PHYSICAL REVIEW A VOLUME 33, NUMBER 3 MARCH 1986

Test of density-functional approximations in an exactly soluble model

Pinchus M. Laufer[*] and J. B. Krieger
Physics Department, Brooklyn College, City University of New York, Brooklyn, New York 11210
(Received 3 October 1985)

We consider an exactly soluble model consisting of two electrons attracted to a common center by harmonic-oscillator forces with mutual Coulomb repulsion between the electrons. The exact wave function and energy for the singlet ground state is obtained by separating the Schrödinger equation in center-of-mass and relative coordinates and numerically integrating the relative-coordinate eigenvalue equation. The exact Kohn-Sham (KS) orbital for the two equivalent electrons with opposite spins is constructed from the exact density, and the Kohn-Sham equation is inverted, yielding the exact exchange-correlation potential as a function of position. The exact correlation potential, as a function of position, is then obtained by subtracting the exact exchange potential from the exact exchange-correlation potential. The exact ground-state energy, exchange potential, correlation potential, KS single-particle energy eigenvalues ϵ_{KS}, exchange energy, and correlation energy are compared to the results given by density-functional theory employing the local-density approximation (LDA) plus correction terms and the exact KS orbitals for values of the harmonic-oscillator spring constant that vary over 4 orders of magnitude. We find that although total energies are accurately given by LDA plus correction terms, the values of ϵ_{KS} are significantly in error. We show that this is mainly due to errors in the exchange potential. In addition we show analytically that in a singlet ground state of a two-electron system, the exact expectation value of the exchange potential equals the exact exchange energy, whereas the LDA expectation value of the exchange potential is only $\frac{2}{3}$ the LDA exchange energy. Furthermore, we show that although the gradient expansion approximations for the exchange energy are significant improvements over the LDA, neither of these approximations significantly decreases the error in the LDA for the expectation value of the exchange potential. Both the correlation energy and the expectation value of the correlation potential in the LDA plus corrections are significantly in error when compared with the results of the exact calculation, the most accurate results being given by the LDA with self-interaction correction.

I. INTRODUCTION

In the Hohenberg-Kohn-Sham[1,2] (HKS) theory of the inhomogeneous electron gas, the exact ground-state energy of the interacting system is calculated from single-particle orbitals describing noninteracting electrons moving in a local effective potential, i.e.,

$$-\tfrac{1}{2}\nabla^2\phi_i(\mathbf{r})+\{v_{\mathrm{ext}}(\mathbf{r})+v_H[n(\mathbf{r})]+v_{\mathrm{xc}}[n(\mathbf{r})]\}\phi_i(\mathbf{r})=\epsilon_i\phi_i(\mathbf{r}) \tag{1}$$

with

$$n(\mathbf{r})=\sum_{i=1}^{N}|\phi_i(\mathbf{r})|^2 ,$$

where the electron density $n(\mathbf{r})$, calculated in this fashion is identically equal to the electron density of the interacting N electron system.

Here $v_{\mathrm{ext}}(\mathbf{r})$ is the external potential present in the interacting problem, $v_H[n(\mathbf{r})]$ is the Hartree potential and $v_{\mathrm{xc}}[n(\mathbf{r})]=\delta E_{\mathrm{xc}}[n(\mathbf{r})]/\delta n$ is the exchange-correlation potential which is the functional derivative of the exchange-correlation energy and is a universal functional of $n(\mathbf{r})$.[2] The total energy of the system can be written[2]

$$E=\sum_{i=1}^{N}\epsilon_i+E_{\mathrm{xc}}[n(\mathbf{r})]-\int v_{\mathrm{xc}}n(\mathbf{r})d\mathbf{r}-\tfrac{1}{2}\int\int\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}' . \tag{2}$$

It is clear that knowledge of this universal functional E_{xc}, and consequently its functional derivative v_{xc}, is of primary concern. However, the theory merely provides for the existence of such a functional but does not prescribe for its construction. Therefore there has been much effort devoted toward developing accurate functionals, often incorporating the result of the uniform electron gas as a starting point.

In light of the above we note that if we could solve a problem for the wave function of the interacting system which included the electron-electron interaction exactly, we could then obtain both the electron density and the ground-state energy as well. Furthermore, because of the simple relationship between $n(\mathbf{r})$ and the single-particle wave function (ϕ_i) of the equivalent Kohn-Sham (KS) Schrödinger equation, if we were dealing with a system of only two particles of opposite spin, we could then obtain the ϕ_i. This could then be used, by inverting Eq. (1), to find the exchange correlation functional v_{xc} as a function of $\mathbf{r}$:

$$v_{\mathrm{xc}}(\mathbf{r})=\epsilon_i-\Phi(\mathbf{r})+\tfrac{1}{2}\nabla^2\phi_i/\phi_i(\mathbf{r}) . \tag{3}$$

This can then be compared to the values obtained in various local and nonlocal approximations to $v_{xc}[n(\mathbf{r})]$.

In seeking improvements to the local-density approximation (LDA) the early belief that the ϵ_{KS} were not physically significant led to a relative neglect of the examination of the accuracy of the v_{xc}. The total energy as calculated using E_{xc} was considered to be the test of the accuracy of the functional, while v_{xc} was simply taken as its functional derivative.

However, recently Perdew *et al.*[3] have argued that the exact $(\epsilon_{KS})_{\max}=E(N)-E(N-1)$ where $E(M)$ is the exact ground-state energy of the M electron system. Thus $(\epsilon_{KS})_{\max}$ is the negative of the ionization energy of a system of N electrons to the totally relaxed state of the remaining $(N-1)$-electron system.

Thus the calculated $(\epsilon_{KS})_{\max}$ provided by Langreth and Mehl[4] can be compared to experimental and self-consistent calculations of the ionization energy of the atoms they treat. For helium, we find that their $(\epsilon_{KS})_{\max}$ is more than an eV too large in magnitude even though their total energy for the helium atom is within only ~ 0.1 eV of the exact value. Similar results obtain for the $(\epsilon_{KS})_{\max}$ of other atoms calculated by them, i.e., their calculated $(\epsilon_{KS})_{\max}$ are greater than the exact value with an error significantly larger than the error in the total energy of the atom.

It thus appears that it would be useful to test the validity of the various density functionals that have been proposed for v_{xc} not merely by seeing whether they produce accurate total energies and good electron densities, but to actually compare the exact values of $v_{xc}(\mathbf{r})$ necessary to give the exact density with that given by the functional, i.e., in a given case a v_{xc} that is considerably different from the exact one might give good overall agreement for $n(\mathbf{r})$ and E because the external potential plus the Hartree term is so large as to make the error in v_{xc} unimportant. However, when this same $v_{xc}[n(\mathbf{r})]$ is used in another calculation where the v_{ext} plus Hartree term is small, these errors in $v_{xc}[n]$ may lead to substantial errors. Moreover, even for the former calculation the KS eigenvalues must be investigated to see how well they are reproduced.

It would therefore be useful to construct an exactly soluble model so this program of comparison could be implemented. Such an analysis of v_c has already been performed by Jagannathan,[5] who considered the two-electron atoms H^-, He, and Li^+ and compared his results to the LDA. The densities he employed were obtained from configuration interaction (CI) wave functions that minimized the energy. However, such analysis on two-electron atoms suffers from certain inherent limitations. Firstly, it is not possible to adjust the nuclear charge Z to make the density arbitrarily slowly varying, because H^- is barely bound relative to H + a free electron and any further decrease in Z (if we allow nonintegral nuclear charge, while maintaining exactly two electrons) leads to a physically unbound state. Secondly, when only integral values of Z are employed, the density varies significantly from one atom to the next, which makes it more difficult to understand the trends in the comparison of the exact and approximate v_{xc}. Thirdly, when a variational calculation is used to obtain a wave function for a two-electron atom it is always possible to add an additional term of the form $Ae^{-\alpha(r_1+r_2)}$ where α is smaller than any other such α in the expansion. Normally, unless this is added to the exact solution, minimizing the energy will result in $A\neq 0$. Thus as $r\rightarrow\infty$ the asymptotic density will be determined by this term which can be quite arbitrary unless one knows what the asymptotic density is prior to starting the calculation. Thus the variational solution can lead to the wrong asymptotic density. As we will show below the ϵ_{KS} are related to the asymptotic density and thus this will lead to incorrect ϵ_{KS} and $v_{xc}(\mathbf{r})$.

