PHYSICAL REVIEW B VOLUME 59, NUMBER 16 15 APRIL 1999-II

ARTICLES

Density-functional correction of random-phase-approximation correlation with results for jellium surface energies

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(Received 11 August 1998)

Since long-range electron-electron correlation is treated properly in the random phase approximation (RPA), we define short-range correlation as the correction to the RPA. The effects of short-range correlation are investigated here in the local spin density (LSD) approximation and the generalized gradient approximation (GGA). Results are presented for atoms, molecules, and jellium surfaces. It is found that (1) short-range correlation energies are less sensitive to the inclusion of density gradients than are full correlation energies, and (2) short-range correlation makes a surprisingly small contribution to surface and molecular atomization energies. In order to improve the accuracy of electronic-structure calculations, we therefore combine a GGA treatment of short-range correlation with a full RPA treatment of the exchange-correlation energy. This approach leads to jellium surface energies close to those of the LSD approximation for exchange and correlation together (but not for each separately). [S0163-1829(99)01315-6]

I. INTRODUCTION AND SUMMARY

The ground-state density and energy of a many-electron system may be found by solving the Kohn-Sham self-consistent one-electron equations.[1–4] Only the exchange-correlation energy as a functional of the density must be approximated. Standard functionals—the local spin density (LSD) approximation and the generalized gradient approximation (GGA)—achieve a useful but limited accuracy. For example, the lattice constants of solids can be in error by several percent, leading to larger errors in the bulk moduli. As a second example, the atomization energies of multiply bonded molecules are overestimated. Much of these errors can be traced, respectively, to errors in the core-valence[5] and valence-valence[6] exchange. We believe that significant improvements in accuracy can be achieved by using the full exact exchange energy from the Kohn-Sham orbitals, but at the cost that the correlation energy must also be constructed from the orbitals, possibly as we propose in this paper. As an application of this approach, we calculate the surface energy of jellium, providing some confirmation for its LSD values.

The LSD and generalized gradient approximations to the exchange-correlation energy of density-functional theory[1–4] are constructed under the assumption of slowly varying densities. But they are surprisingly successful for real atoms and molecules which lie outside this formal domain of validity. Inspection of the separate exchange and correlation components often reveals a cancellation of error[7] between the two pieces. Therefore, it is often better to approximate exchange and correlation together in the same way than to combine exact exchange with the LSD or generalized gradient approximation for correlation.[8,9]

The main ingredient of the exchange-correlation energy, the exchange-correlation hole around an electron, may be expanded in the density derivatives at the electron's position. Analysis of this gradient expansion shows that inclusion of higher-order derivatives typically improves the approximation to the hole close to the electron, while worsening it far away.[10,11] The LSD and generalized gradient approximations are usually most accurate for the ''on-top'' hole density.[12] For many physical systems, the most long-ranged parts of the exact exchange hole and the exact correlation hole tend to cancel one another, leaving the combined exchange-correlation hole relatively short ranged. This explains the error cancellation in the LSD and generalized gradient approximation mentioned above, and suggests that these approximations are most accurate for the short-range part of the exchange-correlation energy.

On the other hand, the random phase approximation (RPA) is exact for long-range correlation,[13] but a poor approximation for short-range correlation.[14] This suggests that an accurate functional may be constructed by combining the RPA with the short-range piece of the GGA correlation.[15] A different separation of long- and short-range effects is presented in Refs. 16 and 17.

In this paper, we are mostly concerned with this short-range correlation energy. Below, we give the formal definition of the RPA in a density-functional context,[10] and describe how the remaining short-range part can be approximated in both LSD and generalized gradient approximations. In Sec. II we give results for atoms and molecules, showing that the effects of gradient corrections to the LSD approximation for the short-range correlation energy are significantly smaller than for the full correlation energy. In Sec. III we treat the jellium surface, for which a full RPA calculation has been reported.[18] For all the systems studied in this paper, we confirm that the short-range piece of the correlation energy is much less sensitive to the inclusion of density gradients than is the full correlation energy. The change in this short-range contribution upon atomization of a molecule is found to be very small compared to experimental atomization energies. Surface exchange-correlation energies for jellium surfaces calculated by combining the RPA with the GGA short-range correlation energy are found to be in good agreement with LSD surface exchange-correlation energies.

