Measuring the effect of density errors when using density functional approximations

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Abstract

Using two different density functionals (one of them can be the exact one) provides two ground state densities. In order to study whether the difference in energies is due to the form of the functional itself, or the difference between the two densities, one may decompose the changes into that due to a change in the density (for given functional), and a change in the functional (at given density). However, the order in which this changes are made matters, yielding different contributions of the individual terms.

The two ways of computing the changes of the functional at given density (ground state density of each of the functionals) brackets the difference between the energies given by the two functionals.

Volentat de dos amichs se concorden a una fi.
Ramon Llull, *Llibre dels Mil Proverbis*, X.13 (1299)

1 Introduction: density and energy errors

A non-relativistic electronic system in its ground state is characterized by the external potential (of the nuclei, v_{ne}), and the number of electrons, N. Once this information is given, the Hamiltonian operator can be constructed, and the Schrödinger equation solved. Density functional theory is based upon the variational principle for obtaining the ground-state energy [1]:

$$E = \min_{n(r)} \left(F[n(r)] + \int v_{ne}(r) n(r) d^3 r \right) \tag{1}$$

where $n(r)$ is a positive function integrating to N. As clear from the notation, the computation of the functional F requires only the knowledge of the density, not that of v_{ne}. The minimizing density is the ground state density of the system characterized by v_{ne} and N.

When $F[n]$ is approximated, neither the ground state energy, nor the ground state density is correct. It is commonly believed that both quantities are quite well approximated, although benchmarks, as a rule, concentrate on energetic quantities. It was argued [2] that the success of density functional approximations is due to the sole use of the density, and not of the wave function that has a more difficult structure to catch. An example, the H_2 molecule in a minimal basis set was given. A single Slater determinant (as used in the Hartree-Fock, or in the Kohn-Sham method) is a poor approximation of the wave function. The density it produces is nevertheless exact.

However, it is not at all clear that the errors introduced by using an approximation for $F[n]$ have less importance for the density than for the energy. Could it happen that the opposite is true? In fact, in the early days of density functional theory, such questions have been asked, and it has been noticed that sometimes using density functional approximations give poorer densities than those obtained at Hartree-Fock level (see, e.g., [3]). A way to understand the source of the problem is to notice that the density is related to the variation of the energy with respect to the potential. Consider, for a trivial analogy, a well know problem from interpolation theory [4]. A polynomial interpolation of $\exp(x)$, with $0 \leq x \leq 1$, on m points gives:

$$f(x) \approx \sum_{k=0}^{m-1} a_k x^k$$

Even if the interpolant works quite well for $f(x)$, its quality deteriorates as derivatives are taken; the derivatives of the interpolant do not approximate well the derivative $f'(x)$, cf. figure 1. A derivative of order larger than m vanishes for the polynomial interpolant, while in the example given, all derivatives of $f(x)$ satisfy $f^{(n)}(x) = f(x)$.

Thus, in a recent series of papers (starting with [5]) the following question is raised:
Is the error of a given density functional approximation due to the inability to produce a good energy, or that of generating a correct density?

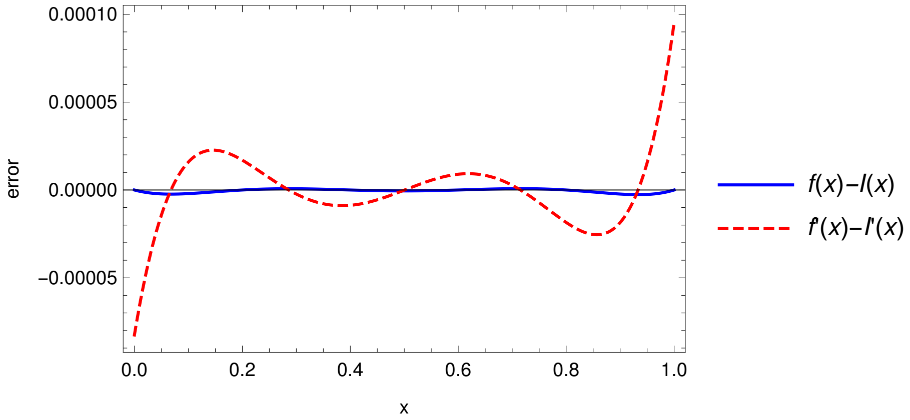

Figure 1: Errors obtained after interpolating $f(x) = \exp(x)$ i) on the function (full curve) ii) on the first derivative, $f'(x) = f(x)$, dashed curve.

