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Easily Implementable Nonlocal Exchange-Correlation Energy Functional

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An exchange-correlation functional for nonuniform electronic systems is developed which provides an easily implementable correction to the local density approximation. It is applied to metallic surface energies, as well as to self-consistent atomic calculations which include the ground-state energies of a number of atoms, plus the removal energies for 1*s*, 2*s*, 3*s*, 4*s*, 2*p*, 3*p*, and 3*d* electrons. In all cases tried a substantial improvement was found.

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For a number of years our group has studied the corrections[1,2] to the local density approximation[3] (LDA) for the exchange-correlation energy for nonuniform electronic systems. The ideas which evolved led to a nonlocal functional[2] which worked well when tested on planar metallic surfaces. Here we apply the same ideas to develop a functional which is easily implementable for any electronic system for which the LDA provides a reasonable starting point. We apply the new functional not only to planar surfaces, but also to the ground-state energy of a number of atoms, as well as the removal energies for a variety of atomic states. We find a systematic improvement over the LDA, and in fact, the improvement was substantial for all atoms tested.

To motivate what follows we begin with a qualitative discussion of length scales. Instead of using electron density n as the basic variable, it is more appropriate for our purposes to use inverse particle spacing or *local* Fermi wave vector $k_F \equiv (3\pi^2 n)^{1/3}$. This makes the coefficient Z_{grad} in the expansion for the energy functional,

$$E^{xc} = E_{LDA}{}^{xc} + \gamma \int Z_{\text{grad}}(k_F)(\nabla k_F)^2\, d^3r + \cdots, \qquad (1)$$

a slowly varying function[2,4] of k_F. The constant $\gamma = e^2/16\pi^3$ makes Z agree with the notation used in Ref. 2 and by Rasolt and Geldart.[4] Of prime importance is a length (call it ξ) which characterizes the scale over which the density varies. This is the surface healing length, the size of the orbital one is in, or whatever. For concreteness imagine a surface whose local k_F varies linearly with distance from its value k_{FB} in the bulk to zero. Then the width of the surface layer is $k_{FB}/|\nabla k_F| = 2k_F/|\nabla k_F|$, where we eliminate k_{FB} in favor of the typical local value in the middle of the layer. We will use this as a definition of ξ (for an arbitrary density variation), that is $\xi^{-1} \equiv \frac{1}{2}|\nabla k_F/k_F|$, where $k_F \equiv k_F(\vec{r})$ and ∇k_F is its gradient. We thus *assume that there is only one important length scale for a given region of space.*

For the LDA to be valid [for the first term of (1) to be a good approximation to the whole series], inequalities like

$$k_F\xi \gg 1, \quad k_{FT}\xi \gg 1 \qquad (2)$$

presumably must hold, where k_{FT} is the local Fermi-Thomas wave vector. For materials of interest k_F and k_{FT} are roughly the same, and the numbers are such that (2) is neither obviously satisfied nor obviously violated. For example,

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at the position of the first Bohr orbit in hydrogen, $k_F\xi \sim 4$. However, because of the vast experience accumulated over the years that the LDA is a reasonable starting point for many systems, we will assume that at the worst (2) does not fail too drastically in regions of importance to us.

Before going on to discuss the second term in (1), it is important to mention an additional implicit assumption. To do this we must consider the exchange-correlation energy functional as a sum over excitations of differing size λ as first done for the uniform electronic systems by Nozières[5] and Pines and by Hubbard,[6] and by our group[2] and others[7] for the nonuniform system. If we let $k=1/\lambda$ then one must assume in using the criteria (2) that the typical k which contributes is not vastly different from k_F or k_{FT}. That this is the case, however, has been amply demonstrated.[1]

Now consider the gradient expansion, that is, the second and higher terms in (1). What is the criterion that the second term is a good approximation to $E^{xc}-E_{LDA}{}^{xc}$? If the assumption of a single ξ in a given region holds, then the criteria (2) are the appropriate ones for this case as well. Then one can ask if the LDA is good, why doesn't the addition of the first gradient correction make it better? The answer lies in the failure[2] of the additional assumption of the above paragraph. Although a part of the gradient contribution is distributed normally in k, so that k_F is a typical value, a significant fraction is concentrated in a narrow range about $k\sim 0$. Although the first equality of (2) may be satisfied, we have shown [Eq. (C7) of Ref. 2] that the second inequality of (2) must be replaced by $k_{FT}\xi \gg 36$ where the number 36 was the result of a detailed numerical estimate. Needless to say this latter criterion clearly fails for situations of interest. The object of the present work is to circumvent this criterion, while still assuming (2).

