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Spin-density gradient expansion for the kinetic energy

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Expressions for the kinetic energy T (and incidentally also for the exchange energy E_x) of a ground-state inhomogeneous electron gas as a functional of the electron density $n(\vec{r})$, and for $n(\vec{r})$ as a functional of the one-electron potential $V(\vec{r})$, are readily generalized to the case of two unequal spin densities $n_\uparrow(\vec{r})$ and $n_\downarrow(\vec{r})$. As an example the authors consider the expansions of T up to fourth order in the gradients of n, and of n up to fourth order in the gradients of V. These expansions are tested for the extreme case of one- and two-electron atoms. It is found that (i) The $n[V]$ expansion contains serious pathologies, while the $T[n]$ expansion leads to much more reasonable results when applied to either the exact density $n(\vec{r})$ or to an $n(\vec{r})$ obtained by minimization of the approximate total-energy functional $E[n]$. (ii) Good approximations to E and $n(\vec{r})$ in one-electron atoms are obtained *only* when the complete spin polarization of a single electron is taken into account via $T[n_\uparrow, n_\downarrow]$. (iii) Within a variational calculation, the inclusion of second- and fourth-order gradient corrections to the zeroth-order (Thomas-Fermi) approximation for T leads to systematic improvements in the analytic behavior of $n(\vec{r})$ near the nucleus. The authors also compare the local-exchange approximation with the local-exchange-correlation approximation in one- and two-electron atoms, and find that correlation should not be neglected.

I. INTRODUCTION

The ground-state properties of a system of interacting electrons are known[1,2] to be functionals of the electron density $n(\vec{r})$, or more generally[3-5] of the spin-up and spin-down electron densities $n_\uparrow(\vec{r})$ and $n_\downarrow(\vec{r})$. In particular the ground-state energy E as a functional of n obeys a well-known variational principle[1,4] which permits the *easy* calculation of E and n (without recourse to the many-body wave function) once the explicit dependence of E upon n is known or approximated. An important ingredient of E is the (noninteracting) kinetic energy, defined as

$$T[n_\uparrow, n_\downarrow] = \sum_\alpha \sum_\sigma \langle \psi_{\alpha\sigma} | -\tfrac{1}{2}\nabla^2 | \psi_{\alpha\sigma}\rangle \theta(\mu - \epsilon_{\alpha\sigma}) \quad (1.1)$$

(in atomic units $\hbar = m = e^2 = 1$), where $\sigma = \uparrow$ or $\downarrow$ and

$$[-\tfrac{1}{2}\nabla^2 + V_\sigma(\vec{r})]\psi_{\alpha\sigma}(\vec{r}) = \epsilon_{\alpha\sigma}\psi_{\alpha\sigma}(\vec{r}) . \quad (1.2)$$

Here $V_\sigma(\vec{r})$ is a self-consistent one-electron potential which is chosen so that the actual spin densities for the interacting system are

$$n_\sigma(\vec{r}) = \sum_\alpha |\psi_{\alpha\sigma}(\vec{r})|^2 \theta(\mu - \epsilon_{\alpha\sigma}) . \quad (1.3)$$

One approach to density-functional theory[2,4] proceeds via the construction of the self-consistent single-particle wave functions $\psi_{\alpha\sigma}$. The *only* approximation in this approach is the approximation for the exchange-correlation energy E_{xc} as a functional of n, for which a local approximation[2,4] is often made. This approach tends to be more accurate but computationally heavier than the second approach to density-functional theory, which approximates the *explicit* functional dependence of T upon n (and sometimes of n upon V) so that even the self-consistent single-particle wave functions are not needed. An example of this second approach is the Thomas-Fermi[6,7] approximation and its systematic generalization as a gradient expansion.[8-11] Following a long period of relative neglect, recent years have seen a rebirth of interest in the gradient expansion[12-16] for calculations in atoms, molecules, solids, and surfaces. It is beginning to appear that the gradient expansion can usefully supplement, and for some limited purposes even replace, the more exact method of Eqs. (1.1)–(1.3). The gradient expansion also admits the possibility of generalizations which will improve its accuracy. One simple and direct example is the spin-dependent generalization of this paper, but further and less direct generalizations may also be possible.