Since the validity of the density-functional theory is not limited to having v_{ext} given by the Coulomb potential due to protons in nuclei, we are free to use any v_{ext} that gives rise to an exactly soluble model. Such a model would be most useful if the v_{ext} contained a parameter which would give rise to a whole family of exactly soluble problems with densities which vary as slowly or rapidly as we wish to study. Such a model is presented in the next section.

Within the framework of the model to be presented we can investigate total energies and their constituents (i.e., exchange, correlation, etc.) as well as the exact eigenvalues and eigenfunctions of the Kohn-Sham equation along with the corresponding expectation values of constituents of the potential (i.e., $\langle\phi_{KS}|v_x|\phi_{KS}\rangle$, $\langle\phi_{KS}|v_c|\phi_{KS}\rangle$).

The exact values which can be obtained for this problem will then be compared to those obtained by evaluating approximate functionals which are in current use, using the exact electron density.

We will demonstrate that although total energies for the system are in quite good agreement for the entire range of densities considered, the corresponding Kohn-Sham eigenvalues are significantly worse. We attribute this to error in the exchange potential functional, and thus conclude that if improvement is to be made in the approximations of density functionals, then the expression for $E_x[n(\mathbf{r})]$ must be changed in a manner that will not affect the energy much, while making a considerable correction to its functional derivative $v_x[n(\mathbf{r})]$.

We have shown analytically[6] for our model, without resorting to the theorem recently proved by Perdew and co-workers, that the energy of the highest occupied Kohn-Sham orbital is of significance, in that it represents the difference in energy between the ground state of the two-electron system and the ground state of the one-electron system including all relaxation effects. Thus, in our case where the only ϵ_{KS} is that of the "highest occupied orbital," it is reasonable to use this energy as a test of the efficacy of various functionals.

II. THE MODEL

To this end we consider two electrons attracted to a force center by a harmonic-oscillator potential.[6] This model has been employed previously by Kestner and Sinanoglou,[7] using the variational principle, to study electron correlation in heliumlike atoms. Thus

$$H=-\frac{\hbar^2}{2m}(\nabla_1^2+\nabla_2^2)+\tfrac{1}{2}k(r_1^2+r_2^2)+\frac{e^2}{|\mathbf{r}_{12}|}\,, \tag{4}$$

where r_i are the coordinates of electron i $(i=1,2)$.

The constant k is a measure of the strength of the attractive center and thus can be adjusted to model an entire range of "physical" situations—from dominance of the electron-electron interaction down to the case where the electron-electron interaction is negligible.

Converting to center-of-mass and relative coordinates, and separating variables, yields

$$\left[-\frac{\hbar^2}{2M}\nabla_R^2+kR^2\right]g(\mathbf{R})=E_{\text{c.m.}}g(\mathbf{R}) , \tag{5}$$

$$\left[-\frac{\hbar^2}{2\mu}\nabla_r^2+\tfrac{1}{4}kr^2+\frac{e^2}{r}\right]f(\mathbf{r})=\epsilon_{\text{rel}}f(\mathbf{r}) , \tag{6}$$

where M is the total mass and μ is the reduced mass of the two electrons. Here the total energy E is given by the sum of $E_{\text{c.m.}}$ and ϵ_{rel}. We may obtain the ground state of the system by finding the ground-state solution of both Eqs. (5) and (6). Then $g(\mathbf{R})$ is the ground state of the spherical harmonic oscillator and $f(\mathbf{r})$ is also an S state since it is the ground state of a spherically symmetric potential.

The density may be obtained from

$$n(\mathbf{r}_2)=2\int|\psi(\mathbf{r}_1,\mathbf{r}_2)|^2 d\mathbf{r}_1 .$$

Then making use of the oscillator wave function, employing a change of variables, and integrating over angles, we obtain (in atomic units)

$$n(r_2)=A^2\frac{e^{-qr_2^2}}{qr_2}\int_0^\infty f^2(r)e^{-qr^2/4}(e^{qrr_2}-e^{-qrr_2})r\,dr , \tag{7}$$

where $q=(4k)^{1/2}$.

The normalization factor A^2 is obtained from the condition $\int n(\mathbf{r})d\mathbf{r}=N$ where $N=2$ is the number of electrons.

Once Eq. (7) is evaluated using the numerical solution of Eq. (6), we are in possession of an exact electron density for a problem with an electron-electron interaction. Because of the simple nature of this problem we can obtain v_{xc}, the exchange and correlation potential of the system. We recall that the same densities would result if we were to solve a system of noninteracting electrons moving in an effective potential $\Phi(\mathbf{r})+v_{\text{xc}}[n(\mathbf{r})]$, where

$$\Phi(\mathbf{r})=v_{\text{ext}}(\mathbf{r})+\int n(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|\,d\mathbf{r}' . \tag{8}$$

Thus we need merely solve the single-particle Schrödinger equation

$$\{-\tfrac{1}{2}\nabla^2+\Phi(\mathbf{r})+v_{\text{xc}}[n(\mathbf{r})]\}\phi_i(\mathbf{r})=\epsilon_i\phi_i(\mathbf{r}) \tag{9}$$

with

$$n(\mathbf{r})=\sum_{i=1}^{N}|\phi_i(r)|^2 ,$$

N the number of electrons.

In our case $N=2$, and we have two equivalent electrons (with opposite spin); therefore,

$$n(\mathbf{r})=2|\phi_i|^2\rightarrow\phi_i=[n(\mathbf{r})/2]^{1/2} .$$

Since we know $n(\mathbf{r})$, we have ϕ_i as well and can use Eq. (3) to find $v_{\text{xc}}(r)$, where $\Phi(\mathbf{r})$ is as defined above, and $v_{\text{ext}}(r)=\frac{1}{2}kr^2$.

From Eq. (3) for $v_{\text{xc}}(\mathbf{r})$ it is clear that the Kohn-Sham single-particle eigenvalue ϵ_{KS} enters into $v_{\text{xc}}(\mathbf{r})$ as an additive constant at all values of r. However, the condition that $v_{\text{xc}}\rightarrow 0$ as $r\rightarrow\infty$ is sufficient to determine the ϵ_{KS} without actually solving the KS equation. In fact, it can be shown analytically that $\epsilon_{\text{KS}}=E_{\text{rel}}$ by assuming the same condition on v_{xc}.[6,8]