In order to formulate more precisely this question, let us consider two methods, using the density functionals F_1 and F_2, yielding after the minimization of equation 1 the energies E_1, E_2, and ground state densities n_1, n_2, respectively. For example, the index 1 can refer to the exact quantities, and 2 to an approximation. Let us consider the expression that is minimized (that is in parentheses) in equation 1,

$$\mathcal{E}_i[n(r)] = F_i[n(r)] + \int v_{ne}(r)n(r)d^3r \tag{2}$$

The potential, v_{ne}, is not explicitly written as argument of $\mathcal{E}$, as it is considered given in the discussions that follow. $\mathcal{E}$ can be computed in principle for any $n(r)$, in particular, the ground state energy $E_i = \mathcal{E}_i[n_i]$. In reference [5], the difference between the energies obtained with the two methods is decomposed:

$$E_2 - E_1 = \Delta E_F + \Delta E_D \tag{3}$$

where $\Delta E_F = \mathcal{E}_2[n_1] - \mathcal{E}_1[n_1]$, $\Delta E_D = \mathcal{E}_2[n_2] - \mathcal{E}_2[n_1]$, and ΔE_F and ΔE_D attributed to errors due to the functional, or due to the density. [1]

In this paper, an alternative decomposition is discussed. It not only provides different numbers for the two contributions, it also provides bounds to the difference $E_2 - E_1$. Furthermore, it will be shown that the origin of effect of the density difference can be traced back to the (exchange-)correlation energy functional.

2 Two path to the same end, and error bounds

Let us consider, as above, $E_2 - E_1$. In the discussion below, one can, but is not obliged to associate index 1 to exact quantities, and 2 to approximate quantities. The attribution could be reversed, or both indices could correspond to approximations. Let us present the possibilities $\mathcal{E}_i[n_j]$, eq. 2, as a diagram (figure

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[1] Please notice that ΔE_F can be also written as a difference $F_2[n_1] - F_1[n_1]$, while ΔE_F also contains the effect of the change in density not only in the universal functional, but also a term depending on v_{ne}.

$$\begin{tikzcd}
E_2=\mathcal{E}_2[n_2] \arrow[r, "\text{change of density}"'] \arrow[d, dashed, "\text{change of functional}"] & \mathcal{E}_2[n_1] \arrow[d, "\text{change of functional}"] \\
\mathcal{E}_1[n_2] \arrow[r, dashed, "\text{change of density}"] & E_1=\mathcal{E}_1[n_1]
\end{tikzcd}$$

Figure 2: Different ways to reach E_2 from E_1. i) First changing the density, next changing the method (as described by the decomposition in ΔE_D, and ΔE_F, eq. 3): full arrows. ii) First changing the method, next changing the density: dashed arrows.

2). The decomposition of $E_2 - E_1$ described above (reference [5]) corresponds to reaching $E_1 = \mathcal{E}_1[n_1]$ starting from $E_2 = \mathcal{E}_2[n_2]$ by passing through $\mathcal{E}_2[n_1]$, i.e., first changing the density from n_2 to n_1, and next changing the method from $\mathcal{E}_2$ to $\mathcal{E}_1$ (full arrows in figure 2). Alternatively, one can first change the method, next change the density (dashed arrows in figure 2), i.e., pass through $\mathcal{E}_1[n_2]$. As in practice it is much easier to compute some approximate density functional with the exact density, i.e., obtain $\mathcal{E}_2[n_1]$, than to compute the exact energy functional with the approximate density, i.e., to obtain $\mathcal{E}_1[n_2]$, the choice of reference [5] is understandable. However,
i) by virtue of the Hohenberg-Kohn theorem [1], the value of the exact functional for a given density is accessible, see, e.g., [6], and
ii) $\mathcal{E}_i$ can correspond to different approximations (useful in practice), and in this case the difficulty mentioned does not show up.[2]

