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Nonlocal Wigner-like correlation-energy density functional through coordinate scaling

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A *nonlocal* Wigner-like correlation-energy functional for electronic systems is presented. The functional is constructed to satisfy certain uniform, as well as nonuniform, coordinate-scaling requirements and is the simplest nonlocal form to do this. Our numerical results appear to compare favorably with those of other functionals.

There is considerable interest in correlation-energy calculations and their corresponding nonlocal electron-density functionals.[1-5] We present a nonlocal correlation functional that is not based on gradient corrections to the local-density approximation (LDA). Instead, in the cases of a nonuniformly scaled electron-density n_λ^x, where $n_\lambda^x(x,y,z)=\lambda n(\lambda x,y,z)$, and a uniformly scaled[6] electron-density n_λ, our formula is the simplest viable nonlocal one that exhibits correct coordinate scaling in the limits of $\lambda \rightarrow 0$ and $\lambda \rightarrow \infty$, as recently derived.[7-10] The functional generates results that appear to be competitive with those of other functionals.[1-3]

The correlation energy in density-functional theory[11,12] is defined as

$$E_c[n]=\langle \Psi_n^{\min} | T+V_{ee} | \Psi_n^{\min}\rangle - \langle \Phi_n^{\min} | T+V_{ee} | \Phi_n^{\min}\rangle , \tag{1}$$

where $\Phi_n^{\min}$ is that wave function which yields n and minimizes just $\langle T\rangle$ and $\Psi_n^{\min}$ is that wave function which yields n and minimizes $\langle T+V_{ee}\rangle$. When the coordinates of an electron-density expression are uniformly scaled such that

$$n_\lambda(x,y,z)=\lambda^3 n(\lambda x,\lambda y,\lambda z) , \tag{2}$$

Levy and Perdew have shown that E_c does *not* scale homogeneously but rather satisfies the inequality[6]

$$E_c[n_\lambda]>\lambda E_c[n];\ \lambda>1 . \tag{3}$$

In addition, Levy has recently derived requirements for the correlation functional in the limits of $\lambda \rightarrow 0$ and $\lambda \rightarrow \infty$. He has shown that, in the limit of $\lambda \rightarrow 0$, $E_c[n_\lambda]$ approaches 0 in the following way:[8,9]

$$\lim_{\lambda\rightarrow 0} E_c[n_\lambda] \sim -\lambda b[n] , \tag{4}$$

where

$$0<b[n]\leq U[n]+E_x[n]<U[n] . \tag{5}$$

In the case of $\lambda \rightarrow \infty$, the functional satisfies[7-9]

$$\lim_{\lambda\rightarrow\infty} E_c[n_\lambda]\geq a[n] , \tag{6}$$

where $a[n]$ is *bounded* from below.[7-9] For a nonuniformly scaled density, the $\lambda \rightarrow \infty$ limit must *also* be *bounded,* at least for two electrons.[10]

It is important to note that most traditional correlation functionals are based on the LDA, with or without gradient corrections. The LDA does not go to a negative constant in the infinity limit. Rather, it goes as $-\ln\lambda$ and is therefore unbounded. This was an important consideration in the development of our proposed functional which has, as its primary constraint, adherence to the uniform and nonuniform limits.

Early in this research, it became apparent that the structure of the simplistic Wigner formula[13] not only satisfied Eq. (3) and both uniform scaling limits, Eqs. (4) (Ref. 14) and (6), but was also the simplest possible local form of such a functional. The functional due to Wigner,[13] with a uniformly scaled density is

$$E_c[n_\lambda]=-\int\frac{0.44n(\mathbf{r})d\mathbf{r}}{7.8+\lambda^{-1}r_s} , \tag{7}$$

where $r_s=(3/4\pi n)^{1/3}$. This functional actually gives better results than the LDA for atoms.[15] Similarly, Brual and Rothstein presented a Wigner formula, with different coefficients, which was parametrized by an exact correlation energy for He. Given its simplicity, the Brual-Rothstein formula gives surprisingly reasonable values for correlation energies for some atoms and ions.[16]

Although the Wigner formula scales correctly, the $\lambda \rightarrow \infty$ limit presents a problem. The negative constant that the functional approaches as $\lambda \rightarrow \infty$ is, unreasonably, always the *same* for a given number of electrons (N), regardless of the density used. In addition, the uniform case gives the *same* constant as the nonuniform case, for all densities. This is also unreasonable.