In their derivations of the second- and fourth-order terms in the gradient expansion, Kompaneets and Pavlovskii,[8] Kirzhnits,[9,10] and Hodges[11] considered only spin-unpolarized electron systems. Thus most tests of the accuracy of the gradient expansion have been restricted to such systems, e.g., the noble gas atoms[12] or the surfaces of paramagnetic metals.[14]

In this paper we show that the spin-unpolarized expressions for T and n may be generalized very simply to the case of arbitrary spin densities. We test the gradient expansions of T and n for the hydrogenic atom, treating it both improperly as a spin-unpolarized system and properly as a polarized system. In fact the original motivation for our work was the observation that Wang, Parr, Murphy, and Henderson[12] obtained accurate results for the kinetic energies of all the noble gases including even helium, but poor results for hydrogen, from the spin-unpolarized gradient expansion of T. As we will see, taking account of the spin-polarization of hydrogen completely removes this anomaly and also greatly improves the density obtained from a variational calculation. We believe that the spin-density gradient expansion of the kinetic energy, or some suitable generalization of it, will have a useful role to play in calculations of many physical and chemical properties of atoms, for which the active outer electrons are often spin polarized.

II. SPIN-DENSITY EXPRESSIONS

Suppose we know the kinetic energy $T[n]$ as a functional of the electron density $n(\vec{r})$ for a spin-unpolarized ($n_\uparrow = n_\downarrow = \frac{1}{2}n$) electron system, and want to know $T[n_\uparrow, n_\downarrow]$ for an arbitrarily-polarized system. By Eq. (1.1),

$$T[n_\uparrow, n_\downarrow] = T[n_\uparrow, 0] + T[0, n_\downarrow], \tag{2.1}$$

and in particular for the unpolarized system

$$T[n] = T[\tfrac{1}{2}n, 0] + T[0, \tfrac{1}{2}n] = 2T[0, \tfrac{1}{2}n]. \tag{2.2}$$

It follows that

$$T[n_\uparrow, n_\downarrow] = \tfrac{1}{2}T[2n_\uparrow] + \tfrac{1}{2}T[2n_\downarrow]. \tag{2.3}$$

As an example of the application of Eq. (2.3), consider the spin-unpolarized gradient expansion[11]

$$T[n] = T_0[n] + T_2[n] + T_4[n] + \cdots, \tag{2.4}$$

where

$$T_0[n] = \tfrac{3}{10}(3\pi^2)^{2/3}\int d^3r\, n^{5/3}, \tag{2.5}$$

$$T_2[n] = \frac{1}{72}\int d^3r\, \frac{|\nabla n|^2}{n}, \tag{2.6}$$

$$T_4[n] = \frac{1}{540(3\pi^2)^{2/3}} \times \int d^3r\, n^{1/3}\left[\left(\frac{\nabla^2 n}{n}\right)^2 - \frac{9}{8}\left(\frac{\nabla^2 n}{n}\right)\left|\frac{\nabla n}{n}\right|^2 + \frac{1}{3}\left|\frac{\nabla n}{n}\right|^4\right]. \tag{2.7}$$

This expansion is expected to converge rapidly when the density $n(\vec{r})$ varies slowly on the scale of the local Fermi wavelength $\lambda_F = 2\pi/(3\pi^2 n)^{1/3}$, i.e., when the gradient of λ_F is small[10]:

$$|\nabla\lambda_F| = \frac{2\pi|\nabla n|}{3(3\pi^2)^{1/3}n^{4/3}} \ll 1. \tag{2.8}$$

Applying Eq. (2.3) to (2.4) gives

$$T[n_\uparrow, n_\downarrow] = \sum_{l=0} T_{2l}[n_\uparrow, n_\downarrow] = \sum_{l=0} \tfrac{1}{2}(T_{2l}[2n_\uparrow] + T_{2l}[2n_\downarrow]). \tag{2.9}$$

A particularly simple result is obtained when the relative spin-polarization x is constant over all space, i.e., when $n_\uparrow(\vec{r}) = \frac{1}{2}(1+x)n(r)$ and $n_\downarrow(\vec{r}) = \frac{1}{2}(1-x)n(\vec{r})$:

$$T_0[n_\uparrow, n_\downarrow] = \tfrac{1}{2}[(1+x)^{5/3} + (1-x)^{5/3}]T_0[n], \tag{2.10}$$

$$T_2[n_\uparrow, n_\downarrow] = T_2[n], \tag{2.11}$$

$$T_4[n_\uparrow, n_\downarrow] = \tfrac{1}{2}[(1+x)^{1/3} + (1-x)^{1/3}]T_4[n]. \tag{2.12}$$

For complete spin polarization ($x = 1$), the leading or Thomas-Fermi[6,7] contribution to the kinetic energy is enhanced by a factor of $2^{2/3}$, while the fourth-order contribution is reduced by a factor of $2^{-2/3}$.