We take now into account that n_i is obtained by minimizing $\mathcal{E}_i[n]$ over n. Thus, by virtue of the variational principle, $\mathcal{E}_i[n \neq n_i] \geq \mathcal{E}_i[n_i] = E_i$. This is presented diagrammatically in figure 3. It shows that the effect of changing the density from n_2 to n_1 is different for the $\mathcal{E}_i$: while the contribution to the density change in equation 3, ΔE_D, is nonpositive, that using the other path, is nonnegative:

$$\begin{aligned} \mathcal{E}_2[n_2] - \mathcal{E}_2[n_1] &\leq 0 \\ \mathcal{E}_1[n_2] - \mathcal{E}_1[n_1] &\geq 0 \end{aligned} \tag{4}$$

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[2] It should be mentioned that the effect of using the Hartree-Fock method constrained to yield the exact density has been also used to provide bonds for the correlation energy [7], and to define and analyze the dynamic/non-dynamic components of the correlation energy [8].

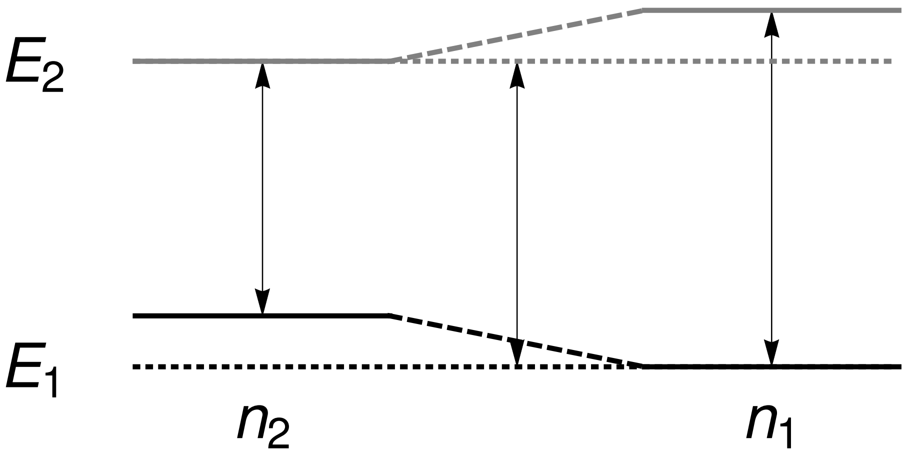

Figure 3: $\mathcal{E}$ for two different methods, and their ground state densities. The black color is used for $\mathcal{E}_1$, while the gray color for $\mathcal{E}_2$. The dashed lines are used to show the raising of $\mathcal{E}_i$ by using a density different from the ground state density. The double arrows shown the quantities showing up in equation 5, $\mathcal{E}_2[n_2] - \mathcal{E}_1[n_2]$, $E_2 - E_1 = \mathcal{E}_2[n_2] - \mathcal{E}_1[n_1]$, $\mathcal{E}_2[n_1] - \mathcal{E}_1[n_1]$.

We further obtain, by applying the above conditions,

$$\mathcal{E}_2[n_2] - \mathcal{E}_1[n_2] \leq E_2 - E_1 \leq \mathcal{E}_2[n_1] - \mathcal{E}_1[n_1] \tag{5}$$

Thus, bounds that bracket the difference between E_2 and E_1 are provided by the two ways of estimating the changes due to functionals, at fixed densities. (The upper bound corresponds to ΔE_F in equation 3.)