As a result of the fact that a Wigner-like formula automatically satisfies Eqs. (3), (4), and (6), the following nonlocal functional was investigated for closed-shell systems using Hartree-Fock densities:[17]

$$E_c[n]=\int\frac{(an+b|\nabla n|/n^{1/3})d\mathbf{r}}{c+d|\nabla n|/(n/2)^{4/3}+r_s} , \tag{8}$$

where a, b, c, and d are coefficients. Equation (8) can be scaled in a variety of ways. With n_λ^x, as $\lambda \rightarrow \infty$, Eq. (8) becomes

$$E_c[n_\lambda^x]=\int\frac{(an+\lambda^{2/3}b|\partial n/\partial x|/n^{1/3})d\mathbf{r}}{c+\lambda^{2/3}d|\partial n/\partial x|/(n/2)^{4/3}+\lambda^{-1/3}r_s} \tag{9}$$

and is thus *bounded* from below as $\lambda \rightarrow \infty$. With n_λ, for all λ, Eq. (8) becomes

$$E_c[n_\lambda]=\int\frac{(an+b|\nabla n|/n^{1/3})d\mathbf{r}}{c+d|\nabla n|/(n/2)^{4/3}+\lambda^{-1}r_s} , \tag{10}$$

and is thus not only bounded as $\lambda \rightarrow \infty$, but also gives, desirably, an asymptotic value which *varies* with n.

Parametrization was achieved by using an identity developed by Levy and Perdew.[6] Namely,

$$\left(\frac{\partial E_c[n_\lambda]}{\partial \lambda} \right)_{\lambda=1} = E_c[n] + T_c[n] , \tag{11}$$

where $T_c[n]$ is the kinetic contribution to $E_c[n]$. The traditional quantum-mechanical definition of correlation energy is

$$E_c^{\mathrm{QM}} = E_{\mathrm{exact}} - E_{\mathrm{HF}} \tag{12}$$

and, for atoms, satisfies $E_c^{\mathrm{QM}} = -T_c^{\mathrm{QM}}$ from the virial theorem. If E_c and E_c^{QM} [Eqs. (1) and (12)] were exactly the same, and if T_c and T_c^{QM} were exactly the same, then[6]

$$\left(\frac{\partial E_c[n_\lambda]}{\partial \lambda} \right)_{\lambda=1} = 0 . \tag{13}$$

Because they are not exactly the same,[18] we cannot expect $(\partial E_c[n_\lambda]/\partial\lambda)_{\lambda=1}$ to be exactly zero; but because the two definitions are close, we can expect $(\partial E_c[n_\lambda]/\partial\lambda)_{\lambda=1}$ to be small in magnitude when n is the Hartree-Fock atomic density. Accordingly, parameters that could minimize

$$\left[\frac{(\partial E_c[n_\lambda]/\partial\lambda)_{\lambda=1}}{E_c[n]} \right]^2 ,$$

subject to other constraints, could be said to be suitable candidates for coefficients in a correlation functional. Here, eight closed-shell Hartree-Fock atomic densities[17] were considered in the minimization process as well as one experimental value, the correlation energy for He.[17,19] Subject to the constraint that our E_c for He agreed with E_c^{QM} for He to five decimal places, the equation that was minimized was

$$G = \sum_{i=1}^{8} \left[\frac{(\partial E_c[n_\lambda^i]/\partial\lambda)_{\lambda=1}}{E_c[n^i]} \right]^2 , \tag{14}$$

where $i =$ He, Li$^+$, Be^{2+}, Be, B$^+$, Ne, Mg, and Ar. The coefficients that resulted from minimizing Eq. (14) are $a = -0.748\,60$, $b = 0.060\,01$, $c = 3.600\,73$, and $d = 0.900\,00$. Table I gives numerical results for our functional, "experimental" correlation energies as defined by Eq. (12), and values obtained from the functionals of Perdew,[1] Becke,[2] and Lee, Yang, and Parr (LYP).[3] It can be seen that the proposed functional gives competitive values for most atoms and ions.

