Improving energies by using exact electron densities

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The exact electronic ground-state density and external potential are used to improve the accuracy of approximate density functionals. Our approach combines the advantages that the exact exchange-correlation energy functional is more local for full-coupling strength than for the coupling-constant average, and that knowledge of the exact virial can be used to reduce the exchange energy error by a factor of 2.

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Recently, several methods [1–8] have been devised that, for a given external potential v and its exact ground-state density ρ, yield the exact Kohn-Sham potential. Subtraction of the external and Hartree potentials then leaves the exact exchange-correlation potential, $v_{XC}([\rho];\mathbf{r}) = \delta E_{XC}/\delta\rho(\mathbf{r})$, whose virial yields [9]

$$-\int d^3 r \rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\nabla} v_{XC}([\rho];\mathbf{r}) = E_{XC} + T_C, \quad (1)$$

where E_{XC} is the exchange-correlation energy and T_C is the correlation contribution to the kinetic energy. We show below how to use the exact $v_{XC}(\mathbf{r})$ to extract E_{XC} (and hence the total energy) more accurately than by any currently used approximate spin-density functional.

We decompose the exchange-correlation energy of a system in terms of the coupling constant in the electron-electron repulsion, $\lambda/|\mathbf{r}-\mathbf{r}'|$, and in terms of the separation between points in the system, $\mathbf{u}$. We define $E_{XC,\lambda} = N\int d^3 u \langle\rho_{XC,\lambda}(\mathbf{u})\rangle/2u$, where $\langle\rho_{XC,\lambda}(\mathbf{u})\rangle = (1/N)\int d^3 r \rho(\mathbf{r})\rho_{XC,\lambda}(\mathbf{r},\mathbf{r}+\mathbf{u})$ is the system-averaged exchange-correlation hole at coupling constant λ [10]. [The external potential is also λ-dependent, being chosen to keep the density $\rho(\mathbf{r})$ independent of λ [11]; at $\lambda=0$, it becomes the Kohn-Sham potential.] The coupling-constant average yields the exact exchange-correlation energy [11,12], $E_{XC} = \int_0^1 d\lambda E_{XC,\lambda}$. At $\lambda=1$, the wave function is the full interacting wave function, and

$$E_{XC,\lambda=1} = E_{XC} - T_C. \quad (2)$$

Adding Eqs. (1) and (2) leads to the exact relation

$$E_{XC} = \frac{1}{2}\left[E_{XC,\lambda=1} - \int d^3 r \rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\nabla} v_{XC}([\rho];\mathbf{r})\right]. \quad (3)$$

In Eq. (3), we suggest using the exact $v_{XC}(\mathbf{r})$ and density $\rho(\mathbf{r})$ to evaluate the virial, and a spin-density functional approximation for $E_{XC,\lambda=1}$. Because Eq. (3) employs the exact

virial, the error made by the functional approximation to the exchange energy is reduced by a factor of 2, as in Eq. (14) of Ref. [13]. Furthermore, because Coulomb-correlated electrons avoid each other, the $\lambda=1$ on-top ($u=0$) hole is deeper than its coupling-constant average. But the system-averaged hole satisfies the charge conservation rule $\int d^3 u \langle\rho_{XC,\lambda}(\mathbf{u})\rangle = -1$, so deeper holes are shorter ranged. Local spin-density (LSD [14]) and semilocal [such as Perdew and Wang (PW91) [15]] approximations to the system-averaged hole are typically most accurate at small u [16], and least accurate at large u [17], as one would expect intuitively. Thus LSD and PW91 typically work better [18] for $E_{XC,\lambda=1}$ than for E_{XC}. We therefore make these approximations for $E_{XC,\lambda=1}$ in Eq. (3), undoing the coupling-constant average as in Ref. [19]. In Table I we give the results of Eq. (3) applied to both LSD and PW91, for the few atoms for which the Kohn-Sham potential has been reliably calculated

TABLE I. Total energy errors in millihartrees for several atoms. We compare functional approximations (LSD and PW91) with improvements thereof (marked by a prime) using Eq. (3). HA denotes the two-electron Hooke's atom [16], with spring constant $k=1/4$. Unless otherwise noted, the approximate functional $E_{XC,\lambda=1}$ is evaluated on the Hartree-Fock density [23]. The last column is the exact E_{XC} (from Ref. [20], unless otherwise noted), also in millihartrees. (1 mhartree = 0.0272 eV = 0.627 kcal/mole.)

