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Phase-space approach to the exchange-energy functional of density-functional theory

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The phase-space distribution function corresponding to a ground-state density of a many-electron system proposed earlier [S. K. Ghosh, M. Berkowitz, and R. G. Parr, Proc. Natl. Acad. Sci. USA 81, 8028 (1984)] is employed to obtain a new approximate exchange-energy functional. This is $K[\rho]=(\pi/2)\int \rho^2(\mathbf{r})\beta(\mathbf{r})d\mathbf{r}$, with $\beta(\mathbf{r})=1/kT(\mathbf{r})$, where $T(\mathbf{r})$ is the local temperature previously defined; $\frac{3}{2}kT(\mathbf{r})$ is the kinetic energy per electron at $\mathbf{r}$. In Thomas-Fermi theory, $\beta=5(3\pi^2\rho)^{-2/3}$, and this formula gives $\frac{10}{9}$ times the classical Dirac formula. This shows why the α parameter in $X\alpha$ theory is normally close to $(\frac{10}{9})(\frac{2}{3})=0.74$. Numerical calculations on atoms are performed, giving excellent results, and the exchange hole associated with the new formula is studied in detail.

I. INTRODUCTION

The phase-space distribution function $f(\mathbf{r},\mathbf{p})$ corresponding to a ground-state electron density $\rho(\mathbf{r})$, proposed earlier[1] in connection with a thermodynamic transcription of density-functional theory, recently has been shown[2] to be highly suitable for predicting momentum-space properties, viz. the Compton profiles for atoms and molecules. In the present work, this same $f(\mathbf{r},\mathbf{p})$ is used to generate a new formula for the exchange energy functional $K[\rho]$.

Consider the ground state of a system with an even number of electrons, for which the exchange energy is given by

$$K[\rho]=\frac{1}{4}\int\int \frac{|\gamma(\mathbf{r},\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}' , \tag{1}$$

where $\gamma(\mathbf{r},\mathbf{r}')$ is the first-order density matrix. The problem is to turn this exact formula for K into a formula for K in terms of the diagonal element of $\gamma(\mathbf{r},\mathbf{r}')$, $\rho(\mathbf{r})=\gamma(\mathbf{r},\mathbf{r})$.

The classical way to do this is due to Dirac; one uses a uniform electron-gas construction for $\gamma(\mathbf{r},\mathbf{r}')$. The result is the well-known local density approximation (LDA) for exchange,[3]

$$K[\rho]=C_x\int \rho^{4/3}(\mathbf{r})d\mathbf{r},\quad C_x=(3/4\pi)(3\pi^2)^{1/3} . \tag{2}$$

This has been much used, for example in the exchange-only version of Kohn-Sham theory.[4] The method due to Slater, the so-called $X\alpha$ method, modifies this by including an empirical multiplicative factor α,[5]

$$K[\rho]=\frac{3}{2}\alpha C_x\int \rho^{4/3}(\mathbf{r})d\mathbf{r} . \tag{3}$$

Values of α have been determined by various means. To reproduce Hartree-Fock energies of atoms, for example, values of α ranging from 0.77 for the atom He to 0.70 for the atom Xe are required.[6] Gradient expansion corrections to Eq. (2) also are known (see below).[7]

For highly nonuniform systems such as atoms or molecules, it is not certain that the uniform electron-gas starting point is so appropriate. We here consider an alternative approach, which makes use of a Gaussian approximation to $\gamma(\mathbf{r},\mathbf{r}')$ (Ref. 1) that elsewhere has already been shown to be highly useful for other purposes.[2] The result is a simple improvement of Eq. (2) and also increased understanding of Eq. (3).

II. EXCHANGE ENERGY

Consider an N-electron system characterized by the ground-state density $\rho(\mathbf{r})$. Associate a phase-space distribution function $f(\mathbf{r},\mathbf{p})$ with this density and assume it to yield the correct kinetic energy density $t(\mathbf{r},\rho)$ as well; that is

$$\rho(\mathbf{r})=\int d\mathbf{p}f(\mathbf{r},\mathbf{p}),\quad \int d\mathbf{r}\rho(\mathbf{r})=N , \tag{4}$$

$$t(\mathbf{r},\rho)=\frac{1}{2}\int d\mathbf{p}p^2f(\mathbf{r},\mathbf{p}),\quad \int d\mathbf{r}\,t(\mathbf{r},\rho)=E_{\text{kin}} . \tag{5}$$