We rewrite (1) as

$$\delta E \equiv E^{xc}-E_{LDA}{}^{xc}=\delta E_{grad}+\cdots, \tag{3}$$

where δE_{grad} is the term involving Z_{grad} in (1). As in our previous work (here we include the phase space factor and angular average in the definition δE) we make a wave-vector decomposition[1,2] for δE and Z_{grad}:

$$\delta E=\int \delta E(k)\,dk, \tag{4}$$

$$Z_{grad}(k_F)=\int_0^\infty z_{grad}(k,k_F)\,dk. \tag{5}$$

A relation similar to (4) also holds for δE_{grad}. The true $\delta E(k)$ approaches zero rapidly with decreasing k when $k\xi$ becomes less than unity, that is when λ becomes greater than ξ. This feature is a consequence of sum rules and is *satisfied* for our previous approximations. However, $\delta E_{grad}(k)$ does *not* have this property. Said another way, the higher-order terms in (3) restore the correct behavior for $k\xi<1$. On the other hand, they make little change for $k\xi>1$, provided that the inequalities (2) are satisfied. Therefore we can get around the severe criterion $k_{FT}\xi\gg 36$ which comes entirely from the region $k\xi<1$ simply by recognizing that the true $\delta E(k)$ goes to zero in this region. Here the contribution of the lowest-order gradient approximation is spurious because it implicitly extrapolates the gradient to distances greater than ξ; since ξ itself depends on nonuniformities, any effective cutoff dependent on it necessarily introduces higher-order gradients.

The approximations of Refs. 1 and 2 are possible ways of dealing with this problem, but lead to functionals so complicated that they are difficult to apply to anything but the planar surface. Here we adopt the simplest approximation that includes the physics described above. We define the exact Z [a functional of $k_F(\vec{r})$], which when inserted instead of Z_{grad} in (1) would give the exact E^{xc} without the higher terms, and its wave-vector decomposition $z(k,k_F)$ in analogy with (5). We then approximate

$$z(k,k_F)=z_{grad}(k,k_F)\,\theta(k-\xi^{-1}) \tag{6}$$

and try to cure any evils of so simple an approximation by using

$$\xi^{-1}\equiv 3f\,|\nabla k_F/k_F|=f\,|\nabla n/n|, \tag{7}$$

where f is a free parameter to be fitted. Actually the value finally adopted for our calculations $f=0.15$ is not much different from the value $f=\frac{1}{6}$ implied by the simple calculation following Eq. (1).

The quantity $z_{grad}(k,k_F)$ has been calculated in random-phase approximation (RPA), and may be written[2]

$$z_{grad}(k,k_F)=z_x(k,k_F)+z_c(k,k_F), \tag{8}$$

where

$$2k_F z_x(k,k_F) = -4x\theta(1-x)+\tfrac{11}{9}\delta(x-1)+\tfrac{1}{9}\delta'(x-1) \tag{9}$$

and $x=k/2k_F$. It would be cumbersome to apply the cutoff procedure (6) to z_x. Fortunately it is also unnecessary, because z_x already vanishes as $k \to 0$, or more generally because it does not involve k_{FT} so that the stringent criterion $k_{\mathrm{FT}}\xi \gg 36$ could not apply. Therefore we use the whole integral (from 0 to ∞) of z_x in (5) and apply (6) only to z_c. Although the quantity z_c is known only numerically we found that the expression

$$z_c(k, k_{\mathrm{F}}) = (4\sqrt{3}/k_{\mathrm{FT}})\exp(-2\sqrt{3}\,k/k_{\mathrm{FT}}) \qquad (10)$$

fitted the calculation[2] to within a few percent for $0 < k < 1.9k_{\mathrm{F}}$ for a wide range of densities. Since the integral of (10) is also close to the calculated value (which is almost density independent), we may use it in (6). We therefore find

$$Z[k_{\mathrm{F}}] = 2\exp[-2\sqrt{3}/k_{\mathrm{FT}}\xi] - \tfrac{7}{9}, \qquad (11)$$

so that

$$E^{\mathrm{xc}} = E_{\mathrm{LDA}}{}^{\mathrm{xc}} + (4.28\times10^{-3})\int d^3r\,|\nabla n|^2/n^{4/3}\{2e^{-F} - \tfrac{7}{9}\}, \qquad (12)$$

where $F = 0.262|\nabla n|/n^{7/6}$. The units are such that energy is in rydbergs and lengths in bohrs, and the value $f = 0.15$ has been incorporated. To apply the Kohn-Sham method[3] one also needs the potential $v^{\mathrm{xc}}(\vec{r}) = \delta E^{\mathrm{xc}}/\delta n(\vec{r})$. We find straightforwardly that

$$v^{\mathrm{xc}}(\vec{r}) = v_{\mathrm{LDA}}{}^{\mathrm{xc}}(\vec{r}) + (8.56\times10^{-3})n^{-1/3}\left\{\frac{7}{9}\left(\frac{\nabla\cdot\vec{K}}{n} - \frac{2K^2}{3n^2}\right) - 2e^{-F}\left[\frac{(1-F/2)\nabla\cdot\vec{K}}{n} - \left(\frac{2}{3} - \frac{11F}{6} + \frac{7F^2}{12}\right)\frac{K^2}{n^2} + \frac{F(F-3)\vec{K}\circ\nabla|\vec{K}|}{2n|\vec{K}|}\right]\right\}, \qquad (13)$$

where $\vec{K} = \nabla n$.