III. EXACT DENSITIES, EXCHANGE, AND CORRELATION FUNCTIONALS

Figure 1 shows $n(r)/n_k(r)$ vs $k^{1/4}r$ for three values of k, where $n_k(r)$ is the electron density of two particles in a harmonic-oscillator potential with the same spring constant but with no e-e interaction. From these figures we see the effect of the e-e interaction on the density profile. We observe that as k decreases, i.e., the relative strength of the e-e interaction increases, the e-e repulsion causes a spreading out of the electron distribution increasing the density at large distances, while dropping the value of the central density in order to conserve the number of particles. This is evident in Fig. 1 as well, since as was to be expected the smaller k values show a larger deviation from the harmonic-oscillator density since it is for this region that the e-e interaction is important. In fact, in the limit $k\rightarrow\infty$ we would expect no deviation at all. For $k^{1/4}r=2.6$, the end point of the plot, the ratio of $n(r)$ to the maximum density, $n(0)$ for $k=100$, 1, and 0.01 is 0.0015, 0.0024, and 0.0081, respectively. The density for $k=10$ corresponds to the "physical range" since if we define an average r_s by

$$(r_s)_{\text{avg}}=\int n(r)r_s(n)d\mathbf{r} ,$$

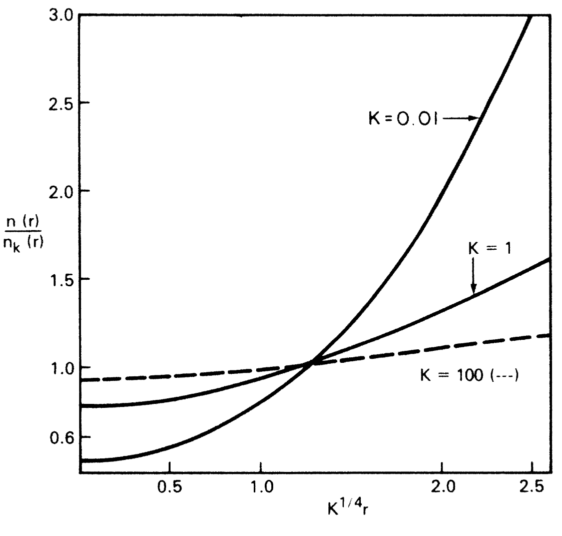

FIG. 1. Scaled density vs $k^{1/4}r$ for $k=0.01$, 1, and 100.

then $(r_s)_{\rm avg} \approx 1$ a.u. for $k=10$. [Using this measure $(r_s)_{\rm avg}$ varies from 0.517 at $k=100$ to 5.87 at $k=0.01$.]

For two electrons of opposite spin

$$\upsilon_x = -\tfrac{1}{2}\int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' , \tag{10}$$

and thus

$$\upsilon_c = \epsilon_i + \frac{\nabla^2\phi_i}{2\phi_i} - v(r) - \tfrac{1}{2}\int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' . \tag{11}$$

In Fig. 2 we present $\upsilon_x^{\rm LDA}$ (the exchange potential in the local-density approximation) and $\upsilon_x^{\rm exact}$ vs r_s. Note that the exchange potential functional is nonlocal, i.e., is not merely a function of r_s, and always of greater magnitude than $\upsilon_x^{\rm LDA}$. As k decreases υ_x appears to approach the free-electron-gas results. However, this way of representing υ_x is deceptive—we know that for large distances the LDA exchange potential exponentially decreases because the density does so, while the exact exchange decreases as $1/r$. Furthermore, for our case we shall see that for the entire range of k values treated the exchange potential in the LDA will not approach the exact value.

In Fig. 3 we present $\upsilon_c^{\rm exact}$ vs r_s for $k=0.01$, 1, and 100; and in Fig. 4 $\upsilon_c^{\rm exact}$ vs r_s for $k=10$ and 0.01, along with the Ceperley-Alder and Wigner local forms of υ_c. It appears from Fig. 4 that for $k=0.01$ the Wigner correlation functional is in close agreement with the exact result for $r_s>5$.

Figure 5 shows $\upsilon_x^{\rm LDA}/\upsilon_x^{\rm exact}$ and $4\pi r^2 n(r)$ vs r for $k=10$. This demonstrates that in the region of interest, i.e., when the weighted density is substantial, the ratio is ~ 0.6. This is the case for all values of k which we studied.

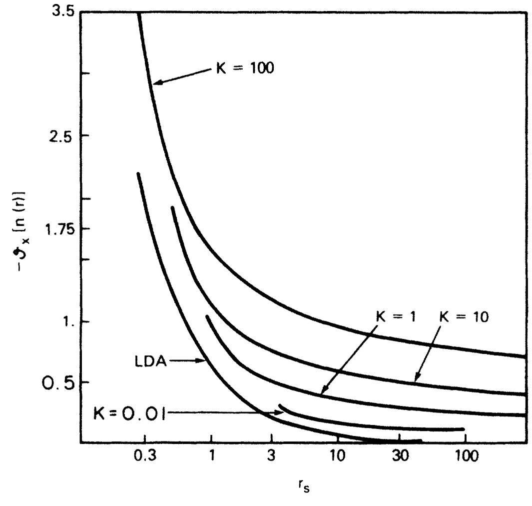

FIG. 2. Exchange potential for various k.

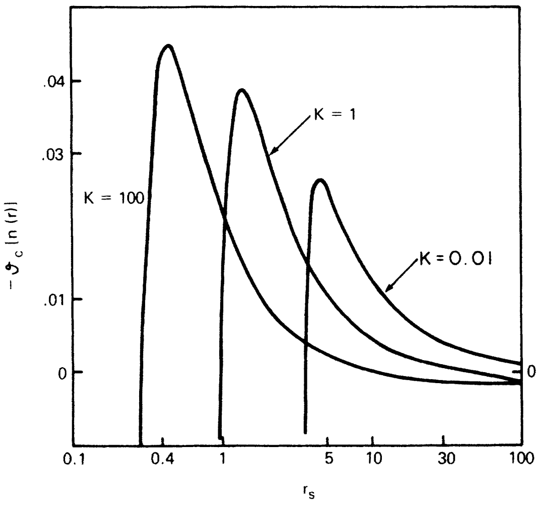

FIG. 3. Correlation potential for $k=100$, 1, and 0.01.

IV. ENERGIES AND EXPECTATION VALUES OF POTENTIALS

We have within the Kohn-Sham theory the following expression:

$$E = \sum_{i=1}^{N}\epsilon_i + E_{\rm xc}[n(\mathbf{r})] - \int \upsilon_{\rm xc} n(\mathbf{r})d\mathbf{r} - \tfrac{1}{2}\int\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}' ,$$

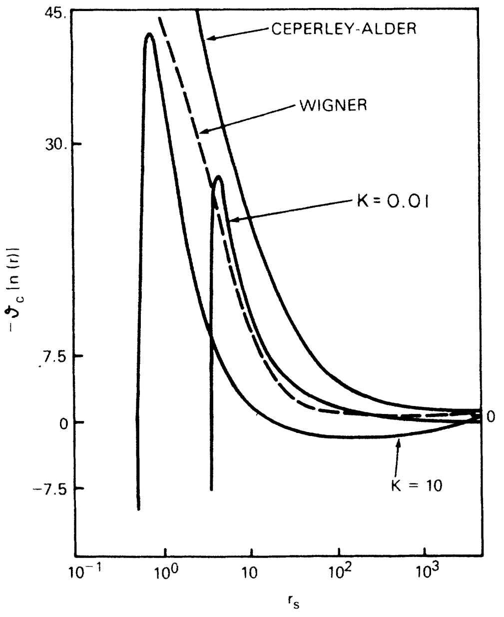

FIG. 4. Correlation potential for $k=10$, 0.01, and local forms.

