

Analysis of the local-density approximation of density-functional theory

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In this paper we perform a configuration-space analysis of the local-density approximation (LDA) for the exchange-correlation energy functional of Kohn-Sham density-functional theory in terms of the corresponding average exchange-correlation charge (hole) and energy densities. According to our analysis, the explanation for the quantitative success of the LDA based on the hole charge-conservation sum rule and the assumed consequent cancellation of errors in the spherical averages of the hole is inadequate. The principal conclusion of our work is that the constraint of charge neutrality is a necessary but not sufficient condition for an approximate energy functional to lead to accurate ground-state energies and ionization potentials. The significant additional requirement for the functional is that it must, at least qualitatively, reproduce correctly the structure of the hole as a function of electron position. We perform our calculations within the exchange-only approximation as applied to atoms and jellium metal surfaces. In atoms the Fermi hole is *localized* about the nucleus; as a consequence the LDA Fermi hole is accurate only for electron positions close to it. However, we show that the spherically averaged LDA hole is accurate for electron positions in the shell regions; it is substantially in error in the intershell and classically forbidden regions. The fact that the principal contribution to the exchange energy comes from the inner-shell region of the atom, where the LDA hole is accurate, explains why the errors in the LDA ground-state energies are small. However, the ionization potential, which depends on the structure of the hole in the outer regions of the atom, is substantially in error in the LDA since here the LDA hole differs significantly from the exact one. For metallic surfaces, on the other hand, as an electron is pulled from within the metal to infinity outside, the Fermi hole is *delocalized* and spread throughout the crystal. As a consequence, the planar-averaged LDA hole, which is accurate for electron positions inside the metal, bears little resemblance to the exact hole for electron positions outside the surface. Thus the planar-averaged LDA energy density in the regions at and outside the surface, from which there is a significant contribution to the energy, is poor, and consequently so is the surface exchange energy. However, the LDA work function is accurate since the surface dipole barrier is fairly insensitive to the choice of the approximate energy functional. Finally, our calculations exhibit a striking similarity in the structure of the exact spherically averaged Fermi holes for the few-electron-atomic and many-electron-metallic-surface nonuniform systems, thus demonstrating the truly universal nature of the exact energy functional.

I. INTRODUCTION AND DISCUSSION

In density-functional theory¹⁻³ (DFT) of a system of interacting electrons in the presence of some external potential, all the many-body effects are incorporated in the universal "exchange-correlation" energy functional $E_{xc}[\rho]$ of the electronic density $\rho(\mathbf{r})$. This functional is defined as

$$E_{xc}[\rho] = \int \epsilon_{xc}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}, \quad (1)$$

where $\epsilon_{xc}(\mathbf{r})$ is the exchange-correlation energy density. The exchange-correlation energy may also be thought of as the Coulomb interaction energy between the electronic density and the exchange-correlation (hole) charge density $\rho_{xc}(\mathbf{r}, \mathbf{r}')$. The hole is a consequence of the reduction in probability of electrons approaching each other due to

the Pauli exclusion principle and Coulomb repulsion between the electrons. Thus (in atomic units: $e = \hbar = m = 1$) we may write⁴⁻⁶

$$E_{xc}[\rho] = -\frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (2)$$

where

$$\rho_{xc}(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r}') \int_0^1 d\lambda [g_\lambda(\mathbf{r}, \mathbf{r}') - 1], \quad (3)$$

and where $g_\lambda(\mathbf{r}, \mathbf{r}')$ is the pair-correlation function⁷ of the system with density $\rho(\mathbf{r})$ and coupling constant λ . The pair-correlation function is the probability of simultaneously finding an electron at \mathbf{r} and \mathbf{r}' . The depletion of charge about each electron is expressed by the charge conservation sum rule

$$\int \rho_{xc}(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = 1. \quad (4)$$

The exchange-correlation energy may also be written as a sum of an exchange $E_x[\rho]$ and a correlation $E_c[\rho]$ energy functional. However, the exchange and correlation energies in DFT differ⁸ from the corresponding values obtained by quantum mechanics. The DFT exchange energy, for example, is defined in terms of Kohn-Sham orbitals from the *full* exchange-correlation potential and must as a consequence differ from the Hartree-Fock value. (For a more detailed discussion of this and other definitions of the exchange and correlation energy functionals of DFT, we refer the reader to Ref. 8.) However, as opposed to $E_{xc}[\rho]$ and $E_c[\rho]$ which are both unknown functionals, the dependence of $E_x[\rho]$ on the Kohn-Sham orbitals is known explicitly via the average exchange charge density or Fermi hole $\rho_x(\mathbf{r}, \mathbf{r}')$. The average exchange charge density at \mathbf{r}' for an electron at \mathbf{r} is defined⁹ as

$$\rho_x(\mathbf{r}, \mathbf{r}') = [\gamma(\mathbf{r}, \mathbf{r}')]^2 / 2\rho(\mathbf{r}), \quad (5)$$

where

$$\gamma(\mathbf{r}, \mathbf{r}') = 2 \sum_{\mathbf{k}} \Psi_{\mathbf{k}}^*(\mathbf{r}') \Psi_{\mathbf{k}}(\mathbf{r}) \quad (6)$$

is the single-particle density matrix with $\gamma(\mathbf{r}, \mathbf{r}) = \rho(\mathbf{r})$. The exchange charge density satisfies the conditions

$$\rho_x(\mathbf{r}, \mathbf{r}) = \rho(\mathbf{r}) / 2, \quad (7)$$

$$\rho_x(\mathbf{r}, \mathbf{r}') \geq 0, \quad (8)$$

and the charge-conservation sum rule of Eq. (4).

Since both the functionals $E_{xc}[\rho]$ and $E_c[\rho]$ are unknown, they must be approximated. As a consequence the mathematical rigor of the Hohenberg-Kohn theorem¹ proof is lost, and bounds obtained for the ground-state energy with the approximate total energy functional are no longer rigorous. Thus in order to interpret accurately the results they generate, it is important to first understand the validity of the approximations invoked. One approach to the evaluation of approximate energy functionals is to make comparisons¹⁰⁻¹³ either with experiment or with results of quantum-mechanical calculations where they exist. Another is to remain within the realm of DFT and to compare^{10,11} with results derived from ex-

actly known functionals such as the exchange energy functional.

The simplest and most extensively used approximation for the functional $E_{xc}[\rho]$ and its exchange $E_x[\rho]$ and correlation $E_c[\rho]$ energy components is the local-density approximation (LDA). In this approximation these energies are represented by uniform electron gas values corresponding to the local value of the density. Thus in the LDA

$$E_i^{\text{LDA}}[\rho] = \int \varepsilon_i[\rho(\mathbf{r})] \rho(\mathbf{r}) d\mathbf{r}, \quad (9)$$

where the subscript i represents exchange (x), correlation (c), exchange-correlation (xc), or screened-Coulomb exchange (sx), respectively, and where ε_i is the corresponding average energy per electron of a uniform electron gas of density ρ . The exchange-correlation charge density in the LDA corresponds to writing Eq. (3) as

$$\rho_{xc}^{\text{LDA}}(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r}) \int_0^1 d\lambda [g_\lambda^{\text{hom}}\{|\mathbf{r} - \mathbf{r}'|; \rho(\mathbf{r})\} - 1], \quad (10)$$

where g_λ^{hom} is the pair-correlation function for the homogeneous electron gas of density $\rho(\mathbf{r})$. Since in the LDA for each electron position \mathbf{r} the local density $\rho(\mathbf{r})$ is assumed uniform, the LDA exchange-correlation hole also satisfies the charge-conservation sum rule [see Eq. (4)], the condition that it is positive everywhere [see Eq. (8)], as well as [see Eq. (7)] for the value of the hole density at the electron position.