An entropy functional, S defined as

$$S=-k\int d\mathbf{r}\int d\mathbf{p}f[\ln f-1] , \tag{6}$$

where k is the Boltzmann constant, is then maximized subject to the constraints of correct density, Eq. (4), and correct kinetic energy density, Eq. (5), to give the unique most-probable distribution function[1]

$$f(\mathbf{r},\mathbf{p})=e^{-\alpha(\mathbf{r})}e^{-\beta(\mathbf{r})p^2/2} . \tag{7}$$

On evaluation of the Lagrange multipliers $\alpha(\mathbf{r})$ and $\beta(\mathbf{r})$ from Eqs. (4) and (5), one obtains

$$f(\mathbf{r},\mathbf{p})=[2\pi kT(\mathbf{r})]^{-3/2}\rho(\mathbf{r})\exp[-p^2/2kT(\mathbf{r})] , \tag{8}$$

where

$$\beta(\mathbf{r})=1/kT(\mathbf{r}) . \tag{9}$$

Here the local temperature $T(\mathbf{r})$ is defined, in analogy with an ideal gas, by

$$\frac{3}{2}\rho(\mathbf{r})kT(\mathbf{r})=t(\mathbf{r},\rho) . \tag{10}$$

The Maxwellian nature of this resulting $f(\mathbf{r},\mathbf{p})$ leads to various simple thermodynamic and fluid-theoretic equations for the electron cloud.[1,8]

The phase-space formulation of quantum mechanics began with the Wigner distribution function,[9] defined through partial Fourier transform of the first-order reduced density matrix $\gamma(\mathbf{r},\mathbf{r}')$,

$$f(\mathbf{r},\mathbf{p})=(2\pi)^{-3}\int \gamma(\mathbf{r}+\tfrac{1}{2}\mathbf{s};\mathbf{r}-\tfrac{1}{2}\mathbf{s})e^{-i\mathbf{p}\cdot\mathbf{s}}d\mathbf{s}\ . \tag{11}$$

The inverse transformation yields the density matrix γ from $f(\mathbf{r},\mathbf{p})$,

$$\gamma(\mathbf{r}+\tfrac{1}{2}\mathbf{s};\mathbf{r}-\tfrac{1}{2}\mathbf{s})=\int f(\mathbf{r},\mathbf{p})e^{i\mathbf{p}\cdot\mathbf{s}}d\mathbf{p}\ . \tag{12}$$

Taking Eq. (8) as an approximation for $f(r,p)$,[1,10] Eq. (12) leads to

$$\gamma(\mathbf{r}+\tfrac{1}{2}\mathbf{s};\mathbf{r}-\tfrac{1}{2}\mathbf{s})=\rho(\mathbf{r})e^{-s^2/2\beta(\mathbf{r})}\ . \tag{13}$$

The exchange energy $K[\rho]$ of Eq. (1) then becomes

$$K[\rho]=\frac{\pi}{2}\int \rho^2(\mathbf{r})\beta(\mathbf{r})d\mathbf{r}\ . \tag{14}$$

This equation is the basic phase-space formula for calculating the exchange energy from the density.

Consider now the functional form of the kinetic energy density $t(\mathbf{r},\rho)$ which defines $\beta(\mathbf{r})$ or $T(\mathbf{r})$ through Eqs. (9) and (10). Although the kinetic energy density is not unique, the most natural form, as has also been adopted in earlier works[1,2] and confirmed by Berkowitz,[10] is

$$\begin{aligned} t(\mathbf{r},\rho)&=\tfrac{1}{8}\sum_i \frac{\nabla\rho_i\cdot\nabla\rho_i}{\rho_i}-\tfrac{1}{8}\nabla^2\rho \\ &=\int \frac{p^2}{2}f(\mathbf{r},\mathbf{p})d\mathbf{p}\ , \end{aligned} \tag{15}$$

where the ρ_i are orbital densities. The orbitals have been here assumed to be real.

