rho] = \int \frac{1}{8}|\nabla\rho|^2/\rho; \int \rho = 1 \text{ or } 2$$

For a subsystem having less than one electron, e.g., one half-space containing one of the H nuclei in the stretched H_2^+ molecule, the density is given by $\omega\rho$ and, correctly, $T_s[\omega\rho] = \omega T_s[\rho_1]$, where ρ_1 is the electron density of the hydrogen atom. If one considers, however, the stretched H_2^- molecule, $\rho = (1-\omega)\rho_1 + \omega\rho_2$, where ρ_2 is the electron density of H^-, a non-linear term shows up (see also Refs. [20,21]):

$$T_s[(1-\omega)\rho_1 + \omega\rho_2] = \int \frac{1}{8} \frac{|\nabla((1-\omega)\rho_1 + \omega\rho_2)|^2}{(1-\omega)\rho_1 + \omega\rho_2}$$
$$= (1-\omega)T_s[\rho_1] + \omega T_s[\rho_2] - \omega(1-\omega)\frac{1}{8}$$
$$\times \int \frac{1}{(1-\omega)\rho_1 + \omega\rho_2} \frac{(\rho_2\nabla\rho_1 - \rho_1\nabla\rho_2)^2}{\rho_1\rho_2}.$$
$$(38)$$

Please notice that the non-linear term would vanish, if ρ_2 were simply twice ρ_1, as for a non-interacting system. The physical density ρ_2 does not have this property, however. Furthermore, as the non-linear term is always non-positive,

$$T_s[(1-\omega)\rho_1 + \omega\rho_2] \leqslant (1-\omega)T_s[\rho_1] + \omega T_s[\rho_2]$$

showing that in the situation considered here the pure state Kohn–Sham solution is preferred to the ensemble (fractionally occupied) solution, for $\rho = (1-\omega)\rho_1 + \omega\rho_2$.

Thus, the non-linear terms in $U[\rho]$ and $T_s[\rho]$ also show up (to be compensated) in $E_{xc}[\rho]$ which is the quantity which is approximated for Kohn–Sham calculations. Splitting is E_{xc} into an exchange and a correlation part also produces non-linear terms. Examples for some simple systems can be found in Ref. [22].

When partial (spin-) densities, $(\rho_\uparrow, \rho_\downarrow)$ are present, the need of treating ensembles correctly shows up even more often. An often given example is the stretched H_2 molecule, where ρ is that of the H atoms, but $\rho_\uparrow = \rho_\downarrow = \rho/2$ are that of an equi-ensemble of H atoms [3,16,17].

3. Workarounds

3.1. Selected members

One possibility to get around this difficulty is to make approximations which allow symmetry breaking, producing thus sets of ρ_i: the functional is applied only for selected members of the ensemble. In fact, this recipe is just what is currently done in density functional calculations (by using the unrestricted Kohn–Sham formalism) and approximations often produce symmetry-broken solutions. It has even been argued that it is more easy to generate approximations for symmetry-broken solutions [23].

As other symmetry broken solutions can be generated by symmetry operations, violating symmetry is not a problem, as it can be restored by producing ensembles of the symmetry broken solutions [3]. Notice that this symmetry restoration is not equivalent to using ensembles in the Kohn–Sham approach (as presented, e.g., in Ref. [24]). In the latter, one uses ensembles for constructing T_s, while in the former, the ensemble shows up in all the terms of the energy, as in Eq. (22) (cf. Ref. [3], Section 4.1, Eqs. (17), (18) in Ref. [1], and a similar treatment for excited state ensembles, Refs. [25–27]).

Breaking symmetry in approximate calculations does not always follow exact theory. An example is that of the stretched H_2 molecule, where all commonly used functionals produce a symmetry broken solution (with $\rho_\uparrow = \rho$ on one atom, $\rho_\downarrow = \rho$ on the other atom), while accurate Kohn–Sham calculations (using Kohn–Sham orbitals $\varphi = \sqrt{\rho/2}$) produce solutions for $\rho_\uparrow = \rho_\downarrow = \rho/2$ [28,29].

One can see from Eq. (38), valid for $1 < \int \rho < 2$, that T_s attains its minimum for $0 < \omega < 1$; the pure state ($\omega = 0$ or 1) or symmetry broken solutions have higher kinetic energy. For $U[\rho]$ we also see that the non-linear terms also favors the formation of an ensemble with ω different from 0 or 1 (cf. Eq. (37)). Thus, the non-linear terms in $E_{xc}[\rho]$ have to be positive enough to make the 'pure state', i.e., $\omega = 0$ or 1, or 'symmetry broken' states at least degenerate with those obtained for $\omega \in (0,1)$.

These considerations 'of principle' may not play a role for a pragmatic person, as often symmetry broken solutions show up in calculations, but there are also some practical limitations:

- symmetric, non-size-consistent solutions turn out to be lower in energy than the symmetry broken ones, and thus not be chosen by the variational procedure, e.g., in X_2^+ molecules [30];
- as in unrestricted Hartree–Fock [31], multiple unrestricted solutions may exist;
- one may have to go further with symmetry breaking, than just using spin-unrestricted Kohn–Sham calculations (see, e.g.,Refs. [3,31,32]).