We start with an exact expression[8] for the exchange-correlation energy of a system of interacting electrons, obtained by adiabatically switching on the electron-electron interaction via a coupling constant λ, i.e., $v^{\lambda}(\mathbf{r}-\mathbf{r}')=\lambda e^2/|\mathbf{r}-\mathbf{r}'|$, while keeping the ground-state density $\rho(\mathbf{r})$ fixed for all values of λ:

$$E_{xc}=\frac{1}{2}\int d^3r\int d^3r'\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\int_0^1 d\lambda\left(-\frac{1}{\pi}\int_0^{\infty}d\omega\,\mathrm{Im}\,\chi^{\lambda}(\mathbf{r},\mathbf{r}',\omega)-\rho(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')\right). \tag{1}$$

$\chi^{\lambda}(\mathbf{r},\mathbf{r}',\omega)$ is the dynamic susceptibility or linear density response function of the system at coupling strength λ. In particular, at $\lambda=0$ it reduces to the Kohn-Sham (KS) or noninteracting response function

$$\chi^{\lambda=0}(\mathbf{r},\mathbf{r}',\omega)=\chi_s(\mathbf{r},\mathbf{r}',\omega)=\lim_{\eta\to 0}\sum_{\sigma}\sum_{j,k}(f_{k\sigma}-f_{j\sigma})\frac{\varphi_{j\sigma}(\mathbf{r})\varphi^{*}_{k\sigma}(\mathbf{r})\varphi^{*}_{j\sigma}(\mathbf{r}')\varphi_{k\sigma}(\mathbf{r}')}{\omega-(\varepsilon_{j\sigma}-\varepsilon_{k\sigma})+i\eta}, \tag{2}$$

where $f_{i\sigma}$ and $\varepsilon_{i\sigma}$ are the occupation numbers and eigenenergies of the KS orbitals $\varphi_{i\sigma}$. From time-dependent density-functional theory,[19–21] one can derive a Dyson-type equation which relates χ^{λ} to the KS response function.[22]

$$\chi^{\lambda}(\mathbf{r},\mathbf{r}',\omega)=\chi_s(\mathbf{r},\mathbf{r}',\omega)+\int d^3x\int d^3x'\,\chi_s(\mathbf{r},\mathbf{x},\omega)\left(\frac{\lambda e^2}{|\mathbf{x}-\mathbf{x}'|}+f^{\lambda}_{\mathrm{xc}}(\mathbf{x},\mathbf{x}',\omega)\right)\chi^{\lambda}(\mathbf{x}',\mathbf{r}',\omega), \tag{3}$$

where $f^{\lambda}_{\mathrm{xc}}(\mathbf{r},\mathbf{r}',\omega)$ is the exchange correlation (xc) kernel at frequency ω.[22]

Equations (1)–(3) are an exact representation of the exchange-correlation energy. In practice, the exact xc kernel is not known and must be approximated. The crudest approximation completely neglects $f^{\lambda}_{\mathrm{xc}}$. This is the random phase approximation, and the corresponding response function is (in short-hand notation)

$$\chi^{\lambda,\mathrm{RPA}}=(1-\chi_s v^{\lambda})^{-1}\chi_s\,. \tag{4}$$

For a one-electron system, $\chi^{\lambda}=\chi_s$, and the correction to the RPA is a self-correlation correction. Equation (4) is the simple ''RPA without exchange'' or sum of ring diagrams, but in a density-functional context:[10] χ_s is constructed from Kohn-Sham orbitals and not from Hartree orbitals. When the ''RPA without exchange'' approximation for the response function is used in Eq. (1) for the exchange-correlation energy, the leading term χ_s in the series expansion of Eq. (4) yields the exact exchange energy functional.

Via Eqs. (1)–(3), E_{xc} is defined as an explicit functional of the Kohn-Sham orbitals and orbital energies. A fully self-consistent treatment would require a calculation of the corresponding exchange-correlation potential with the optimized effective potential method,[23] generalized to include correlation.[24,25] (For a review of this method, see Ref. 25. For an RPA-like application of the method, see Ref. 26.) The equation for the exchange-correlation potential is hard to solve numerically. Experience shows, however, that the final results for total exchange-correlation energies differ little when evaluating the energy functional with, e.g., Hartree-Fock, LSD, or GGA orbitals and densities. Hartree orbitals are typically more delocalized and less realistic than LSD or GGA orbitals, and their use in Eq. (2) is not recommended.

In the RPA, both exchange and long-range correlation are treated exactly. However, the RPA is a poor approximation for short-range correlation. For the uniform electron gas at metallic densities, the RPA on-top correlation hole is much too deep.[14] We use the RPA to define the short-range correlation energy

$$E_{c,\mathrm{sr}}=E_{\mathrm{xc}}-E^{\mathrm{RPA}}_{\mathrm{xc}}=E_c-E^{\mathrm{RPA}}_c\,. \tag{5}$$

In the following we will argue that $E_{c,\mathrm{sr}}$ can be treated conveniently and accurately within the LSD approximation or, better, the GGA.