Thus the LDA is exact in the limit of slowly varying densities and should be accurate for densities which do not change appreciably over a Fermi or screening wavelength. However, most real systems show a considerable variation of the density over these lengths. The implicit assumptions in the application of this approximation to realistic systems are that either errors in local exchange and local correlation cancel, or that in those cases where correlation effects are small, local exchange is adequate.³ These expectations are weakly founded in light of the fact that in this approximation one employs in classically forbidden regions expressions derived from the uniform electron gas model. The expressions for the average exchange or screened-Coulomb exchange energies are derived using plane waves. For the average correlation energy one usually employs a parametrization¹¹ of results obtained from correlated wave function calculations.¹⁴ However, these wave functions are again approximations for the uniform gas and not for the inhomogeneous systems usually under consideration. For the various successes and failures of the LDA as applied to atoms, molecules, metals, semiconductors, metal and semiconductor surfaces, we refer the reader to the review articles of Refs. 3 and 15-17. More recently,¹⁸ the cancellation of errors in local exchange and correlation taken separately has been demonstrated for realistic metal surfaces where correlation energies are a substantial fraction¹⁸ (34-97%) of the exchange energy. In these calculations it is assumed that the "exact" surface exchange-correlation energies are those obtained via the wave-vector analysis scheme of Langreth and Perdew.^{19,20} In this scheme where the surface exchange-correlation energy is analyzed in terms of the wavelength of the fluctua-

tions which contribute to it, it has been shown that the LDA is exact at large wave vectors, but fails for small wave vectors for which an exact result exists. This may be understood on the basis of the fact that short-wavelength excitations must be insensitive to a variation in the density. We again refer the reader to the original literature for details of this momentum-space analysis.

The first insightful configuration-space analysis of the LDA was performed by Gunnarsson, Jonson, and Lundqvist.¹⁰ They explained the quantitative success of the LDA in atoms in terms of the spherical average of the exchange-correlation charge density. Additional physical arguments in support of the explanation are given in Ref. 15. However, since this real-space analysis and explanations bear directly on our present work, we discuss them here in some detail. In their work Gunnarsson *et al.* consider the exchange-only system,⁸ since in atoms exchange effects dominate those due to correlation. Furthermore, since within this approximation the exact orbitals are known, it is possible to make comparisons with the exact results. They first make comparisons of a cross section (along the axis of electron removal) through the Fermi hole of neon for two positions ($r=0.09$ and 0.4 a.u.) of the electron in the interior of the atom. The cross section through the LDA Fermi hole is obtained by employing the uniform electron gas pair-correlation function due to the Pauli exclusion principle. This is given as

$$\begin{aligned} g_x(k_F R) &= 1 - \frac{1}{2} j^2(k_F R), \quad \mathbf{R} = \mathbf{r} - \mathbf{r}' \\ j(y) &= 3j_1(y)/y, \\ g_x(0) &= \frac{1}{2}, \end{aligned} \quad (11)$$

where $j_1(y)$ is the first-order spherical Bessel function, and where in the LDA it is the local value of the Fermi momentum $k_F(\mathbf{r}) = [3\pi\rho(\mathbf{r})]^{1/3}$ which must be used. What they observed was that the cross section through the LDA hole bore little resemblance to the cross section through the exact hole. (Whereas the exact hole is localized²¹ about the nucleus for all electron positions, the LDA hole is extended, spherically symmetric and centered on the electron. Thus the further out an electron, the less the resemblance between the LDA and exact holes.)

The next step in their analysis was to note that the exchange energy density $\varepsilon_x(\mathbf{r})$, and hence the exchange energy $E_x[\rho]$ [see Eq. (1)], could also be expressed in terms of the spherical average $\rho_x(\mathbf{r}, R)$ of the average exchange charge density $\rho_x(\mathbf{r}, \mathbf{r}')$. Thus the exchange energy density (per electron) is

$$\varepsilon_x(\mathbf{r}) = \int_0^\infty dR R \rho_x(\mathbf{r}, R), \quad (12)$$

where

$$\rho_x(\mathbf{r}, R) = \frac{1}{2} \int d\Omega_{\mathbf{R}} \rho_x(\mathbf{r}, \mathbf{r} + \mathbf{R}), \quad \mathbf{R} = \mathbf{r} - \mathbf{r}' \quad (13)$$

is the spherically averaged exchange charge density. In terms of the spherically averaged hole, the charge-conservation sum rule of Eq. (4) is

$$4\pi \int_0^\infty dR R^2 \rho_x(\mathbf{r}, R) = 1. \quad (14)$$

For the same two electron positions considered before, they then made comparisons of the exact and LDA results for the quantity $R\rho_x(\mathbf{r}, R)$ [see Eq. (12)], and observed that there was a substantial cancellation of errors for large and intermediate distances from the electron. They attributed this cancellation to the fact that a similar cancellation *must* occur in the plots of the quantity $R^2\rho_x(\mathbf{r}, R)$ since both the exact and LDA holes satisfy the charge-conservation sum rule [see Eq. (14)]. Or equivalently, the argument¹⁵ is that exact cancellation in the $R^2\rho_x(\mathbf{r}, R)$ curves is only slightly affected by dividing by R . Thus it is the fact that the LDA satisfies the charge-conservation sum rule which is the significant factor underlying the success of the approximation. That the LDA hole is not localized about the nucleus was not considered significant. For completeness we note that the LDA exchange energies for H, He, Ne, Ar, and Kr are in error²² by -14.2% , -13.6% , -8.8% , -7.5% , and -5.4% , respectively.

Now the exchange energy arises due to the interaction between the electronic and exchange charge densities, *both* of which in atoms are concentrated within a region of approximately 1 a.u. of the nucleus. For most of this region the LDA hole is a poor approximation to the exact one. Thus the argument¹⁵ that due to the long-range nature of the Coulomb force, the interaction energy between two charge distributions is weakly dependent on the shape of the charge distributions and depends only on the total charge is inapplicable to this situation. Thus although it is possible to rewrite the expression for the exchange energy in terms of the spherically averaged Fermi hole, the exchange energy does in fact depend explicitly on the average exchange charge density. In those cases where the various charge densities *overlap substantially*, if an approximation does not give rise to an accurate representation of the average exchange charge density, the corresponding exchange energy will not be accurate.

A qualitative rationalization^{3,23} for the use of the LDA for exchange correlation in the Kohn-Sham equations that has been suggested is to think of the quantity $R(\mathbf{r})$, where

$$\frac{1}{R(\mathbf{r})} = - \int \frac{\rho_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad (15)$$

as an average range of the hole. The average range of the corresponding LDA hole is, of course, obtained by replacing $\rho_{xc}(\mathbf{r}, \mathbf{r}')$ in Eq. (15) by its LDA counterpart. The argument is that provided the range of the LDA and exact holes are similar, the corresponding energies will be too. (For two specific positions of a spin-up electron in the nitrogen atom at $r=0.13$ and 0.63 a.u., Gunnarsson²³ has shown that in the exchange-only approximation the range of the LDA hole closely approximates that of the exact hole.) Thus again the conclusion arrived at is that the details of the shape of the hole are not significant and that $R(\mathbf{r})$ is in general a fairly insensitive functional of the density $\rho(\mathbf{r})$. However, the quantity $1/R(\mathbf{r})$ of Eq. (15) is the exchange energy density at position \mathbf{r} . Now in order to determine the exchange energy one requires the exchange energy density at *all* points in space. Thus in all of the above analysis there is the implication that the

results obtained for the two electron positions considered are representative of all points within the atom; contributions to the energy from classically forbidden regions, whether they be in atoms or metallic surfaces, are in any event negligible.

Finally, we note the following facts which tend to weaken the contention of the lack of significance of the structure of the hole relative to its spherical average. When a self-interaction correction (SIC) within the LDA is included,¹¹ it is observed that for *both* electron positions in the case of the Ne atom, the SIC-LDA cross sections of the Fermi hole closely approximate the exact hole. However, although the corresponding SIC-LDA results for $R\rho_x(r,R)$ are also superior to the LDA when the electron is close to the nucleus at $r=0.09$ a.u., the results are substantially *inferior* to the LDA when the electron is further out at $r=0.4$ a.u. The self-interaction corrected exchange energies for the atoms H, He, Ne, Ar, and Kr are in error by 0%, 0%, 2.6%, 3.0%, and 3.0%, respectively. (The SIC-LDA hole¹¹ satisfies charge conservation, but for large distances from the nucleus it does not satisfy the requirement that it be positive everywhere.) Thus these facts would seem to indicate that it is the hole rather than its spherical average which is of greater significance. Of course, once again, this is a conclusion based on an analysis of only two points in space. But there is another important fact to be noted. In this exchange-only approximation, the highest occupied eigenenergy (which is the only physically meaningful eigenenergy of Kohn-Sham DFT as the chemical potential²⁴) as obtained within SIC-LDA is also vastly superior to that of the LDA value. In comparison to the Hartree-Fock result for the $2p$ eigenenergy which is -23.1 eV, the LDA and SIC-LDA values¹¹ are -12.1 and -22.0 eV, respectively. All the results discussed in this paragraph thus tend to the conclusion of greater significance of the Fermi hole, not only for the determination of the exchange-correlation energy but also for the ionization potential.