The expressions we have developed above for the nonlocal v^{xc} and E^{xc} are based on the RPA. We argued previously[2] that there were no large (like the compressibility correction to the static RPA dielectric function) corrections to the fundamental nonlocal approximation, just as there are no such large corrections to the RPA energy for the uniform system (or LDA). However there are smaller corrections to the RPA energy which come at least in the high-density limit[8-10] from the second-order exchange diagram and which (for uniform systems) account for the difference (which is nearly density independent at high densities) between the RPA and RPA-like[11] approximations and approximations like the recent Ceperly[12] calculation. These are *not* included in our nonlocal approximation and thus it is *not* consistent to include them in the $v_{\mathrm{LDA}}{}^{\mathrm{xc}}$ or $E_{\mathrm{LDA}}{}^{\mathrm{xc}}$ used in Eqs. (12) and (13). Not only is it not consistent to use anything but RPA here, but it would almost surely make the results worse to do so, because for localized states there is strong cancellation between local and nonlocal effects (for nearly constant density; on the other hand, the near density independence of the correction to the RPA in question means that only the total energy will be affected). Thus Eqs. (12) and (13) should be used only with RPA values for $E_{\mathrm{LDA}}{}^{\mathrm{xc}}$ and $v_{\mathrm{LDA}}{}^{\mathrm{xc}}$, for which the von Barth-Hedin[13] parametrization is an adequate approximation, and which was used in the calculations which follow.

We first used (12) to calculate the deviation of the surface energy from the LDA using profiles from the linear potential model[14] (in a non-self-consistent calculation as in Ref. 2). For typical values of that model's parameter y_F ($y_F = 3.5$ for $r_s = 2$ and $y_F = 2$ for $r_s = 4$) we find respective nonlocal surface energies of 90 and 20 ergs/cm^2. This compares with 120 and 22 ergs/cm^2 for the average-slope approximation[2] which we take as a standard. These values are for $f = 0.15$. For this surface case the results are sensitive to f and presumably to the crudeness of the approximation (6), because the two terms in (11) nearly cancel. The comparison with the average-slope approximation is improved for smaller f ($f \sim 0.14$ or 0.13). We found, however, that the results for very small atoms ($Z < 5$) were also sensitive to the choice of f and were fitted better with the choice $f = 0.15$ or 0.16. Since the experimental values are known unequivocally for the atoms, we settled on $f = 0.15$ as a value for the rest of our calculations, which were not sensitive to f and hopefully therefore not to the approximation (6). We could not use the infinite-barrier limit ($y_F = 0$) of the surface case to fix f, because of the failure of (2) in this limit, as clearly demonstrated by the recent calculation of Sahni, Gruenebaum, and Perdew.[15]

To test further the functional equations (11) and (12) we have made self-consistent calculations of the ground-state energies and ionization energies of a number of atoms. For the former (see

TABLE I. Ground-state energies of atoms in various approximations (in rydbergs). A minus sign is implied for all entries.

	He	Be	Ne	Mg	Ar
LDA[a]	5.67	28.9	256.4	398.2	1052
LDA[b]	5.74	29.0	256.8	398.7	1053
HF[c]	5.73	29.1	257.1	399.2	1054
Present[d]	5.80	29.2	257.4	399.4	1054
Expt.[e]	5.81	29.3	257.9	400.1	1055
SIC[f]	5.84	29.4	258.6	401.1	1057

[a] Ceperly E^{xc}, Ref. 12.

[b] von Barth–Hedin E^{xc}, Ref. 13.

[c] Hartree-Fock values of Ref. 17.

[d] Present nonlocal calculation.

[e] Experimental values "corrected" for relativistic effects, see Ref. 16.

[f] Self-interaction–corrected values of Ref. 10.

TABLE II. Average removal energies per electron (in rydbergs) for all the electrons in the atomic shell indicated. No relativistic corrections were made. Values in parentheses are extrapolations with large uncertainty.

	Local[a]	Nonlocal[b]	Expt.[c]
He (1*s*)	2.87	2.91	2.91
Be (2*s*)	1.04	1.00	1.01
Mg (3*s*)	0.88	0.83	0.83
Ca (4*s*)	0.71	0.66	0.66
Zn (4*s*)	1.07	1.02	1.01
Ne (2*p*)	6.29	6.24	6.22
Ar (3*p*)	3.83	3.80	3.80
Cu^+ (3*d*)	9.69	9.64	(9.55)
Zn^{++} (3*d*)	12.1	12.0	(11.9)

[a] Ref. 13.

