# Understanding and Reducing Errors in Density Functional Calculations

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We decompose the energy error of any variational density functional theory calculation into a contribution due to the approximate functional and that due to the approximate density. Typically, the functional error dominates, but in many interesting situations the density-driven error dominates. Examples range from calculations of electron affinities to preferred geometries of ions and radicals in solution. In these abnormal cases, the error in density functional theory can be greatly reduced by using a more accurate density. A small orbital gap often indicates a substantial density-driven error.

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Density functional theory (DFT) began with the Thomas-Fermi (TF) approximation [1,2], which is now used in many branches of physics [3]. For electronic structure, the Kohn-Sham (KS) scheme [4] is now applied in many other disciplines, from chemistry to materials science and beyond. In all practical calculations, some form of density functional approximation is used, leading to errors in the property being calculated. A persistent weakness of the method has been an inability to control these errors or systematically improve approximations [5]. There are no error bars on DFT energies. Traditionally, all that can be used to judge the reliability of a calculation [6] is experience with specific classes of systems and properties.

Many researchers worldwide are focused on improving approximations to the ground-state energy functional, but no such improvements are reported here. On the contrary, we introduce a general method for analyzing the error in *any* such approximate DFT calculation. We find the somewhat surprising result that entire classes of errors are often misclassified. We also show how such errors can often be greatly reduced with relatively little computational cost. We demonstrate the power of our method by curing the infamous self-interaction error (SIE) that bedevils DFT calculations of ions and radicals in solution. We illustrate with numerous examples from the chemical literature, but our reasoning applies to approximate DFT calculations in *any* situation.

In ground-state DFT, the energy is written as

$$E = \min_n \left\{ F[n] + \int d^3r\, n(\mathbf{r}) v(\mathbf{r}) \right\}, \tag{1}$$

where $v(\mathbf{r})$ is the one-body potential of the system (e.g., the sum of attractions to the nuclei), while $F[n]$ is a functional [7] of the one-electron density $n(\mathbf{r})$ and is independent of $v(\mathbf{r})$. In practical DFT calculations, $F[n]$ is approximated, call it $\tilde{F}[n]$. The minimizing density $\tilde{n}(\mathbf{r})$ is therefore also approximate, so the energy error is

$$\Delta E = \tilde{E} - E = \Delta E_F + \Delta E_D, \tag{2}$$

where $\Delta E_F = \tilde{F}[n] - F[n]$ is the functional error, because it is the error made by the functional on $n(\mathbf{r})$. The density-driven error is due to the error in $\tilde{n}(\mathbf{r})$, and $\Delta E_D$ is defined by Eq. (2).

A Thomas-Fermi calculation is a pure DFT calculation, in which $F[n]$ itself is approximated. Because of the inability to treat quantum oscillations leading to shell structure, the density-driven error dominates and is typically much larger than $\Delta E_F$. Modern attempts at pure DFT approximations (i.e., orbital-free DFT [8–10]) are rarely tested self-consistently, for precisely this reason. Modern calculations employ the KS scheme in which only a small fraction of $F[n]$ is approximated, the so-called exchange-correlation contribution, $E_{\mathrm{XC}}[n]$. Even with the simple local density approximation (LDA), $\Delta E_F$ usually dominates over $\Delta E_D$. Densities are often so accurate that it is common practice to test a new approximation with orbitals from a less accurate one [11–13]. We denote such calculations as *normal*, as their energetic errors largely reflect the true error in the approximation.

But in a small fraction of calculations, $\Delta E_D$ dominates over $\Delta E_F$. In such *abnormal* calculations the typical error of a given approximation appears abnormally large. Our analysis shows that this is a qualitatively different (and more insidious) error, due to an unusual sensitivity to the XC potential, leading to a poor-quality density. Such errors should not be directly attributed to the given approximation, but rather to the type of calculation, and can be greatly reduced by using more accurate densities, sometimes at little additional cost.

The infamous SIE [14] made by standard DFT approximations is well known to be extreme when an extra electron is added to a neutral atom or molecule. In LDA, $H^-$ is unbound because of this [15]. But recently [16] it has been shown that, if more accurate densities are used instead of self-consistent densities, the errors are reduced so much that they are *less* than those of ionization potentials. The SIE is reduced by adding an extra electron.

