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Exchange and correlation energies in density-functional theory: Bounds from available data

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It is pointed out that the Kohn-Sham orbitals, for the exact interacting ground-state energy and density for the external potential of interest $v(\mathbf{r})$, are *simultaneously* the optimum orbitals of the exact *exchange-only* computation for the modified external potential $v(\mathbf{r})+v_c(\mathbf{r})$, where $v_c(\mathbf{r})$ is the correlation potential. This theorem is used to derive necessary bounds that the exact density-functional-theory correlation energy must satisfy in terms of approximate correlation energies which are obtained from available data. Numerical examples of one of the bounds is given with respect to the surface correlation energies of jellium metal.

In the Hohenberg-Kohn-Sham density-functional theory,[1-3] it is $E_x[\rho]+E_c[\rho]$ which has to be approximated for variational calculations, where $E_x[\rho]$ is the universal exchange-energy functional of density ρ and $E_c[\rho]$ is the universal correlation-energy functional of ρ. In this paper we focus upon the definitions of $E_x[\rho]$ and $E_c[\rho]$ and then exhibit necessary bounds that the exact $E_c[\rho]$ must satisfy in terms of available data.

$E_c[\rho]$ is commonly defined explicitly or implicitly in density-functional theory as[4-8]

$$E_c[\rho]=E[\rho]-E_{xo}[\rho]\ , \tag{1}$$

with

$$E[\rho]=\langle\Psi\,|\,\hat{T}+\hat{V}_{ee}+\sum_i v(\mathbf{r}_i)\,|\,\Psi\rangle\ , \tag{2}$$

where $\hat{T}$ and $\hat{V}_{ee}$ are the kinetic and electron-electron interaction operators, respectively, and where

$$E_{xo}[\rho]=\langle\Phi\,|\,\hat{T}+\hat{V}_{ee}+\sum_i v(\mathbf{r}_i)\,|\,\Phi\rangle\ , \tag{3}$$

where ρ comes from Ψ, the interacting ground-state[9] wave function of external potential $V=\sum_i v(\mathbf{r}_i)$, and where Φ, which also yields ρ, is the corresponding Kohn-Sham ground-state single determinant. Note that Φ is generated by the full exchange-correlation potential. xo signifies exchange only.

Equation (3) is a natural choice for the definition of the exchange-only part of Eq. (1) in that the gradient expansion exists[6,10] for the nonclassical repulsive part of Eq. (3) and this nonclassical part has also been shown to scale homogeneously.[11] That is, $E_x[\lambda^3\rho(\lambda\mathbf{r})]=\lambda E_x[\rho(\mathbf{r})]$.

An active area of density-functional-theory research concerns the generation of accurate functional forms of $E_c[\rho]$. For this purpose, numerical estimates of $E_c[\rho]$'s are presently available for ground-state Coulomb ρ's but only by using data obtained outside of density-functional theory. Specifically *available* as good estimates of $E_c[\rho]$ are the exact values for $E_c'[\rho]$ and $E_c^{\mathrm{HF}}[\rho]$, where

$$E_c'[\rho]=E[\rho]-E_{xo}'[\rho] \tag{4}$$

and

$$E_c^{\mathrm{HF}}[\rho]=E[\rho]-E_{xo}^{\mathrm{HF}}[\rho]\ . \tag{5}$$

(Note that for atoms and molecules, $E_c[\rho]$, $E_c'[\rho]$, and $E_c^{\mathrm{HF}}[\rho]$ have all been defined to be negative here.)

In Eq. (4), $E_{xo}'[\rho]$ is the exact "exchange-only" total energy[6,7] for external potential V. That is,

$$E_{xo}'[\rho]=\langle\Phi'\,|\,\hat{T}+\hat{V}_{ee}+\sum_i v(\mathbf{r}_i)\,|\,\Phi'\rangle\ , \tag{6}$$

where Φ' is that single determinant which is constrained to be a ground state[9] of some noninteracting Hamiltonian of the form $\hat{T}+\sum_i w'(\mathbf{r}_i)$, and which simultaneously minimizes $\langle\hat{T}+\hat{V}_{ee}+\sum_i v(\mathbf{r}_i)\rangle$. The potential $w'(\mathbf{r})$ is restricted to be local.