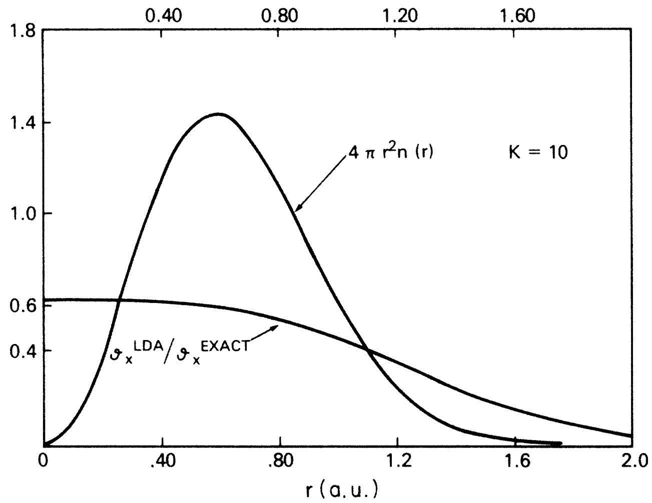

FIG. 5. Ratio of LDA to exact exchange potential for $k=10$.

which gives the total energy of the interacting N electron system in terms of the single-particle eigenvalues and various functionals of the derived density.

For our model system E is known exactly, as is $\epsilon_{\rm KS}$, $n(r)$, $\upsilon_x[n(r)]$, and $\upsilon_c[n(r)]$. In fact, we can invert the preceding equation to write

$$E_{\rm xc}[n(\mathbf{r})]=E-\sum_{i=1}^{N}\epsilon_i+\int \upsilon_{\rm xc}n(\mathbf{r})d\mathbf{r}+\tfrac{1}{2}\int\int\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}' \qquad (12)$$

and obtain $E_{\rm xc}$ exactly. Moreover, for the two-particle case it follows from Eq. (10) that

$$E_x[n]=-\tfrac{1}{4}\int\int\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}' \qquad (13)$$

enabling us to obtain $E_x[n]$ and $E_c[n]=E_{\rm xc}[n]-E_x[n]$ exactly.

We wish to investigate the accuracy of various approximate functionals in predicting energies and related potentials. One approach would be to use these approximate functionals for the potential, $\upsilon_{\rm xc}$, in the Kohn-Sham equations and solve for the density $n(r)$ and the corresponding $\epsilon_{\rm KS}^{\rm app}$. These could then be used to obtain total energies as well.

An alternative approach—the one which we employ—is to evaluate the approximate functionals using the exact density, $n(r)^{\rm ex}$, generated by the solution of the Schrödinger equation, to obtain potentials (as projected on r space), energies, and potential-energy expectation values to be compared to the correct ones. We note that if we use this second method the only terms in which error can be introduced (in considering energies) are E_x, E_c, $\langle\Psi_{\rm KS}|\upsilon_x|\Psi_{\rm KS}\rangle$, and $\langle\Psi_{\rm KS}|\upsilon_c|\Psi_{\rm KS}\rangle$, since the other terms are exact, i.e., the $\epsilon_{\rm KS}$ and the expectation value of the external potential and the Hartree potential are obtained exactly from the exact density. Thus we are actually testing the functional forms of exchange-correlation energies and potentials.

A. Exchange only

Because correlation makes a contribution to the total energy which is never more than $\sim 5\%$ for our model, a first approximation of interest is to consider exchange only.

(a) *LDA.* The LDA (Ref. 1) treats exchange by taking the energy density at each point in space as if there were a uniform electron gas of the local electron density, i.e., the exchange energy density, $\epsilon_x=-\frac{3}{4}(3n/\pi)^{1/3}$:

$$E_x[n]=\int \epsilon_x n(\mathbf{r})d\mathbf{r}=-\tfrac{3}{4}(3/\pi)^{1/3}\int n^{1/3}(\mathbf{r})n(\mathbf{r})d\mathbf{r}\ ,$$

and since

$$\upsilon_x=\delta E_x/\delta n(r)=\frac{d}{dn}[n\epsilon_x]\ ,$$

in the local approximation

$$\upsilon_x(r)=-[3n(r)/\pi]^{1/3}\ .$$

(b) *Nonlocal.* LDA with gradient-energy expansion[1,9–11] (GEA):

$$E_x[n]=E_x^{\rm LDA}-C_x\int|\nabla n|^2 n^{-4/3}d\mathbf{r}+\cdots\ ,$$

$$C_x=7\pi(3\pi^2)^{-4/3}/144=0.001\,667 \text{ a.u.}\ ,$$

and the corresponding potential term is

$$\upsilon_x=\upsilon_x^{\rm LDA}-C_x\left[\frac{4}{3}\frac{|\nabla n|^2}{n^{7/3}}-2\frac{\nabla^2 n}{n^{4/3}}\right]\ .$$

(c) *Nonlocal.* LDA plus Langreth-Mehl[12,4] approximation (LM):

$$E_x^{\rm LM}=E_x^{\rm LDA}-a(\tfrac{7}{9}+18f^2)\int|\nabla n(\mathbf{r})|^2 n^{-4/3}dr\ ,$$

where $a=\pi/[16(3\pi^2)^{4/3}]=2.144\times10^{-3}$ a.u. and we used $f=0.15$ as suggested by LM.

B. Exchange and correlation

1. Local

Here, $E_{\rm xc}[n]=E_x[n]+E_c[n]$, where exchange is given by LDA [as in condition (a) above] and E_c has a local form as well, i.e.,

$$E_c=\int n(\mathbf{r})\epsilon_c(n)d\mathbf{r}\ ,$$

where ϵ_c, the correlation energy density per electron, is given by the parametrization of Perdew and Zunger[13] of a form due to Ceperley and Alder:[14]

$$\epsilon_c=\begin{cases}A\ln(r_s)+B+Cr_s\ln(r_s)+Dr_s, & r_s\le 1\\ \gamma/[1+\beta(r_s)^{1/2}+\beta_2 r_s], & r_s\le 1\end{cases}$$

where $4(\pi r_s^3)/3=n^{-1}$.

2. *Nonlocal*

Here we have

$$E_{xc}[n]=E_x^{\mathrm{LDA}}+E_c^{\mathrm{RPA}}+\Delta E_x^{\mathrm{LM}}+\Delta E_c^{\mathrm{LM}} .$$

In this case it is necessary to use the random-phase approximation (RPA) parametrization of the Ceperley-Alder parametrization as given by Cole and Perdew.[15] This is because LM has been derived within the RPA scheme:

$$E_c^{\mathrm{LM}}=E_c^{\mathrm{LDA}}+a\int n^{-4/3}(2e^{-F}+18f^{2})\,|\nabla n(\mathbf{r})|^{2}d\mathbf{r} .$$

a and f are as noted previously [see condition (c) above] and $F=b\,|\nabla n(\mathbf{r})|\,/[n(\mathbf{r})]^{7/6}$, where $b=(9\pi)^{1/6}f=0.2618$.

C. Self-interaction correction (SIC)

We employ a local spin density (LSD) formalism in this instance. This is designed such that for a two-fermion system the exchange cancels half the Hartree term, thus ensuring that at least in this simple case there is no electrostatic self-interaction remaining.

