

Degeneracy and size consistency in electronic density functional theory

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Abstract. The electronic structure calculations based upon energy density functionals are highly successful and widely used both in solid state physics and quantum chemistry. Moreover, the Hohenberg-Kohn theorems and the Kohn-Sham method provide them with a firm basis. However, several basic issues are not solved, and hamper the progress to achieve high accuracy. In this paper we focus on the conceptual problem of size consistency, basing our analysis on the non-intensive character of the (spin) electronic density in the presence of degeneracy. We also briefly discuss some of the issues concerning fractional electron numbers from the same point of view, analyzing the behavior of the exact functionals for the He and the Hooke's atom series when the number of electrons fluctuates between one and two.

1. Introduction

Density functional theory (see, e.g., [1]) (DFT) is by now the most popular method for electronic structure calculations in condensed matter physics and quantum chemistry, because of its unique combination of low computational cost and reasonable accuracy for many molecules and solids. However, despite its large success in scientific areas ranging from material science to biology, several basic issues in DFT are still unsolved, and hamper further developments towards high accuracy. Besides, some of these issues are often overlooked or simply ignored. We believe that raising them is a necessary step towards further improvement of DFT performances. To this purpose, in this paper we concentrate on a critical issue in this regard, namely the problem of size consistency in DFT in the presence of degeneracy.

The Hohenberg-Kohn theorems [2] and the Kohn-Sham method [3] provide a firm basis for DFT calculations, in which the ground state energy and density of a many-electron system is obtained by using energy density functionals that can be rigorously defined. Unfortunately, the exact definition does not give a prescription that can be followed in practice. Approximations are needed for the exchange-correlation energy $E_{xc}[n]$ as a functional of the electronic density $n(\mathbf{r})$, together with the corresponding exchange-correlation part of the Kohn-Sham potential, i.e., the functional derivative of $E_{xc}[n]$ with respect to $n(\mathbf{r})$. It is worth stressing that none of the available approximate $E_{xc}[n]$ satisfies two basic requirements:

- to provide reasonable error estimates;
- to allow systematic improvement, meaning that one knows how to reduce the errors by means of a well defined procedure.

Moreover, size consistency in DFT, which is often taken for granted (at least for systems composed of closed-shell fragments) can still be an issue, as discussed in the following sections. This paper is organized as follows. Section 2 discusses the general form of many approximate energy density functionals, focusing on the size consistency problem in the Hohenberg-Kohn framework. A similar analysis within the Kohn-Sham theory is then carried out in Sec. 3. Systems with fractional electron number are discussed from the same point of view in Sec. 4. The last Sec. 5 is devoted to concluding remarks.

2. Size consistency and density functional theory

The Hohenberg-Kohn theorems [2] state that the energy of a many-electron system is a variational functional of the density, $E[n]$, given by the sum of a universal part, $F[n]$, and a linear functional determined by the external potential $\hat{V}_{ne} = \sum_i v_{ne}(\mathbf{r}_i)$ acting on the electrons,

$$E[n] = F[n] + \int d\mathbf{r} v_{ne}(\mathbf{r}) n(\mathbf{r}). \quad (1)$$

Although the great success of DFT comes essentially from the introduction of the Kohn-Sham kinetic energy functional, orbital-free DFT is appealing for its lower computational cost, and is nowadays an active field of research (see, e.g., [4]). It is thus worth to first analyze the size-consistency issue in the pure Hohenberg-Kohn framework. In orbital-free DFT the universal functional $F[n]$ of Eq. (1) is rewritten as

$$F[n] = E_{\text{kxc}}[n] + E_{\text{H}}[n], \quad (2)$$

where $E_{\text{H}}[n]$ is the usual Hartree classical repulsion energy, $E_{\text{H}}[n] = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' n(\mathbf{r}) n(\mathbf{r}') |\mathbf{r} - \mathbf{r}'|^{-1}$, and $E_{\text{kxc}}[n]$ is the remaining part of the energy, the kinetic and exchange correlation functional, that needs to be approximated. The simplest approximations to $E_{\text{kxc}}[n]$ have the form

$$E_{\text{kxc}}^{\text{APPR}}[n] = \int d\mathbf{r} f(n(\mathbf{r}), |\nabla n(\mathbf{r})|, \dots), \quad (3)$$

where the function f is chosen to yield accurate properties for selected systems, e.g., the energy of the uniform electron gas, and/or to satisfy some known exact constraints, like scaling relations.