One also has various approximate kinetic energy density functionals, for example, the Thomas-Fermi form[11]

$$t_0(\mathbf{r},\rho)=C_K\rho(\mathbf{r})^{5/3},\quad C_K=\tfrac{3}{10}(3\pi^2)^{2/3}\ , \tag{16}$$

for which Eq. (14) gives

$$K[\rho]=\frac{5}{6\pi}(3\pi^2)^{1/3}\int \rho(\mathbf{r})^{4/3}d\mathbf{r}\ . \tag{17}$$

Note that this expression differs from the familiar Dirac expression of Eq. (2) by a multiplicative factor of $\frac{10}{9}$. That is, $\alpha=(\frac{10}{9})(\frac{2}{3})=0.74$ is predicted for Eq. (3). Equation (17) is a modified local density approximation for exchange.

Although using the closed form of Eq. (14) clearly is to be preferred, it is of some interest to generate gradient corrections to Eq. (17) from Eq. (14) by augmenting the Thomas-Fermi kinetic energy with correction terms. Thus, inclusion of the second-order Weizsacker-Kirzhnits correction,[12]

$$t_2(\mathbf{r},\rho)=\tfrac{1}{9}t_w(\mathbf{r},\rho)=\frac{1}{72}\frac{\nabla\rho\cdot\nabla\rho}{\rho}+\tfrac{1}{6}\nabla^2\rho \tag{18}$$

leads to the exchange energy

$$\begin{aligned} K[\rho]=\frac{3\pi}{4}\frac{1}{C_K}\int \rho^{4/3}\Bigg[1&+\frac{1}{72}\frac{1}{C_K}\frac{\nabla\rho\cdot\nabla\rho}{\rho^{8/3}} \\ &+\frac{1}{24C_k}\frac{\nabla^2\rho}{\rho^{5/3}}\Bigg]^{-1}d\mathbf{r}\ , \end{aligned} \tag{19}$$

which, on expansion and retention of second-order terms, becomes

$$\begin{aligned} K[\rho]=&\frac{5}{6\pi}(3\pi^2)^{1/3}\int \rho^{4/3}d\mathbf{r} \\ &-\frac{25\pi}{108}(3\pi^2)^{-4/3}\int \frac{\nabla\rho\cdot\nabla\rho}{\rho^{4/3}}d\mathbf{r}\ . \end{aligned} \tag{20}$$

This expression can be compared with the conventional gradient expansion[7]

$$\begin{aligned} K[\rho]=&\frac{3}{4\pi}(3\pi^2)^{1/3}\int \rho^{4/3}d\mathbf{r} \\ &+\frac{7\pi}{144}(3\pi^2)^{-4/3}\int \frac{\nabla\rho\cdot\nabla\rho}{\rho^{4/3}}d\mathbf{r}\ , \end{aligned} \tag{21}$$

where the second coefficient is due to Sham[13] and is about three times smaller than that found empirically by Herman *et al.*[14] Note that the coefficients of both the first and the second terms are different. One can generate higher order terms similarly. Equation (19) itself is an interesting closed expression for exchange.

III. EXCHANGE HOLE

Now consider the behavior of the exchange hole corresponding to the exchange energy of Eq. (14). The exchange energy of Eq. (1) can be written in the form

$$K[\rho]=-\tfrac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{\rho(\mathbf{r})\rho_x(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{22}$$

and can be visualized as the interaction energy of an electron with its associated exchange hole. The exchange-hole density $\rho_x(\mathbf{r},\mathbf{r}')$ is given by

$$\rho_x(\mathbf{r},\mathbf{r}')=-\frac{1}{2}\frac{|\gamma(\mathbf{r};\mathbf{r}')|^2}{\rho(\mathbf{r})}\ . \tag{23}$$

The exact exchange hole is always negative and satisfies two important other conditions,[15,16]

$$\rho_x(\mathbf{r},\mathbf{r}')=-\rho(\mathbf{r})/2 \tag{24}$$

and

$$\int \rho_x(\mathbf{r},\mathbf{r}')d\mathbf{r}'=1\quad \text{for all } \mathbf{r}\ . \tag{25}$$

Rewriting the density matrix of Eq. (13) as

$$\gamma(\mathbf{r};\mathbf{r}')=\rho\left[\frac{\mathbf{r}+\mathbf{r}'}{2}\right]\exp\left[-|\mathbf{r}-\mathbf{r}'|^2\Big/2\beta\left[\frac{\mathbf{r}+\mathbf{r}'}{2}\right]\right], \tag{26}$$

the present exchange hole is seen to be given by

$$\rho_x(\mathbf{r},\mathbf{r}')=-\frac{1}{2}\frac{\rho^2\left[\frac{\mathbf{r}+\mathbf{r}'}{2}\right]}{\rho(\mathbf{r})}\times\exp\left[-|\mathbf{r}-\mathbf{r}'|^2/\beta\left[\frac{\mathbf{r}+\mathbf{r}'}{2}\right]\right], \tag{27}$$

which clearly is always negative and satisfies Eq. (24).