In this formalism, we define $\zeta=(n_u-n_d)/n$, as the degree of polarization (where u and d denote spin up and down, respectively). Then $\zeta=0$ corresponds to an unpolarized system, while $\zeta=1$ corresponds to a completely polarized configuration. For intermediate polarizations $(0<\zeta<1)$, the interpolation formula of von Barth and Hedin[16] is employed:

$$\epsilon_c(r_s,\zeta)=\epsilon_c^{u}(r_s)+f(\zeta)[\epsilon_c^{p}(r_s)-\epsilon_c^{u}(r_s)] , \tag{14}$$

where

$$f(\zeta)=[(1+\zeta)^{4/3}+(1-\zeta)^{4/3}](2^{4/3}-2) .$$

We implement this using the Ceperley-Alder form for ϵ_c. The expression for the self-interaction-corrected correlation is[13,17,18]

$$E_c^{\mathrm{SIC}}=\int\left[\epsilon_c(n_u,n_d)n(\mathbf{r})-\sum_{\alpha,\sigma}\epsilon_c(n_{\alpha\sigma},0)n_{\alpha\sigma}(\mathbf{r})\right]d\mathbf{r} . \tag{15}$$

The parameters used can be found in Table I. In this case, because there is only one particle with spin up and one with spin down, exchange is given exactly and thus the only source of error is in the approximation for correlation. In our case of two electrons of opposite spin this reduces to

$$\begin{aligned}E_c^{\mathrm{SIC}}&=\int\epsilon_c(n/2,n/2)n(\mathbf{r})d\mathbf{r}\\&\quad-\int[\epsilon_c(n/2,0)+\epsilon_c(0,n/2)]\tfrac{1}{2}n(\mathbf{r})d\mathbf{r}\\&=\int n(\mathbf{r})\epsilon_c^{u}(n)d\mathbf{r}-2\int\tfrac{1}{2}n(\mathbf{r})\epsilon_c^{p}(n/2)d\mathbf{r}\\&=\int[\epsilon_c^{u}(n)-\epsilon_c^{p}(n/2)]n(\mathbf{r})d\mathbf{r} .\end{aligned} \tag{16}$$

In the next section we consider the following quantities to ascertain the efficacy of the various approximations:

$$E_x=\int n(\mathbf{r})\epsilon_x[n]d\mathbf{r} ,$$

$$E_c=\int n(\mathbf{r})\epsilon_c[n]d\mathbf{r} ,$$

$$V_x=\langle\Psi_{\mathrm{KS}}\,|\,v_x\,|\,\Psi_{\mathrm{KS}}\rangle ,$$

$$V_c=\langle\Psi_{\mathrm{KS}}\,|\,v_c\,|\,\Psi_{\mathrm{KS}}\rangle ,$$

$$E_{\mathrm{tot}}=(E_{\mathrm{tot}}-E_{\mathrm{xc}})^{\mathrm{exact}}+E_{\mathrm{xc}}^{\mathrm{app}} ,$$

$$\epsilon_{\mathrm{KS}}=(\epsilon_{\mathrm{KS}}-V_{\mathrm{xc}})^{\mathrm{exact}}+V_{\mathrm{xc}}^{\mathrm{app}} .$$

V. RESULTS AND CONCLUSIONS

We recall that over the range of k values under consideration, the central density varies by a factor of almost 2000. While in r space the densities evolve with increasing k, from slowly to rapidly varying, the criterion for applicability of the LDA or the GEA expansion based on the local Fermi wave vector, $|\nabla n|/(k_F n)\ll 1$, is never satisfied for our model. However, since this is the case

TABLE I. Parameters used in the Ceperley-Alder form of the correlation energy density as given by Perdew and Zunger (Ref. 13) and Cole and Perdew (Ref. 15). (U denotes unpolarized, while P denotes completely polarized.)

	RPA		Ceperley-Alder	
Parameter	U	P	U	P
A	0.0311	0.015 55	0.0311	0.015 55
B	−0.071	−0.0499	−0.048	−0.0269
C	0.0021	0.0005	0.0020	0.0007
D	−0.0078	−0.0020	−0.0116	−0.0048
γ	−0.2044	−0.1104	−0.1423	−0.0843
β_1	1.5023	1.1102	1.0529	1.3981
β_2	0.0916	0.0170	0.3334	0.2611

for other systems as well in which LDA has achieved some success, we will apply it here as well. Various arguments have been proposed to explain the success of LDA and GEA in such systems where the aforementioned criterion is not satisfied.[19–21]

A. Total energy and Kohn-Sham single-particle eigenvalues

Figure 6 compares the total energy of our model system, for a series of k values, calculated exactly and within various approximations. The total energy $E_{\rm tot}$ is given along the top border of the figure, and each curve represents the percentage error in the calculations of $E_{\rm tot}$ using the stated approximation. As can be seen by reference to the figure, the discrepancies in the total energy are quite small—on the order of hundredths of a.u. (i.e., $\sim 5\%$) in the worst case ($k=0.01$) and in the range of 1% or better over the remainder of the range.

That is, for the entire range, any approximation we use for exchange-correlation is quite good for the calculation of the total energy. Referring to the figures on exchange and correlation energies (Figs. 8 and 10), we see that exchange-correlation ranges from 8% to 48% of the magnitude of the total energy. Thus the good agreement of $E_{\rm tot}$, irrespective of the approximation for $E_{\rm xc}$, cannot be attributed to exchange-correlation being a small component of the energy in this problem.

Note that using a strictly local [$({\rm LDA})_{\rm xc}$] approximation the error is always on the order of 1%. Of course SIC yields even better results since it eliminates the error in exchange and thus limits the introduction of error to the correlation term alone, which only varies from 0.2% to 5.8% of the total energy.

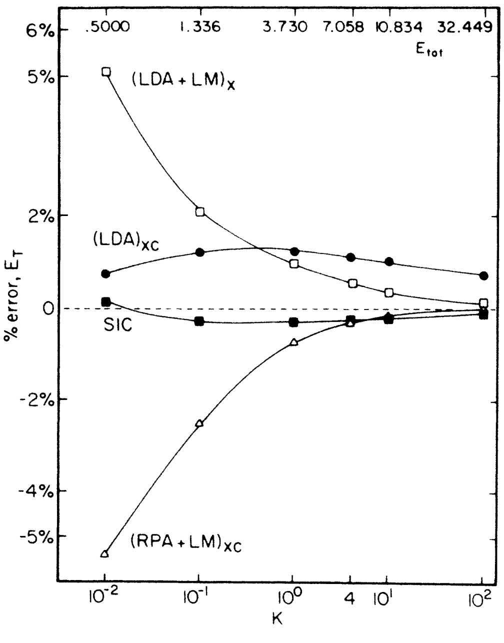

FIG. 6. Percentage error in the total energies.

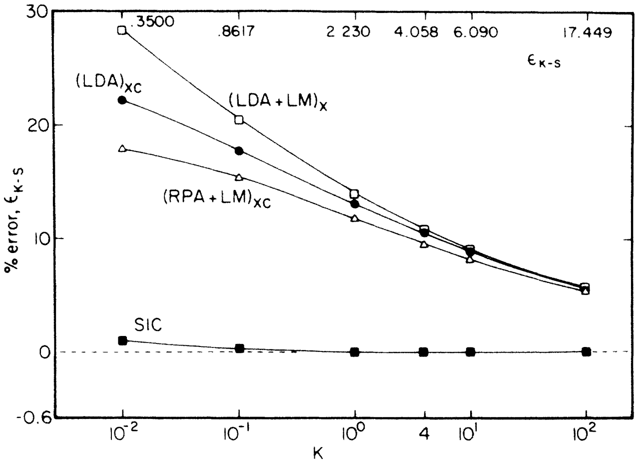

FIG. 7. Percentage error in the Kohn-Sham eigenvalues.

We next consider the Kohn-Sham eigenvalue $\epsilon_{\rm KS}$ (Fig. 7). Figure 7 shows the percentage error in the calculation of the eigenvalue within the given approximations. From the values of $\epsilon_{\rm KS}$ listed along the top border we can see that the discrepancy in $\epsilon_{\rm KS}$ can be comparatively large—on the order of 1 a.u.

We observe that although the SIC gives remarkable agreement (0.2% or better, ~ 0.1 a.u. or better), all the other approximations, both local and nonlocal, are quite poor. That is, for high k where the error in the total energy is $\sim 1\%$, the error in the corresponding $\epsilon_{\rm KS}$ is $>5\%$, while for low k where $E_{\rm tot}$ is in error from 1–5 % depending on the approximation employed, $\epsilon_{\rm KS}$ is in error by approximately 20–30 %.