The requirement of size consistency for a quantum chemistry method is that the result for the energy $E(A+B)$ of two non-interacting systems A and B (e.g., which are at infinite distance from each other) be equal to the sum of their individual energies, $E(A) + E(B)$. Size consistency is evidently crucial when computing dissociation energies.

When approximations of the form of Eq. (3) are used, one is tempted to believe that size-consistency is guaranteed if the function f is intensive, i.e., if its value in the domain of space pertaining to system A , Ω_A , is not changed by the presence of the system B very far from A . A corresponding statement can be made for the integration Ω_B over the region of system B . As the integral in the composite system is the sum over the regions of the individual (sub-)systems,

$$\int d\mathbf{r} f(n(\mathbf{r}), |\nabla n(\mathbf{r})|, \dots) = \int_{\Omega_A} d\mathbf{r} f(n(\mathbf{r}), |\nabla n(\mathbf{r})|, \dots) + \int_{\Omega_B} d\mathbf{r} f(n(\mathbf{r}), |\nabla n(\mathbf{r})|, \dots) \quad (4)$$

size consistency would be guaranteed (for the Hartree and the external potential terms the same partition obviously holds for non-interacting subsystems). The basic belief behind this statement is that the density itself be an intensive quantity, i.e., that the total density $n_{A+B}(\mathbf{r})$ of the composite system $A + B$ be equal to

$$n_{A+B}(\mathbf{r}) = \begin{cases} n_A(\mathbf{r}) & \mathbf{r} \in \Omega_A \\ n_B(\mathbf{r}) & \mathbf{r} \in \Omega_B \end{cases} \quad (5)$$

However, this is not true when one of the two systems (or both) has a degenerate ground state with different densities. In this case, even an infinitesimal interaction with the other system can select one of the states (or a specific ensemble of some of the degenerate states). This change is not infinitesimal, and depends on the nature of the other system. Simple examples are diatomic molecules in which the individual atoms have partially filled shells with $\ell > 0$ (e.g. B₂, C₂, ...). An even simpler example is one of such atoms (with degenerate non-spherical densities) perturbed by a proton placed at a large distance. Thus, for degenerate systems, Eq. (5) should be replaced by

$$n_{A+B}(\mathbf{r}) = \begin{cases} \sum_i w_i(B) n_{Ai}(\mathbf{r}) & \mathbf{r} \in \Omega_A \\ \sum_i w_i(A) n_{Bi}(\mathbf{r}) & \mathbf{r} \in \Omega_B \end{cases} \quad (6)$$

where $n_{Ai}(\mathbf{r})$ and $n_{Bi}(\mathbf{r})$ are, respectively, the i^{th} degenerate densities of A and B , and the notation $w_i(B)$ (and $w_i(A)$) explicits the dependence of the weights of each ensemble ($\sum_i w_i = 1$ and $0 \leq w_i \leq 1$) on the presence of the other system, even if very far away. Equation (6) shows the non intensive character of the density in the presence of degeneracy.

The *exact* $F[n]$, of course, would preserve the degeneracy so that it would give for any linear combination of the degenerate densities, say, $n_{Ai}(\mathbf{r})$ the same energy for the system A , leading to size consistency. But none of the available approximate functionals is able to preserve the degeneracy of the physical system, as none is invariant within the set of degenerate densities. Typically, when treating the isolated systems with an approximate functional, one obtains a lower energy with one of the degenerate densities, or for a particular ensemble. This means that the approximation is size consistent only for some very specific choices of A and B , not in general.