[b] Present calculation, Eqs. (12) and (13).

[c] Ref. 18.

Table I) our method when compared with experiment (corrected for relativistic effects)[16] gives not only a substantial improvement over the LDA, but is comparable or better than Hartree-Fock[17] and self-interaction correction[10] methods. Notice that our functional correctly predicts *positive* nonlocal corrections for surfaces, as well as *negative* corrections for atoms. For ionization energies (Table II) we had to remove whole shells because we have not yet full developed a spin-dependent version of the theory. However, preliminary work on the spin-dependent version convinces us that the substantial improvement in comparison with experiment[18] is not specific to the whole-shell case. Notice that our functional correctly predicts the *positive* correction for He, as well as the *negative* corrections for the other atoms considered.

We illustrate the degree of sensitivity of the results to f by the following examples. First the nonlocal entries (row 4) in Table I have been calculated for various f's. For Be and Ar the respective (unrounded) values for $f = (0.10, 0.15, 0.20, 0.25)$ are (29.08, 29.21, 29.28, 29.35) and (1053.1, 1053.7, 1054.0, 1054.2). For the same f values the respective nonlocal entries for Mg in Table II are (0.826, 0.827, 0.833, 0.839).

The reader wishing to apply our functional should read Herman, van Dyke, and Ortenburger,[19] who discuss some technical points [see especially Eq. (6)] which we found useful here as well.

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Determination of Symmetry of Localized Orbitals in Solids

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It is shown that the center of localized orbitals and their symmetry can be deduced from experimental or computational information about the symmetry of Bloch functions at different points in the Brillouin zone.

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When using localized orbitals in band calculations the question often arises of choosing the center and the proper symmetry of these orbitals. This question was first raised in the early work of Hall[1] and of Slater and Koster,[2] and later it was considered in a number of papers[3-6] that dealt with band calculations for crystals with well-separated valence and conduction bands. There is apparently much freedom in choosing the "correct" localized orbitals and the controversy in the literature since the early work on the subject[1,2] was discussed in detail in Ref. 4.

In a recent publication[7] it was shown that the symmetry of a band can be labeled by a couple of indices ($\vec{q}$, l), where $\vec{q}$ is a symmetry center in the Wigner-Seitz cell and l labels the irreducible representation of the point group of G_q, the symmetry group of q. Having the band symmetry, one can uniquely define the symmetries of the Bloch states at all the points in the Brillouin zone. In this Letter we solve the inverse problem: Given the symmetries of Bloch states at different points in the Brillouin zone, one can reconstruct the symmetry type of the band, or, equivalently, find the center $\vec{q}$ and the symmetry l of the localized orbitals from which the band is built. It follows that by knowing the symmetries of Bloch states for a given band at different points in the Brillouin zone (this can, in principle, be measured experimentally or obtained from calculations) one should be able to determine the symmetry center $\vec{q}$ and the symmetry of the localized orbitals for the same band. As an example we consider the diamond structure.

Representation theory of space groups enables one to specify the symmetry of Bloch states at each point in the Brillouin zone.[8] Thus, one can specify the Bloch states at the points Γ, L, X, and so on. Then by using the compatibility[8] or connectivity[9] relations it becomes possible to connect Bloch states at different points in the Brillouin zone that can belong to the same band. However, the conventional specification of Bloch states by space-group representations gives no symmetry label for a band as a whole entity. The reason for this is as follows. Space groups consist of two kinds of symmetries: translations and point-group elements (rotations, reflections). These two kinds of symmetries are noncommuting. Because of this there are two alternatives in specifying states. The conventional alternative is to specify states in solids as eigenstates of translations of the space group. This leads to Bloch states $\psi_k(\vec{r})$ corresponding to a given $\vec{k}$ vector. In this approach, for each $\vec{k}$ one can find a group of $\vec{k}$, G_k, for assigning different symmetry labels Γ_i, L_j, and so on to the Bloch states $\psi_k^{(j)}(\vec{r})$ (here j stands for one of the labels Γ_i, L_j, etc.). Such a specification is local in k space and no symmetry label can be assigned in this scheme to a band as a whole entity in a solid.

An alternative way to specify states in solids is to start with the point-group symmetry of the space group. This idea originated with Hall[1] and was later developed by Des Cloizeaux.[3] By using the point-symmetry approach one can define the concept of band representations.[7] In this approach states in solids are specified by a symmetry center $\vec{q}$ and a representation label l of the symmetry group of $\vec{q}$, G_q. Correspondingly,

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