The LSD correlation energy is defined by

$$E^{\mathrm{LSD}}_c[\rho_{\uparrow},\rho_{\downarrow}]=\int d^3r\,\rho(\mathbf{r})\epsilon^{\mathrm{unif}}_c(r_s,\zeta), \tag{6}$$

where r_s is the local Wigner-Seitz radius $[\rho=3/(4\pi r_s^3)=k_F^3/(3\pi^2)]$, $\zeta=(\rho_{\uparrow}-\rho_{\downarrow})/\rho$, and $\epsilon^{\mathrm{unif}}_c(r_s,\zeta)<0$ is the correlation energy per particle of a uniform electron gas.[27] For the GGA correlation energy, we use the nonempirical form proposed by Perdew, Burke, and Ernzerhof (PBE),[28]

$$E^{\mathrm{GGA}}_c[\rho_{\uparrow},\rho_{\downarrow}]=\int d^3r\,\rho(\mathbf{r})\{\epsilon^{\mathrm{unif}}_c(r_s,\zeta)+H(r_s,\zeta,t,\epsilon^{\mathrm{unif}}_c(r_s,\zeta))\}. \tag{7}$$

Here $t=|\nabla\rho|/([(1+\zeta)^{2/3}+(1-\zeta)^{2/3}]k_s\rho)$ is a dimensionless density gradient, $k_s=\sqrt{4k_F/(\pi a_0)}$ is the Thomas-Fermi screening wave number, and a_0 is the Bohr radius. The curly bracket in Eq. (7) varies between $\epsilon_c^{\mathrm{unif}}(r_s,\zeta)+\beta(\zeta)t^2$ as $t\to 0$, and zero as $t\to\infty$, where β is a positive gradient coefficient. Both the LSD approximation of Eq. (6) and the GGA of Eq. (7) are constructed beyond the RPA. It is easy, however, to construct the RPA version of each approximation (E_c^{LSDRPA} and E_c^{GGARPA}), replacing $\epsilon_c^{\mathrm{unif}}(r_s,\zeta)$ by the RPA correlation energy per particle of a uniform electron gas, $\epsilon_c^{\mathrm{RPA}}(r_s,\zeta)$.[27] No further change is needed for the PBE-GGA correlation functional, because it uses the high-density limit of the gradient coefficient, which is the same within or beyond the RPA.[10]

The short-range correlation energy $E_{c,\mathrm{sr}}$ can now be approximated in the LSD approximation,

$$E_{c,\mathrm{sr}}^{\mathrm{LSD}}=E_c^{\mathrm{LSD}}-E_c^{\mathrm{LSDRPA}}, \tag{8}$$

or in the GGA,

$$E_{c,\mathrm{sr}}^{\mathrm{GGA}}=E_c^{\mathrm{GGA}}-E_c^{\mathrm{GGARPA}}. \tag{9}$$

The results presented in the following sections indicate that the short-range correlation energy $E_{c,\mathrm{sr}}$ is more local than the full correlation energy. This suggests that treatment of short-range correlation via Eq. (9), combined with a full RPA calculation, is more accurate than the use of the LSD or generalized gradient approximation for the full correlation energy.

The weak nonlocality of the short-range correlation energy can be seen in Fig. 1(a), where we show the short-range correlation energy per particle for a spin-unpolarized system as a function of the dimensionless density gradient t, i.e.,

$$\begin{aligned}\epsilon_{c,\mathrm{sr}}^{\mathrm{GGA}}(r_s,t,\zeta=0)=&\,\epsilon_c^{\mathrm{unif}}(r_s,\zeta=0)\\&+H(r_s,\zeta=0,t,\epsilon_c^{\mathrm{unif}}(r_s,\zeta=0))\\&-\{\epsilon_c^{\mathrm{RPA}}+H(r_s,\zeta=0,t,\epsilon_c^{\mathrm{RPA}}(r_s,\zeta=0))\}.\end{aligned} \tag{10}$$

For all r_s, the curves start out very flat, i.e., the effect of the density gradient is negligible for small t. Only beyond a certain (r_s-dependent) value of t does nonlocality alter $\epsilon_{c,\mathrm{sr}}^{\mathrm{GGA}}$ significantly from its LSD value. In the high-density limit $(r_s\to 0), \epsilon_{c,\mathrm{sr}}^{\mathrm{GGA}}$ becomes a constant for all finite t, the second-order exchange constant of the uniform electron gas which corrects the RPA correlation in this limit.[29]