3.2. Back to wave functions

When analyzing size-consistency, we only looked up to now at what happens when a system completely dissociates. However, the treatment should be correct also for a finite distance, and this is by no means guaranteed by semi-local approximations. In fact, long-range interactions are dominated by R^{-n}-dependent terms, which do not show up even when there are no degeneracy effects at infinity. One can see this e.g., from Eq. (19), where i takes only the value one, and thus $\kappa_i = 1$,

$$\frac{1}{2} \int \int P(r_1,r_2)/|r_1 - r_2| \to \frac{1}{2}\frac{1}{R} \int \int \rho_A(r_1)\rho_B(r_2) = \frac{N_A N_B}{2} \frac{1}{R}.$$

Using a semi-local form produces for energies, to the same order R, a sum of terms, cf. Eq. (35), without $1/R$ terms.

As a side-remark, this also is a reason for using the exact form of $U[\rho]$, Eq. (32), which introduces such a term.

In order to introduce a more flexible form of $P(r_1,r_2)$ it is possible to generalize the Kohn–Sham ground state energy expression,

$$E_0 = \min_\Psi \left\langle \Psi \left| -\frac{1}{2}\sum_{i=1,N} \nabla_i^2 \right| \Psi \right\rangle + \int \rho_\Psi v_{ne} + U[\rho_\Psi] + E_{xc}[\rho_\Psi],$$
$$(39)$$

where ρ_Ψ is the density produced by Ψ, into

$$E_0 = \min_\Psi \left\langle \Psi \left| -\frac{1}{2}\sum_{i=1,N} \nabla_i^2 + w(|r_1 - r_2|) \right| \Psi \right\rangle + \int \rho_\Psi v_{ne}$$
$$+ U[\rho_\Psi; w] + E_{xc}[\rho_\Psi; w],$$
$$(40)$$

where the interaction w is hopefully weak enough to both produce a flexible form of $P(r_1,r_2)$ and not to require a computationally to heavy burden (see, e.g., Refs. [3,33–48]). Of course, U and E_{xc} will now depend on the interaction used. (For $w = 0$, they fall back into the Kohn–Sham expressions.) A simple and useful form for w is [13,36]:

$$w(r_{12}) = \text{erf}(\mu r_{12})/r_{12}.$$
$$(41)$$

This interaction is nearly constant (and thus with no effect on Ψ) for r_{12} smaller than $\approx 1/\mu$, and decays as $1/r_{12}$ beyond $r_{12} \approx 1/\mu$. It is a long-range interaction. The remaining part (the 'short range') has to be described by the density functional.

An advantage of introducing an interaction w is that, even weak, it selects the proper form of the wave function which is allowed to be constructed from several Slater determinants. Recall that in Kohn–Sham, one traditionally works with a single Slater determinant, or with an ensemble. In Kohn–Sham, this can produce a wave function which in spite of producing the right $\rho(r)$ produces $P(r_1,r_2)$ which is far from that of the exact one, and cannot reproduce the features required by Eq. (19). An example might be the stretched H_2 molecule [28,29], mentioned above, which has in accurate Kohn–Sham a solution described by a single Slater determinant. Thus, when the subsystems considered are at large separations,
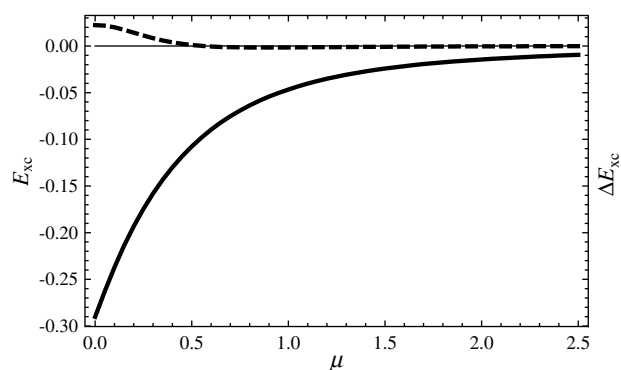
Fig. 1. Exchange–correlation energy, $E_{xc}[\rho;\mu]$, as in Eq. (40), full curve, and the error made by the LDA approximation, dashed curve, as a function of the range parameter μ, for the interaction given in Eq. (41); for the H atom, in atomic units.

Fig. 2. Error in the LDA exchange–correlation energy as a function of the weight ω, and the range parameter μ, for a density ω times that of a hydrogen atom.

long-range interactions, like that in Eq. (41), describe their interaction correctly, via the physical Coulomb interaction operator. Furthermore, as the wave function is constructed from several Slater determinants, $P(r_1,r_2)$ can have the correct form, and this allows a better description of the energy for a large separation between subsystems. This has been confirmed by numerical calculations for van der Waals systems (see, e.g., Refs. [37–41]).