In order to better understand the LDA we perform in this paper a more detailed configuration-space analysis of the approximation for the inhomogeneous electron gas in the Ne atom and at metallic surfaces and surfaces in general. In particular we wish to resolve whether the condition of charge neutrality of the average exchange-correlation hole of an approximate energy functional is sufficient to lead to accurate results or whether in addition other physical requirements must be met. Recall that all the arguments in terms of the spherically averaged hole have charge conservation as the fundamental building block. We perform our calculations in the exchange-only approximation. We do this not only because exact results are available for comparison, but also because the behavior of the average exchange charge density is strikingly different in the two systems. As an electron is removed from an atom, its Fermi hole is localized about the nucleus, whereas as an electron is removed from within a metal to infinity outside, the Fermi hole expands and in the asymptotic limit is spread over the entire volume of the crystal.²⁵⁻²⁷ Thus it would be possible to determine how important it is for an approximate en-

ergy functional which satisfies charge conservation to also reproduce the correct physics of the structure of the Fermi hole as a function of the electron position.

II. RESULTS AND ANALYSIS

A. Neon atom

For our analysis of the LDA in the Ne atom we employ the analytical Hartree-Fock wave functions due to Clementi and Roetti.^{28,29} In Fig. 1 we plot the electronic density $\rho(r)$ due to these wave functions, and in Fig. 2 the radial probability density. We consider four representative electron positions which we treat in pairs. The first pair corresponds to the two maxima of the radial probability density at $r=0.104$ and 0.651 a.u. The second pair constitutes the point at the intershell minimum of the radial probability density at $r=0.307$ a.u. and to a point in the classically forbidden region at $r=2.000$ a.u. All these positions are indicated by arrows in Figs. 1 and 2.

In Figs. 3(a) and 3(b) we plot the exact and LDA spherically averaged exchange charge densities for the first pair of electron positions. Observe that for both these posi-

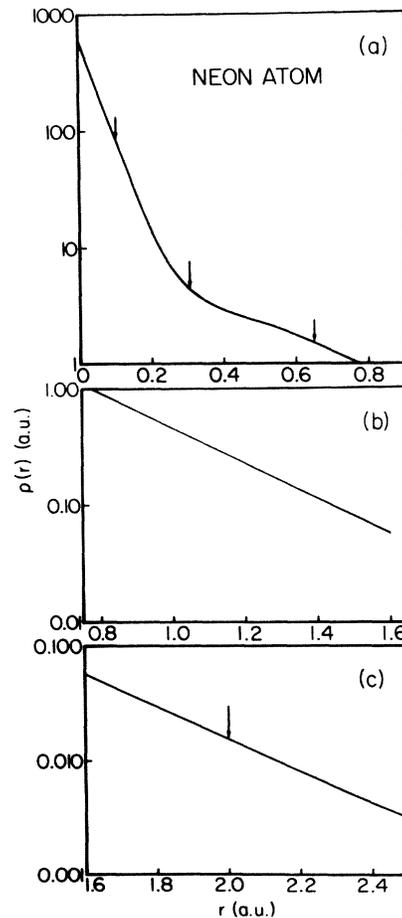


FIG. 1. The electronic density $\rho(r)$ of the Ne atom within Hartree-Fock theory. The wave functions used are those due to Clementi and Roetti, Ref. 28. The arrows represent the four electron positions considered in the text.

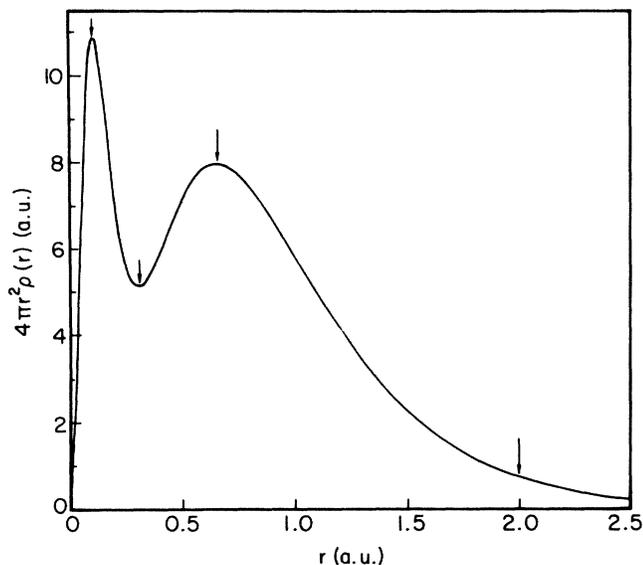


FIG. 2. The radial probability density of the Ne atom within Hartree-Fock theory obtained using the Clementi-Roetti wave functions of Ref. 28. The arrows at the maxima, the intershell, and classically forbidden regions correspond to the four electron positions considered in the text.

tions of high-radial probability density, the LDA is a good approximation. However, it more closely approximates the exact result at the second maximum. This is because although the electronic density corresponding to the electron position at the first maximum is higher than that at the second maximum, the gradient of the density

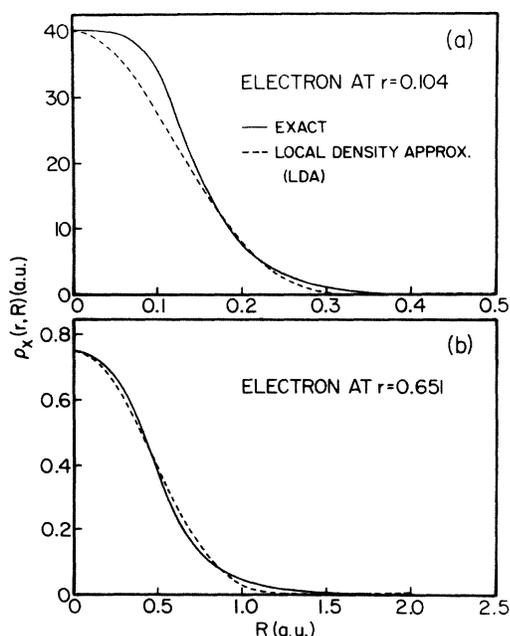


FIG. 3. The exact and local-density approximation spherically averaged exchange charge densities $\rho_x(r,R)$ for electron positions r at the maxima of the K and L shells of the Ne atom as a function of the distance R from the electron.

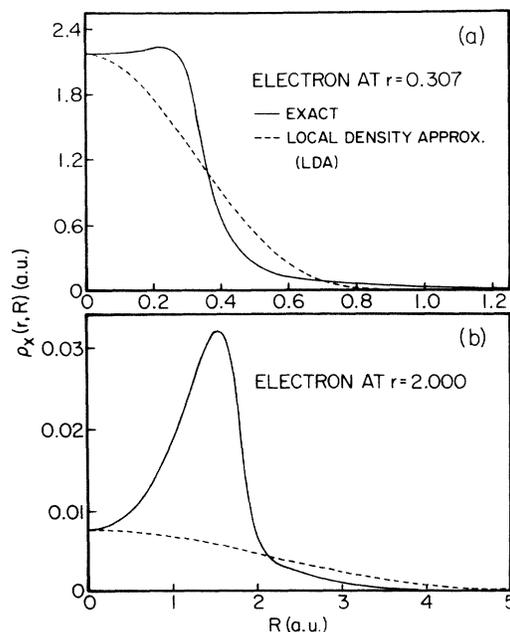


FIG. 4. The exact and local-density approximation spherically averaged exchange charge densities $\rho_x(r,R)$ for electron positions r at the intershell and at a point in the classically forbidden region of the Ne atom as a function of the distance R from the electron.

at the former point is far greater. The electronic density at $r = 0.651$ a.u. (see Fig. 1) more closely approximates a uniform electron gas than it does at $r = 0.104$ a.u. This occurs because in the region of the second maximum of the radial probability density there are eight electrons in a large volume (see Fig. 2), whereas in the region of the first maximum there are two electrons in a very small volume.

In Figs. 4(a) and 4(b) we plot the spherically averaged exchange charge densities for the electron positions corresponding to the intershell and classically forbidden regions. Note the structure developing in the exact curve of Fig. 4(a) and its prominence in Fig. 4(b). The corresponding LDA curves are poor approximations in these regions of low-radial probability density, though it is far worse in the classically forbidden region. Furthermore, the LDA possesses none of the structure of the exact curves.