II. CORRELATION ENERGIES FOR ATOMS AND MOLECULES

In Table I, we show total and short-range correlation energies [Eqs. (8) and (9)] for various atoms in the LSD approximation and the PBE-GGA of Eq. (7). Görling and Levy showed[30] that under a uniform scaling of the density,

$$\rho\to\rho_\gamma=\gamma^3\rho(\gamma\mathbf{r}), \tag{11}$$

the correlation energy scales to a finite value as $\gamma\to\infty$, i.e.,

$$\lim_{\gamma\to\infty}E_c[\rho_\gamma]=E_c^{(2)}[\rho], \tag{12}$$

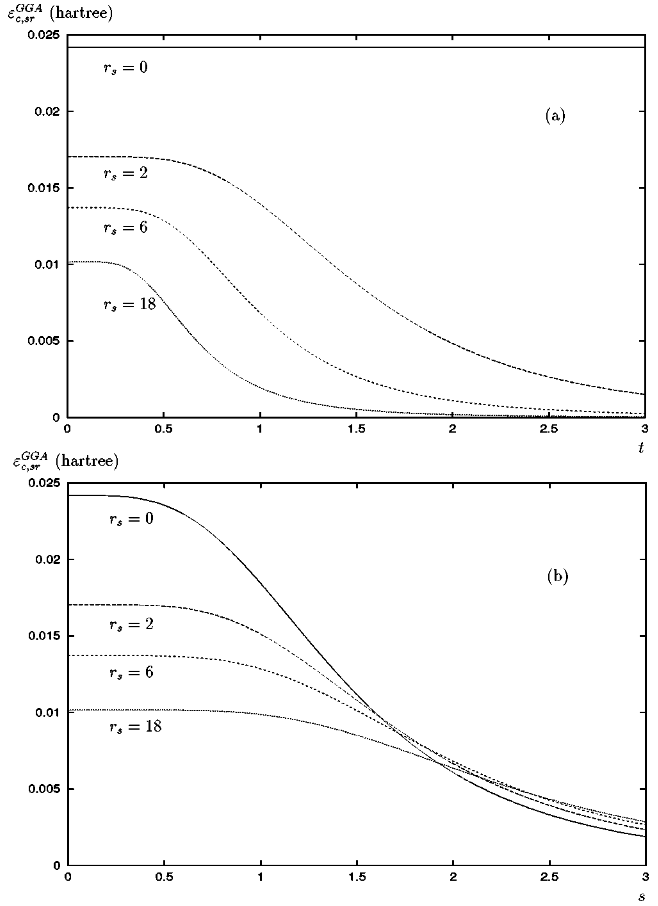

FIG. 1. PBE-GGA short-range correlation energy per particle $\epsilon_{c,\mathrm{sr}}^{\mathrm{GGA}}$ of Eq. (10), as a function of the dimensionless reduced density gradient t defined after Eq. (7) (upper panel) and as a function of another reduced density gradient $s=|\nabla n|/(2k_Fn)=(r_s/a_0)^{1/2}t/c$ (lower panel) for different values of the density parameter r_s. a_0 is the Bohr radius and $c=(3\pi^2/16)^{1/3}$. t and s measure how fast the density varies on the scales of the local screening length and Fermi wavelength, respectively. The $t\to 0$ or $s\to 0$ limit is $\epsilon_{c,\mathrm{sr}}^{\mathrm{LSD}}$.

where $E_c^{(2)}$ is the second-order energy of Görling-Levy perturbation theory (GL2). For both RPA and beyond-RPA versions of the PBE-GGA approximation, the left-hand side of Eq. (12) can be evaluated [Eq. (9) of Ref. 28 with $\omega=0.070\,823$ within the RPA and $\omega=0.046\,644$ beyond the RPA], and the results are also given in Table I. In the LSD approximation the correlation energy scales to $-\infty$ in this limit.

Table I shows that the magnitude of the correlation energy is reduced drastically as one moves from the LSD approximation to the GGA, indicating that $E_c[\rho]$ is not a very local functional. The GGA correlation energy is typically between 35% and 55% of the corresponding LSD correlation energy. Table I also shows that the second-order contribution captures the full GGA result within 10–15%.

The nonlocality of the short-range contribution to the correlation energy, $E_c-E_c^{\mathrm{RPA}}$, is much less pronounced, as can be seen from the sixth and seventh columns of Table I. The short-range correlation energy in the GGA ranges from 75% to as much as 97% (for Xe) of that in the LSD approximation. This supports the argument that the short-range correlation energy is treated with sufficient accuracy in the GGA.

TABLE I. Correlation energies E_c, and short-range corrections $E_{c,\mathrm{sr}}=E_c-E_c^{\mathrm{RPA}}$ to the RPA correlation energy of atoms and ions in the LSD approximation, the GGA, and the GGA second-order Görling-Levy perturbation theory. All functionals were evaluated with the Hartree-Fock densities of Ref. 45. Energies in hartrees. Experimental values from Ref. 46.