Notice that here we consider the simple case in which different degenerate wavefunctions yield different densities. The interesting case of different denegerate wavefunctions corresponding to the same density is deeply analyzed in [5].

3. Kohn-Sham framework

In their foundational work, Kohn and Sham [3] split the functional $E_{\text{kxc}}[n]$ of Eq. (2) into

$$E_{\text{kxc}}[n] = T_s[n] + E_{\text{xc}}[n], \quad (7)$$

where $T_s[n]$ is the kinetic energy of a system of non-interacting fermions with density $n(\mathbf{r})$ [6],

$$T_s[n] = \max_v \left\{ \min_{\Phi} \langle \Phi | \hat{T} + \hat{V} | \Phi \rangle - \int d\mathbf{r} n(\mathbf{r}) v(\mathbf{r}) \right\}, \quad \text{with } \hat{V} = \sum_{i=1}^N v(\mathbf{r}_i), \quad (8)$$

where Φ is in most cases a single Slater determinant. The N spin-orbitals ϕ_i entering in Φ are determined via the self-consistent equations

$$\left[-\frac{1}{2} \nabla^2 + v_{\text{H}}(\mathbf{r})[n] + v_{\text{xc}}(\mathbf{r})[n] + v_{ne}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}), \quad n(\mathbf{r}) = \sum_i f_i |\phi_i(\mathbf{r})|^2, \\ v_{\text{H}}(\mathbf{r})[n] = \frac{\delta E_{\text{H}}[n]}{\delta n(\mathbf{r})}, \quad v_{\text{xc}}(\mathbf{r})[n] = \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})}. \quad (9)$$

The Kohn-Sham potential $v_{\text{KS}} = v_{\text{H}}[n] + v_{\text{xc}}[n] + v_{ne}$ is the maximizing potential of Eq. (8). Common approximations for the exchange-correlation energy $E_{\text{xc}}[n]$ are typically of the form of Eq. (3), so that as far as size consistency in the presence of degeneracy is concerned, we can apply to the Kohn-Sham $E_{\text{xc}}[n]$ the same considerations of the previous section, although in this case the situation is complicated by the presence of the functional $T_s[n]$, which depends

on the density in a rather complex way. $T_s[n]$ can have different values for different densities $n_i(\mathbf{r})$ that are degenerate in the physical system. The work of Fertig and Kohn [7] clearly shows that to different degenerate $n_i(\mathbf{r})$ can correspond different Kohn-Sham potentials $v_{KS,i}(\mathbf{r})$. For example, in an open shell atom with several degenerate non-spherical densities we have different non-spherical Kohn-Sham potentials, one for each symmetry. And for an ensemble of these densities, we usually need yet another Kohn-Sham potential [8].

The requirement for approximate $E_{xc}[n]$ to recover the degeneracy of the physical system has been recognized by several authors. Usually, it is written in the form (see, e.g., Ref. [9])

$$T_s[\sum_i w_i n_i] + E_{xc}[\sum_i w_i n_i] + E_H[\sum_i w_i n_i] = \sum_i w_i (T_s[n_i] + E_{xc}[n_i] + E_H[n_i]), \quad (10)$$

where n_i are the densities of the physical system corresponding to a set of orthonormalized degenerate ground-state wavefunctions Ψ_i , and Eq. (10) should hold for any set of the weights w_i . However, as noted in Refs. [10, 8], imposing Eq. (10) to approximate $E_{xc}[n]$ is probably a daunting task: the Hartree energy $E_H[\sum_i w_i n_i]$ contains cross terms ij , and must be compensated by a complex interplay between T_s and E_{xc} . This is illustrated with simple examples in the next Sec. 4.