The corresponding normalization integral,

$$\begin{aligned}N_x(\mathbf{r})&\equiv\int\rho_x(\mathbf{r},\mathbf{r}')d\mathbf{r}'\\&=-\frac{1}{2}\int\frac{\rho^2\left[\frac{\mathbf{r}+\mathbf{r}'}{2}\right]}{\rho(\mathbf{r})}\\&\quad\times\exp\left[-|\mathbf{r}-\mathbf{r}'|^2/\beta\left[\frac{\mathbf{r}+\mathbf{r}'}{2}\right]\right]d\mathbf{r}',\end{aligned} \tag{28}$$

can be simplified on change of variable

$$(\mathbf{r}+\mathbf{r}')/2=\mathbf{R} \text{ and } \mathbf{r}-\mathbf{r}'=2(\mathbf{r}-\mathbf{R}),\quad d\mathbf{r}'=8d\mathbf{R} \tag{29}$$

to yield

$$N_x(\mathbf{r})=-\frac{4}{\rho(\mathbf{r})}\int\rho^2(\mathbf{R})\exp[-4|\mathbf{r}-\mathbf{R}|^2/\beta(\mathbf{R})]d\mathbf{R}\,. \tag{30}$$

For spherically symmetric densities (e.g., atoms), angular integration can be performed leading to the simplified form

$$N_x(r)=-\frac{\pi}{r\rho(r)}\int dR\,R\rho^2(R)\beta(R)\left[\exp\left[-\frac{4(r-R)^2}{\beta(R)}\right]-\exp\left[-\frac{4(r+R)^2}{\beta(R)}\right]\right]. \tag{31}$$

This is not necessarily equal to -1 for all r values. The normalization condition of Eq. (25) is not necessarily exactly satisfied by the exchange hole of the present scheme.

A most important aspect of the exchange hole is that its spherical average that determines the exchange energy. Thus Eq. (22) can be rewritten as

$$K[\rho]=-\tfrac{1}{2}\int d\mathbf{r}\rho(\mathbf{r})\int d\mathbf{s}\frac{\rho_x(\mathbf{r},\mathbf{r}+\mathbf{s})}{s} \tag{32}$$

$$=-\tfrac{1}{2}\int d\mathbf{r}\rho(\mathbf{r})\int ds\frac{\rho_x^{\mathrm{SA}}(\mathbf{r},s)}{s}\,, \tag{33}$$

where the spherically averaged exchange hole is given by

$$\rho_x^{\mathrm{SA}}(\mathbf{r},s)\equiv\frac{1}{4\pi}\int\rho_x(\mathbf{r},\mathbf{r}+\mathbf{s})d\Omega_s\,. \tag{34}$$

For the exchange hole of Eq. (27),

$$\rho_x^{\mathrm{SA}}(\mathbf{r},s)=-\frac{1}{2}\frac{1}{r\rho(r)}\frac{1}{s}\times\int_{|r-s/2|}^{|r+s/2|}dr'\,r'\rho^2(r')\exp[-s^2/\beta(r')] \tag{35}$$

which determines the exchange energy through the simple formula, for spherically symmetric densities,

$$K[\rho]=-4\pi^2\int_0^\infty dr\,r^2\rho(r)\int_0^\infty ds\,s\rho_x^{\mathrm{SA}}(\mathbf{r},s)\,. \tag{36}$$

The normalization integral is similarly given by

$$N_x(r)=4\pi\int ds\,s^2\rho_x^{\mathrm{SA}}(\mathbf{r},s)\,. \tag{37}$$

The integration in these formulas generally must be performed numerically.

IV. RESULTS

The present theory is readily tested for atoms by evaluating the exchange energies based on Eq. (14) using electron densities from the Hartree-Fock atomic wave functions of Clementi and Roetti.[17] The local temperature is calculated from the kinetic energy density, employing Hartree-Fock orbital densities in Eq. (15). For the noble-gas atoms, the results are compared in Table I with the exact exchange energies, the LDA result [Eq. (2)], the modified LDA (i.e., using Thomas-Fermi kinetic energy) [Eq. (17)], and some recent results of Perdew.[18]

Table I shows that (as is well known) the traditional LDA underestimates the exchange energies; the underestimation varying from -13.8% for He to -4.7% for Xe. In the present method, on the other hand, the underestimation (-11% for He) turns into overestimation (1.5% for Xe) as one goes to higher atoms. The modified LDA also shows the same trend. The considerable overall improvement over conventional LDA is clear.