Atom	E_c^{expt}	E_c^{LSD}	E_c^{GGA}	E_c^{GGAGL2}	$E_{c,\mathrm{sr}}^{\mathrm{LSD}}$	$E_{c,\mathrm{sr}}^{\mathrm{GGA}}$	$E_{c,\mathrm{sr}}^{\mathrm{GGAGL2}}$
H	−0.0000	−0.0222	−0.0060	−0.0050	0.0177	0.0129	0.0056
He	−0.0420	−0.1125	−0.0420	−0.0438	0.0367	0.0291	0.0330
Li^+	−0.0435	−0.1346	−0.0448	−0.0454	0.0392	0.0302	0.0332
Be^{+2}	-	−0.1504	−0.0461	−0.0460	0.0406	0.0308	0.0334
Li	−0.0455	−0.1508	−0.0514	−0.0544	0.0541	0.0421	0.0405
Be^+	−0.0477	−0.1727	−0.0542	−0.0553	0.0574	0.0439	0.0414
Be	−0.0950	−0.2240	−0.0856	−0.1059	0.0719	0.0579	0.0682
Ne^{+6}	-	−0.3336	−0.1040	−0.1114	0.0829	0.0647	0.0702
N	−0.1858	−0.4273	−0.1812	−0.2113	0.1361	0.1172	0.1222
Ne	−0.3929	−0.7428	−0.3513	−0.4018	0.2008	0.1799	0.2036
Ar	−0.7314	−1.4242	−0.7067	−0.8368	0.3654	0.3371	0.3821
Zn^{+12}	-	−1.7995	−0.8237	−0.9077	0.3929	0.3607	0.3888
Zn	-	−2.6553	−1.4057	−1.5961	0.6297	0.5984	0.6615
Kr	-	−3.2693	−1.7671	−2.0018	0.7598	0.7275	0.8077
Xe	-	−5.1773	−2.9181	−3.3366	1.1531	1.1181	1.2354

Furthermore, the short-range correlation energy per electron, $(E_c-E_c^{\mathrm{RPA}})/N$, is typically close to 0.024 hartree, the second-order exchange constant of the uniform electron gas.[29]

We also calculated total and short-range correlation energies for a set of small molecules. The general trends are much as for the atoms: total correlation energies in the GGA are about half those in the LSD approximation. Again, the nonlocality is much weaker for the short-range part of the correlation energy. For the molecules in this set, the GGA reduces this short-range part by only about 10% relative to the LSD approximation.

For an accurate description of chemical processes, atomization energies are of much greater interest than total energies. In Table II we give total and short-range correlation contributions to the atomization energies of molecules. Comparison with experimental data (the last column of Table II) shows that total correlation contributions are a significant part of total atomization energies. However, short-range correlation contributions are much smaller. This suggests that combination of an exact treatment of long-range correlation (i.e., a full RPA calculation) with a GGA functional for the short-range piece could give very accurate results in quantum chemistry. We note that RPA-like correlation energies have already been evaluated for jellium clusters.[31]

III. EXCHANGE AND CORRELATION ENERGIES FOR JELLIUM SURFACES

As a simple and useful model for metal surfaces, jellium has been investigated with various approaches over the years. In a landmark study, Lang and Kohn[32] reported the first self-consistent calculations of surface energies for jellium. They employed the LSD approximation for the exchange-correlation energy. However, since the exact surface energies are not known for this problem, it is difficult to assess the quality of the LSD results. From a wave-vector analysis of the surface exchange-correlation energy, Langreth and Perdew[13] estimated a small positive correction to the LSD results. Krotscheck and Kohn[33] performed a Fermi

TABLE II. Total Δ_c and short-range $\Delta_{c,\mathrm{sr}}$ correlation contributions to the atomization energies Δ of some small molecules in the LSD approximation, the GGA, and the GGA second-order Görling-Levy perturbation theory. Experimental total atomization energies are given in the last column. All functionals were evaluated with self-consistent GGA densities for the atoms and for the molecules at experimental geometries. The calculations were performed with a modified version of the CADPAC program (Ref. 47). The Gaussian basis sets used are of triple-zeta quality with *p*- and *d*-type polarization functions for hydrogen and *d*- and *f*-type polarization functions for the other elements. Energies in kcal/mole. Experimental values were taken from Ref. 28. (1 kcal/mole $=1.594\times10^{-3}$ hartree.)