Atom	LSD	LSD′	PW91	PW91′	E_{XC}
H[a]	22	5	-2	-3	-312
H$^-$[a]	14	3	-2	1	-423[b]
HA[a]	27	5	8	1	-554[c]
He	71	20	5	2	-1068
Li	138	41	6	-2	-1827
Be^{++}	214	78	23	9	-2321
Be	236	86	33	17	-2772[b]
Be[a]	227	81	24	12	-2772
N	460	170	10	5	-6780
Ne	700	280	-20	10	-12480[d]

[a]Approximate $E_{XC,\lambda=1}$ evaluated on exact density.
[b]Exact results from Ref. [21].
[c]Exact results from Ref. [22].
[d]Exact results from Ref. [6].

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[6,20–22]. We see that both LSD and PW91 errors are typically reduced, often by a factor of 2 to 3.

In constructing the table, the virial had to be evaluated on the exact density (see below), but we evaluated the density functional $E_{XC,\lambda=1}$ on the spin-restricted Hartree-Fock density, for convenience sake. For the Be atom, in which the difference between the Hartree-Fock and exact densities is greatest, we show results for the density functionals evaluated on both densities. We find that, while the results of the functionals change noticeably, the improvement due to Eq. (3) is present in either case. This justifies our use of Hartree-Fock densities for the functional evaluation in other parts of the table, where these differences are expected to be much smaller.

To see why $v_{XC}(\mathbf{r})$ and its virial had to be constructed from the exact density, consider the results when inexact densities are used. Application of Eq. (1) to the self-consistent density and potential for an approximate functional yields the functional approximation to $E_{XC}+T_C$, so that Eq. (3) simply recovers the original approximation. On the other hand, if we start from the Hartree-Fock density, the corresponding potential is essentially the exact $v_X(\mathbf{r})$, and the right-hand side of Eq. (1) becomes essentially the exact E_X. (We assume the slight differences between the exact exchange-only and Hartree-Fock densities to be negligible here [24].) Inserted into Eq. (3), this Hartree-Fock approximation for the virial of Eq. (1) yields $E_{XC} \simeq (E_{XC,\lambda=1}+E_X)/2$. (In the particular case where $E_{XC,\lambda=1}$ is calculated within LSD, this is Becke's half-and-half hybrid [25–27].) This procedure typically improves upon the energy of LSD, but is not as good as using the exact virial in Eq. (3), except when $(E_C+T_C)/E_C \approx 0$, i.e., in the tightly bound or high-density limit.

In fact, if the exact density and external potential are known, the accuracy of Eq. (3) may be obtained for the total energy directly, without constructing $v_{XC}(\mathbf{r})$ at all. For this purpose, the exact relation of Eq. (14) of Ref. [13] may be rewritten as

$$E_0 = \int d^3r \rho(\mathbf{r})v(\mathbf{r})$$
$$+ \frac{1}{2}\left[\int d^3r \rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\nabla}v(\mathbf{r}) + U + E_{XC,\lambda=1}\right], \quad (4)$$

where E_0 is the total electronic ground-state energy, and U is the Hartree energy, $\int d^3r \int d^3r' \rho(\mathbf{r})\rho(\mathbf{r}')/2|\mathbf{r}-\mathbf{r}'|$. For an atom, the virial theorem of Eq. (4) asserts that the total energy is half the potential energy. Since $E_{XC,\lambda=1}/2$ is approximated in either Eq. (3) or Eq. (4), these equations make the same absolute errors. However, to go back and extract E_{XC} from E_0 requires knowledge of T_S, the noninteracting kinetic energy. Again, to obtain the accuracy of Table I from Eq. (4), the Hartree-Fock density can be used instead of the exact density *only* in the evaluation of $E_{XC,\lambda=1}$.

We close by noting that, while Eq. (3) represents a systematic improvement on both LSD and PW91 exchange correlation, it does not provide a new functional in the normal sense. This is because the procedures used here require as input both the exact density and the external potential of the system. There is no obvious way to modify them to produce a self-consistent scheme that *yields* the exact density and, through Eq. (4), a highly accurate energy. Equations (3) and (4) may become of more direct interest once sufficiently accurate experimental valence densities are available [28].

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