Much detailed insight into the nature of the functional can be obtained through the study of the properties of the exchange hole. In Figs. 1 and 2, the exchange holes in the present scheme are compared with the exact and the LDA results. The last two are taken from a paper by Perdew and Zunger.[16] In Fig. 1, $\rho_x(\mathbf{r},\mathbf{r}')$ for the neon atom is plotted against $(r'-r)$ at $r=0.09$ and 0.39 a.u., where $\mathbf{r}'$ lies on the line joining the point r and the nucleus. The asymmetry of the exact exchange hole is much better reproduced by the present method than by the conventional LDA method. When $\mathbf{r}$ and $\mathbf{r}'$ are on the same side of the nucleus, nearly exact coincidence with the correct hole is observed, although, for points on opposite sides of the

TABLE I. Exchange energies for noble-gas atoms (a.u.).

Atom (Z)	Exact exchange[a]	Present exchange[b]	LDA exchange[c]	Modified LDA exchange[d]	Modified present exchange[e]	Perdew exchange[a]
He (2)	1.026	0.9129	0.8841	0.9823	1.022 (1.119)	1.033
Ne (10)	12.11	11.57	11.03	12.26	12.15 (1.050)	12.24
Ar (18)	30.18	29.24	27.86	30.96	30.97 (1.059)	30.36
Kr (36)	93.9	94.26	88.62	98.47	97.46 (1.034)	94.5
Xe (54)	179.1	181.7	170.6	189.5	188.1 (1.035)	180.5

[a] Reference 18.

[b] Equations (9), (10), (14), and (15) of text.

[c] Equation (2) of text.

[d] Equation (17).

[e] Equations (40), (41), and (45), with f=const (values of f indicated in parentheses). See text.

nucleus the present hole decreases too fast. Figure 2 shows that the present scheme also reproduces the spherical average of the exchange hole [Eq. (35)] very well, in good agreement with the exact result regardless of whether the hole center is located near ($r=0.09$) or far ($r=0.39$) from the nucleus.

The next important characteristic of the exchange hole after its shape is its normalization. As has already been stated, the present exchange hole is everywhere negative, satisfies the condition of Eq. (24), compares with the exact behavior quite well, but does not exactly satisfy the normalization condition of Eq. (25). The normalization integral $N_x(r)$ of Eq. (37) for the krypton atom is given in Fig. 3. Although $-N_x(r)$ is not identically unity, it is near the exact value in the important region. However, at distances far away or very close to the nucleus, it is much smaller than unity. It is interesting that the shell structure in the radial density is reflected in the normalization curve (showing maxima at the points of radial density minima).

Various schemes can be introduced to improve the normalization. An exact normalization can, for example, be realized by changing the density matrix of Eq. (26) to

$$\gamma^M(\mathbf{r},\mathbf{r}')=\rho\left[\frac{\mathbf{r}+\mathbf{r}'}{2}\right]\times\exp\left[-|\mathbf{r}-\mathbf{r}'|^2\Big/2f\beta\left[\frac{\mathbf{r}+\mathbf{r}'}{2}\right]\right], \quad (38)$$

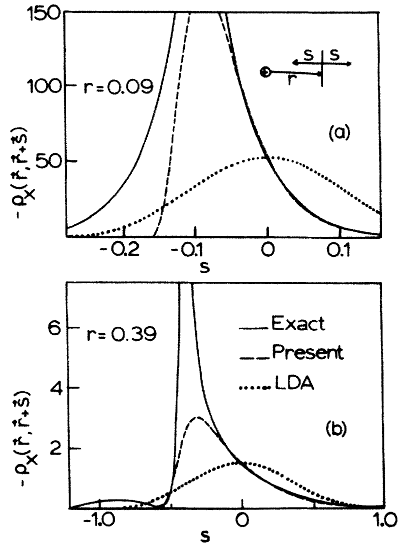

FIG. 1. Exchange hole for neon atom. The observation point $\mathbf{r}'=\mathbf{r}+\mathbf{s}$ lies on a line joining the reference point $\mathbf{r}$ and the nucleus. (a) and (b) correspond to two different values of r.