Molecule	Δ_c^{LSD}	Δ_c^{GGA}	$\Delta_c^{\mathrm{GGAGL2}}$	$\Delta_{c,\mathrm{sr}}^{\mathrm{LSD}}$	$\Delta_{c,\mathrm{sr}}^{\mathrm{GGA}}$	$\Delta_{c,\mathrm{sr}}^{\mathrm{GGAGL2}}$	Δ^{expt}
H_2	31.7	19.7	27.3	0.5	−1.5	−13.9	109
N_2	56.0	59.0	96.9	0.1	−5.0	−23.8	229
O_2	27.5	39.3	65.0	−0.7	−4.8	−13.7	121
F_2	14.2	21.0	30.5	−0.5	−3.6	−8.5	39
CH_4	92.4	83.8	136.2	4.3	−10.6	−44.2	419
NH_3	82.3	74.3	114.0	−0.1	−8.2	−38.1	297
H_2O	53.6	50.3	74.0	−0.4	−6.0	−24.7	232
HF	26.2	25.0	35.3	−0.4	−3.1	−11.9	141

TABLE III. Exchange and correlation parts of surface energies σ (in ergs/cm^2) for the jellium surface. r_s is the bulk density parameter. All functionals were evaluated using LSD orbitals and densities. Results for the exact surface exchange energies (second column) and for the RPA surface correlation energies (last column) are from Pitarke and Eguiluz (Ref. 35), who also used LSD orbitals. (1 erg/cm^2=6.423 $\times 10^{-7}$ hartree/bohr^2.)

r_s	σ_x^{exact}	σ_x^{LSD}	σ_x^{GGA}	σ_c^{LSD}	σ_c^{GGA}	σ_c^{LSDRPA}	σ_c^{GGARPA}	σ_c^{RPA}
2.00	2624	3037	2437	317	824	367	914	843
2.07	2296	2674	2127	287	754	333	834	768
2.30	1521	1809	1395	210	567	245	630	577
2.66	854	1051	770	137	382	160	427	386
3.00	526	669	466	95	275	112	309	275
3.28	364	477	316	72	215	86	243	215
4.00	157	222	128	39	124	47	142	121
5.00	57	92	40	19	67	23	77	62
6.00	22	43	12	10	40	13	47	36

hypernetted-chain (FHNC) calculation, and obtained surface energies significantly higher than in the LSD approximation. Acioli and Ceperley[34] studied the problem using the diffusion Monte Carlo (DMC) method, and also obtained surface energies higher than in the LSD approximation. Recently Pitarke and Eguiluz[18] performed a full RPA calculation for the jellium surface. This allows a comparison of the RPA versions of LSD and generalized gradient approximations with the exact RPA results.

In Table III we show the exchange and correlation contributions to the surface energy in different approximations. The exact surface exchange energies (σ_x^{exact}) and RPA correlation energies (σ_c^{RPA}) were provided by Pitarke and Eguiluz.[35] They were obtained from Eqs. (2), (4), and (1), with the Kohn-Sham response function χ_s constructed from self-consistent LSD orbitals. (In contrast, the ''RPA'' results reported in Ref. 18 employed self-consistent Hartree orbitals to construct the noninteracting response function.) No result for the second-order Görling-Levy perturbation theory is shown here, because $E_c^{(2)}=-\infty$ for the uniform electron gas.

Table III shows that the LSD approximation overestimates the surface exchange energies, while the GGA underestimates them. The surface correlation energies in the GGA are roughly a factor of 3 larger than the corresponding LSD values. This is another indication that the correlation energy is a highly nonlocal functional of the density. The RPA version of the GGA gives surface correlation energies which differ by typically less than 20% from the exact RPA values. (The fact that the beyond-RPA results in the GGA are even closer to the exact RPA results is probably fortuitous.)

The short-range contribution $\sigma_c-\sigma_c^{\text{RPA}}$ to the surface correlation energy in the LSD and generalized gradient approximations is easily calculated from the results given in Table III. Its magnitude is 10–20 % of the total surface correlation energy. This contrasts with the results for atoms and molecules, where the short-range correlation energy contributed between 30% and 40% of the total correlation energy, and shows the importance of long-range effects in the surface problem. GGA short-range contributions to the surface correlation energy are about a factor of 2 larger than LSD values. This is very different from the situation for atoms and molecules, where the GGA short-range correlation energy was only 10–20 % less than its LSD counterpart. The difference can be understood with the help of Fig. 1(b): the reduced density gradient s is usually less than 1 in the interior of an atom, but much greater in the jellium surface.