In practical Kohn-Sham calculations, the individual spin densities, $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$, are used as two independent variables. In this case the total energy is rewritten as

$$E[n_\uparrow, n_\downarrow] = T_s[n_\uparrow, n_\downarrow] + E_H[n] + E_{xc}[n_\uparrow, n_\downarrow] + \int d\mathbf{r} v_{ne}(\mathbf{r}) n(\mathbf{r}). \quad (11)$$

As the total density, the spin densities are also non-intensive. Besides, degeneracy can occur more often than when considering the total density only. The simplest example is the hydrogen atom, which has two degenerate set of spin densities, $n_\uparrow = n$, $n_\downarrow = 0$ and $n_\uparrow = 0$, $n_\downarrow = n$. In the stretched hydrogen molecule, we have the equi-ensemble of the two on each atom.

4. Fractional number of electrons

The behavior of density functionals in the presence of a fractional number of electrons has been widely investigated [11, 12, 13]. Nowadays, there is a renovated interest in this issue (see, e.g., [14, 15, 16]), which has lead to the definition of the “many-electron self-interaction error”.

Fractional number of electrons can be recast in the same class of problems (degeneracy and size-consistency) discussed in the previous sections (see also Ref. [9]). To understand why, consider the simple example of the stretched He_2^+ molecule, where now system A is the He nucleus plus its electronic cloud on the left, and system B is the one on the right. We can take the two degenerate densities $n_{2,1}(\mathbf{r})$ and $n_{1,2}(\mathbf{r})$,

$$n_{2,1}(\mathbf{r}) = \begin{cases} n_{\text{He}}(\mathbf{r}) & \mathbf{r} \in \Omega_A \\ n_{\text{He}^+}(\mathbf{r}) & \mathbf{r} \in \Omega_B \end{cases} \quad n_{1,2}(\mathbf{r}) = \begin{cases} n_{\text{He}^+}(\mathbf{r}) & \mathbf{r} \in \Omega_A \\ n_{\text{He}}(\mathbf{r}) & \mathbf{r} \in \Omega_B \end{cases} \quad (12)$$

and form any ensemble of the two. We should always get the same energy. In particular, we can choose the symmetric one, $n_{3/2,3/2}(\mathbf{r}) = \frac{1}{2}n_{2,1}(\mathbf{r}) + \frac{1}{2}n_{1,2}(\mathbf{r})$, which yields $\frac{3}{2}$ electrons on A and $\frac{3}{2}$ electrons on B . Since the two degenerate wavefunctions corresponding to $n_{1,2}(\mathbf{r})$ and $n_{2,1}(\mathbf{r})$ have zero overlap, we must have, for any $0 \leq w \leq 1$,

$$E[w n_{2,1} + (1 - w) n_{1,2}] = w E[n_{2,1}] + (1 - w) E[n_{1,2}]. \quad (13)$$

If we now only look at the region pertaining to system A , we find [11, 9]

$$E_A[(1 - w) n_{\text{He}^+} + w n_{\text{He}}] = (1 - w) E_A[n_{\text{He}^+}] + w E_A[n_{\text{He}}], \quad (14)$$