On the basis of the analysis of Figs. 3 and 4 we conclude that the LDA is accurate in the shell regions of an atom; the wider a shell (with more electrons) the better the approximation. The LDA fails in the intershell and classically forbidden regions.

The next question which arises is from what regions of space does the -8.8% error in the LDA exchange energy come from? In order to answer this question we have plotted in Figs. 5 and 6 the quantity $R\rho_x(r,R)$ (for the same two pairs of electron positions) since the area under these curves gives the energy density at these points. A study of these graphs indicates that comments with regard to the accuracy of the LDA similar to those made in connection with Figs. 3 and 4 can again be made. How-

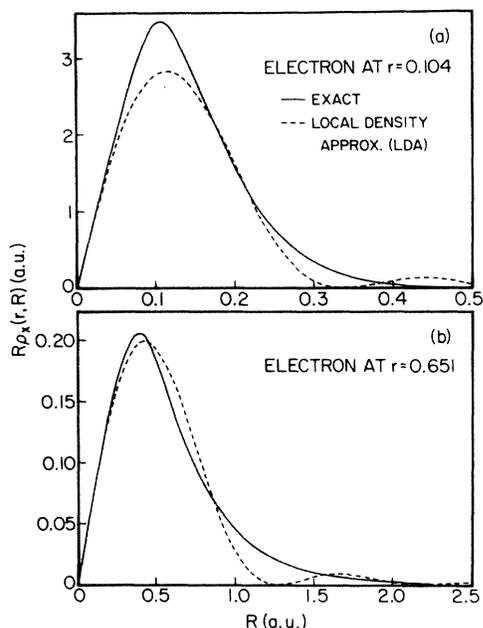


FIG. 5. The exact and local-density approximation integrands $R\rho_x(\mathbf{r},R)$ of the exchange energy density of Eq. (12), where $\rho_x(\mathbf{r},R)$ is the spherically averaged exchange charge density, as a function of the distance R from the electron for electron positions r at the maxima of the K and L shells of the Ne atom.

ever, what should be noted is that although the LDA in Fig. 5(b) is superior to that in Fig. 5(a), the former graphs are an order of magnitude smaller. At the intershell point Fig. 6(a), where the LDA is poor, the order of magnitude of the curves is the same as those of Fig. 5(b). Finally, in the classically forbidden region Fig. 6(b) where the LDA fails, the results are a further order of magnitude smaller. In Table I we quote the exact and LDA values of the integral for the energy density

$$4\pi \int_0^\infty dR R\rho_x(\mathbf{r},R)$$

and the percent LDA error for the four electron positions considered. For determination of the energy, the more significant quantity, however, is the product

$$\rho(\mathbf{r})4\pi \int_0^\infty dR R\rho_x(\mathbf{r},R),$$

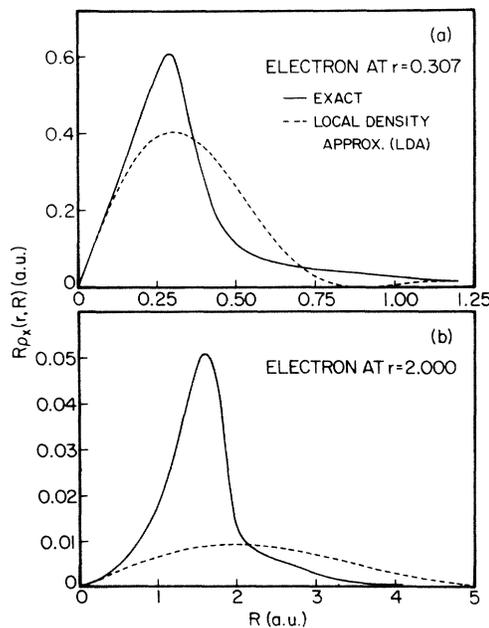


FIG. 6. The same as in Fig. 5 except that these graphs have been plotted for electron positions at the intershell and at a point in the classically forbidden region of the Ne atom.

and these values are also given in the table. It is evident from the table that the principal region where the error in the LDA exchange energy arises is the deep interior of the atom. This occurs both from the high-density K shell region as well as the intershell region. Not only is the value of the integral large in this region, but when multiplied by the density, the resulting product is very large. In the L shell region, the LDA error is the smallest as expected, but the contribution to the energy from this region is also small. Finally, even though the energy density in the classically forbidden region at $r=2.000$ is larger than the L shell value at $r=0.651$, the contribution to the energy is negligible from this region. Observe also that for all four electron positions considered, the LDA exchange energy density consistently underestimates the exact results. All these errors in the same direction are thus additive in the determination of the energy.

Thus in addition to the conclusions arrived at above,

TABLE I. Ne atom exact and local-density approximation (LDA) values for the energy-density integral $4\pi \int_0^\infty R\rho_x(\mathbf{r},R)dR$ and the quantity $\rho(\mathbf{r})4\pi \int_0^\infty R\rho_x(\mathbf{r},R)dR$ for the four different electron positions considered in the text. Here $\rho(\mathbf{r})$ is the electronic density and $\rho_x(\mathbf{r},R)$ the spherically averaged exchange charge density.

Electron position r (a.u.)	$4\pi \int_0^\infty R\rho_x(\mathbf{r},R)dR$		$\rho(\mathbf{r})4\pi \int_0^\infty R\rho_x(\mathbf{r},R)dR$		% LDA error
	Exact	LDA	Exact	LDA	
0.104	7.065	6.389	566.8	512.5	-9.6
0.307	2.542	2.414	11.06	10.51	-5.2
0.651	0.1740	0.1694	0.2607	0.2537	-2.9
2.000	0.6288	0.3777	0.009692	0.005821	-39.9

we note that although the LDA graphs for both the spherically averaged hole $\rho_x(r, R)$ and the quality $R\rho_x(r, R)$ look good for electron positions near the nucleus [Figs. 3(a) and 5(a)], this is the region from which the principal contributions to the exchange energy arise. Consequently, for the LDA or any approximate energy functional to give accurate results for the exchange energy, it must reproduce very accurately the spherically averaged exchange charge density in the deep interior of the atom. Even small differences in this region can lead to large errors in the energy. This conclusion implies that for electron positions close to the nucleus in particular and even in the first intershell region, if the average exchange charge density were obtained accurately, the spherical average would be accurate. A study of the one cross section through the LDA Fermi hole given in the work of Gunnarsson *et al.*^{10,23} shows the hole not to be very good.

Finally, we also conclude from the above analysis that although the charge-conservation sum rule of Eq. (4) must necessarily be satisfied by an approximate energy functional, it is not a sufficient condition for the accurate estimation of energies or eigenenergies.

B. Surfaces

We perform our analysis of the LDA at solid surfaces in the jellium model approximation of a crystal. The wave functions we employ are those generated by the linear-potential model³⁰ of a surface. With this model it is possible to consider a wide range of electronic density profiles existing at surfaces ranging from very rapidly to very slowly varying and including those typically existing at metallic surfaces. The behavior of the exact Fermi hole as an electron is removed from within the crystal to infinity outside is described in Refs. 25–27, and we refer the reader to Ref. 26 for expressions pertinent to the surface physics problem to the extent discussed here as well as for notational details. We note, however, that the electron position is given by the coordinate $y = \bar{k}_F x$ and that of the hole by $y' = \bar{k}_F x'$. (Here \bar{k}_F is the Fermi momentum in the bulk, and x the electron coordinate perpendicular to the surface.) The parameter y_F controls the profile of the density at the surface. All properties in the linear-potential model may be expressed in terms of universal functions of this parameter. As a consequence, the graphs of this subsection are presented in terms of the corresponding universal functions. In these figures the vacuum region is to the right of the jellium edge. As in Ref. 26 we consider the profiles corresponding to $y_F = 0$, the infinite barrier model; $y_F = 3$, a typical metallic density profile;³¹ and $y_F = 8$, a very slowly varying profile. The LDA surface exchange energies for these values of y_F are in error³² by 55%, 17%, and 4%, respectively.