It should be pointed out that, in light of the previous discussion of the different definitions of the correlation energy, the two definitions cannot *always* be considered close, especially when the Hartree-Fock density is markedly different from the true density. This may explain[20] the rather large difference between "experimental" and Eq. (8) values for B$^+$ and Ne^{6+}. Our functional is possibly not inadequate for these ions. Instead, the exact E_c^{QM} and the exact $E_c[n_{\mathrm{HF}}]$ are perhaps significantly different due to a certain near $2s$-$2p$ degeneracy.[20,21]

TABLE I. Correlation energies E_c of closed-shell species. Energies are in atomic units.

Species	P[a]	B[b]	LYP[c]	Eq. (8)[d]	Expt.[e]
He	−0.044[f]	−0.042[f]	−0.0437[g]	−0.0420	−0.0420
Li$^+$	−0.045[h]	−0.050[d]	−0.0475[g]	−0.0442	−0.0435
Be^{2+}	−0.049[h]	−0.055[d]	−0.0490[g]	−0.0452	−0.0443
Li$^-$		−0.070[i]	−0.073[i]	−0.0805	
Be	−0.095[f]	−0.092[f]	−0.095[g]	−0.095	−0.094
B$^+$		−0.107[i]	−0.107[g]	−0.100	−0.111
Ne^{6+}	−0.136[h]			−0.108	−0.18[j]
F$^-$		−0.364[i]	−0.361[i]	−0.364	
Ne	−0.395[f]	−0.391[f]	−0.383[g]	−0.383	−0.387
Mg	−0.471[f]	−0.466[f]	−0.459[d]	−0.444	−0.444
Ar	−0.810[f]	−0.785[f]	−0.751[g]	−0.787	−0.787
Kr	−2.01[h]		−1.748[d]	−1.899	
Xe	−3.31[h]		−2.743[d]	−3.151	

[a] Perdew's functional (Ref. 1).
[b] Becke's functional (Ref. 2).
[c] Lee-Yang-Parr functional (Ref. 3).
[d] Obtained by integration program by J. P. Perdew.
[e] From Refs. 2 and 3, and references therein. These values refer to E_c^{QM}.
[f] Reported in Ref. 2.
[g] Reported in Ref. 3.
[h] Reported in Ref. 1.
[i] Reported in Ref. 22.
[j] See Ref. 23.

An open-shell functional for the correlation energy that is an elaboration on the closed-shell functional is also presented here. It is spin-dependent and includes an additional factor in the numerator that was found empirically to give good agreement with experiment,

$$E_c[n_\alpha,n_\beta] = \int \frac{(an+b|\nabla n|/n^{1/3})(1-\zeta^2)^{1/2}d\mathbf{r}}{c+d(|\nabla n_\alpha|/n_\alpha^{4/3}+|\nabla n_\beta|/n_\beta^{4/3})+r_s} , \tag{15}$$

where $\zeta = (n_\alpha - n_\beta)/(n_\alpha + n_\beta)$ and where the coefficients are those for Eq. (8). Here α signifies up spin and β signifies down spin. Results of this functional and relevant comparisons appear in Table II.

As emphasized earlier, the functional of Eq. (8) satisfies both the uniform and nonuniform coordinate-scaling requirements for $\lambda \rightarrow 0$ and $\lambda \rightarrow \infty$, as Eqs. (9) and (10) demonstrate. It can be identified as the simplest viable nonlocal functional to satisfy these conditions and the condition that the infinite uniform limit be *dependent* upon n. The nonlocal terms not only scale correctly in the uniformly scaled $\lambda \rightarrow \infty$ limit, but must also be present in the numerator *and* denominator to offset each other in the nonuniformly scaled $\lambda \rightarrow \infty$ limit. It should not be a great surprise, therefore, that Eq. (8) gives reasonable values and values better than a purely local functional. In the *nonuniform* infinite limit, however, Eq. (8) has a similar problem to that of the Wigner functional; namely, Eq. (8) goes to the same constant for a given N, regardless of the density and for any nonuniform case. The open-shell functional, Eq. (15), on the other hand, does not have this problem for the nonuniform case, for systems with spin polarization, while also correctly scaling for both limits.