As each of the bounds in equation 5 uses the same density, the term containing v_{ne} in the definition of $\mathcal{E}$, equation 2, disappears from the bounds: only $F_2[n] - F_1[n]$ is used. In practice, most of the density functional calculations are performed using the method of Kohn and Sham [9]. In this method method, a kinetic energy functional of the density is defined, $T_s[n]$, subtracted it from $F[n]$, as is the classical Coulomb or Hartree term, $E_h[n]$. These terms are determined by the density alone, and are thus - for a given n - the same no matter what approximation is used for the remaining term, the exchange-correlation energy. We obtain that

$$E_{xc,2}[n_2] - E_{xc,1}[n_2] \leq E_2 - E_1 \leq E_{xc,2}[n_1] - E_{xc,1}[n_1] \tag{6}$$

In a variant of the Kohn-Sham method, the exchange energy is obtained exactly (like T_s and E_h), and for this category of approximations, only the approximation of the correlation energy produces the inequalities:

$$E_{c,2}[n_2] - E_{c,1}[n_2] \leq E_2 - E_1 \leq E_{c,2}[n_1] - E_{c,1}[n_1] \tag{7}$$

3 Illustration: the hydrogen atom

In order to illustrate the results obtained, let us now consider some specific example. We choose a very simple one that can be constructed analytically: the hydrogen atom. [3] As further simplifications, the local density approximation (LDA) is used, and a minimal basis set, $\psi = (\zeta^3/\pi)^{1/2} \exp(-\zeta r)$ in which the exponent of the hydrogen wave function, ζ, can be optimized. The optimal value, ζ_{min} depends on the approximation. Please notice that this ansatz corresponds to a scaling of the wave function.

Let us first consider exchange-only approximations (spin-restricted, or unrestricted). The energy expression is given by

$$\frac{1}{2}\zeta^2 - \zeta + \frac{5}{16}\zeta + c_x\zeta \tag{8}$$

The term in ζ^2 comes from the kinetic energy, the linear terms from the interaction with the nucleus, the Hartree, and the exchange term. An exchange term linear in ζ is provided by any approximation that satisfies the exact relationship required by scaling (equation 102 of reference [10]), in particular by LDA. The value of the coefficient c_x depends on the approximation. In LDA, c_x are known exactly, both for the spin-restricted, or -unrestricted approximation ($c_x \approx -0.2127$ and ≈ -0.2680, respectively).

The exact energy of the hydrogen atom is $E_1 = \mathcal{E}_1[n_1] = -1/2$ atomic units, and the exact density is obtained by using $\zeta = 1$ in the wave function ψ. The (exchange-only) LDA energy expression using the exact density of the H atom is obtained by choosing $\zeta = 1$ in equation 8, $\mathcal{E}_2[n_1] = -3/16 + c_x$.

As the LDA expression for the energy, equation 8, is quadratic, the lowest value is reached when using $\zeta_{min} = 11/16 - c_x$: $E_2 = \mathcal{E}_2[n_2] = -\zeta_{min}^2/2$.

To obtain the exact energy obtained for the LDA-optimized density, n_2, we consider a one-electron system, and need to find the potential that has the density $n = \psi^2 = (\zeta_{min}^3/\pi)\exp(-2\zeta_{min} r)$. We know it, this solution corresponds to the hydrogen-like atoms, and the potential is $-\zeta_{min}/r$. For this potential, the ground state energy is the same as for the approximation, $\mathcal{E}_1[n_2] = -\zeta_{min}^2/2$.

The numerical values are given in Table 1, where results obtained by adding a correlation functional [11] are also shown. One can notice that due to the incomplete cancellation of the Hartree term by the LDA exchange, the densities become too diffuse ($\zeta_{min} < 1$). The results are also summarized in form of an energy-level diagrams in figure 4. At first sight, the diagrams in figure 4 and figure 3 look different. However, the bounding properties shown by the inequalities 5 remain valid. The confusion is produced by the degeneracy of the approximate and exact energies for the approximate density (in the exchange-only case), and a significant stabilization produced by the correlation functional at LDA level (for the exchange-correlation case) making the lower bound become negative.

We now go a step further, and approach the exact value by modifying the Kohn-Sham model, by treating the contribution of the long-range interaction to exchange and correlation exactly; the long-range part of the interaction is defined by replacing the Coulomb repulsion between electrons by $\mathrm{erf}(\mu r)/r$ [12]. When the parameter μ vanishes, we recover the Kohn-Sham approximation, while when $\mu \to \infty$, the exact Schrödinger equation is obtained. In our hydrogen atom example, this means that the (fictitious self-interaction) Hartree (classical) repulsion between electrons is exactly compensated for the long range. The

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[3] One can imagine this also as a study of the limit of dissociation of the H_2 molecule, and analyze the problems that can occur when (semi-)local approximations are used.