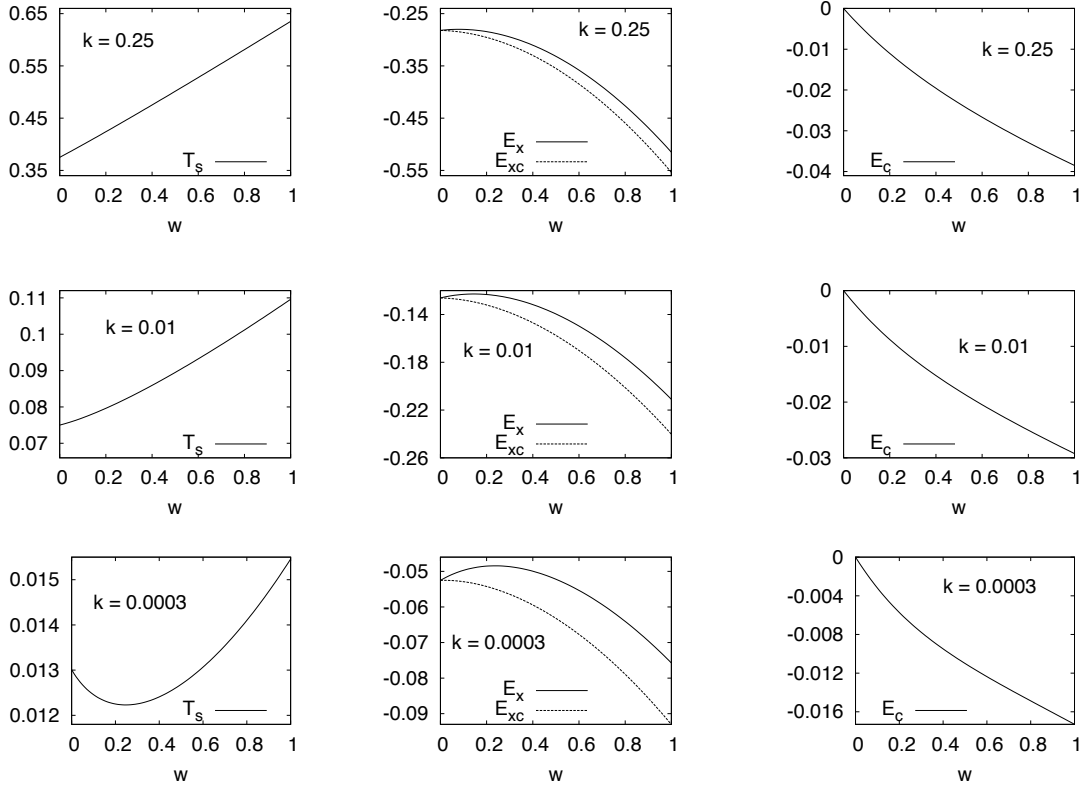


Figure 1. The non-interacting Kohn-Sham kinetic energy functional T_s , the exchange functional E_x , the correlation functional E_c , and their sum E_{xc} for the ensemble $n = (1 - w)n_1 + wn_2$ formed by the $N = 1$ and $N = 2$ densities of the Hooke's atom series, as a function of the weight w . All quantities are exact, calculated from the analytical solutions given by Taut [17], and are reported in Hartree atomic units.

which is the usual result for the energy of a fractional number of electrons [11, 12, 13], corresponding to the well-known requirement for density functionals as a function of w ,

$$T_s[(1 - w)n_N + wn_{N+1}] + E_H[(1 - w)n_N + wn_{N+1}] + E_{xc}[(1 - w)n_N + wn_{N+1}] = (1 - w)(T_s[n_N] + E_H[n_N] + E_{xc}[n_N]) + w(T_s[n_{N+1}] + E_H[n_{N+1}] + E_{xc}[n_{N+1}]), \quad (15)$$

where n_N and n_{N+1} are the densities of the physical system (same v_{ne}) with N and $N + 1$ electrons, respectively. Equation (15) is formally equivalent to Eq. (10). We have only two densities n_N and n_{N+1} , non-degenerate on the same region A , coming from the degeneracy arising in systems composed of many sub-systems [9].

Again, we may wonder whether Eq. (15) can ever be attained by approximate functionals. To illustrate the complicated interplay between T_s and E_{xc} as a function of w , we consider here the simple cases of the Hooke's atom series (two interacting electrons in an harmonic external potential, $v_{ne}(\mathbf{r}) = \frac{1}{2}kr^2$), and of the He isoelectronic series (two interacting electrons with $v_{ne}(\mathbf{r}) = -Z/r$). When a closed-shell two-electron system is weakly correlated (i.e., its wavefunction is well approximated by a single Slater determinant) we have $n_2(\mathbf{r}) \approx 2n_1(\mathbf{r})$. The Hooke's atoms and the He-like ions become, respectively, more and more correlated as k and Z decrease, i.e., as the electron-electron repulsion becomes important with respect to

