

Density-functional approximation for the correlation energy of the inhomogeneous electron gas

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Langreth and Mehl (LM) and co-workers have developed a useful spin-density functional for the correlation energy of an electronic system. Here the LM functional is improved in two ways: (1) The *natural* separation between exchange and correlation is made, so that the density-gradient expansion of each is recovered in the slowly varying limit. (2) Uniform-gas and inhomogeneity effects beyond the random-phase approximation are built in. Numerical results for atoms, positive ions, and surfaces are close to the exact correlation energies, with major improvements over the original LM approximation for the ions and surfaces.

The major obstacle toward an accurate self-consistent-field theory for atoms, molecules, and solids is the electron correlation problem, since everything else may be treated more or less exactly (as in the spin-unrestricted Hartree-Fock approximation). Ground-state density-functional^{1,2} approximations, starting from the limit of the electron gas of slowly varying density, have traditionally made serious errors in the correlation energy E_c for realistically inhomogeneous systems. For example, the local-spin-density (LSD) approximation^{2,3}

$$E_c^{\text{LSD}}[n_\uparrow, n_\downarrow] = \int d^3r n(\mathbf{r}) \epsilon_c(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r})) \quad (1)$$

predicts correlation energies for atoms that are about twice the exact values, and the gradient-expansion approximation^{1,4} predicts correlation energies of the wrong sign.⁴ Self-interaction corrections⁵⁻⁷ to the LSD approximation have been useful, but not entirely satisfactory. Recently, Langreth and Mehl (LM) and co-workers⁸⁻¹¹ have developed a generalized gradient approximation which predicts rather accurate correlation energies for atoms^{9,10} and molecules.¹²

$$E_c^{\text{LM}}[n_\uparrow, n_\downarrow] = \int d^3r n \epsilon_c^{\text{RPA}}(n_\uparrow, n_\downarrow) + 0.004287 \int d^3r [d^{-1} e^{-F} |\nabla n|^2 / n^{4/3} + 9f^2 2^{-1/3} (|\nabla n_\uparrow|^2 / n^{4/3} + |\nabla n_\downarrow|^2 / n^{4/3})] \quad (2)$$

(in atomic units), where

$$F = 1.745f |\nabla n| / n^{7/6}, \quad (3)$$

$$d = 2^{1/3} \left[\left(\frac{1+\zeta}{2} \right)^{5/3} + \left(\frac{1-\zeta}{2} \right)^{5/3} \right]^{1/2}, \quad (4)$$

$n = n_\uparrow + n_\downarrow$, $\zeta = (n_\uparrow - n_\downarrow) / n$, and $f = 0.15$. When applied in concert with the LM approximation for exchange,⁹ Eq. (2) has also improved the LSD description of the density and energy of solids.¹³ There is good fundamental physics in the LM approximation, which may be the most significant development in the field since the advent of the LSD approximation, but there are also a few theoretical and practical drawbacks which it is the aim of this communication to point out and correct.

First, the fundamental physics of the LM approximation will be briefly reviewed. The gradient-expansion approximation (GEA) for the correlation energy is analyzed⁸ into contributions from dynamic density fluctuations of various wave vectors k , and a strong exponential peak is found to lie around $k = 0$. More precisely, the coefficient of the gradient term in the correlation energy in the random-phase approximation (RPA) is roughly

$$C^{\text{RPA}}(n) \approx \int_0^\infty dk A(n) e^{-B(n)k}. \quad (5)$$

Since the GEA is valid only when the inhomogeneity wave vector $|\nabla n|/6n$ is small compared to k , Eq. (5) contains a spurious contribution from the region $k < f|\nabla n|/n$ which Langreth and Mehl⁹ replace by zero. Transparently, the

spatial extent of a dynamic density fluctuation must be relatively small before this fluctuation can effectively sample the local density $n(\mathbf{r})$ and its gradient $\nabla n(\mathbf{r})$.