This clearly demonstrates the following: Although a given approach may yield highly accurate total energies, this does not ensure the accuracy of the corresponding Kohn-Sham eigenvalues. We now endeavor to obtain an understanding of this phenomenon by investigating the exchange and correlation terms (the only terms which are being approximated) individually.

B. Exchange

Figure 8 shows the negative of the exchange energy and the percentage error in the calculated values for each case and approximation.

Before examining these displays we digress to make an observation with regard to the LM and GEA approximations. If we refer to Sec. IV in which we define the different approximations, we find that both LM and the second-order gradient-energy expansion for exchange can be written as

$$E_x^i = E_x^{\rm LDA} + C_x^i \int |\nabla n|^2 n^{-4/3} d\mathbf{r} ,$$

where i equals GEA or LM. Thus the correction to LDA

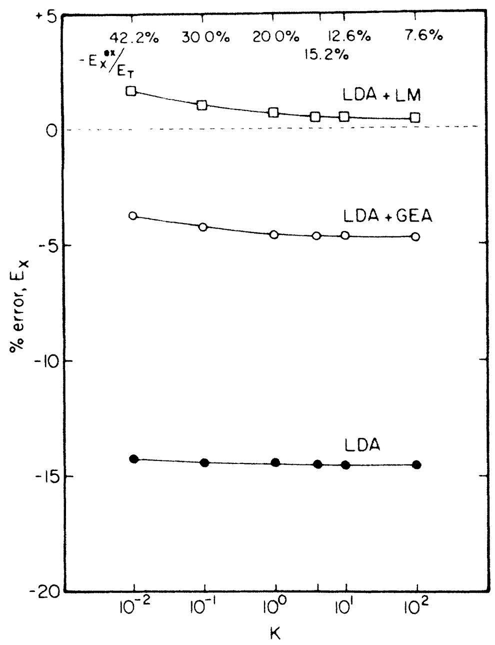

FIG. 8. Percentage error in the exchange energies.

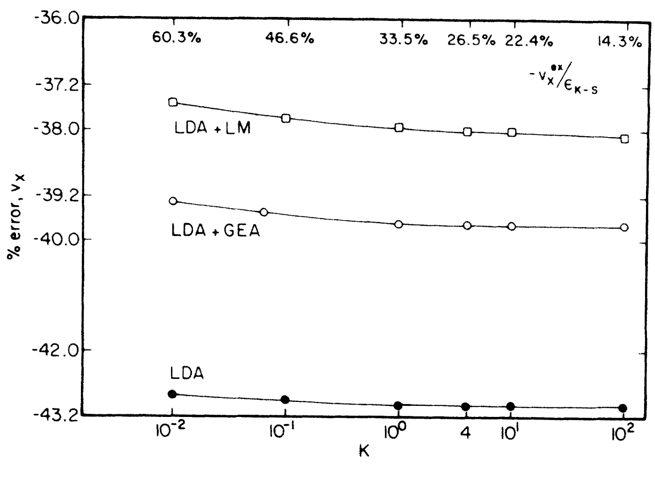

FIG. 9. Percentage error in the exchange potential expectation values.

afforded by each of these differs only through the multiplicative constant C^i, i.e.,

$$\frac{\Delta E_x^{\mathrm{LM}}}{\Delta E_x^{\mathrm{GEA}}}=\frac{C_x^{\mathrm{LM}}}{C_x^{\mathrm{GEA}}}=\frac{a(\frac{7}{9}+18f^2)}{7\pi/[144(3\pi^2)^{4/3}]}\ ,$$

where $a=\pi/[16(3\pi^2)^{4/3}]$, thus

$$\frac{\Delta E_x^{\mathrm{LM}}}{\Delta E_x^{\mathrm{GEA}}}=\tfrac{9}{7}(\tfrac{7}{9}+18f^2)=1+\tfrac{162}{7}f^2=1.521$$

for $f=0.15$, the value given by LM.

Figure 8 shows the percentage error for $-E_x$. Along the upper border is the percentage of E_{tot}, in the magnitude that E_x represents. This is not an alternate scale (x axis) for the plot, but only shows the values we have calculated, and can be used at most as a guide to determine the relative importance of exchange for the given k region. We observe that in the LDA the exchange energy is 14% less than the exact value throughout. The GEA correction reduces the error to ~5% and the LM form overcompensates, slightly yielding values between 0.2% and 2% too large.

When considering the companion quantity $-V_x$, the negative of the expectation value of $\upsilon_x[n]$, we see a very different picture. Figure 9 makes it evident that the exchange potential is not being modeled well at all. We find that for the LDA the percentage error is ~43% throughout (as compared to 14% for E_x), and although both the GEA and the LM improve E_x considerably they have a much smaller effect on the expectation value V_x. In fact, the percentage error even after the corrections is never less than 37% as compared to roughly 1% error in the total energy for the corresponding k value within the same approximation (LM).

Some of the points which have been touched upon in the discussion of results for exchange can be understood with a little analysis:

(a) $E_x^{\mathrm{LDA}}\cong 85\%$ of E_x^{exact} for the entire range of k values.

(b) $V_x^{\mathrm{LDA}}\cong 57\%$ of V_x^{exact} for the entire range of k values.

Two questions present themselves here. (1) Why does LDA (and its corrections) work so well for the energy E_x, but not for V_x? (2) Why does LDA give approximately the same value—i.e., the same percentage of the exact answer—over the entire spectrum of densities we have investigated?

The second question can be answered by reference to Fig. 5, which shows that for the region of space where the quantity $4\pi r^2 n(r)$ is substantial, the ratio $\upsilon_x^{\mathrm{LDA}}$ to $\upsilon_x^{\mathrm{exact}}$ is ~0.6. In addition, we shall present a calculation which should make this plausible on analytic grounds as well.

To address the first question, it follows from Eqs. (10) and (13) that

$$V_x=\langle\Psi_{\mathrm{KS}}|\upsilon_x|\Psi_{\mathrm{KS}}\rangle=-\tfrac{1}{2}\int\int\frac{n(\mathbf{r})}{2}\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}'$$
$$=E_x\ .$$

Thus

$$V_x^{\mathrm{exact}}=E_x^{\mathrm{exact}}\ . \tag{17}$$

However, in the LDA

$$E_x^{\mathrm{LDA}}=-\frac{3}{4}\left[\frac{3}{\pi}\right]^{1/3}\int n^{4/3}(\mathbf{r})d\mathbf{r}\ ,$$

$$\upsilon_x^{\mathrm{LDA}}=-\left[\frac{3}{\pi}\right]^{1/3}n^{1/3}(\mathbf{r})\ ,$$

so

$$V_x^{\rm LDA}=\langle \Psi_{\rm KS}\,|\,v_x^{\rm LDA}\,|\,\Psi_{\rm KS}\rangle=-\frac{1}{2}\left[\frac{3}{\pi}\right]^{1/3}\int n^{4/3}(\mathbf{r})d\mathbf{r}\ .$$

Therefore

$$V_x^{\rm LDA}=\tfrac{2}{3}E_x^{\rm LDA}\ . \tag{18}$$

Thus comparing Eqs. (17) and (18), it is evident that if the LDA is a good first approximation for E_x, as it is in heliumlike atoms,[4] it is necessarily poor for the exchange potential V_x. (It is interesting to note that the Slater exchange, i.e., $\frac{3}{2}v_x^{\rm LDA}$, will give very good results for the exchange potential in the case of two-electron atoms, when LDA is a good approximation for the exchange energy.) This points out the inadequacy in attempts to improve LDA by addressing the issue of the energy alone. It is clear that merely seeking a correction to $E_x^{\rm LDA}$ which is assumed small without reference to v_x will not necessarily lead to improvement in the V_x, thus leaving a major source of error in the calculation of $\epsilon_{\rm KS}$.