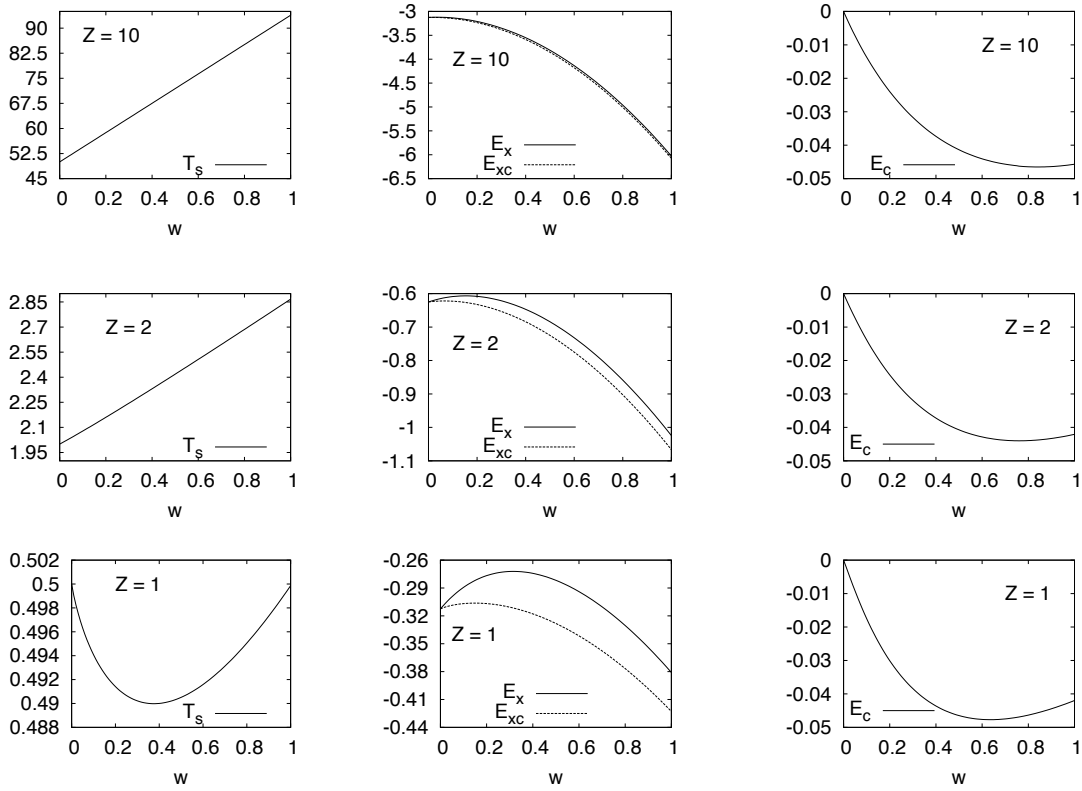


Figure 2. The non-interacting Kohn-Sham kinetic energy functional T_s , the exchange functional E_x , the correlation functional E_c , and their sum E_{xc} for the ensemble $n = (1 - w)n_1 + wn_2$ formed by the $N = 1$ and $N = 2$ densities of the He atom series, as a function of the weight w . All quantities are very accurate, calculated from the variational wavefunctions of Ref. [19] (see also [20] and [21]), and are reported in Hartree atomic units.

the external potential. The Hooke's atom series has a set of analytical solutions for specific values of the spring constant k [17]. Thus, we can calculate the exact densities and energies for $N = 1$ and $N = 2$ electrons, and, by inversion (see [18]), all the exact Kohn-Sham functionals corresponding to the ensemble density $(1 - w)n_1 + wn_2$. In Figure 1 we report, as a function of w , the exact $T_s[(1 - w)n_1 + wn_2]$ and $E_{xc}[(1 - w)n_1 + wn_2]$ (with its two components, exchange and correlation, separately) for three different values of k . The non-interacting kinetic energy T_s as a function of w changes from being almost linear in the less correlated case $k = \frac{1}{4}$, to displaying a minimum in the more correlated case $k = 4 \left(\frac{35 - 3\sqrt{57}}{1424} \right)^2 \approx 0.0003$. The functional E_{xc} must compensate the quadratic behavior of E_H with w ,

$$E_H[(1 - w)n_1 + wn_2] = (1 - w)^2 E_H[n_1] + w^2 E_H[n_2] + w(1 - w) \int d\mathbf{r} \int d\mathbf{r}' \frac{n_1(\mathbf{r})n_2(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (16)$$

as well as the non-linear behavior of T_s for correlated systems.