Another advantage of introducing an interaction w is that it can – if carefully chosen – improve the quality of the density functionals, as these now do not have to describe features for which they are not adapted and represent the short ranged features which are imposed onto them by the nature of the semi-local approximation. In the exact theory, the parameter μ can take any value. However, as one uses approximations, the value of μ might become very important. For example, for $\mu = 0$, the interaction disappears, so we are back at the Kohn–Sham method. However, it can be shown that for very short range (very large μ) even the local density approximation (LDA) becomes exact for exchange, and very accurate for correlation [36,43,44]. Fig. 1 shows that the errors made by the LDA (exchange functional in Refs. [3,36], correlation functional from Ref. [49]), become small even for values of μ which are not very large, and the contribution of the functional is significant. For the atom of H for which the results are shown in Fig. 1, the errors are less than $\approx$1 mhartree for μ larger than $\approx$0.5. In different applications μ has been chosen to be close to 0.5 bohr (see, e.g., Refs. [45–48]). Using range separation also brings improvement for problems where a single determinant provides a good (even exact) description of the wave function [42].

Let us now see what happens when degeneracy shows up. A simple example is that of the stretched H_2^+ molecule, or $H^{+1/2}$, the equi-ensemble of the H^+ ions and H atoms (a situation similar to that in Eq. (8)). The exact $E_{xc}[\rho]$ is known in this case, at is has to compensate exactly $U[\rho = 1/2\ \rho_1]$ where ρ_1 is the density of the H atom:

$$E_{xc}[\rho] \rightarrow -\frac{1}{2} \int\int \rho(r_1)\rho(r_2)/r_{12} = -\frac{1}{8}\int \rho_1(r_1)\rho_1(r_2)/r_{12}$$
$$= -\frac{1}{8}\frac{5}{8}\text{hartree} \approx -0.078\,\text{hartree} \qquad (42)$$

Fig. 2 shows that the error in E_{xc} produced for $\omega \neq 0$ is drastically reduced when the range parameter μ is larger than $\approx$0.5.

The range separation reduces, but does not eliminate all the problems of the density functional approximations. For example, using a semi-local form for the approximations still does not solve the problem of obtaining different values for the functional when different degenerate densities are used.
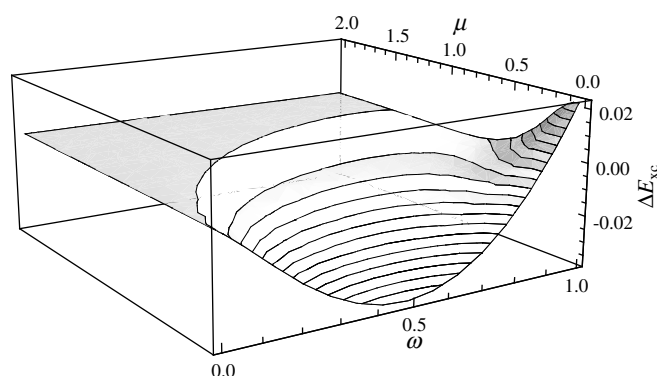
4. Conclusions

The size-consistency requirement, Eq. (1), is not automatically satisfied with density functional approximations when degeneracy is present. This is easily seen when the first-order density matrix, Eqs. (16) and (18), the one-particle density, Eq. (13), and the two-particle density, Eq. (19), are written using field operators. Although the energy seems to be partitionable into subsystem quantities, Eqs. (23) and (24), the dependence of the ensemble weights, ω_i, is explicit, and determined by the 'preparation' of the system. The situation gets even more complicated when the distance between subsystems becomes finite, as the proper description of the interaction between electrons located in different subsystems needs a proper two-particle density matrix, and this not only depends on the weights, but also on signs of the coefficients which showed up in the wave function, cf. Eqs. (19) and (25).

In order to avoid this problem, two paths were considered. The first one is in fact hidden in most practical calculations: one gives up describing ensemble densities, and uses functionals which induce symmetry broken solutions. Restoration of symmetry is no problem, but other problems, mainly how to induce the symmetry-broken solution, remain to be clarified. The other path is to generalize the Kohn–Sham method by permitting some interaction between particles. Although this is not a complete solution of the problem, a clear improvement has been seen in practical calculations.

This paper has not dealt with related issues, like the lack of correspondence between degeneracy in real systems and that in the Kohn–Sham system (see, e.g., Refs. [15,50–53]), or the effect of molecular dissociation on the Kohn–Sham potential (see, e.g., Refs. [2,21,53–55]).

Finally, it should be mentioned that the formalism presented here can be applied to degeneracy produced by spins, and also degeneracies showing up on a potential energy surface.

As this volume is dedicated to Prof. W. Kutzelingg, and this paper is on density functional theory, one may ask here whether Prof. Kutzelnigg is a friend of density functional theory [56]. Maybe one

can answer with Proverbs 27.6: 'Faithful are the wounds of a friend'.

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