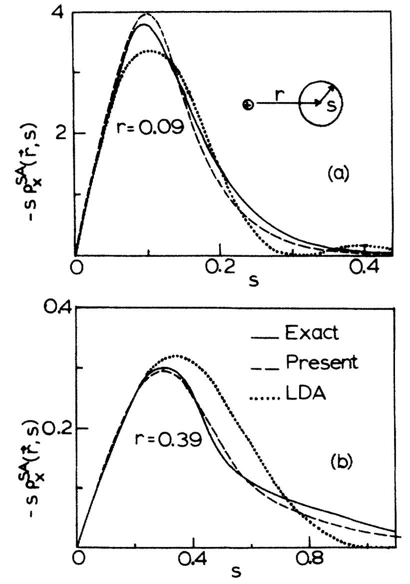

FIG. 2. Spherical average of the exchange hole for neon atom. (a) corresponds to $r=0.09$ a.u.; the hole normalizes to -0.87 at this point. (b) corresponds to $r=0.39$ a.u., where the normalization is -0.79.

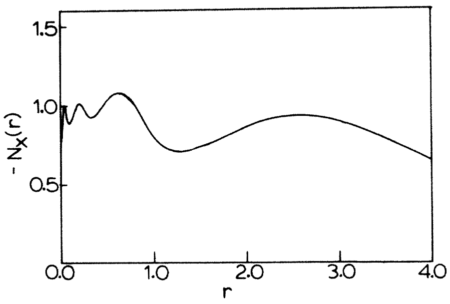

FIG. 3. Normalization of the exchange hole vs the distance from the nucleus for krypton atom.

where f is a function. To preserve the symmetry of the density matrix, f should actually be $f((\mathbf{r}+\mathbf{r}')/2)$ or $f(|\mathbf{r}-\mathbf{r}'|)$; or $[f(\mathbf{r})+f(\mathbf{r}')]/2$, $f(\mathbf{r})f(\mathbf{r}')$, or some other suitable symmetrized form. One simple choice is

$$f \equiv f(\mathbf{r}+\mathbf{r}')/2$$

which amounts to assuming a modified β; i.e., an effective temperature which is somewhat different from the one defined through the kinetic energy and is determined so as to give a correct normalized exchange hole. The exchange hole corresponding to the density matrix modified in this way is

$$\rho_x^M(\mathbf{r},\mathbf{r}')=-\frac{1}{2}\frac{\rho^2\left[\dfrac{\mathbf{r}+\mathbf{r}'}{2}\right]}{\rho(\mathbf{r})} \times\exp\left[-|\mathbf{r}-\mathbf{r}'|^2\Big/ f\beta\left[\frac{\mathbf{r}+\mathbf{r}'}{2}\right]\right], \tag{39}$$

and the normalization is given by

$$N_x^M(r)=-\frac{\pi}{r\rho(r)}\int dR\, R\rho^2(R)f(R)\beta(R)\left[\exp\left[-\frac{4(r-R)^2}{f(R)\beta(R)}\right]-\exp\left[-\frac{4(r+R)^2}{f(R)\beta(R)}\right]\right], \tag{40}$$

with $f(R)$ as yet undetermined, but to be determined to give the correct normalization of Eq. (25). By imposing this correct normalization, one obtains a set of nonlinear simultaneous equations which can be solved for f. The modified exchange energy then may be obtained from

$$K[\rho]=\frac{\pi}{2}\int \rho^2(\mathbf{r})f(\mathbf{r})\beta(\mathbf{r})d\mathbf{r}\,. \tag{41}$$

A second renormalization scheme follows if one assumes $f \equiv f(r)$ only. In that case at each point r, one single $f(r)$ is uniquely determined by the normalization

$$-1=-\frac{\pi}{r\rho(r)}\int dR\, R\rho^2(R)f(r)\beta(R) \times\left[\exp\left[-\frac{4(r-R)^2}{f(r)\beta(R)}\right]-\exp\left[-\frac{4(r+R)^2}{f(r)\beta(R)}\right]\right]. \tag{42}$$