Some light may be shed on the second question through consideration of limiting cases. First, let us consider two electrons in a spherical harmonic-oscillator potential with no e-e interaction. This can be thought of as the $k\rightarrow\infty$ limit, or alternatively we can think of it as a first approximation to our model where the e-e term $1/|\mathbf{r}|$ is treated as a perturbation. Then

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=(\alpha/\pi)^{3/4}\exp[-\tfrac{1}{2}\alpha(r_1^2+r_2^2)]\ ,$$

where $\alpha=k^{1/2}$, and

$$n(r)=2(\alpha/\pi)^{3/2}e^{-\alpha r^2}\ .$$

Then a calculation of the exchange energies and potentials yields

$$E_x^{\rm exact}=-(2\alpha/\pi)^{1/2}=V_x^{\rm exact}\ ,$$

$$E_x^{\rm LDA}=-\tfrac{9}{16}(6/\pi)^{1/3}(3\alpha/\pi)^{1/2}\ ,$$

$$V_x^{\rm LDA}=-\tfrac{3}{8}(6/\pi)^{1/3}(3\alpha/\pi)^{1/2}\ .$$

Thus

$$E_x^{\rm LDA}/E_x^{\rm ex}=\frac{9}{16}\left[\frac{6}{\pi}\right]^{1/3}\left[\frac{3}{2}\right]^{1/2}=0.855$$

and

$$V_x^{\rm LDA}/V_x^{\rm ex}=0.570\ .$$

In addition,

$$\Delta E_x^i=[27(3\pi\alpha/2)^{1/2}/2^{1/3}]C_x^i\ ,$$

where i equals LM or GEA; then the correction term due to LM or GEA is

$$\Delta E_x^{\rm GEA}/E_x^{\rm ex}=0.0972\quad\text{while}\quad \Delta E_x^{\rm LM}/E_x^{\rm ex}=0.1478\ ,$$

$$\Delta V_x^i=-[9(3\pi\alpha/2)^{1/2}\times 2^{1/6}]C_x^i\ ,$$

$$\Delta V_x^{\rm GEA}/V_x^{\rm ex}=0.0648\quad\text{while}\quad \Delta V_x^{\rm LM}/V_x^{\rm ex}=0.0985\ .$$

The analysis above shows that for large k (or to first order for all k), the LDA will give 85.5% of the correct exchange energy. This explains why we find a percentage error of approximately 14% + throughout regardless of k. In addition, it shows that when GEA is taken for the correction, the energy is then 95% of the correct value, while LM yields approximately 100.3%, which is consistent with our findings.

In a similar manner, we find that for the expectation value of the exchange potential the LDA is 57.0% of the exact value—corresponding to the -43% error we found in our calculations. For the V_x we see that the GEA only brings us to 63.5% and the LM to 66.9% of the exact result. Thus we see that the exchange potential is not as well given as the exchange energy. It is interesting to note that the correction to the expectation value of the potential as calculated deviates from the limiting value to a far greater extent than is the case for the energy.

We can also consider another two-electron model in which the e-e interaction is negligible compared to the strength of the central potential; i.e., a heliumlike ion in the limit of large Z:

$$H=-\tfrac{1}{2}\nabla_1^2-\tfrac{1}{2}\nabla_2^2-Z(1/r_1+1/r_2)\ .$$

Then

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=(Z^3/\pi)\exp[-Z(r_1+r_2)]$$

and

$$n(r)=2(Z^3/\pi)e^{-2Zr}\ .$$

Then a calculation of the exchange energies and potentials yields

$$E_x^{\rm exact}=-\tfrac{5}{8}Z=V_x^{\rm exact}\ ,$$

$$E_x^{\rm LDA}=-\tfrac{81}{64}(3^{1/3}/2^{2/3})\pi^{-2/3}Z\ ,$$

$$V_x^{\rm LDA}=-27(3^{1/3}/2^{17/3})\pi^{-2/3}Z\ .$$

Thus

$$E_x^{\rm LDA}/E_x^{\rm ex}=\frac{81}{40}\frac{3^{1/3}}{2^{1/3}\pi^{1/3}}=0.8577\ ,$$

and

$$V_x^{\rm LDA}/V_x^{\rm ex}=0.5718\ .$$

In addition,

$$\Delta E_x^i=-[27(\pi/2)^{1/3}]C_x^iZ\ ,$$

$$\Delta V_x^i=-9(\pi^{1/3}2^{1/6})C_x^iZ\ ,$$

where i equals LM or GEA. Then the correction term due to LM or GEA is

$$\Delta E_x^{\rm GEA}/E_x^{\rm ex}=0.0837\quad\text{while}\quad \Delta E_x^{\rm LM}/E_x^{\rm ex}=0.1274\ ,$$

$$\Delta V_x^{\rm GEA}/V_x^{\rm ex}=0.0333\quad\text{while}\quad \Delta V_x^{\rm LM}/V_x^{\rm ex}=0.0507\ .$$

In this case as well, the LDA exchange energy is 85.8% of the exact exchange energy, and GEA and LM bring that value to 94.4% and 98.5%, respectively. For the ex-

TABLE II. Hartree-Fock (HF) and Kohn-Sham (KS) exchange energies for a series of atoms and the percentage errors (relative to Kohn-Sham) of the local-density (LDA), second-order gradient-expansion (GEA), and Langreth-Mehl (LM) approximations for the exchange energy ($-E_x$). All entries except LM were obtained from Ref. 9.

	Exact values (a.u.)		Percentage error		
Atom	HF	KS	LDA	GEA	LM
H	0.3125	0.3125	−14.2	−5.9	−1.6
He	1.03	1.03	−13.6	−5.3	−1.0
Ne	12.13	12.10	−8.8	−4.6	−2.4
Ar	30.30	30.16	−7.5	−4.2	−2.5
Kr	94.63	93.78	−5.4	−3.2	−2.1

change potential the percentages of the exact expectation value for LDA, GEA, and LM are 57.2%, 60.5%, and 62.3%, respectively. These values are similar to those obtained in the exact calculations and our other model calculation as well. The LM value of 62.3% is indeed what we find in the exact calculation over almost all of the range. The results of these two limiting cases substantiate the reliability of the numerical calculations. It also shows that for a totally different central potential we get similar results. Thus, our results cannot be considered as merely an artifact of the harmonic-oscillator potential, as we see it persists for the physical Coulomb attractive center as well.

The above results for two electrons are examples of a more general conclusion that large errors in the expectation value of the functional derivative

$$\frac{\delta E_{\mathrm{xc}}}{\delta n(r)}=v_{\mathrm{xc}}(r)$$

are not inconsistent with accurate total energies. The "exact" functional derivative as defined here is evaluated from the electron-deficient side of the integer electron number. Because of the derivative discontinuity discussed in Ref. 3 the functional derivative from the electron-rich side "exceeds" this "exact" value by a positive constant C. Continuous approximations such as LDA, GEA, and LM represent averages over this discontinuity.[22]

We observed earlier that second-order GEA and LM differ only in the constant used in the correction term. For all our two-particle model systems the LM coefficient yields far more accurate results. We investigate this further by looking at results for real systems as well. Table II is a display from Ref. 9 of the exact Kohn-Sham and Hartree-Fock exchange energies and the percentage errors obtained when calculating the E_x in the LDA or GEA. (The values were obtained from various sources as noted in Ref. 9). Exact in this context means exchange only Kohn-Sham. Expanding the table we have added a column labeled "LM." This is the percentage error an LM calculation would have resulted in for these noble atoms. The method of obtaining these values was

$$\mathrm{LM}=\mathrm{LDA}+(\mathrm{GEA}-\mathrm{LDA})C_x^{\mathrm{LM}}/C_x^{\mathrm{GEA}}\ . \tag{19}$$

Once again we see LM yielding results superior to GEA.