Functional approximated	restricted LDA	unrestricted LDA
exchange only	-0.405 (0.900)	-0.456 (0.955)
exchange and correlation	-0.444 (0.921)	-0.477 (0.965)

Table 1: Results obtained by optimizing the scaled density of the H atom in the local density approximation. The ground state energies are followed by the optimized exponent, ζ_{min}, in parentheses; atomic units used.

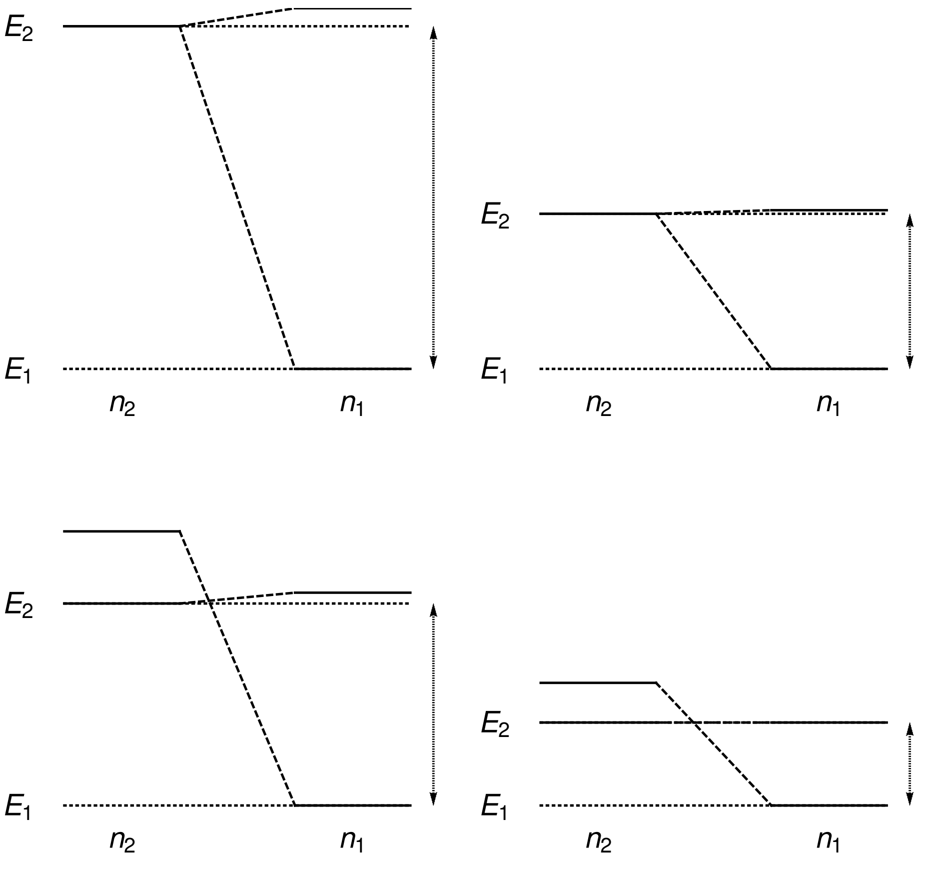

Figure 4: Energy level diagram, cf. figure 3, comparing the LDA and exact ground state energies (vertically), and the effect of density change, for the H atom, from LDA to the exact (horizontally, in each panel. The results using the exchange-only approximation are on the top panels, the exchange-correlation approximations are in the bottom panels; the spin-restricted form for the left panels, the spin-unrestricted form for the right panels.