In order to determine whether the various rationales for the accuracy of the LDA described in the Introduction are applicable to the surface physics problem, we begin our analysis by first considering the spherically averaged exchange charge densities. (For the infinite barrier model wave functions an analytical expression for the spherically averaged Fermi hole is given in Ref. 26.) In

Fig. 7 we compare the exact and LDA holes for four representative electron positions. The graphs are plotted as a function of $\mathcal{R} = \bar{k}_F R$, where R is the distance from the electron. (The infinite barrier is at $y = 0$, and the jellium edge at $y = -3\pi/8$.) Inside the solid at $y = -4.0$ [Fig. 7(a)] where the Fermi hole is spherically symmetric,

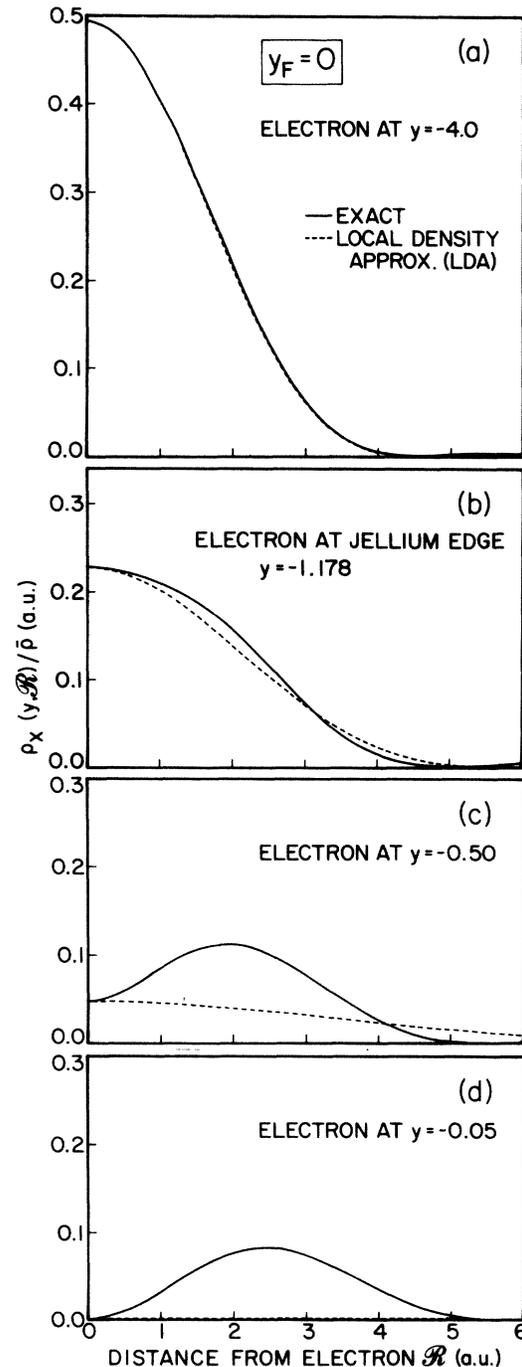


FIG. 7. Variation of the function $\rho_x(y, \mathcal{R})/\bar{\rho}$ for the infinite barrier model ($y_F = 0$), where $\rho_x(y, \mathcal{R})$ is the spherically averaged exchange charge density, and the corresponding function in the local-density approximation vs the distance from the electron for different positions y of the electron.

it is difficult to distinguish between the LDA and exact results. This, of course, must be the case. Even when the electron is at the surface [Fig. 7(b)] where the gradients of the density are large, the LDA is still very accurate. However, as the electron is pulled out beyond the surface to $y = -0.50$ [Fig. 7(c)], the Fermi hole is no longer spherically symmetric, and the LDA hole deviates significantly from the exact results, possessing none of its structure. In the low-electronic density region at $y = -0.05$ there is, as expected, no similarity at all between the LDA and exact holes. If one were to consider only the two electron positions corresponding to panels Figs. 7(a) and 7(b), one might conclude that the LDA was very accurate. But recall that the LDA surface exchange energy is in error by 55% in this case. Consequently, it is evident from Figs. 7(c) and 7(d) that a substantial fraction of the error arises from the region outside the solid. (Note that in Fig. 7 the ordinate scale is the same in all four panels.) This is also the region where the shape of the LDA spherically averaged hole deviates substantially from the exact hole. Thus, once again, we conclude that for an approximate exchange-correlation energy functional to be accurate, the hole to which it gives rise must be accurate for all electron positions.

The obvious next question is how well does the actual LDA Fermi hole compare with exact hole? However, prior to making this comparison we note the striking similarities between the results for the spherically averaged Fermi holes in the few-electron-atomic system (Figs. 3 and 4) and the many-electron-surface system (Fig. 7). The graphs of Fig. 3 corresponding to the regions of high-radial probability and electronic density in the Ne atom are similar to those of Figs. 7(a) and 7(b) which also correspond to regions of high-probability and electronic density. The development of structure in the graphs of Fig. 4 in the intershell and classically forbidden regions is also strikingly similar to the structure exhibited in Figs. 7(c) and 7(d) in the regions of low electronic density at the surface. The implications of the similarities of this property in the quite different nonuniform systems discussed is that approximate exchange and correlation energy functionals must be truly universal in the spirit of Hohenberg, Kohn, and Sham. The concept of a different functional for each different kind of inhomogeneity violates the fundamental density-functional theory tenet of universality.

Due to the symmetry of the surface physics problem, we make comparisons in this paper for the *planar-averaged* Fermi holes²⁵⁻²⁷ as a function of electron position. (Note, however, that although in the jellium model approximation the electronic density in the planes parallel to the surface is uniform, this is not the case²⁷ for the average exchange charge density.) In Fig. 8 we compare the LDA and exact holes for the rapidly varying density profile of the infinite barrier model. (See Ref. 26 for analytical expressions for the exact planar-averaged hole for these model potential wave functions and for the plane waves of a uniform electron gas, the latter being required for the LDA calculations.) Inside the metal [Fig. 8(a)], the LDA as expected closely approximates the exact result. However, even at the jellium edge [Fig. 8(b)],

the difference between the two is quite significant. [Note that the information of this rather substantial difference is completely lost in the process of spherically averaging. See Fig. 7(b).] As the electron is pulled out of the surface [Fig. 8(c)], all similarity ceases. (In this model potential, although the wave functions vanish at $y=0$, the LDA hole extends into the region $y > 0$, since it is symmetric about the electron position and must also satisfy the charge-conservation sum rule.) The behavior of the LDA hole for a typical metallic density profile as the electron is pulled from inside to outside the metal, is very similar [see Figs. 9(a)–9(c)]. For a very slowly varying profile

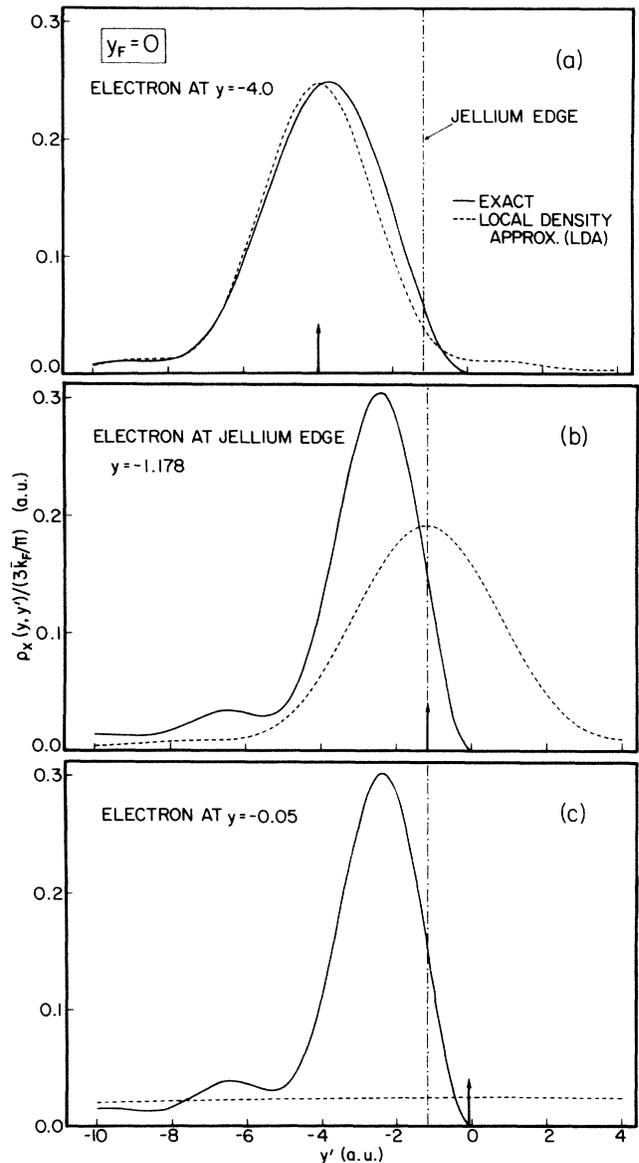


FIG. 8. Variation of the universal function $\rho_x(y, y') / (3\bar{k}_F / \pi)$ for the infinite barrier model $y_F = 0$, where $\rho_x(y, y')$ is the planar-averaged exchange charge density, and the corresponding function in the local-density approximation vs y' for different positions y of the electron.