Of course these simple results have not been unanticipated in the literature. Golden[17] used an expression equivalent to Eqs. (2.10) and (2.11) with $x = 0$ or 1 (and without T_4), although his version of $T_2[n]$ was too large (by a factor of $\frac{13}{5}$) to be correct in the slowly varying limit. Kautz and Schwartz[18] gave correct general expressions for $T_0[n_\uparrow, n_\downarrow]$ and $T_2[n_\uparrow, n_\downarrow]$, in agreement with Eqs. (2.9), (2.5), and (2.6), but their derivation of $T_2[n_\uparrow, n_\downarrow]$, which is based on the random-phase-approximation (RPA) linear response function, cannot be applied to yield $T_4[n_\uparrow, n_\downarrow]$, which contains contributions from nonlinear response [viz., the second and third terms in Eq. (2.7)].

Incidentally, if we choose to define[19] the exchange energy E_x of the inhomogeneous system in terms of density-functional orbitals $\psi_{\alpha\sigma}(\vec{r})$ instead of Hartree-Fock orbitals, then the same argument leading to Eq. (2.3) gives

$$E_x[n_\uparrow, n_\downarrow] = \tfrac{1}{2}E_x[2n_\uparrow] + \tfrac{1}{2}E_x[2n_\downarrow], \tag{2.13}$$

and the analog of Eq. (2.10) becomes

$$E_x[n_\uparrow, n_\downarrow] = \tfrac{1}{2}[(1+x)^{4/3} + (1-x)^{4/3}]E_x[n], \tag{2.14}$$

within the local approximation[2,20] for exchange. While the long range of the Coulomb interaction does not admit[21] a gradient expansion for E_x, other nonlocal approximations for $E_x[n]$ have been proposed recently.[22,23]

Next, suppose we know the electron density $n([V]; \mu, \vec{r})$ as a functional of the one-electron potential $V(\vec{r})$ (and as a function of the chemical potential μ) for a spin-unpolarized system, and want to know the up-spin density $n_\uparrow([V_\uparrow]; \mu_\uparrow, \vec{r})$ for a spin-polarized system. The analog of Eq. (2.1) is simply

$$n(\vec{r}) = n_{\uparrow}(\vec{r}) + n_{\downarrow}(\vec{r}) , \tag{2.15}$$

with $n_\sigma(\vec{r})$ given by Eq. (1.3). Proceeding by the analog of Eq. (2.2), we find the analog of Eq. (2.3):

$$n_{\uparrow}([V_{\uparrow}]; \mu_{\uparrow}, \vec{r}) = \tfrac{1}{2} n([V]; \mu, \vec{r})\big|_{V=V_{\uparrow},\, \mu=\mu_{\uparrow}} . \tag{2.16}$$

As an example, consider the spin-unpolarized gradient expansion[11]

$$n([V]; \mu, \vec{r}) = \sum_{l=0} n_{2l}([V]; \mu, \vec{r}) , \tag{2.17}$$

where

$$n_0 = k_0^3/3\pi^2 , \tag{2.18}$$

$$n_2 = -\frac{1}{\pi^2}\left(\frac{(\nabla V)^2}{24k_0^3} + \frac{\nabla^2 V}{12k_0}\right) , \tag{2.19}$$

$$\begin{aligned} n_4 = \frac{1}{\pi^2}\Bigg[& \frac{\nabla^2(\nabla^2 V)}{240k_0^3} + \frac{1}{k_0^5}\left(\frac{(\nabla^2 V)^2}{96} + \sum_{i=1}^{3}\sum_{j=1}^{3}\frac{(\nabla_i\nabla_j V)^2}{120} + \frac{\nabla V\cdot\nabla(\nabla^2 V)}{40}\right) \\ & + \frac{1}{k_0^7}\left(\frac{5(\nabla V)^2\nabla^2 V}{96} + \frac{\nabla V\cdot\nabla(\nabla V)^2}{32}\right) + \frac{35(\nabla V)^4}{384k_0^9}\Bigg] , \end{aligned} \tag{2.20}$$

and

$$k_0 = [2(\mu - V)]^{1/2} . \tag{2.21}$$

Applying the spin-polarized generalization (2.16) to this expression introduces only a trivial factor of $\frac{1}{2}$. $\mu_{\uparrow}$ is determined by the condition

$$\int d^3r\, n_{\uparrow}([V_{\uparrow}]; \mu_{\uparrow}, \vec{r}) = N_{\uparrow} , \tag{2.22}$$

where $N_{\uparrow}$, the total number of spin-up electrons, is constrained to be some positive integer, and $N_{\uparrow} + N_{\downarrow}$ is a fixed positive integer. In evaluating Eq. (2.17), care must be taken to evaluate the right-hand side only over a region of space in which it is real, positive, and integrable; the density must be set equal to zero in any regions where Eq. (2.17) does not satisfy these physical constraints.