In Eq. (5),

$$E_{xo}^{\mathrm{HF}}[\rho]=\langle\Phi_{\mathrm{HF}}\,|\,\hat{T}+\hat{V}_{ee}+\sum_i v(\mathbf{r}_i)\,|\,\Phi_{\mathrm{HF}}\rangle\ , \tag{7}$$

where Φ_{HF} is that single determinant which minimizes $\langle\hat{T}+\hat{V}_{ee}+\sum_i v(\mathbf{r}_i)\rangle$, without further restriction. Note that while Φ' and Φ_{HF}, as well as Φ, are all determined by ρ, in general Φ, Φ', and Φ_{HF} are all different, and only $\langle\Phi\,|\,\hat{\rho}\,|\,\Phi\rangle=\rho$, where $\hat{\rho}$ is the density operator. The densities ρ' and ρ_{HF} are generally different from each other and different from ρ.

The exact value of $E_c^{\mathrm{HF}}[\rho]$ is often available when ρ is the ground-state density of an atom or a small molecule,[12,13] and the exact value of $E_c'[\rho]$ is available for a variety of atoms.[6,7,14] In contrast, exact values for $E_c[\rho]$, the density-functional correlation energy of interest, are unavailable for comparison.[13]

$E_c^{\mathrm{HF}}[\rho]$, based upon the Hartree-Fock reference point, is the traditional quantum chemistry definition of the correlation energy for external potential V, and $E_c'[\rho]$ is the correlation energy based upon the reference point of Aashamar, Luke, Shadwick, and Talman (see also Refs. 6 and 7).[14] It is the purpose of this article to exhibit necessary bounds, in terms of $E_c'[\rho]$ and $E_c^{\rm HF}[\rho]$, that the exact $E_c[\rho]$ must satisfy. We shall also discuss the tightness of the bounds.

The main rigorous bounds are

$$E_c[\rho] < E_c'[\rho] < E_c^{\rm HF}[\rho] \,, \tag{8}$$

and we shall prove that

$$0 < E_c'[\rho] - E_c[\rho] = \int [\rho'(\mathbf{r}) - \rho(\mathbf{r})] v_c(\mathbf{r}) d\mathbf{r} - \delta_2 \,, \tag{9}$$

where δ_2 is a positive number, so that

$$0 < E_c'[\rho] - E_c[\rho] < \int [\rho'(\mathbf{r}) - \rho(\mathbf{r})] v_c(\mathbf{r}) d\mathbf{r} \,. \tag{10}$$

Actual numerical bounds on $E_c'[\rho] - E_c[\rho]$ may thus be obtained via Eq. (10) because v_c, ρ, and ρ', are now available for atoms,[14,15,16] where $v_c(\mathbf{r})$ is the correlation potential associated with the ground-state density of $v(\mathbf{r})$ which is ρ. The rightmost inequality in Eq. (8) results from the fact that $E_{\rm xo}'$ has the local potential restriction associated with it while $E_{\rm xo}^{\rm HF}$ is unrestricted in this sense. (For two electrons, the inequality actually becomes an equality because the Fock potential is local for two electrons.)

Equation (9) and the leftmost inequality in Eq. (8) are now proven. For the key starting point in the proof, we now state the theorem that the Kohn-Sham Φ is the minimizing single determinant of the interacting *exchange-only* calculation for the *modified external potential* $v(\mathbf{r}) + v_c(\mathbf{r})$, where

$$v_c(\mathbf{r}) = \delta E_c[\rho] / \delta\rho(\mathbf{r}) \,. \tag{11}$$

That is, Φ is that single determinant which minimizes

$$\langle \hat{T} + \hat{V}_{ee} + \sum_i v(\mathbf{r}_i) + \sum_i v_c(\mathbf{r}_i) \rangle$$

and is simultaneously constrained to be the ground state of some noninteracting Hamiltonian of the form $\hat{T} + \sum_i w(\mathbf{r}_i)$, with $w(\mathbf{r})$ restricted to be a local potential. Throughout this minimization process it is assumed that the $v_c(\mathbf{r})$ retains its ground-state form, always corresponding to the ground-state density ρ, thereby playing the role of a component of the modified external potential. Thus, while Φ' is the constrained minimizing single determinant for the interacting Hamiltonian $\hat{T} + \hat{V}_{ee} + \sum_i v(\mathbf{r}_i)$, Φ is the constrained minimizing single determinant for the *different* interacting Hamiltonian

$$\hat{T} + \hat{V}_{ee} + \sum_i v(\mathbf{r}_i) + \sum_i v_c(\mathbf{r}_i) \,.$$