In Table IV we compile different estimates for the surface exchange-correlation energies. The LSD results were obtained using the parametrization of Perdew and Wang[27] for the correlation energy of the uniform electron gas. They differ slightly from the values of Lang and Kohn,[32] where the Wigner parametrization was used. The numbers in the fourth column ($\sigma_{\text{xc}}^{\text{WVI}}$) were calculated by combining the LSD results with the interpolation correction of Langreth and Perdew,[13] obtained from a wave-vector analysis of the surface exchange-correlation energy. This positive correction is of the order of 10% of $\sigma_{\text{xc}}^{\text{LSD}}$ or less. The fifth column combines the FHNC results of Krotscheck and Kohn[33] with the exact surface exchange energies of Pitarke and Eguiluz (Ref. 35, see also Table III), resulting in surface exchange-correlation energies significantly higher than the LSD results. For $r_s=4$ the deviation from the LSD approximation is more than 40%. The Monte Carlo calculation gives lower surface exchange-correlation energies than the FHNC calculation for $r_s \lesssim 3.25$, while both methods give similar results for lower densities ($r_s \gtrsim 3.25$). The eighth column shows the Pitarke-Eguiluz results[18] from the time-dependent local-density approximation (TDLDA), also known as the adiabatic LDA.[22] In this approximation, Eq. (3) is solved with the (frequency-independent) exchange-correlation kernel f_{xc}^{λ} of the static LDA. In the final two columns of Table IV, we combine exact RPA results (the seventh column of Table IV) with short-range correlation energies in the LSD and generalized gradient-approximations, respectively, and find the RPA+GGA results very close to those of the LSD approximation for exchange and correlation together; for $r_s \leqslant 4$, the difference is less than 1%. On this basis, and assuming that $\sigma_{\text{xc}}^{\text{RPA}}$ was calculated accurately in Ref. 35, we conclude that the LSD approximation works surprisingly well for the exchange-correlation contribution σ_{xc} to the jellium surface energy. This conclusion was also reached in Ref. 36, which compares LSD surface energies for real metals against experiment. Skriver and Rosengaard,[37] who calculated surface energies for real simple metals (see also Ref. 38), found that ''local density theory . . . can provide surface energies which are at least as accurate as those derived from experi-

TABLE IV. Estimates of the exact surface exchange-correlation energies σ_{xc} (in ergs/cm^2) for realistic density profiles of the jellium surface. For $r_s = 2.07$, the diffusion Monte Carlo calculation of Ref. 48 gives a surface energy about 50 ergs/cm^2 lower than that of Ref. 34, and within the error bars of both calculations.

r_s	$\sigma_{\mathrm{xc}}^{\mathrm{LSD}}$	$\sigma_{\mathrm{xc}}^{\mathrm{GGA}}$	$\sigma_{\mathrm{xc}}^{\mathrm{WVI}}$ [a]	$\sigma_{\mathrm{xc}}^{\mathrm{FHNC}}$ [b]	$\sigma_{\mathrm{xc}}^{\mathrm{DMC}}$ [c]	$\sigma_{\mathrm{xc}}^{\mathrm{RPA}}$ [d]	$\sigma_{\mathrm{xc}}^{\mathrm{TDLDA}}$ [e]	$\sigma_{\mathrm{xc}}^{\mathrm{RPA+LSD}}$ [f]	$\sigma_{\mathrm{xc}}^{\mathrm{RPA+GGA}}$ [g]
2.00	3354	3261	3527			3467	3533	3417	3377
2.07	2961	2881		3347	3152	3064	3125	3018	2984
2.30	2019	1962		2376		2098		2063	2035
2.66	1188	1152		1452	1394	1240		1217	1195
3.00	764	741	813			801	840	784	767
3.28	549	531		719	719	579		565	551
4.00	261	252	281	377	390	278	295	270	260
5.00	111	107	121	178		119	130	115	109
6.00	53	52	58			58	65	55	51

[a] LSD approximation plus correction from wave-vector interpolation of Ref. 13.

[b] Exact exchange plus FHNC correlation from Ref. 33.

[c] Exact exchange plus DMC correlation from Ref. 34.

[d] RPA from Ref. 35.

[e] TDLDA from Rev. 18.

[f] RPA with LSD short-range correction.

[g] RPS with GGA short-range correction.

ments,'' although the experimental values are old and uncertain. We note that σ_{xc} is an extremely important contribution to the total surface energy σ, the former being typically three times larger than the latter.

In both the LSD approximation and the PBE-GGA, the short-range correction to the RPA surface energy is *negative*. Both corrections are small, with the GGA correction more negative than the LSD approximation. (Roughly the same pattern can be seen in the atomization energies of Table II, as the liquid drop model[39,38] would suggest.) We see no physical origin for a positive correction, as in the WVI, FHNC, DMC, and TDLDA numbers in Table IV, although we cannot rule out such a correction.

If the last column in Table IV gives an accurate estimate of σ_{xc} for jellium, then we find that the LSD value of σ_{xc} is fortuitously a little more realistic than the PBE-GGA value, which is about 3% off, although the PBE-GGA gives more realistic results for σ_x and σ_c separately. The PBE-GGA nonlocalities of exchange and correlation tend to cancel for metallic densities, as shown in Fig. 1 of Ref. 28.