III. APPLICATIONS TO ONE- AND TWO-ELECTRON ATOMS

In an interesting recent paper, Wang and Parr[13] have applied the spin-unpolarized gradient expansion of the kinetic energy ($T_0 + T_2$) in a variational calculation of the total energy and electron density of first- and second-row atoms. They find good values for the total energy, and even obtain the correct shell structure of the density when the density is constrained to be a piecewise exponentially decaying function of r (the distance from the nucleus), with the number of distinct exponential regions equal to the number of shells. However, since the total energy is dominated by the spin-paired inner electrons, the suitability of this approach for the description of the physically and chemically active (and often spin-polarized) outer electrons remains uncertain.

In order to test the spin-density gradient expansion of Sec. II, we will apply it to one- and two-electron atoms, for which *all* of the electrons are "outer." For these atoms, the Wang-Parr[13] variational form for the density reduces to a single exponential

$$n(r) = N(\zeta^3/\pi)e^{-2\zeta r} , \tag{3.1}$$

where the variational parameter ζ can be regarded as an "effective nuclear charge," and where $N = 1$ or 2 is the number of electrons. Two *caveats* are in order here. First, the formal validity condition (2.8) for the gradient expansion is not satisfied by the density (3.1); in fact,

$$|\nabla\lambda_F| = 1.98N^{-1/3}e^{(2/3)\zeta r} \tag{3.2}$$

is greater than 1 even at $r = 0$, and diverges as $r \to \infty$. Second, the (unknown) sixth-order (T_6) and higher-order contributions to the kinetic energy are divergent for the density (3.1): From the definitions (1.1)–(1.3) it follows that, under the number-conserving scale transformation

$$n(\vec{r}) \to \gamma^3 n(\gamma\vec{r}) , \tag{3.3}$$

the kinetic energy transforms as

$$T[n] \to \gamma^2 T[n] . \tag{3.4}$$

Thus, if we write the $2l$th order gradient term T_{2l} in terms of a kinetic energy density[15,16] t_{2l}:

$$T_{2l}[n] = \int d^3r\, t_{2l} , \tag{3.5}$$

we find that t_{2l} is homogeneous in n of degree

$$\tfrac{1}{3}(5 - 2l) . \tag{3.6}$$

For $2l \geq 6$, t_{2l} diverges exponentially at large r. Nevertheless, the fourth-order expansion is known to work well for other problems to which both *caveats* apply; in particular, Ma and Sahni[14] obtained good results for the kinetic energy of the metal surface from $T[n] = T_0 + T_2 + T_4$.

The spin-density gradient expansion in the form (2.10)–(2.12) applied to the density profile (3.1) gives

$$T[n_{\uparrow}, n_{\downarrow}] = A(N, x)N\zeta^2 , \tag{3.7}$$

where $x = 0$ (spin unpolarized) or 1 (fully polarized). (Here we do not consider the possibility of nonuniform relative polarization.) Table I shows the values of $A(N, x)$ so obtained, which may be com-

TABLE I. Kinetic energy T of an N-electron atom with exponential density profile (3.1) and uniform relative spin polarization x is $T = A(N, x)N\xi^2$. Values of $A(N,x)$ given by the spin-density gradient expansion of T are here compared to the exact value. The first column is for a (hypothetical) spin-unpolarized one-electron atom, while the second column is for a spin-polarized one-electron atom or a spin-unpolarized two-electron atom.

	(a.u.)	
Order	$N=1$, $x=0$	$N=1$, $x=1$ or $N=2$, $x=0$
T_0	0.2891	0.4590
$T_0 + T_2$	0.3447	0.5145
$T_0 + T_2 + T_4$	0.3696	0.5302
Exact	···	0.5000

pared with the exact value $A = \frac{1}{2}$ (for $N = 1$ or 2) given by the definitions (1.1) and (1.3). Note that while inclusion of T_2 improves the value of $A(N, x)$, the further inclusion of T_4 slightly worsens it (in contrast to the situation for the metal surface,[14] where T_4 improves the kinetic energy). Note further that reasonable results for one-electron atoms are obtained *only* when the complete spin polarization of a single electron is taken into account; in fact $A(N, x)$ is the same for spin-polarized one-electron atoms as it is for spin-unpolarized two-electron atoms.

We next ask whether reasonable total energies and density profiles can be obtained variationally from the spin-density gradient expansion of T. First we discuss the simpler case of one-electron atoms of nuclear charge Z, for which the total energy is

$$E[n_\uparrow, n_\downarrow] = T[n_\uparrow, n_\downarrow] + U[n] , \tag{3.8}$$

where

$$U[n] = \int d^3r \left(\frac{-Z}{r}\right) n(r) . \tag{3.9}$$

TABLE II. Results of variational calculations for one-electron atoms of nuclear charge Z, using the exponential density profile (3.1). ξ is the variational parameter, and E the total energy. Results obtained with the fourth-order spin-density gradient expansion of the kinetic energy are here compared with the exact results. The first row is for a (hypothetical) spin-unpolarized ($x = 0$) one-electron atom, and the second and third rows are for a spin-polarized ($x = 1$) one-electron atom.