Thus, unless $v_c(\mathbf{r})$ is a constant, it follows directly that[17]

$$E_{\rm xo}[\rho] - E_{\rm xo}'[\rho] = \delta_1, \quad \delta_1 > 0 \,, \tag{12}$$

or equivalently

$$\langle \Phi | \hat{T} + \hat{V}_{ee} + \sum_i v(\mathbf{r}_i) | \Phi \rangle - \langle \Phi' | \hat{T} + \hat{V}_{ee} + \sum_i v(\mathbf{r}_i) | \Phi' \rangle = \delta_1, \quad \delta_1 > 0 \,. \tag{13}$$

And it also follows that

$$\langle \Phi' | \hat{T} + \hat{V}_{ee} + \sum_i v(\mathbf{r}_i) + \sum_i v_c(\mathbf{r}_i) | \Phi' \rangle - \langle \Phi | \hat{T} + \hat{V}_{ee} + \sum_i v(\mathbf{r}_i) + \sum_i v_c(\mathbf{r}_i) | \Phi \rangle = \delta_2 \,, \quad \delta_2 > 0 \,. \tag{14}$$

Now, add Eqs. (13) and (14). Obtain

$$\int [\rho'(\mathbf{r}) - \rho(\mathbf{r})] v_c(\mathbf{r}) d\mathbf{r} = \delta_1 + \delta_2 > 0 \,. \tag{15}$$

Equations (12) and (15) yield

$$E_{\rm xo}[\rho] - E_{\rm xo}'[\rho] = \int [\rho'(\mathbf{r}) - \rho(\mathbf{r})] v_c(\mathbf{r}) d\mathbf{r} - \delta_2 > 0 \,. \tag{16}$$

Finally, the combination of Eqs. (1) and (4) with Eqs. (12)

TABLE I. Jellium-metal surface correlation energies as a function of the Wigner-Seitz radius r_s. In the table σ is the total surface energy for the fully correlated system; $\sigma_{\rm xo}$ and $\sigma_{\rm xo}'$ the surface energies in the exchange-only approximation with $\sigma_{\rm xo}$ determined for densities that minimize the total energy and $\sigma_{\rm xo}'$ for those that minimize the total exchange-only energy; σ_c and σ_c' are the corresponding surface correlation energies.

Wigner-Seitz radius r_s (a.u.)	Surface energies (ergs/cm^2) σ	$\sigma_{\rm xo}$	$\sigma_{\rm xo}'$	σ_c	σ_c'
2.0	−664[a]	−1549	−1643[b]	885[a]	979
2.5	187[a]	−288	−332[b]	475[a]	519
3.0	278[a]	−7	−26[b]	285[a]	304
3.5	240[a]	56	49[b]	184[a]	191
4.0	189[a]	65	57[b]	124[a]	132
4.5	146[a]	58	55[b]	88[a]	91
5.0	113[a]	50	47[b]	63[a]	66
5.5	89[a]	41	39[b]	48[a]	50
6.0	71[a]	33	33[b]	38[a]	38

[a] See Ref. 8.

[b] See Ref. 18.

and (16) proves Eq. (9) and the leftmost inequality in Eq. (8).

The rightmost side in Eq. (9),

$$\int [\rho'(\mathbf{r})-\rho(\mathbf{r})]v_c(\mathbf{r})d\mathbf{r}-\delta_2 \, ,$$

is a positive number which is the difference between two numbers that are always positive and generally small in a relative sense. Hence, Eq. (9) dictates that while $E_c[\rho]$ should always be more negative than $E_c'[\rho]$, the former should be reasonably close to the latter, at least in a relative sense. We expect in general, however, that $E_c[\rho]$ should be farther from $E_c'[\rho]$ than $E_c'[\rho]$ is from $E_c^{\mathrm{HF}}[\rho]$. Namely, the rightmost bound in Eq. (8) should be tighter than the leftmost bound. That is,

$$E_c'[\rho]-E_c[\rho]>E_c^{\mathrm{HF}}[\rho]-E_c'[\rho] \, . \tag{17}$$

Equation (17) is conjectured because Φ' and Φ_{HF} are minimizing determinants with respect to the *same* Hamiltonian, $\hat{T}+\hat{V}_{ee}+\sum_i v(\mathbf{r}_i)$, while as stated earlier, Φ is the minimizing function for a different Hamiltonian,