(Fig. 10), note that as expected the LDA hole is accurate even for electron positions outside the surface [Fig. 10(b)]. It begins to fail only far out in the classically forbidden region [Fig. 10(c)]. Observe also [Figs. 9(c) and 10(c)] that the structure the exact hole develops within the metal when the electron is in the classically forbidden region is absent in the LDA.

However, what is more significant is that the LDA does not reproduce an important feature of the physics of this problem: As an electron is removed from within the metal, the exchange charge remains behind and begins to spread throughout the semi-infinite half-space of the crystal.²⁵⁻²⁷ Even for electron positions near and outside the surface well over 90% of the exchange charge lies inside the metal.²⁵⁻²⁷ Thus there is substantial overlap between the electronic density and the Fermi hole, their Coulomb

interaction giving rise to the surface exchange energy. In the LDA for *all* electron positions outside the surface, over 50% of the exchange charge must be outside the metal since the LDA hole is symmetric about the electron. The incorrect overlap between the LDA hole and electronic density at and outside the surface is what gives rise to the 17% error in the surface energy for the metallic density case (Fig. 9). For very slowly varying densities (Fig. 10), the LDA hole is in error only in the region where the electronic density is negligible, and consequently the error in the surface energy is small (4%). Thus we see that although the LDA hole satisfies charge conservation, its description of the hole for metallic surfaces is inaccurate. Again, as in the atomic case, we conclude that charge conservation is necessary but not sufficient. An approximate functional must correctly

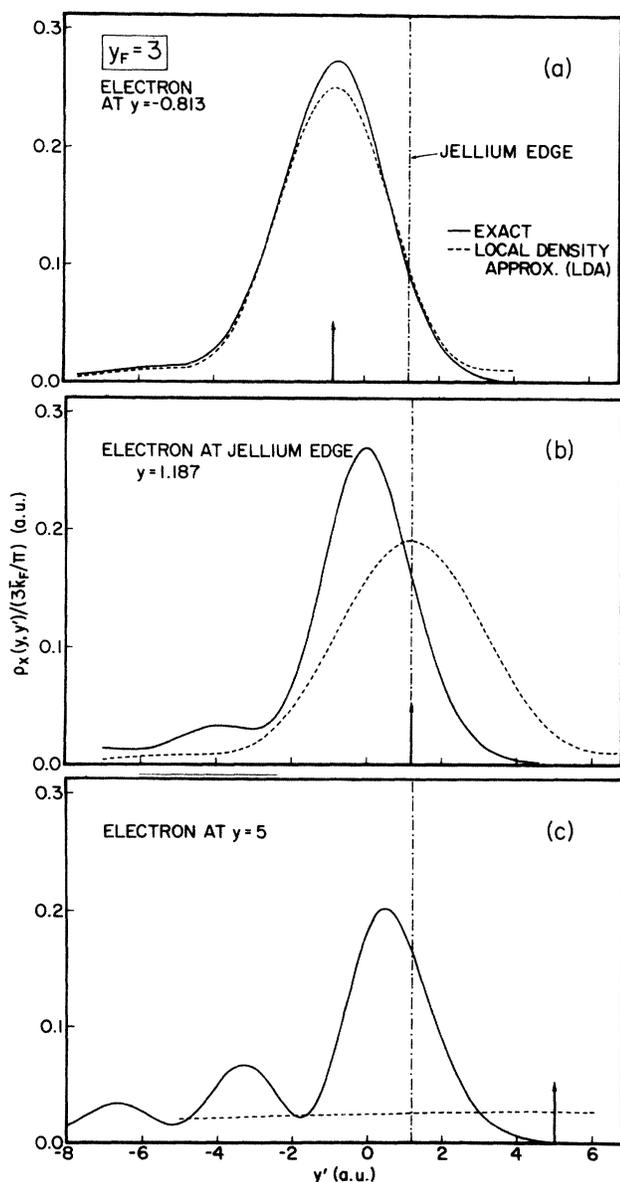


FIG. 9. Same as in Fig. 8 except that these graphs are drawn for a typical metallic surface electronic density profile ($y_F = 3$).

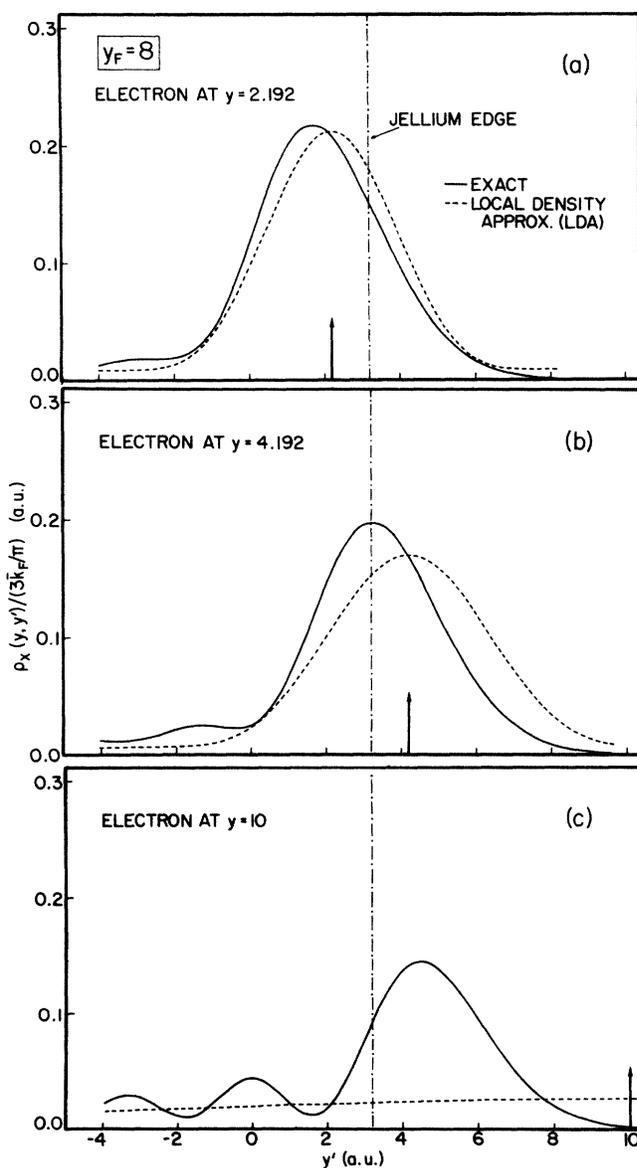


FIG. 10. Same as in Fig. 8 except that these graphs are drawn for a very slowly varying electronic density profile at a surface ($y_F = 8$).

reproduce the structure of the Fermi hole.

In the atomic case, it is natural to write the exchange energy in terms of the spherically averaged exchange charge density as in Eq. (12). Since in the surface physics problem, the inhomogeneity in the electronic density is only in the direction perpendicular to the surface, we write the exchange energy density in terms of the quantity $\Gamma_x(x, x')$ as

$$\epsilon_x = \frac{1}{2} \int_{-\infty}^{\infty} dx' \Gamma_x(x, x'), \quad (16)$$

where

$$\Gamma_x(x, x') = \int d\mathbf{x}_{\parallel} \int d\mathbf{x}'_{\parallel} \frac{\rho_x(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (17)$$

$$\frac{\Gamma_x(y, y')}{3\bar{k}_F^2/\pi} = \frac{1}{f(y)} \frac{2}{\pi} \int_0^1 dq \int_0^1 dq' \phi_{qq'}(y, y') \int_0^2 dp \mathcal{H}(p, q, q') e^{-p|y-y'|}, \quad (19)$$

where

$$\mathcal{H}(p, q, q') = \begin{cases} \pi(1-q^2) - 2 \left[(1-q'^2) \sin^{-1} \frac{\xi}{(1-q'^2)^{1/2}} + \xi(1-q'^2 - \xi^2)^{1/2} \right] & \text{for } \xi^2 < 1 - q'^2 \\ \pi(q'^2 - q^2) & \text{for } \xi^2 > 1 - q'^2 \text{ and } \xi > 0 \\ \pi[(1-q'^2) + (1-q^2)] & \text{for } \xi^2 > 1 - q'^2 \text{ and } \xi < 0 \end{cases}$$

$$\xi = \frac{1}{2p}(p^2 + q^2 - q'^2), \quad \phi_{qq'}(y, y') = \phi_q^*(y) \phi_q^*(y') \phi_q(y') \phi_q(y),$$

$$f(y) = \int_0^1 dq (1 - q^2) |\phi_q(y)|^2,$$

and where $\phi_q(y)$ is the component of the wave function in the direction perpendicular to the surface. The expression Eq. (19) is general in that it has been written in terms of arbitrary wave functions $\phi_q(y)$ which may depend upon various parameters. For the linear-potential model²⁶ the wave function depends upon the field strength parameter y_F , and consequently Eq. (19) is a universal function of this parameter. The equation for Γ_x can be easily derived by following the Appendix of Ref. 32.