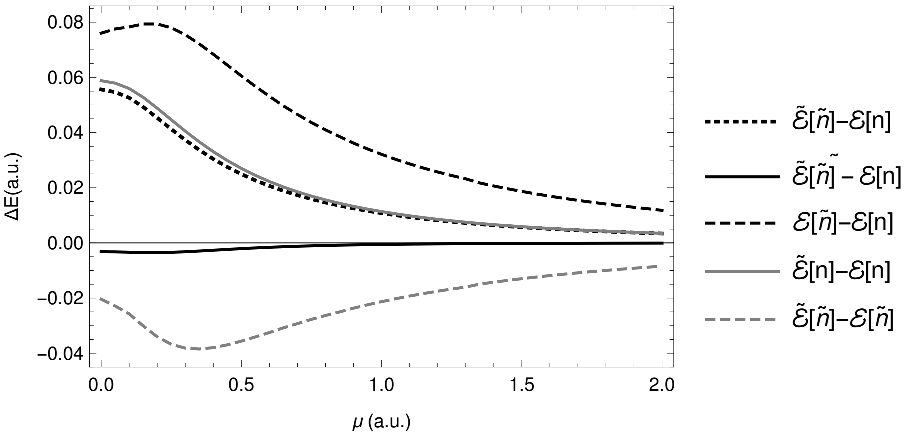

Figure 5: Evolution of energy differences with the range parameter μ. The difference between the LDA approximation and the exact value is shown as a dotted curve; the effect of changing between the exact and the LDA functional, at given density, is shown in gray, the effect of changing the density, for a given functional in black; the values on the path shown by full arrows in the diagram in figure 2 correspond to full curves, those corresponding to the path shown by dashed arrows in this diagram to dashed curves.

remaining part uses an LDA-type approximation for exchange and correlation that depends on the parameter μ [12, 13].

The resulting curves of the various energy differences as a function of μ are shown in figure 5. We notice that the attribution to changes due the functional, and due to the density, corresponding to the two paths in figure 2, full vs. dashed curves, are quite different. As show in inequalities 5, a given change of the density, produces opposite effects (different) signs for the contributions to the energy differences corresponding to a change in functionals. The path described by full arrows in the diagram in figure 2, i.e., the path of reference [5], attributes a weak change due to the density, while it is significant for the other path (black curves, full, and dashed, in figure 5). So, on one path the difference between curves is explained mainly by the error in the functional, while on the other, both contributions are significant. The bounds given by the inequalities 5 are shown in gray on figure 5. In accordance with the observation above, the upper bound is tighter than the lower bound.

4 Conclusion

The question addressed is whether the difference in the energies obtained using two density functional methods (one possibly the exact one) is due to i) the difference in the (exchange-)correlation functionals used, or ii) the differences in ground state densities produced by these functionals. It turns out that the order in which this change is made (first change the density, or first change the functional) matters, and a simple example (H atom), shows quite a substantial difference. The signs for the changes due to changing the densities in the two functionals (on the two paths) are different, (cf. inequalities 5). The changes produced by the functionals, when using the corresponding two ground state densities, produce bounds (cf. inequalities 5).

References

[1] P. Hohenberg, W. Kohn, *Phys. Rev* **136**, B864 (1964).

[2] M. Cook, M. Karplus, *J. Phys. Chem.* **91**, 31 (1987).

[3] A. Savin, U. Wedig, H. Stoll, H. Preuss, *Chem. Phys. Letters* **92**,503 (1982); erratum **94**, 536 (1983).

[4] C. Runge, *Zeitschrift für Mathematik und Physik*, **46**, 224 (1901).

[5] M.-C. Kim, E. Sim, K. Burke, *Phys. Rev. Lett.* **111**, 073003 (2013).

[6] F. Colonna, A. Savin, *J. Chem. Phys.* **110**, 2828 (1999).

[7] A. Savin, H. Stoll, H. Preuss, *Theor. Chim. Acta* **70**, 407 (1986).

[8] E. Valderrama, E. V. Ludeña, J. Hinze, *J. Chem. Phys.* **110**, 2343 (1999).

[9] W. Kohn, L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).

[10] M. Levy, J. P. Perdew, *Phys. Rev. A* **32**,2010 (1985).

[11] S. H. Vosko, L. Wilk, M. Nusair, *Canadian Journal of Physics* **58**, 1200 (1980).

[12] A. Savin, in *Recent Developments and Applications of Modern Density Functional Theory*, edited by J. M. Seminario, Elsevier, Amsterdam, 1996.

[13] S. Paziani, S. Moroni, P. Gori-Giorgi, G. B. Bachelet, *Phys. Rev. B* **73**, 155111 (2006).