$$\hat{T}+\hat{V}_{ee}+\sum_i v(\mathbf{r}_i)+\sum_i v_c(\mathbf{r}_i) \, .$$

As a numerical illustration of the leftmost inequality of Eq. (8) we consider the corresponding surface correlation energies $\sigma_c[\rho]$ and $\sigma_c'[\rho]$ of jellium metal (for the surface, we have replaced E_c by σ_c and E_c' by σ_c'). The surface energy σ which is the work required, per unit area of the new surface formed, to split a crystal in two, involves the difference in energies between the split and unsplit crystal. Consequently the surface correlation energy is positive, since the correlation energy of the uniform electron gas of the unsplit crystal is lower than that of the lower electron density system at and about the surface of the split crystal.

The results quoted in Table I are gleaned from the work of Mohammed and Sahni,[8] and Sahni and Ma.[18] The work of these authors for the total surface energy[8] $\sigma[\rho]$ for the fully correlated system and the total surface energy $\sigma_{\mathrm{xo}}'[\rho]$ in the exchange-only (Pauli-correlated) approximation[18] is variational in nature. (A fully self-consistent optimized local-effective-potential calculation of the jellium-metal surface physics problem in the exchange-only approximation has yet to be performed, as has the more formidable fully self-consistent Hartree-Fock calculation.) The accuracy of the results of these authors is guaranteed both by their use of physically realistic wave functions as well as the application of the variational principle for the energy. For details of these calculations, we refer the reader to the appropriate references.[8,18]

In the second column of Table I we quote the results[8] for the total surface energy over the metallic range of densities, $r_s=2$–6, where r_s is the Wigner-Seitz radius. This is the sum of the surface kinetic energy of a system of noninteracting electrons, the surface electrostatic energy, and the surface exchange-correlation energy as determined by the *nonlocal* wave-vector analysis scheme of Langreth and Perdew.[19] In the next two columns we give the exchange-only results $\sigma_{\mathrm{xo}}[\rho]$ and $\sigma_{\mathrm{xo}}'[\rho]$ (which are the sum of the surface kinetic, surface electrostatic, and *nonlocal* surface exchange energies), the former[8] being determined for those orbitals which minimize the total surface energy, and the latter[18] for those that minimize the total exchange-only surface energy. In the last two columns we give the corresponding correlation energies $\sigma_c[\rho]$ and $\sigma_c'[\rho]$. We observe that σ_c' closely approximates the "exact" result σ_c with σ_c' being greater than σ_c as expected on the basis of Eq. (8). The difference between $\sigma_c[\rho]$ and $\sigma_c'[\rho]$, on the average, is about 5% although for higher density metals it is as high as 10%. Finally, the fact that the bounds are as tight as they are is indicative of the accuracy of these variational calculations.

TABLE II. Theoretical values for the Hartree-Fock (conventional wave function) and exchange-only (density-functional-theory) correlation energies E_c^{HF} and E_c', respectively.

		Correlation energies (Ry)	
Atom	Atomic number Z	Hartree-Fock $-E_c^{\mathrm{HF}}$	Exchange only $-E_c'$
He	2	$0.0843^{a,b}$	$0.0843^{b,c}$
Li	3	$0.0906^{a,d}$	$0.0913^{c,d}$
Be	4	$0.1887^{a,e}$	$0.1899^{c,e}$

[a] See Ref. 23.
[b] See Ref. 20.
[c] See Ref. 13.
[d] See Ref. 21.
[e] See Ref. 22.

For atoms and molecules, as mentioned earlier, results for the density-functional-theory correlation energy $E_c[\rho]$ are presently unavailable. Consequently, it is not possible for us, at present, to demonstrate the extent of the inequality $E_c[\rho]<E_c'[\rho]$. However, it is possible to demonstrate the extent of the rightmost inequality of Eq. (8), $E_c'[\rho]<E_c^{\mathrm{HF}}$. In Table II we present values for E_c' and E_c^{HF} for the atoms He, Li, and Be based on many-parameter correlated wave-function calculations[20–22] for the nonrelativistic ground-state energies. E_c^{HF} is greater than E_c' by less than 1%.

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