There are, however, at least two drawbacks of the LM approximation for the correlation energy. The first is the $9f^2$ term in Eq. (2), which is really a piece of the gradient expansion for the exchange energy, incorporated via a somewhat artificial separation⁹ of exchange and correlation. As a result, the LM approximation in the slowly varying limit recovers the LSD, as it should, but not the GEA. The second drawback is that the LM approximation does not go beyond the random-phase approximation for the correlation energy. The RPA may be adequate for atoms,^{11,14} but is not really good enough for the valence electrons in simple metals. (A possible third drawback, the simplification¹⁰ made in the spin dependence of the gradient term, will not be addressed here. Perhaps this is no more serious than a similar interpolation between $\zeta = 0$ and 1 made in the LSD term.)

Thus, two modifications of the LM functional are proposed here. The first is simply to make the *natural* separation between exchange and correlation. The second is more speculative, since the wave-vector decomposition of the gradient expansion has not been carried beyond RPA. Here the simplest reasonable assumption will be made, that this decomposition would still be dominated by the exponential peak around $k = 0$ [as in Eq. (5)], but with $B(n)$ altered to yield the beyond-RPA gradient coefficient for the correlation energy $C(n)$. (The expectation^{8,11} is that the RPA becomes exact for $k \rightarrow 0$, as in the uniform gas.) This coeffi-

TABLE I. Correlation energies of atoms and ions, in a.u.

Atom	LSD	GEA	LM	Eq. (8)	Experiment
H	-0.022	0.033	-0.008	-0.003	0
He ⁺¹	-0.030	0.092	0.002	0.002	0
Li ⁺²	-0.034	0.154	0.012	0.004	0
He	-0.112	0.088	-0.050	-0.044	-0.042 ^{a,b}
Li ⁺¹	-0.134	0.201	-0.039	-0.045	-0.044 ^c
Be ⁺²	-0.150	0.320	-0.025	-0.049	-0.044 ^c
Be	-0.224	0.233	-0.099	-0.094	-0.094 ^{a,b}
Ne ⁺⁶	-0.333	0.965	-0.026	-0.136	-0.18 ^c
Ne	-0.74	0.56	-0.41	-0.39	-0.39 ^{a,b}
Ar	-1.42	1.11	-0.80	-0.80	-0.79 ^{a,b}
Kr	-3.27	2.12	-1.92	-2.01	...
Xe	-5.18	3.26	-3.07	-3.31	...

^aReference 18.^bReference 19.^cReference 21.

cient is known,^{11,15} and has been parametrized by Rasolt and Geldart:¹⁶

$$C(n) = 0.001667 + \frac{(0.002568 + \alpha r_s + \beta r_s^2)}{(1 + \gamma r_s + \delta r_s^2 + 10^4 \beta r_s^3)}, \quad (6)$$

where

$$n = (4\pi r_s^3/3)^{-1}, \quad (7)$$

$\alpha = 0.023266$, $\beta = 7.389 \times 10^{-6}$, $\gamma = 8.723$, and $\delta = 0.472$. [Note that $C^{\text{RPA}}(n) \approx C(\infty)$.]

The proposed correlation-energy functional is therefore

$$E_c[n_\uparrow, n_\downarrow] = \int d^3r n \epsilon_c(n_\uparrow, n_\downarrow) + \int d^3r d^{-1} e^{-\Phi} C(n) |\nabla n|^2 / n^{4/3}, \quad (8)$$

where

$$\Phi = 1.745 \tilde{f} [C(\infty)/C(n)] |\nabla n| / n^{7/6}. \quad (9)$$

The correlation energy per particle of the uniform electron gas, $\epsilon_c(n_\uparrow, n_\downarrow)$, is taken from a parametrization⁶ of the Ceperley-Alder¹⁷ results, and the cutoff parameter $\tilde{f} = 0.11$ is chosen to fit the exact correlation energy of the neon atom.^{18,19} Equation (8) recovers the beyond-RPA gradient expansion in the unpolarized slowly varying limit.

Table I presents numerical results for the correlation energies of atoms and ions. The theoretical values were calculated from Hartree-Fock densities,²⁰ while the experimental values come from Veillard and Clementi's^{18,21} analysis of measured total energies, but with the sign of the Lamb-shift correction reversed.¹⁹ For the neutral atoms, Eq. (8) is

slightly more accurate than the LM approximation, but some of the difference would be removed by choosing $f = 0.17^9$ in Eq. (2). More significant is the error of the LM result which occurs within the one-, two-, and four-electron isoelectronic series of Table I. The LM approximation predicts that the correlation energy within an isoelectronic series becomes *less* negative as the nuclear charge Z increases. This misbehavior is also evident in Table III of Ref. 22. It results from the $9f^2$ term in Eq. (2), which is absent from Eq. (8). Note also the rather precise cancellation of the self-interaction in the one-electron ions which Eq. (8) achieves.