		(a.u.)	
Order	x	ξ/Z	E/Z^2
$T_0 + T_2 + T_4$	0	1.35	−0.676
$T_0 + T_2 + T_4$	1	0.94	−0.472
Exact	1	1.00	−0.500

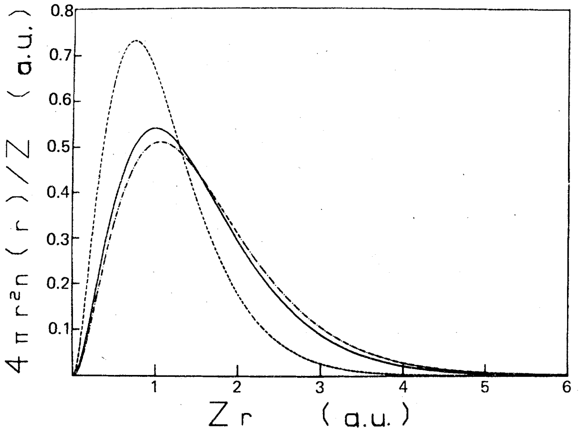

FIG. 1. Density profiles for one-electron atoms of nuclear charge Z found from variational calculations with the exponential density profile (3.1). Dashed curve: found from the fourth-order gradient expansion ($T_0 + T_2 + T_4$) of the kinetic energy assuming no spin polarization ($x = 0$); dash-dotted curve: same expansion assuming full spin polarization ($x = 1$); solid curve: exact profile for hydrogenic atoms.

For the density profile (3.1), we have

$$U[n] = -NZ\xi . \tag{3.10}$$

The results of minimizing (3.8) with respect to ξ, using the fourth-order gradient expansion of T, are shown in Table II and in Fig. 1. Note that application of the spin-unpolarized gradient expansion to this spin-polarized system leads to an energy that is far too low and a density that is far too localized near the nucleus, while the spin-polarized gradient expansion remedies these defects.

It is of some interest to ask how the truncation of the gradient series for T at various orders affects the shape of the electron density profile. We anticipate that higher-order gradient corrections will mainly improve the density in the vicinity of the nucleus for one- and two-electron atoms, since (a) the "small parameter" (3.2) of the expansion is smallest there, and (b) the series dependence on powers of n [see Eq. (3.6)] suggests best convergence in regions of highest density. In order to investigate this idea, we have considered the three-parameter power-law density profile

$$n(r) = \begin{cases} Cr^\alpha(1 - r/a)^\beta \ (r < a) , \\ 0 \ (r > a) \end{cases} \tag{3.11}$$

(where C normalizes the density to $N = 1$). This is a rather versatile profile which recovers the correct Thomas-Fermi Amaldi[24] ($T = T_0$) profile when $\alpha = -\frac{3}{2}$ and $\beta = +\frac{3}{2}$, and also recovers the exponential profile (3.1) when $\alpha = 0$ and β, $\alpha \to \infty$ with

TABLE III. Results of variational calculations for the spin-polarized ($x=1$) one-electron atom of nuclear charge Z, using the power-law density profile (3.11). The parameters α, β, a, and C of the density profile, and the total energy E, are shown for the zeroth, second-, and fourth-order spin-density gradient expansions as well as for an exact treatment of the kinetic energy.

Order	α	β	(a.u.) Za	C/Z^3	E/Z^2
T_0	-1.5	1.5	4.16	0.0478	-0.721
T_0+T_2	-0.62	$0.72(2Za)$	∞	0.153	-0.518
$T_0+T_2+T_4$	0.00	$0.94(2Za)$	∞	0.267	-0.472
Exact	0.00	$1.00(2Za)$	∞	0.318	-0.500

$\beta/2a=\xi$. All the required integrals can be done analytically, using the formula

$$\int_0^1 dy\, y^{\alpha'}(1-y)^{\beta'}=\frac{(\alpha')!(\beta')!}{(\alpha'+\beta'+1)!}\,, \tag{3.12}$$

where $x!=\Gamma(x+1)$ and Γ is the gamma function. These integrals converge for $\alpha'>-1$ and $\beta'>-1$.