We begin with pure DFT, such as TF calculations for total atomic energies. For Ra ($Z = 88$), the TF error is about $-3.4$ kilohartree out of $-23$ kilohartree, and the relative error vanishes as $Z \to \infty$ [17]. But $\Delta E_F$ is only $-0.62$ kilohartree, and so $\Delta E_D$ is about 4 times larger. The errors in self-consistent TF atomic calculations are mainly due to the error in the density, and the main aim of orbital-free approaches should be to reduce this error.

But most modern calculations use the KS scheme, solving self-consistently

$$\{-\nabla^2/2 + v_S(\mathbf{r})\}\phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}), \tag{3}$$

where $\phi_i(\mathbf{r})$ is a KS orbital and $\epsilon_i$ its eigenvalue. Here, the density of the orbitals is defined to match the true density, and the energy can be found from

$$F[n] = T_S[n] + U[n] + E_{XC}[n], \tag{4}$$

where $T_S$ is the kinetic energy of the orbitals, $U$ their Hartree energy, and

$$v_S(\mathbf{r}) = v(\mathbf{r}) + \int d^3r \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} + v_{XC}(\mathbf{r}),$$
$$v_{XC}(\mathbf{r}) = \frac{\delta E_{XC}}{\delta n(\mathbf{r})}. \tag{5}$$

Approximations in common use are LDA [4], the generalized gradient approximation, such as the Perdew-Burke-Ernzerhof (PBE) functional [18], and hybrid functionals [19,20]. The energy-functional error is transmitted to the density via $v_{XC}(\mathbf{r})$. The SIE of standard approximations causes $v_{XC}(\mathbf{r})$ to decay too rapidly with $r$, so that $v_S(\mathbf{r})$ is too shallow [21], and the $\epsilon_i$ are insufficiently deep by several eV. However, an almost constant shift in $v_S(\mathbf{r})$ has little effect on $\tilde{n}(\mathbf{r})$ and therefore on $E$.

To illustrate our method, we apply it to the simplest nontrivial system, two-electron ions, with nuclear charge $Z$ varying down to 1 ($\mathrm{H}^-$). For He (and any $Z \geq 2$) with standard approximations, $\tilde{n}(r)$ is indistinguishable from $n(r)$, despite the large errors in $v_S(r)$ and $\epsilon_i$. Thus, $\Delta E_F$ is 0.3 eV, while $\Delta E_D$ is only $-0.04$ eV, and the calculation is *normal*. But the energy error for $Z \leq 2$ in Fig. 1 behaves rather smoothly until around $Z_c \approx 1.23$, where it suddenly changes behavior. As $Z$ is reduced from 2 (He) to 1 ($\mathrm{H}^-$), a fraction of an electron [15] unbinds (about 0.3) in a standard DFT calculation [18], greatly increasing the error.

Our analysis explains the origin of this error in general terms. The solid colored lines decompose the error into $\Delta E_F$ and $\Delta E_D$. Around $Z_c \approx 1.23$, where $\epsilon_{1s}$ vanishes and the system begins to ionize, $\Delta E_D$ grows and leads to the qualitative change in $\Delta E$. Nothing special happens to $\Delta E_F$, which is almost zero for $\mathrm{H}^-$ and is far less than for He. A DFT calculation with an accurate two-electron density produces a smaller error for the electron affinity of H than for the ionization energy of He [16].

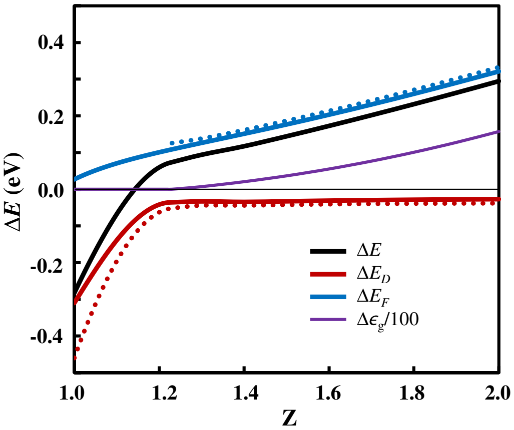

FIG. 1 (color online). Errors in ground-state energies of two-electron ions as a function of nuclear charge: PBE energies evaluated on exact [53,54] (solid lines) and Hartree-Fock (dotted lines) densities [55].