A comparison between the LDA and exact results for Γ_x in the infinite barrier approximation is made in Fig. 11. The trends are similar to those discussed for the hole. In the interior [Fig. 11(a)] the LDA is accurate but as the electron approaches and passes through the surface its deviation from the exact results becomes more pronounced. The function Γ_x in the LDA is symmetric about the electron position and consequently extends into the forbidden region $y > 0$. The exact function Γ_x , on the other hand, tends to remain principally in the crystal. For the more realistic metallic density profile case (Fig. 12), at the jellium edge [Fig. 12(b)] the maxima of the two functions differ by a factor of 2. Even just outside the surface [Fig. 12(c)], the LDA does not resemble at all the exact curve, the maxima differing by an order of magnitude. [Note that the electron position in Fig. 12(c) is closer to the surface than in Fig. 9(c) for the hole.] Similar remarks can be made about the slowly varying electronic density profile case shown in Fig. 13. Since the

is the planar average of $[\rho_x(\mathbf{r}, \mathbf{r}')/|\mathbf{r} - \mathbf{r}'|]$. The exchange energy may then be written as

$$E_x[\rho] = \int_{-\infty}^{\infty} dx \rho(x) \epsilon_x(x). \quad (18)$$

As such we may think of $\Gamma_x(x, x')$ for the surface inhomogeneity as being the equivalent, in a sense, of R times the spherically averaged hole for atoms. Consequently, we now make comparisons between the LDA and exact results for $\Gamma_x(x, x')$. In terms of the variables $y = \bar{k}_F x$, $y' = \bar{k}_F x'$, $q = k/\bar{k}_F$, $q' = k'/\bar{k}_F$, and $p = P/\bar{k}_F$, where $\mathbf{P} = \mathbf{k}_{\parallel} - \mathbf{k}'_{\parallel}$, and where k, k_{\parallel} are components of the electron momenta perpendicular and parallel to the surface, we may write the universal quantity $\Gamma_x(y, y')/(3\bar{k}_F^2/\pi)$ per unit surface area as

area under the Γ_x curves is the energy density at that point, we see that the LDA energy density is in error not only at and about the surface but also beyond it to some extent. These differences will increase the further out the electron. However, the differences become of little significance only far out in the classically forbidden region since there the electronic density is negligible [see Eq. (18)]. We see once again how important it is for an approximate energy functional to reproduce accurately the behavior of the Fermi hole. Only then will the function Γ_x and consequently the significant quantity, the energy density, be obtained correctly.

III. CONCLUSIONS AND FUTURE WORK

In this paper we have performed a real-space analysis of the local-density approximation of density-functional theory. The analysis, performed for the Ne atom and jellium surface, is in terms of the Fermi hole along lines similar to those of Gunnarsson *et al.*^{5,10} According to these authors, the principal reason for the quantitative success of this approximation is that the corresponding Fermi hole satisfies the charge-conservation sum rule. Furthermore, the actual shape of the Fermi hole is considered insignificant since charge conservation ensures to a great extent that the LDA spherically averaged Fermi hole is relatively accurate. Undoubtedly, if for all electron positions the spherically averaged hole is accurate,

the energy will be too. However, the mere satisfaction of charge neutrality does not guarantee this to be the case. Our analysis indicates that a considerable amount of information is lost by the process of spherically averaging, and that although charge conservation is a necessary condition, it is not a sufficient criterion. An additional condition of prime importance is that an approximate energy functional must accurately reproduce the behavior of the Fermi hole. The structure of the Fermi hole as a function of electron position describes a fundamental aspect of the physics of the problem. As such, it is imperative that approximate functionals not only satisfy sum rules such as

charge conservation, but that they also correctly reproduce this intrinsic property of the nonuniform electron gas. It is only then that one could apply these functionals with confidence to systems in which the exact results are unknown because then both the ground-state energy as well as the ionization potential will be obtained accurately. Furthermore, by demonstrating the striking similarity in the structure for the spherically averaged Fermi hole in the few-electron-atomic and many-electron-surface nonuniform systems, we reemphasize that it is also imperative for this functional to be universal in the spirit of Hohenberg, Kohn, and Sham.

Our study has shown that for atoms the LDA is accurate for the wider shells which have many electrons, but that it fails in the classically forbidden and intershell re-

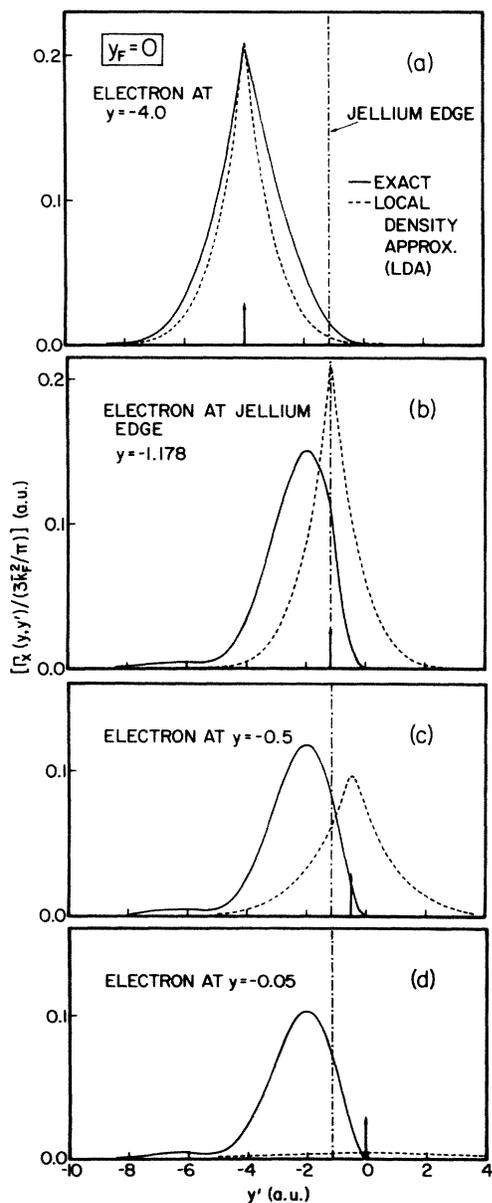


FIG. 11. Variation of the universal function $\Gamma_x(y, y') / (3\bar{k}_F^2/\pi)$ for the infinite barrier model ($y_F=0$) and the corresponding function in the local-density approximation vs y' for different positions y of the electron. See text [Eqs. (17) and (19)] for the definition of the function $\Gamma_x(y, y')$.