We also note that, since U is properly homogeneous, i.e.,

$$U[n]\rightarrow\gamma U[n] \tag{3.13}$$

under the scale-transformation (3.3), the result of minimizing E with respect to a automatically satisfies the viral theorem $U=-2T$. The minimizing a is proportional to $1/Z$, while the minimizing α and β are independent of Z. The results of such a minimization for the spin-polarized one-electron atom are shown in Table III and in Fig. 2. Note that for $T=T_0$ the density at the origin diverges as $r^{-3/2}$, while for $T=T_0+T_2$ this divergence is considerably weakened to $\sim r^{-1/2}$. Since the total energy equals $-\frac{1}{2}\langle Z/r\rangle$, this improvement in n at small r leads to a significant improvement in the energy. Finally for $T=T_0+T_2+T_4$, the divergence at the origin is completely eliminated, i.e., $n\sim r^0$, and in fact the minimizing profile is exponential, as in Eq. (3.1).

One peculiarity of T_4 deserves mention. Unlike T_0 and T_2, T_4 can be negative, and this can lead to instabilities for certain pathological density profiles. With the profile (3.11), T_4 is finite only when α is strictly zero or else greater than three. A true minimum was found only for $\alpha=0$, but a negative divergence of E was found for the (unphysical) case $\alpha>3$. Specifically, $E\rightarrow-\infty$ when $\alpha\rightarrow 10.3$, $\beta\rightarrow 24.3$ and $a\rightarrow 0$.

We turn now to the expansion of the spin-density n in gradients of the potential V, i.e., to the evaluation of Eqs. (2.16)–(2.21). We have evaluated these expressions for the spin-polarized one-

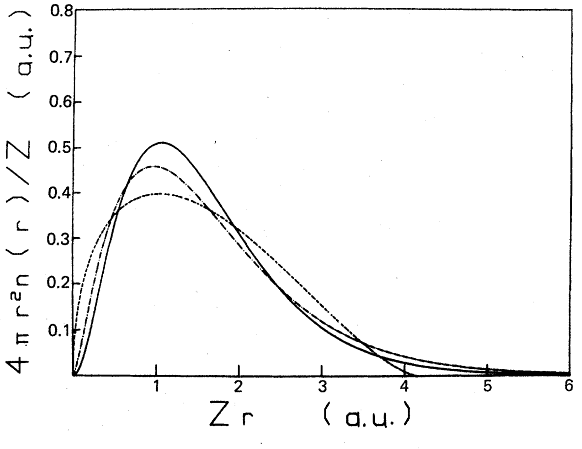

FIG. 2. Density profiles for one-electron atoms of nuclear charge Z found from variational calculations with the power-law density profile (3.11), employing the spin-polarized ($x=1$) gradient expansion of the kinetic energy to zeroth, second, and fourth orders. Dashed curve: $T=T_0$; dash-dotted curve: $T=T_0+T_2$; solid curve: $T=T_0+T_2+T_4$.

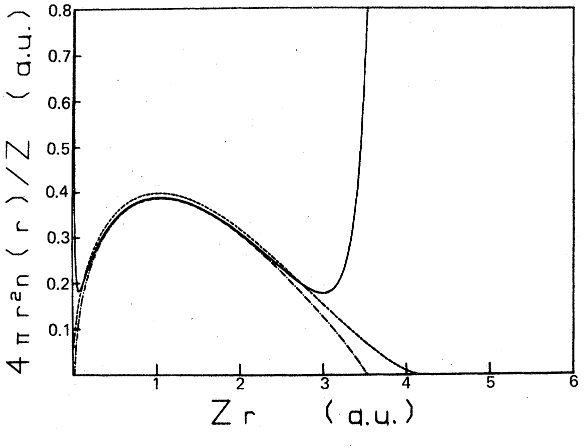

FIG. 3. Density profiles predicted for one-electron atoms of nuclear charge Z from the expansion of the spin density in gradients of the one-electron potential, to zeroth, second, and fourth orders. Dashed curve: $n=n_0$, for which $\mu=-0.240Z^2$; dash-dotted curve: $n=n_0+n_2$ for which $\mu=-0.237Z^2$; solid curve: $n=n_0+n_2+n_4$, for which no normalizing value of μ was found.

electron atom, for which $V=-Z/r$; the results are displayed in Fig. 3. The zero-order term n_0 is of course just the Thomas-Fermi-Amaldi[24] density [(3.11) with $\alpha=-\frac{3}{2}$, $\beta=\frac{3}{2}$, and $\mu=-Z/a=-0.240Z^2$]. Inclusion of n_2 hardly changes $\mu(=-0.237Z^2)$, but forces the density to zero for $r<0.016$ a.u. The further inclusion of n_4 leads to positive divergences of the density at both large and small r, so that no normalizing value of μ was found; the figure shown is for $\mu=-0.237Z^2$. The small-r singularities of this $n[V]$ expansion arise from the $-Z/r$ singularity of V, while the larger-r singularities arise from the existence of a classical turning point $[k_0(\vec{r})=0]$. Thus the $n[V]$ expansion, unlike the $T[n]$ expansion, appears to be useless for atomic problems. Even though the $T[n]$ expansion was derived from the $n[V]$ expansion in the work of Kirzhnits[9] and Hodges,[11] the $T[n]$ expansion is much less singular.