TABLE II. Correlation energies E_c of open-shell species. Energies are in atomic units.

Species	P[a]	B[b]	LYP[c]	Eq. (15)[d]	Expt.[e]
H	−0.002[f]	0.000[f]	0.000[g]	0.000	0.000
He^+	−0.002[h]	0.000[f]	0.000[g]	0.000	0.000
Li^{2+}	−0.004[h]	0.000[f]	0.000[g]	0.000	0.000
Li	−0.054[f]	−0.055[f]	−0.053[g]	−0.046	−0.046
B	−0.130[f]	−0.129[f]	−0.128[g]	−0.129	−0.125
C	−0.168[f]	−0.166[f]	−0.161[g]	−0.160	−0.157
N	−0.206[f]	−0.202[f]	−0.193[g]	−0.188	−0.189
C^-		−0.179[i]	−0.171[i]	−0.177	
Na	−0.421[f]	−0.419[f]	−0.408[d]	−0.399	−0.398
P	−0.608[f]	−0.590[f]	−0.566[d]	−0.554	−0.553

[a] Perdew's functional (Ref. 1).
[b] Becke's functional (Ref. 2).
[c] Lee-Yang-Parr functional (Ref. 3).
[d] Spherically averaged values obtained by integration program of J. P. Perdew.
[e] From Refs. 2 and 3, and references therein. These values refer to E_c^{QM}.
[f] Reported in Ref. 2.
[g] Reported in Ref. 3.
[h] Reported in Ref. 1.
[i] Reported in Ref. 22.

TABLE III. Correlation energies E_c and $(\partial E_c[n_\lambda]/\partial\lambda)_{\lambda=1}$ for Becke's functional and Eq. (8).

	E_c			$\left(\frac{\partial E_c[n_\lambda]}{\partial\lambda}\right)_{\lambda=1}$	
Species	B[a]	Eq. (8)[b]	Expt.[c]	B[a]	Eq. (8)[b]
He	−0.0419	−0.0420	−0.0420	−0.0165	−0.0023
Li^+	−0.0498	−0.0442	−0.0435	−0.0150	−0.0015
Be^{2+}	−0.0546	−0.0452	−0.0443	−0.0134	−0.0012

[a] Obtained from Becke's functional.
[b] Obtained from the functional in Eq. (8) by the integration program of J. P. Perdew.
[c] This value is E_c^{QM}

The LDA functionals with gradient corrections, such as the ones by Langreth and Mehl[5] (LM) and Perdew,[1] have the advantage that they give, of course, the correct result in the uniform-density limit, but they do not satisfy the $\lambda \rightarrow \infty$ scaling requirement. (It should be noted, however, that Perdew has a recent unpublished functional which is bounded as $\lambda \rightarrow \infty$.) Now, our Eqs. (8) and (15) are obviously *not correct* in the uniform-density limit. Two recent correlation functionals that also do not reduce to the correct result in the uniform-density limit, but that do scale correctly in the $\lambda \rightarrow \infty$ limit for uniformly scaled electron densities, are the functionals of Becke[2] and Lee, Yang, and Parr.[3] They also scale correctly for the $\lambda \rightarrow 0$ uniform limit. However, the LYP functional does not obey the nonuniform $\lambda \rightarrow \infty$ limit because it is unbounded for two electrons and Becke's approaches 0 in this limit for two electrons, which is probably unreasonable. Also, although bounded from below, our functionals in Eqs. (8) and (15) actually become slightly positive in the $\lambda \rightarrow \infty$ nonuniform limit because b turns out to be positive upon optimization. Becke's functional is not very accurate for Li^+ and Be^{2+}. This is likely due to the fact that Becke's functional gives a larger value for $|(\partial E_c[n_\lambda]/\partial\lambda)_{\lambda=1}|$ than does Eq. (8). (See Table III.) Finally, the functionals of LYP and Becke and our Eq. (15) have the desirable feature that they vanish for all one-electron densities. Becke's functional and those of Perdew and LM have the desirable feature that they do not vanish for completely spin-polarized systems with more than one electron. Our Eq. (15) and the open-shell functional of LYP always vanish for these systems.

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