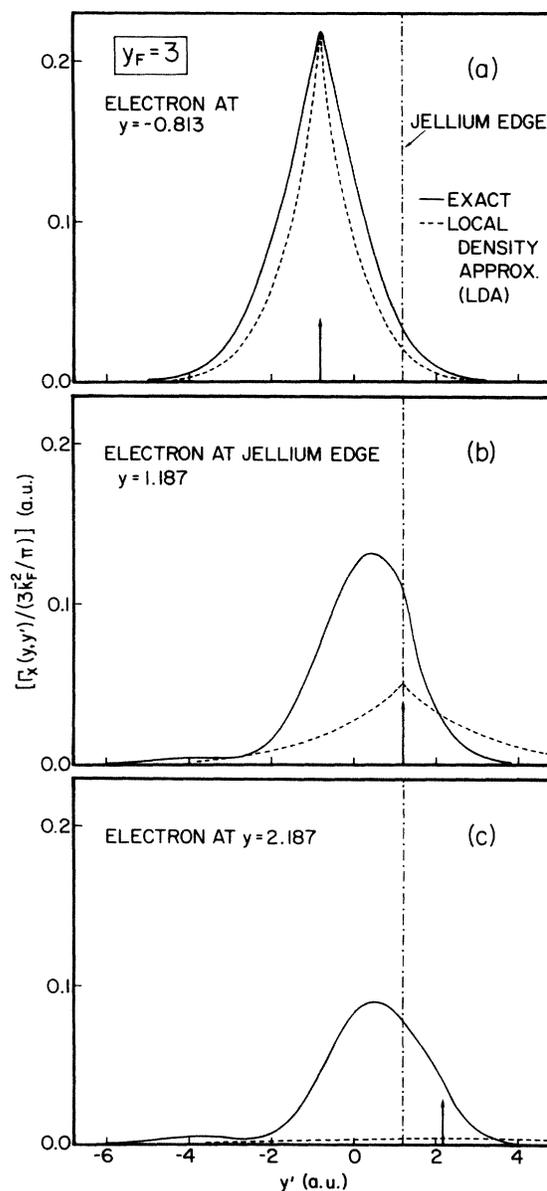


FIG. 12. Same as in Fig. 11 except that these graphs are drawn for a typical metallic surface electronic density profile ($y_F=3$).

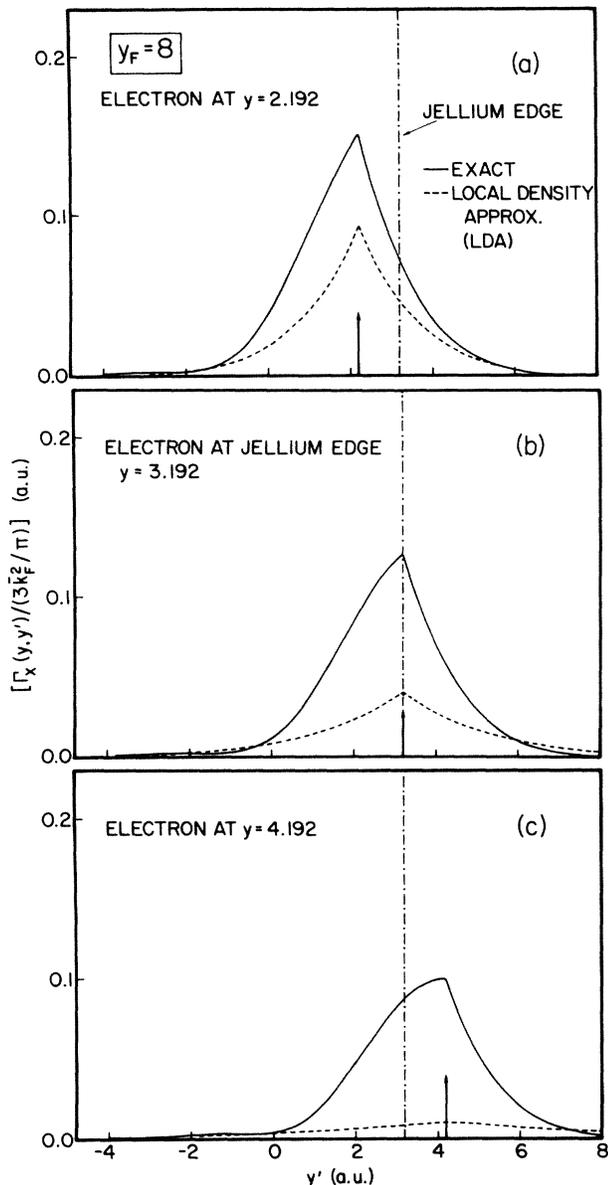


FIG. 13. Same as in Fig. 11 except that these graphs are drawn for a very slowly varying electronic density profile at a surface ($y_F = 8$).

gions. In the deep interior such as in the K shell region it is also fairly accurate. But this is the region where the principal contribution to the exchange energy arises; it is the differences here that cause the error in the LDA result for the energy. We know from the one cross section studied that the LDA Fermi hole is a poor approximation to the exact hole and that it becomes worse as an electron is pulled out from an atom. However, it best approximates the exact hole only when the electron is in the deep interior. Now the exchange energy is the Coulomb interaction energy between the electronic charge density and the Fermi hole. Thus in the deep interior the three-dimensional overlap between the LDA hole and the electronic density is obviously substantial enough for the LDA to lead to a less than 15% error in the exchange en-

ergy of atoms. On the other hand, the highest occupied eigenenergy depends upon a potential which is derived from the average exchange charge density in the region at and outside the corresponding atomic shell. Outside the shell the LDA hole is very poor (see Table I), and as a consequence the LDA value of the highest occupied level for Ne is in error¹¹ by 48%. The improvement of the hole via the self-interaction correction scheme¹¹ reduces this error to 4.8%.

For the nonuniform system at jellium metal surfaces our study has shown that the LDA hole is accurate inside the crystal as well as up to near the surface when approached from the interior. However, whereas for electron positions at and outside the surface, most of the exchange and electronic charge lie inside the metal, over half of the LDA Fermi hole lies outside. Significant contributions to the surface energy also come from the region at and outside the surface. Thus we understand why for metallic surfaces the LDA surface exchange energy is in error¹⁸ by 15–46%. The LDA work functions³³ in the exchange-only case, on the other hand, differ from the exact results by less than two-tenths of an electron volt. This difference is small because the contributions to the chemical potential due to exchange effects (which are substantial) are fixed at the bulk value; it is only the shape of the effective potential at the surface which is different for different exchange charge densities. The differences in effective potential lead to differences in the surface electrostatic dipole barrier, and it is only this component of the work function which changes.

The significance of the additional requirement that an approximate functional lead to an accurate Fermi hole as a function of the electron position is evident from the present work and the discussion above. It is also clear that a considerable amount of additional work needs to be done before the LDA is fully understood. For one, it is important to make three-dimensional comparisons between the exact and approximate holes. For example, it is important to learn how the LDA and exact holes compare in planes perpendicular to that of electron removal both in atoms as well as at metallic surfaces. Comparisons between the corresponding exchange charge densities and the respective potentials would also lead to further insights. In recent work³⁴ on the gradient expansion approximation (GEA) for the exchange energy, Perdew has imposed real-space cutoffs on the corresponding hole to ensure charge neutrality and positiveness—the generalized gradient approximation. (The GEA hole satisfies neither of these conditions.) For atoms the exchange energies are within 1% of the Hartree-Fock value, and for the infinite barrier model of a surface the error in the surface exchange energy is –44%, which is a substantial improvement over the –155% error³³ in the GEA result. It would be interesting to determine whether this improved functional, which satisfies exactly the same conditions as the LDA, leads to improved Fermi holes. Perdew³⁴ has, however, indicated that the truncated hole in an atom always encompasses the nucleus and that its center of gravity is shifted towards the nucleus.

In order to understand the LDA for exchange correlation or correlation separately, comparisons between the

exact and LDA Coulomb holes must be made. When Coulomb correlations are included in the uniform electron gas, the electron digs a deeper hole about itself, i.e., the probability of finding two electrons close to each other is further reduced. The pair-correlation function for exchange correlation $g_{xc}(\vec{k}_F R)$ must now have a value at the electron position of between 0 and $\frac{1}{2}$. As a consequence, the spatial extent of the pair-correlation function is reduced. It is thus assumed¹⁵ that on introducing Coulomb correlations the LDA exchange-correlation hole becomes more localized about the electron position. Does this localization occur, and if so, does it make the hole superior in those regions where the contributions to the correlation energy are a maximum? What is the relationship between the localization of the exchange-correlation hole in the outer shell and classically forbidden regions and the highest occupied eigenenergy? How does the fact that in the LDA both the exchange and correlation holes are centered about the electron position, and now presumably more localized about it, explain the

cancellation¹⁸ of energy errors in local exchange and correlation at surfaces? Calculations to answer such questions must be carried out if we are to better understand the LDA and thereby to improve upon it meaningfully. As for the exact results, we know from the literature^{5,35} that the size of the Coulomb hole for atoms such as He and Be is similar to that of the electronic charge distribution. For surfaces, it is only recently that the three-dimensional structure of the exact Fermi hole has been studied.²⁷ The structure of the exact Coulomb hole at a metal surface has yet to be determined.³⁶ This work is in progress.³⁷

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