We believe that $\sigma_{\mathrm{xc}}^{\mathrm{LSD}}$ is very accurate, not only within an exact treatment of electron correlation, but also to some extent within the RPA treatment (compare $\sigma_x^{\mathrm{LSD}} + \sigma_c^{\mathrm{LSDRPA}}$ from Table III with $\sigma_{\mathrm{xc}}^{\mathrm{RPA}}$ from Table IV) or within a TDLDA treatment (as stressed in Ref. 18). These observations are made for realistic density profiles, but they can also be made (less strongly) for the rapidly varying profiles of the infinite barrier model (Table V). Finally, we note that a GGA correction can be made, not only to the RPA correlation energy, but also to the RPA correlation hole, along the lines of Ref. 40.

IV. CONCLUSIONS

In density functional theory as usually practiced, the whole exchange-correlation energy E_{xc} is approximated in the LSD or generalized gradient approximation. Despite many remarkable successes, this approach is not accurate enough for all applications. We have proposed an alternative approach, more computationally demanding but probably more accurate, in which exchange is treated exactly, long-range correlation is treated in the RPA, and only the short-range correction to the RPA is treated in the LSD approximation or, better, the GGA.

We believe that our approach combines the strongest aspects of the RPA with those of the LSD or generalized gradient approximation. For example, the RPA naturally recovers the van der Waals interaction, the subject of several recent investigations.[16,41–44] The LSD or generalized gradient approximation should work best for the short-range part of the correlation hole, where the RPA is deficient. As expected, we have found that gradient corrections to the LSD aproximation are much smaller for the short-range part than for the whole correlation energy.

An alternative correction to the RPA is provided by the TDLDA for the exchange-correlation kernel f_{xc}, as applied in Ref. 18. Unlike the TDLDA, our LSD and GGA corrections are exact for the uniform electron gas, and nearly exact

TABLE V. Surface exchange-correlation energies σ_{xc} (in ergs/cm^2) for the rapidly varying density profiles of the infinite barrier model. Comparison of the second and third columns was made in Ref. 13.

r_s	$\sigma_x^{\mathrm{LSD}} + \sigma_c^{\mathrm{LSDRPA}}$	$\sigma_{\mathrm{xc}}^{\mathrm{RPA}}$ [a]	$\sigma_{\mathrm{xc}}^{\mathrm{LSD}}$	$\sigma_{\mathrm{xc}}^{\mathrm{RPA+GGA}}$ [b]
2.07	1245	1388	1227	1314
4.00	185	203	181	187
6.00	58	63	56	57

[a] From Refs. 13 and 49.

[b] RPA with GGA short-range correction.

for the gas of slowly varying density. Although we have not used the optimized effective potential method[23–26] here, it can be combined with our approach to construct a realistic approximation for the Kohn-Sham exchange-correlation potential $v_{\mathrm{xc}}(\mathbf{r})$.

While the RPA is not a very good approximation for the total correlation energy, we have suggested that it may be a much better approximation for the changes in correlation energy upon atomization or surface formation (since our calculated LSD or GGA short-range corrections to these changes turn out to be small). In an oversimplified picture, short-range correlation raises the energy of each valence electron by the same amount, and so has no effect on atomization or surface energies.

Our best estimate for the jellium surface energy is close to that of the LSD approximation for exchange and correlation together, and thus considerably lower than the diffusion Monte Carlo estimate.[34] We regard this as an interesting (although not definitive) confirmation of density-functional theory as usually practiced. While the Monte Carlo[34] surface energy is higher than the RPA (Ref. 35) surface energy, our LSD and GGA short-range corrections to the RPA surface energy are small and *negative*, in accord with intuition: Short-range correlation raises the energy of a bulk electron a little more than it raises the energy of a surface electron.

Note added in proof Recently, a more reliable GGA for the RPA correlation energy was found by Z. Yan, J. P. Perdew, and S. Kurth, who applied the real-space cutoff construction of Ref. 40 within RPA. Thus the GGA results of the present work will be updated and improved in a future publication. The short-range correlation energy is more local than Fig. 1 suggests, but the qualitative conclusions of the present work are unchanged.

ACKNOWLEDGMENTS

S.K. gratefully acknowledges financial support through the Deutsche Forschungsgemeinschaft. This work was supported by the National Science Foundation under Grant No. DMR 98-10620, by the Petroleum Research Fund under Grant ACS-PRF No. 33001-AC6, and by NATO Collaborative Research Grant No. CRG 960759. We thank J. M. Pitarke and A. G. Eguiluz for sending us their unpublished results, Z. Yan for help with some of the calculations, and E. K. U. Gross and K. Burke for discussions.

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