In an *abnormal* calculation, the system is peculiarly sensitive to the error in $v_{XC}(\mathbf{r})$, so that $\tilde{n}(\mathbf{r})$ differs significantly from $n(\mathbf{r})$, enhancing $\Delta E_D$. The large error in density is very visible in Fig. 2, where the PBE density integrates to only 1.7 electrons. From Fig. 1, one sees that the PBE calculation is (somewhat accidentally) almost exact for $\mathrm{H}^-$ when evaluated on the exact density.

Our method can be applied to any small system where accurate densities can be calculated via quantum chemical methods, and it will show when an error is density driven. But much of the value of DFT is in its relatively low computational cost, allowing large systems to be treated, where highly accurate densities are prohibitively expensive. However, if we apply linear response theory to the KS system:

$$\delta n(\mathbf{r}) = \int d^3r' \chi_S(\mathbf{r}, \mathbf{r}')\delta v_S(\mathbf{r}'), \tag{6}$$

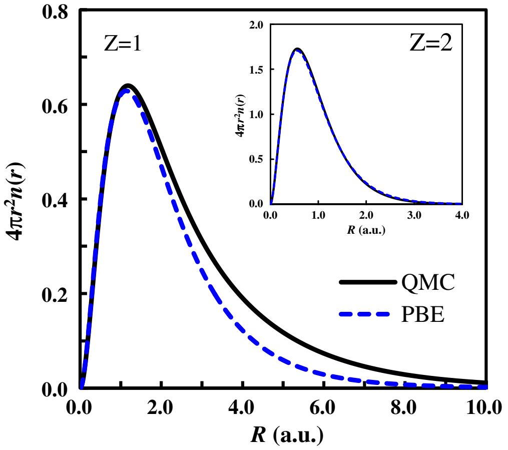

FIG. 2 (color online). Exact [Quantum Monte Carlo (QMC) calculations [53,54]] and PBE radial densities for $\mathrm{H}^-$ ($Z = 1$) and He ($Z = 2$).

where $\delta n(\mathbf{r})$ is the change in density induced by $\delta v_S(\mathbf{r})$,

$$\chi_S(\mathbf{r},\mathbf{r}') = \sum_{i,j}(f_i - f_j)\frac{\phi_i^*(\mathbf{r})\phi_j^*(\mathbf{r})\phi_i(\mathbf{r}')\phi_j(\mathbf{r}')}{\epsilon_i - \epsilon_j + i0_+} \quad (7)$$

is the static density-density KS response function and $f_i$ is the KS orbital occupation factor [22]. The smallest denominator is $\Delta\epsilon_g$, the HOMO-LUMO gap. Normally, the difference between the exact and approximate $v_S(\mathbf{r})$ is small, ignoring any constant shift. If $\Delta\tilde{\epsilon}_g$ is not unusually small, this error leads to a small error in $\tilde{n}(\mathbf{r})$. But if $\Delta\tilde{\epsilon}_g$ is small, even a small error in $v_S(\mathbf{r})$ can produce a large change in the density, and self-consistency only increases this effect. Thus, small $\Delta\tilde{\epsilon}_g$ suggests a large density error, and we plot $\Delta\epsilon_g^{\text{PBE}}$ in Fig. 1. For two-electron ions, the PBE LUMO is unbound, so that $\Delta\epsilon_g^{\text{PBE}} = |\epsilon_{\text{HOMO}}^{\text{PBE}}|$. At $Z_c$ this vanishes. For other atomic anions with standard approximations, $\tilde{\epsilon}_{\text{HOMO}} > 0$, i.e., a resonance [16]. Finite atom-centered basis sets turn this resonance into an eigenstate with an accurate density and produce accurate electron affinities [23].