The corresponding exchange energy is given by

$$\begin{aligned}K[\rho]&=-\tfrac{1}{4}\int d\mathbf{r}\int d\mathbf{r}'\,|\mathbf{r}-\mathbf{r}'|^{-1}\rho^2\left[\frac{\mathbf{r}+\mathbf{r}'}{2}\right]\exp\left[-|\mathbf{r}-\mathbf{r}'|^2\Big/ f(\mathbf{r})\beta\left[\frac{\mathbf{r}+\mathbf{r}'}{2}\right]\right]\\&=-\tfrac{1}{4}\int d\mathbf{R}\int d\mathbf{s}\,s^{-1}\rho^2(\mathbf{R})\exp\left\{-s^2\Big/\left[f\left[\left|\mathbf{R}+\frac{\mathbf{s}}{2}\right|\right]\beta(\mathbf{R})\right]\right\}\\&=-2\pi^2\int_0^\infty dR\,R^2\rho^2(R)\int_0^\infty ds\,s\int_0^\pi d\theta\,\sin\theta\exp\left\{-s^2\Big/\left[\beta(R)f\left[\left|R^2+\frac{s^2}{4}+sR\cos\theta\right|\right]\right]\right\}.\end{aligned} \tag{43}$$

The main drawback of this second scheme is that the density matrix no longer is symmetric in $\mathbf{r}$ and $\mathbf{r}'$. The situation is comparable to the case of the weighted density scheme for nonlocal exchange correlation (XC) density functional as discussed, e.g., by Gunnarsson *et al.*[15] and Alonso and Girifalco,[19] where the XC hole is assumed to depend on a density $\bar{\rho}(\mathbf{r})$ which is determined through the normalization condition, i.e.,

$$\begin{aligned}-1&=\int d\mathbf{r}'\rho_{\mathrm{XC}}(\mathbf{r},\mathbf{r}')\\&=\int d\mathbf{r}'\rho(\mathbf{r}')g^h_{\bar{\rho}(\mathbf{r})}(\mathbf{r},\mathbf{r}')\,,\end{aligned} \tag{44}$$

where g^h is the correlation function for the homogeneous electron gas. This introduction of asymmetry in the exchange hole (since $\bar{\rho}$ depends only on $\mathbf{r}$ and is not a symmetrized function of $\mathbf{r}$ and $\mathbf{r}'$) amounts to assuming the density matrix to be asymmetric.

There is a third alternative, which is simple to implement. One can choose f to be a constant, a scale factor. Of course, normalization at each point cannot then be accomplished. However, one can choose the constant so as to minimize the deviations of the normalization integrals from their actual values in some least-squares sense. To incorporate the dominating effect of the most important region, the radial density can be used as the weighting factor in the least square procedure. That is, one may determine the scale factor by minimizing the quantity

$$F=N^{-1}\int d\mathbf{r}\,\rho(\mathbf{r})[1+N_x^M(\mathbf{r})]^2\ . \tag{45}$$

Results of doing this are included in Table I. They are exceedingly good for lighter atoms but for heavier atoms some overestimation of the exchange is found.

The numerical results reported here have been obtained by evaluating the functionals using the Hartree-Fock densities. However, this is only a convenience; one can as well employ the Kohn-Sham orbital densities[4] and, as has been pointed out by Perdew,[18] the difference is small. Of course, the ultimate purpose is to employ the new exchange formula in the self-consistent procedure itself. The exchange potential corresponding to the exchange energy of Eq. (14) is given by

$$v_x=-\frac{\delta K}{\delta\rho}=-\frac{\pi}{2}\left[2\rho(\mathbf{r})\beta(\mathbf{r})+\int\rho^2(\mathbf{r}')\frac{\delta\beta(\mathbf{r}')}{\delta\rho(\mathbf{r})}d\mathbf{r}'\right]\ . \tag{46}$$

Evaluating v_x using Eqs. (9), (10), (15), and (46), and incorporating the result into the Kohn-Sham scheme, one will obtain a modified self-consistent density-functional procedure. A simpler modified self-consistent scheme would follow from the modified local exchange of Eq. (17). The exchange potential then is $\frac{10}{9}$ times the conventional Kohn-Sham exchange.

V. ASSESSMENT

There can be other methods to go from the density and kinetic energy density to an approximate first-order density matrix. For example, one may follow the method of Negele and Vautherin,[20] which gives interesting results.[21] Why is the present method so good? Because of all such methods it is the best in an information theoretic sense, as has already been discussed elsewhere.[2,10]

Further insight is provided by consideration of the uniform electron-gas case. At first sight this presents a problem: Should one not recover the classical uniform gas result if one goes to the limit?[22] Note that Eq. (30) gives for the uniform gas $N_x=-\frac{1}{2}\rho(\pi\beta)^{3/2}=-1.05$, five percent in error. K itself is 11% in error.