Of course, no simple density functional can be even qualitatively correct for an isoelectronic series in the *limit* $Z \rightarrow \infty$,²³ since the exact correlation energy must ultimately vary as Z^1 or Z^0 , depending upon whether or not another orbital configuration of the same symmetry becomes degenerate with the ground-state configuration in this limit. As $Z \rightarrow \infty$, Eq. (8) reduces to the LSD approximation, which compromises with a $\ln Z$ limiting behavior.

Table II presents numerical results for the correlation contribution to the jellium surface energy in the infinite-barrier model. This model is somewhat unfair to the GEA and LM approximations, which contain spurious contributions from an integrable singularity (at the barrier) which is absent in the LSD approximation and in Eq. (8). Since the exact correlation energy is not known, comparison is made in Table II with the RPA results²⁴ for the infinite barrier model, and satisfactory agreement with the results of Eq. (8) is observed. Equation (8) should indeed lead to some

TABLE II. Jellium surface correlation energy for the infinite barrier model, in erg/cm². The bulk density is characterized by r_s .

r_s	LSD	GEA	LM	Eq. (8)	RPA
2.07	118	2604	1319	535	688 ^a
4	27	323	215	84	103 ^a
6	10	90	71	26	33 ^a

^aReference 24.

underestimation of the surface correlation energy, since Eq. (8) contains *no* contribution from $k \approx 0$, while the exact surface correlation energy should include a contribution from a small (compared to what the GEA predicts) positive limit²⁵ as $k \rightarrow 0$. (Unfortunately, the RPA must be regarded with a measure of skepticism, in view of a recent suggestion²⁶ of large beyond-RPA contributions to the jellium surface energy.)

In summary, Eq. (8) predicts correlation energies of useful accuracy for the electron gas of slowly varying density, atoms, ions, and (perhaps) metal surfaces. For general applications (including the calculation of densities and binding energies for molecules and solids), Eq. (8) might be used in concert with spin-unrestricted Hartree-Fock or other exact-exchange methods.²⁷⁻²⁹ In principle, Hartree-Fock theory

with a nonlocal exchange potential is different from exact exchange-only density-functional theory with a local exchange potential; in practice, the numerical difference between the two differently defined exchange energies is slight.^{30,31} Alternatively, Eq. (8) might be applied along with the new generation of accurate generalized gradient approximations³²⁻³⁵ for the exchange energy as a functional of the density. (Note, however, that when exchange and correlation are approximated separately, the usual "cancellation of errors" between the two cannot always be relied upon.)

The spin-dependent correlation potential, for use in self-consistent calculations, is the functional derivative $\delta E_c / \delta n_\sigma(\mathbf{r})$. Neglecting the small derivatives of $C(n)$, this may be transcribed rather directly from Ref. 10:

$$\frac{\delta E_c}{\delta n_\sigma(\mathbf{r})} = \mu_c^\sigma(n_\uparrow, n_\downarrow) - d^{-1} e^{-\Phi} C(n) n^{-1/3} \left[\frac{(2-\Phi)\nabla^2 n}{n} - \left(\frac{4}{3} - \frac{11\Phi}{3} + \frac{7\Phi^2}{6} \right) \frac{|\nabla n|^2}{n^2} + \frac{\Phi(\Phi-3)\nabla n \cdot \nabla |\nabla n|}{n|\nabla n|} - \frac{5n^{1/3}(n_\sigma^{2/3} - n_\sigma^{2/3})}{6d^2 n^4} [(1+\Phi-\Phi^2)n_{-\sigma}|\nabla n|^2 - (2+2\Phi-\Phi^2)n\nabla n_{-\sigma} \cdot \nabla n] \right], \quad (10)$$

where $\mu_c^\sigma(n_\uparrow, n_\downarrow)$ is the LSD correlation potential.⁶

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