Additionally, we need only a more accurate density than the poor density of the abnormal DFT calculation itself. For SIE, we know that most of the error in $v_S(\mathbf{r})$ can be cured with orbital-dependent functionals [14,24,25], and the Hartree-Fock density is often sufficient and is available in all quantum chemical codes. Thus, the SIE density-driven error of standard approximations will often be cured by evaluating DFT energies on HF densities, called HF-DFT [16], which are not much more expensive than self-consistent DFT calculations. This method yields extremely small errors (about 0.05 eV) for the electron affinities of atoms and small molecules [16,26]. Occasionally, spin contamination make HF calculations yield poor density, and so HF-DFT fails.

Our next abnormality is well known [27]. DFT calculations of molecular dissociation energies ($E_b$) are usefully accurate with generalized gradient approximations, and more so with hybrid functionals. These errors are often about 0.1 eV/bond [28], found by subtracting the calculated molecular energy at its minimum from the sum of calculated atomic energies. This is because, if one simply increases the bond lengths to very large values, the fragments fail to dissociate into neutral atoms. The prototypical case is NaCl, which dissociates into $\text{Na}^{0.4}$ and $\text{Cl}^{-0.4}$ in a PBE calculation [27]. The large error in density for the stretched bond yields $\Delta E_b \approx 1$ eV, as shown as the difference between PBE and HF-PBE calculations in Fig. 3. In this case, the HF density spontaneously suddenly switches to neutral atoms at about 5.6 Å, but is correct in the dissociation limit. The common practice of using isolated atomic calculations is inconsistent, but removes the density-driven error, because isolated atoms are normal. Incorrect dissociation occurs whenever the approximate HOMO of one is below the LUMO of the other [27], which guarantees a vanishing $\Delta\tilde{\epsilon}_g$ when the bond is greatly stretched. The exact $v_{\text{XC}}(\mathbf{r})$ contains a step between the atoms which is missed by semilocal approximations.

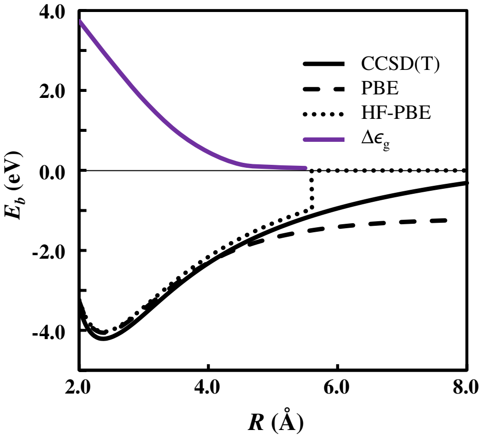

FIG. 3 (color online). Energy of NaCl as a function of Na-Cl distance in several calculations, and the PBE HOMO-LUMO gap.

When modern functionals were first being adopted for molecular calculations, they were sometimes evaluated on HF densities [11–13], so as to compare only functional errors. More recently, Janesko and Scuseria [29] showed that this led to substantial improvement in transition-state barriers. The prototype of such barriers is the symmetric H—$H_2$ transition state, which is improved by almost a factor of 2 by using HF-PBE instead of PBE. Here $\Delta\epsilon_g^{\text{PBE}}$ is not quite as small (2.5 eV) as in other cases, but the improvement upon using the HF densities is still substantial. High-level *ab initio* calculations yield an energy barrier of 0.43 eV [29], where the PBE calculation gives a value of 0.16 eV and that of HF-PBE gives 0.25 eV. Analysis of a collection of barriers in Table 1 of Ref. [30] shows that, in cases where the HF DFT barrier differs from the self-consistent barrier by more than, for instance 25%, the mean absolute error is more than 3 times smaller than DFT. The sole exception is the $t$-$N_2H_2$ hydrogen transfer forward reaction barrier, where the HF density is spin contaminated (just as in the molecule CN [26]).

Finally, we report new applications where we drive out the density-driven error. The potential energy surfaces (PES) of odd-electron radical complexes like $\text{OH}\cdot\text{Cl}^-$ and $\text{OH}\cdot\text{H}_2\text{O}$ are important in radiation, atmospheric and environmental chemistry, as well as in cell biology [31–34]. For example, how anions behave in droplets is critical to understanding aerosols in the atmosphere [35]. Accepted wisdom is that anions near an air-water interface, being less screened, have lower concentrations [36]. But recent classical molecular dynamics (MD) simulations have shown the opposite [36,37].