Consider the well-known integral which enters the calculation of Dirac exchange,[23]

$$\int_0^\infty\frac{(\sin x-x\cos x)^2}{x^5}dx=\frac{1}{4}\ . \tag{47}$$

Reevaluate this by approximating the integral by the Berkowitz expansion and resummation procedure:[10]

$$\frac{(\sin x-x\cos x)^2}{x^5}\approx\frac{1}{9}xe^{-x^2/5}\ , \tag{48}$$

$$\int_0^\infty\frac{1}{9}xe^{-x^2/5}dx=\frac{5}{18}=\frac{10}{9}\left(\frac{1}{4}\right)\ . \tag{49}$$

Here is the $\frac{10}{9}$ factor, in this case clearly in error. However, consider the integrands in Eqs. (47) and (49); these are shown in Fig. 4. What the phase-space procedure has done is average out the oscillations for large $x\sim|\mathbf{r}-\mathbf{r}'|$, and it is highly likely that the real behavior of the density matrix for an atom conforms more to the smoothly decreasing integrand of Eq. (49) than to the oscillating integrand for the uniform gas, Eq. (47).[24]

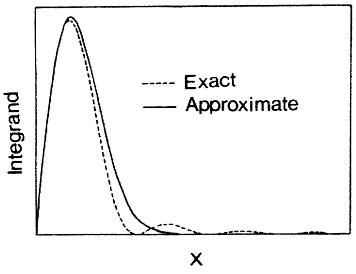

FIG. 4. Integrand for exchange energy for uniform electron gas. Exact: Eq. (47). Approximate: Eq. (49). x is proportional to $|\mathbf{r}-\mathbf{r}'|\,1-$; see Ref. 23.

The foregoing paragraph, it must be emphasized does not provide the fundamental rationale for the phase-space approach, or an acceptable derivation of the factor $\frac{10}{9}$. The real justification is the entropic or information theoretic derivation of the much more general result of Eq. (14). It is a best or least-biased approximation that has been made, and the factor $\frac{10}{9}$ is a consequence of that.

VI. FINAL REMARKS

The conclusion is that Eq. (14) is a most promising generalization of the local density approximation for exchange. It is a new nonlocal exchange function, but with the whole effect of nonlocality packed into the local temperature. It may be employed in self-consistent calculations without basic difficulty, in contrast with gradient expansions, which have divergence difficulties.

A highly promising new method for computing exchange, due to Perdew,[18] appears sometimes to surpass Eq. (14) in accuracy. However, it has the problem that the functional derivative $\delta K/\delta\rho$ is not easily computed, whereas the functional derivative of Eq. (14) can be dealt with straightforwardly (although it is not trivial). That the α parameter in $X\alpha$ theory should be assigned a value about 10% greater than $\frac{2}{3}$ would appear now to be understood.

It should not be presumed that Eq. (14) will be as accurate for molecules as for atoms. Indeed, it is evident from the history of our derivation of Eq. (14), in the work of Refs. 1, 2, and 10, that modification of Eq. (14) must be expected when the symmetry is less than purely spherical. For then the kinetic energy components in the three directions are not equivalent, and more than one effective temperature will be required for good accuracy. See for example the calculations of Compton profiles in Ref. 2.

The lovely derivation of Berkowitz[10] in fact brings in off-diagonal as well as diagonal elements of the local kinetic energy tensor; these must be investigated in detail.

The most interesting questions of all, however, have to do with the phase-space approach itself. Can the whole exchange-correlation functional be treated similarly? What theory of the many-body problem gives rise to Eq. (8) or Eq. (13), and can such a theory effectively incorporate correlation effects?

Discussions with Professor Max Berkowitz and Mr. Weitao Yang have been very helpful. Professor Berkowitz kindly provided a prepublication copy of Ref. 10, which in fact inspired the present work. This research has been aided by a grant from the National Science Foundation to The University of North Carolina at Chapel Hill.

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[23] For example, pp. 323—332 in J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill, New York, 1960), Vol. II.

[24] The substance of this paragraph has been independently found and communicated to the authors by Professor Robert Harris of the University of California at Berkeley.