A very similar trend of the functionals is observed for the He isoelectronic series, as shown in Fig. 2. In this case we have used an improved version [20] of the accurate variational wavefunctions and energies of Ref. [19] (see also [21]) to calculate the exact functionals. Notice in particular the behavior of T_s for the more correlated case, $Z = 1$.

As said, a closed shell interacting system of two-electrons is weakly correlated when $n_2(\mathbf{r}) \approx 2n_1(\mathbf{r})$. In this case, the ensemble density with the corresponding $N = 1$ system is simply given by $w n_1 + (1 - w) n_2 \approx (1 + w) n_1$, and $T_s[(1 - w) n_1 + w n_2] \approx (1 - w) T_s[n_1] + w T_s[n_2]$. This is the case, e.g., of the Ne^{8+} system of Fig. 2, for which T_s is almost linear. However, the deviation of the Hartree term from linearity,

$$\begin{aligned} & E_H[(1 - w)n_1 + wn_2] - (1 - w)E_H[n_1] - wE_H[n_2] = \\ & = -\frac{w(1-w)}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{[n_2(\mathbf{r})-n_1(\mathbf{r})][n_2(\mathbf{r}')-n_1(\mathbf{r}')]}{|\mathbf{r}-\mathbf{r}'|} = -w(1-w) E_H[n_2 - n_1] \end{aligned} \quad (17)$$

is significantly different from zero when $n_2 \approx 2n_1$, while it could become smaller when n_2 is much more diffuse than $2n_1$. For example, for an ensemble of H and H^- we have $E_H[n_2 - n_1] = 0.1203$ Hartree, while $E_H[n_1] = 0.3125$ Hartree. That is, if the $N = 2$ system were less correlated so that $n_2 - n_1$ were equal (or close) to n_1 , E_H would be further from the linear behavior. So (in the simple systems considered here) when T_s is closer to linearity E_H can be further from it. The exchange-correlation functional should compensate these two different sources of deviation from linearity, a task that approximate functionals are not able to accomplish (see, e.g., Fig. 1 of Ref. [15]). As an example, consider the simple case of LDA: in the weakly correlated case ($n_2 \approx 2n_1$) the exchange LDA functional yields $E_x^{\text{LDA}}[(1 + w) n_1] = (1 + w)^{4/3} E_x^{\text{LDA}}[n_1]$, while the exact exchange functional is equal to $E_x[(1 + w) n_1] = (1 + w^2) E_x[n_1]$.

Notice that while the relative deviation of T_s from linearity decreases as the $N = 2$ system becomes less correlated (as shown in Figs. 1 and 2), the maximum absolute value of $T_s[(1 - w)n_1 + wn_2] - (1 - w)T_s[n_1] - wT_s[n_2]$ is always of the same order of magnitude, i.e. ≈ 2 mHartree for the Hooke's series and ≈ 15 mHartree for the He series.

5. Conclusions

Size-consistency in DFT is often taken for granted with approximate functionals of the form of Eq. (3), because the density is believed to be an intensive quantity. However, the density is not intensive in the presence of degeneracy. An attempt to build a correct description of ensembles in DFT seems in order [22], but using Eqs. (10) and (15) is probably not the best starting point. The alternative path of building ensembles of Kohn-Sham systems (e.g., using different Kohn-Sham potentials for each symmetry of the degenerate system [10]) deserves further investigation.

Acknowledgments

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