IV. EXCHANGE AND CORRELATION

So far we have discussed mainly the one-electron atom, for which we can use the energy functional (3.8), in which *only* the kinetic energy $T[n_\uparrow, n_\downarrow]$ is approximated. For atoms with arbitrary numbers of electrons, the total energy[2] becomes

$$E[n_\uparrow, n_\downarrow]=T[n_\uparrow, n_\downarrow]+U[n]+U_H[n]+E_{xc}[n_\uparrow, n_\downarrow], \qquad (4.1)$$

where

$$U_H[n]=\frac{1}{2}\int d^3r\int d^3r'\,\frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|}, \qquad (4.2)$$

and where the exchange-correlation energy $E_{xc}[n_\uparrow, n_\downarrow]$ must also be approximated. Gunnarsson and Lundqvist[25] have presented a strong case for the spin-density version[4] of the local exchange-correlation approximation[2] (LXCA),

$$E_{xc}[n_\uparrow, n_\downarrow]=\int d^3r\, n(\vec{r})\,\epsilon_{xc}(n_\uparrow(\vec{r}), n_\downarrow(\vec{r})), \qquad (4.3)$$

where $\epsilon_{xc}(n_\uparrow, n_\downarrow)$ is the exchange-correlation energy per electron of an electron gas with uniform spin densities $n_\uparrow$ and $n_\downarrow$. Here we compare the LXCA with the local-exchange approximation[2,20] (LXA) used in the atomic calculations of Wang and Parr.[13] The LXA is the same as the LXCA except that correlation is omitted, i.e.,

$$\begin{aligned}\epsilon_{xc}(n_\uparrow, n_\downarrow)&\rightarrow\epsilon_x(n_\uparrow, n_\downarrow)\\&=-\tfrac{1}{2}[(1+x)^{4/3}+(1-x)^{4/3}](3/4\pi)(3\pi^2n)^{1/3}. \qquad (4.4)\end{aligned}$$

To investigate exchange and correlation, we apply the energy functional (4.1) to N-electron atoms where $N=1$ or 2. We rewrite (4.1) as

$$E=T+U+(1-1/N)U_H+\Delta, \qquad (4.5)$$

where

$$\Delta=U_H/N+E_{xc}. \qquad (4.6)$$

For $N=1$ the "self-interaction" U_H/N should ideally be cancelled by E_{xc} so that $\Delta=0$, while for $N=2$ we still expect a near cancellation and a small value of Δ. (Complete cancellation is achieved in the Hartree and Hartree-Fock approximations.)

To test the LXA and LXCA, we have used the exponential density profile (3.1), for which

$$U_H[n]=0.3125N^2\zeta, \qquad (4.7)$$

and (in the LXA)

$$E_x[n]=-0.212\,74N^{4/3}\zeta, \qquad (4.8)$$

with $E_x[n_\uparrow, n_\downarrow]$ given by Eq. (2.14). The correlation energy $\epsilon_c(n_\uparrow, n_\downarrow)$ was taken from the work of Gunnarsson and Lundqvist.[25] We have minimized (4.1) with respect to ζ, using now the *exact* kinetic energy $T[n_\uparrow, n_\downarrow]$ [Eq. (3.7) with $A=\frac{1}{2}$] instead of the gradient expansion.

Results of this variational calculation are presented in Table IV. While the density profiles found in the LXA are similar to those found in the LXCA, the LXCA gives better energies because it does a better job of cancelling the self-interaction

TABLE IV. Results of variational calculations for one- and two-electron atoms, using the energy functional (4.1) and the exponential density profile (3.1). E is the total energy, and Δ is the sum of the self-interaction U_H/N and the exchange-correlation energy E_{xc}. The kinetic energy is treated exactly, and the results of various approximations for E_{xc} are compared with each other and with experiment. LXA: local exchange. LXCA: local exchange correlation. H: Hartree. HF: Hartree-Fock. $X\alpha$: Slater $X\alpha$ with $\alpha=0.777$. One-electron atoms are regarded as spin polarized ($x=1$), and two-electron atoms as unpolarized ($x=0$). (Experimental energies from Ref. 25.)