This controversy invites an *ab initio* MD approach, to either reinforce or debunk classical MD. However, DFT approximations have problems here [25,38–40]. Several

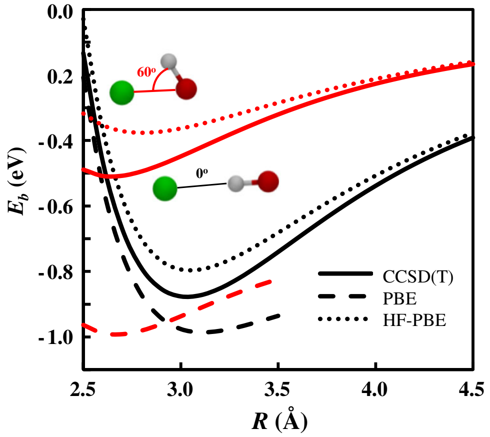

FIG. 4 (color online). Potential energy surface scans for the $HO \cdot Cl^-$ complex along Cl—O—H angle of 0° (hydrogen-bonding structure, black lines) and 60° [hemibonding structure, gray (red) lines] using various methods; $R$ is the Cl—O separation.

studies show two minima in the ground-state PES: a normal hydrogen bond and a two-center, three-electron interacting hemibond [41]. High-level quantum chemical calculations [41] and self-interaction corrected DFT calculations [25,42] reveal that the true PES has only one minimum, the hydrogen-bonding structure. Hemibonding is overstabilized in approximate DFT because three electrons incorrectly delocalize over two atoms.

In Fig. 4, we show plots of the PES of the $HO \cdot Cl^-$ complex using different methods. The O—H bond length was fixed at 1 Å. The binding energy is

$$\Delta E_b = E_{HO \cdot Cl^-}(R, \theta) - (E_{HO\cdot} + E_{Cl^-}), \tag{8}$$

where $E_{HO \cdot Cl^-}(R, \theta)$ is the energy on a given geometry with Cl—O distance $R$, and Cl—O—H angle $\theta$, $E_{HO\cdot}$ is the energy of the OH radical, and $E_{Cl^-}$ is the energy of the Cl anion. The difference between the energy minima of hydrogen-bonding and hemibonding structures in the PBE calculation is less than 0.01 eV. A small $\Delta\epsilon_g^{\rm PBE}$ in the hydrogen-bonding structure ($\sim 0.32$ eV) suggests a large density-driven error. We find that the HF-PBE calculation follows the same trends and produces the same minima as the coupled-cluster method with singles, doubles, and perturbative triples [CCSD(T)], although the binding energies themselves have errors of up to 0.09 eV. Similar conclusions are found for the PES of the $HO \cdot H_2O$ complex [43].

In every example of density-driven error in this Letter, the HOMO-LUMO gap of the DFT calculation is small. We end with an example in which a small gap does not produce a density-driven error. Much recent research is focused on localization errors of approximations [44], and many failures can be related to such errors. Consider the classic example of a severe SIE, namely, stretched $H_2^+$ with a standard functional. As the bond is stretched, the gap rapidly shrinks, suggesting abnormality, but when a HF-DFT calculation is performed, the error barely changes. Thus, this is a normal calculation whose error is functional driven, not density driven, and the HF-DFT calculation does not reduce the error. The small gap is due to stretching the bond, not a sign of an incipient density-driven error [45].

Our method for classifying DFT errors is general. Declaring a calculation abnormal depends on both the energy being calculated (total, ionization, bond, etc.) and the approximation being used. The error in *any* approximation can be studied in this way. For example, methods that begin from exact exchange (such as RPA [46–48] or *ab initio* DFT [49]) which yield better potentials could be examined to see if such improvements yield better energies. We focused here on the SIE because of its ubiquity, but one can apply the same reasoning to, e.g., the correlation energy itself [50,51] or the error in the KS kinetic energy in orbital-free approximations [9]. The classic examples of stretched $H_2$ and $H_2^+$ are normal, because self-consistent densities (restricted in the case of $H_2$) are close to exact densities. The myriad materials and molecules where standard DFT fails should now be reexamined to distinguish between true errors (i.e., large energy errors even on exact densities) and density-driven errors, which are system and property dependent.

Calculation details are given in the Supplemental Material [52].

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