C. Correlation

The contribution to the total energy due to correlation is shown in Fig. 10. The correlation as a percentage of the total energy is given inside the upper border for each of the points actually calculated. We see that correlation varies from 0.2% to 5.8% of the total energy, and thus it is a significantly smaller percentage of the total energy than is exchange. However, it is worth noting that with the exception of the SIC none of the approximations for correlation gives reasonable results—the errors varying from 50% to more than 300%. Among these the RPA + LM is best in that its error ranges between −50% and +80%. This is because the sign on the LM correction for correlation is opposite that of all other terms, and for large k the correction term is even greater in magnitude than the RPA value. Furthermore, the error in correlation is 2 orders of magnitude worse than that in exchange for the LM, therefore the relative success of LM does not indicate that it is a satisfactory approximation.

Even the SIC which does give better results is not very promising. For low k the error is on the order of 6%, but this grows with k until at $k=100$ it is on the order of 70%. However, as we have noted previously this will not affect the very fine results for total energy because SIC treats exchange exactly for the two-particle problem and

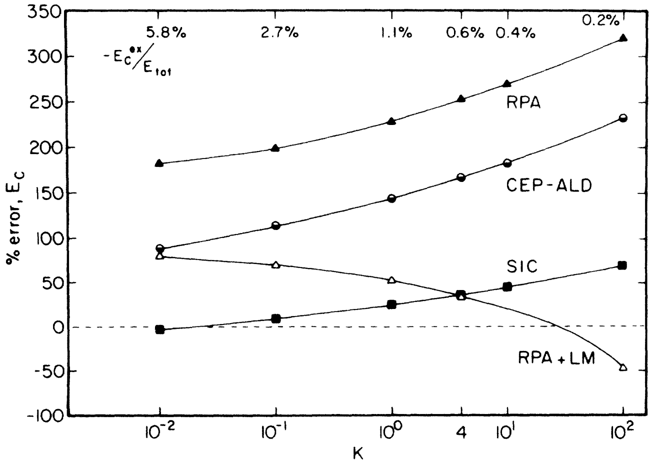

FIG. 10. Percentage error in the correlation energies.

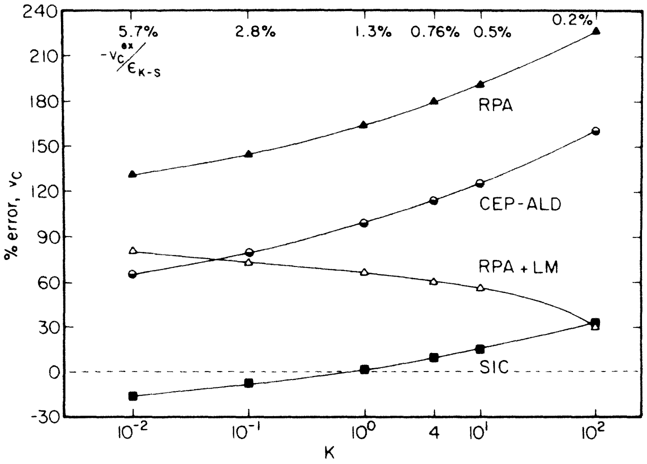

FIG. 11. Percentage error in the correlation potential expectation values.

the correlation energy for $k=100$ is only 0.2% of the total energy. Figure 11 gives the results for $-V_c$. The upper border of the figure contains $-V_c$ as a percentage of the Kohn-Sham eigenvalue. Unlike exchange, the expectation value of the correlation potential is more accurate than the correlation energy, though when dealing with such large errors it is doubtful whether there is any significance to this at all. It is evident from these results that neither E_c nor V_c is modeled satisfactorily by any of the functionals.

However, we do now have an explanation for the excellent agreement for the values of total energy. Referring to the figures, we see that the correlation energy is overestimated by large relative amounts (which are not large in absolute terms since correlation is only a small part of the total energy). For exchange exactly the opposite is the case—the energy was consistently underestimated. Thus, the errors in exchange and correlation being of opposite sign cooperate to give very good results for total energy through large cancellation. It also becomes clear that if correlation, although small, was given accurately, then the error in total energy as given by LDA would increase appreciably, while the LDA + LM result would improve.

D. Summary

In summary we collect the results in a concise manner. Total energies and exchange energies are obtained to good accuracy in the LDA along with standard correction schemes. On the other hand, Kohn-Sham maximal energy eigenvalues, expectation values of both exchange and correlation potentials, and correlation energies are given very poorly by these same approximations. The SIC gives good results for the exchange-correlation potential and thus for the Kohn-Sham eigenvalues as well.

The results quoted above lead us to conclude the following.

(1) Total energies are not an adequate measure of the efficacy of an energy functional. The functional derivative, i.e., the potential functional, must be considered as well.

(2) From the large errors in exchange potential expectation values we infer that improving correlation alone will not cure the difficulties of density-functional theory, but rather improvement of exchange potentials is still the first priority.

ACKNOWLEDGMENTS

This research work was supported in part through a City University of New York (CUNY) Professional Staff Congress—Board of Higher Education (PSC—BHE) grant.

---

*Present address: Naval Research Laboratories, Washington, D.C., 20375-5000.

[1] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[2] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[3] J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Phys. Rev. Lett. **49**, 1691 (1982).

[4] D. C. Langreth and M. J. Mehl, Phys. Rev. B **28**, 1809 (1983).

[5] S. Jagannathan, Ph.D. thesis, University of Georgia, Athens, GA, 1979 (unpublished).

[6] J. B. Krieger and P. M. Laufer (unpublished).

[7] N. R. Kestner and O. Sinanoglou, Phys. Rev. **128**, 2687 (1962).

[8] Pinchus M. Laufer, Ph.D. thesis, City University of New York, 1984 (unpublished).

[9] V. Sahni, J. Gruenebaum, and J. P. Perdew, Phys. Rev. B **26**, 4371 (1982).

[10] L. J. Sham, in *Computational Methods in Band Theory*, edited by P. Marcus, J. F. Janak, and A. R. Williams (Plenum, New York, 1971).

[11] A. R. E. Mohammed and V. Sahni, Phys. Rev. B **29**, 3687 (1984).

[12] D. C. Langreth and M. J. Mehl, Phys. Rev. Lett. **47**, 446 (1981).

[13] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[14] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[15] Lee A. Cole and J. P. Perdew, Phys. Rev. B **25**, 1265 (1982).

[16] U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).

[17] J. P. Perdew, Chem. Phys. Lett. **64**, 127 (1979); J. P. Perdew, E. R. McMullen, and A. Zunger, Phys. Rev. A **23**, 2785 (1981).

[18] H. Stoll, C. M. E. Pavlidou, and H. Preuss, Theor. Chim. Acta **49**, 143 (1978); H. Stoll, E. Golka, and H. Preuss, *ibid.* **55**, 29

(1980).

[19] N. D. Lang and L. J. Sham, Solid State Commun. **17**, 581 (1975).

[20] O. Gunnarsson, M. Johnson, and B. I. Lundqvist, Solid State Commun. **24**, 765 (1977); Phys. Rev. B **20**, 3136 (1979).

[21] A. R. E. Mohammed and V. Sahni, Phys. Rev. B **28**, 3014 (1983); see this article for further discussion of this topic.

[22] J. P. Perdew and M. Levy, in *Many-Body Phenomena at Surfaces,* edited by D. Langreth and H. Suhl (Academic, New York, 1984) p. 82.