			(a.u.)	
Atom	Approximations	ζ	Δ	E
H	LXA	0.96	0.043	−0.457
	LXCA	0.97	0.008	−0.492
	H, HF, $X\alpha$	1.00	0.000	−0.500
	Expt.	1.00	0.000	−0.500
He$^+$	LXA	1.96	0.087	−1.912
	LXCA	1.97	0.040	−1.959
	H, HF, $X\alpha$	2.00	0.000	−2.000
	Expt.	2.00	0.000	−2.000
He	LXA	1.64	0.146	−2.700
	LXCA	1.66	0.008	−2.839
	H, HF, $X\alpha$	1.69	0.000	−2.848
	Expt.	···	···	−2.90
H$^-$	LXA	0.64	0.057	−0.414
	LXCA	0.68	−0.032	−0.505
	H, HF, $X\alpha$	0.69	0.000	−0.473
	Expt.	···	···	−0.529

(i.e., $\Delta \approx 0$). (This remarkable cancellation in the LXCA was first observed for hydrogen by Gunnarsson, Lundqvist, and Wilkins.[26]) Note in particular that only the LXCA (and not the LXA or the Hartree or Hartree-Fock approximations) correctly predicts that the negative hydrogen ion H^- is stable with respect to the neutral atom H. It is also worth noting that the LXA results can be improved (and in fact made equal to the Hartree and Hartree-Fock results) if the LXA approximation to the exchange-correlation energy is multiplied by $\frac{3}{2}\alpha$, where $\alpha = 0.777$, in the spirit of the Slater $X\alpha$ method.[20]

V. CONCLUSIONS

We have presented a spin-density gradient expansion of the kinetic energy (up to fourth order in ∇), and have shown that it gives reasonable results in variational calculations of the ground-state energy and density, even for one- and two-electron atoms which are formally well outside the domain of convergence of the expansion. Reasonable results for the one-electron atom are obtained *only* when its complete spin polarization is taken into account. We believe that this expansion, or some suitable generalization of it, will prove to be useful, along with the spin-density local exchange-correlation approximation (in preference to the local exchange approximation) for *easy* calculations of the physical and chemical properties of atoms and molecules. In particular, we believe that a proper treatment of the active outer electrons of atoms cannot neglect spin polarization. Variational calculations employing the spin-density gradient expansion of the kinetic energy may also provide a useful zeroth approximation for the spin densities in the iterative solution of the self-consistent single-particle equations (1.2) and (1.3).

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[1] P. Hohenberg and W. Kohn, Phys. Rev. B 136, 864 (1964).

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

[3] J. C. Stoddart and N. H. March, Ann. Phys. (N.Y.) 64, 174 (1971).

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

[5] A. K. Rajagopal and J. Callaway, Phys. Rev. B 7, 1912 (1973).

[6] L. H. Thomas, Proc. Cambridge Philos. Soc. 23, 542 (1926).

[7] E. Fermi, Rend. Lincei 6, 602 (1927).

[8] A. S. Kompaneets and E. S. Pavlovskii, Sov. Phys.-JETP 4, 328 (1957).

[9] D. A. Kirzhnits, Sov. Phys.-JETP 5, 64 (1957).

[10] D. A. Kirzhnits, *Field Theoretical Methods in Many-Body Systems* (Pergamon, New York, 1967).

[11] C. H. Hodges, Can. J. Phys. 51, 1428 (1973).

[12] W.-P. Wang, R. G. Parr, D. R. Murphy, and G. A. Henderson, Chem. Phys. Lett. 43, 409 (1976).

[13] W.-P. Wang and R. G. Parr, Phys. Rev. A 16, 891 (1977).

[14] C. Q. Ma and V. Sahni, Phys. Rev. B 16, 4249 (1977); Phys. Rev. B 19, 1290 (1979).

[15] J. A. Alonso and L. A. Girifalco, Chem. Phys. Lett. 53, 190 (1978).

[16] Y. Tal and R. F. W. Bader (unpublished).

[17] S. Golden, Phys. Rev. 105, 604 (1957).

[18] R. L. Kautz and B. B. Schwartz, Phys. Rev. B 14, 2017 (1976).

[19] J. Harris and R. O. Jones, J. Phys. F 4, 1170 (1974).

[20] J. C. Slater, in *Advances in Quantum Chemistry*, Vol. 6, edited by P. O. Löwdin (Academic, New York, 1972).

[21] D. J. W. Geldart, M. Rasolt, and C.-O. Almbladh, Solid State Commun. 16, 243 (1975).

[22] J. A. Alonso and L. A. Girifalco, Solid State Commun. 24, 135 (1977); Phys. Rev. B 17, 3735 (1978).

[23] O. Gunnarsson, M. Jonson, and B. Lundqvist, Solid State Commun. 24, 765 (1977).

[24] E. Fermi and E. Amaldi, referenced by L. Szasz, I. Berrios-Pagan and G. McGinn, Z. Naturforsch. 30a, 1516 (1975).

[25] O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B 13, 4274 (1976).

[26] O. Gunnarsson, B. I. Lundqvist, and J. W. Wilkins, Phys. Rev. B 10, 1319 (1974).