PHYSICAL REVIEW A VOLUME 46, NUMBER 5 1 SEPTEMBER 1992

Quantities $T_s[n]$ and $T_c[n]$ in density-functional theory

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(Received 17 January 1992)

Levy's constrained-search procedure [Proc. Natl. Acad. Sci. U.S.A **76**, 6062 (1979)] is employed to show how to determine Kohn-Sham and Hartree-Fock-Kohn-Sham orbitals and kinetic energies T_s and T_c, for the two-electron, four-electron, and the general case starting from the electron density. Numerical results are presented for the species H^- through F^{7+} and the atom Be. The Pauli potential is also determined for Be. The small differences among Kohn-Sham, Hartree-Fock, and Hartree-Fock-Kohn-Sham orbitals suggest that determination of Kohn-Sham orbitals from the density in this way is an attractive procedure for getting an orbital description from an electron density.

PACS number(s): 31.20.Sy, 31.20.Tz, 71.10.+x

I. INTRODUCTION

Three important quantities in the Kohn-Sham implementation of the density-functional theory of the ground state of an electronic system are $T[n]$, $T_s[n]$, and $T_c[n]$ [1]. $T[n]$ is the exact kinetic energy as a functional of the electron density n, $T_s[n]$ is the exact kinetic energy for the ground state of a corresponding noninteracting system with the same density n, and $T_c[n]$ is their difference,

$$T_c[n]=T[n]-T_s[n] \ . \tag{1}$$

$T_c[n]$ is the kinetic-energy part of the exchange-correlation energy $E_{xc}[n]$ of Kohn-Sham theory. It is not the kinetic-energy part of the correlation energy in Hartree-Fock theory, though it is (as we shall see) numerically fairly close to it. $T[n]$ and $T_s[n]$ are universal functionals of n.

Also a universal functional, this time of the Hartree-Fock electron density n_{HF}, is the restricted Hartree-Fock kinetic-energy $T^{\mathrm{HF}}[n_{\mathrm{HF}}]$. For Hartree-Fock theory, too, there is a corresponding noninteracting system with the same density, with kinetic energy $T_s^{\mathrm{HF}}[n_{\mathrm{HF}}]$. A corresponding "correlation" energy is

$$T_c^{\mathrm{HF}}[n_{\mathrm{HF}}]=T^{\mathrm{HF}}[n_{\mathrm{HF}}]-T_s^{\mathrm{HF}}[n_{\mathrm{HF}}] \ . \tag{2}$$

This is a very different quantity than $T_c[n]$. Indeed (as we shall see), T_c^{HF} is small relative to T_c.

This paper is concerned with T_s, T_s^{HF}, and T_c^{HF}—their calculation for two- and four-electron systems and their calculation generally. Almbladh and Pedroza [2]. Aryasetiawan and Stott [3], and March and co-workers [4,14,15] already have gone over similar ground.

The calculations of T, n, T^{HF}, and n_{HF} are standard problems which we need not here go into. We assume that we are dealing with an N-electron system of interest having a nondegenerate ground state, for which we know the numbers T and T^{HF} and the functions $n(\mathbf{r})$ and $n_{\mathrm{HF}}(\mathbf{r})$. The problem we address here is the determination of T_s and T_s^{HF}.

The general prescription for solution was given by Levy [5]. Namely, for any physically acceptable density n—exact, Hartree-Fock, or approximation to either—one may take

$$T_s[n]=\min_{\Phi_D\to n}\langle\Phi_D|\hat{T}|\Phi_D\rangle \ , \tag{3}$$

where $\hat{T}$ is the N-electron kinetic-energy operator, Φ_D is a normalized N-electron Slater determinant, and the "constrained search" is over all Slater determinants that give the density n.

With this formula for $T_s[n]$, one immediately recognizes that

$$T_s[n_{\mathrm{HF}}]=T_s^{\mathrm{HF}}[n_{\mathrm{HF}}] \ . \tag{4}$$

This means that one need only evaluate $T_s[n]$. There also are rigorous inequalities,

$$T>T_s \ , \quad T^{\mathrm{HF}}>T_s^{\mathrm{HF}} \ . \tag{5}$$

In actual density-functional calculations, one needs functional derivatives of the various energy components. Accordingly we are necessarily concerned with the functional derivative $\delta T_s[n]/\delta n$.

For a one-electron system, since $\psi=n^{1/2}$, the Schrödinger equation itself immediately gives

$$T[n]=T_s[n]=\tfrac{1}{8}\int\frac{|\nabla n|^2}{n}d\mathbf{r}\equiv T_w[n] \ . \tag{6}$$

Here the notation T_w is introduced for historical reasons; the W stands for Weizsacker. This same formula also holds for a system of N bosons in its ground state. This prompts us to write, for a system of fermions,

$$T_s[n]=T_w[n]+T_p[n] \tag{7}$$

where $T_p[n]$ is the extra kinetic energy required of the fermions by the Pauli exclusion principle. Then

$$\frac{\delta T_s[n]}{\delta n}=\frac{1}{8}\frac{|\nabla n|^2}{n^2}-\frac{1}{4}\frac{\nabla^2 n}{n}+v_p[n] \ , \tag{8}$$

where

$$v_p[n]=\frac{\delta(T_s[n]-T_w[n])}{\delta n} \tag{9}$$

is what has been called the Pauli potential. Knowledge of $T_s[n]$ thus provides knowledge of $v_P[n]$, as will be illustrated in Sec. III C. The Pauli potential is important because it is an essential ingredient in the differential equation for n [6–8],

$$(-\tfrac{1}{2}\nabla^2 + v_{\rm KS} + v_P) n^{1/2} = \mu n^{1/2} , \tag{10}$$

where $v_{\rm KS}$ is the Kohn-Sham effective potential and μ is the chemical potential.

II. TWO-ELECTRON SYSTEMS

A. Theory

Assuming its ground state to be a singlet, a two-electron system will have only one Hartree-Fock or Kohn-Sham orbital, say $\phi(\mathbf{r})$, in each case equal to the square root of one-half the density. That is,

$$\phi(\mathbf{r}) = \sqrt{n(\mathbf{r})/2}\exp[i\theta(\mathbf{r})] , \tag{11}$$

where $\theta(\mathbf{r})$ is an arbitrary function of $\mathbf{r}$. Equation (7) then gives

$$T[n] = T_w[n] + \tfrac{1}{2}\int n(\mathbf{r})|\nabla\theta(\mathbf{r})|^2 d\mathbf{r} , \tag{12}$$

where T_w is given by Eq. (6). Minimizing with respect to $\theta(\mathbf{r})$ in accord with the demand of Eq. (3), we find that $\theta(\mathbf{r})$ should be a constant, which we may set equal to zero. There results

$$T_s[n] = T_w[n] = \tfrac{1}{8}\int \frac{|\nabla n|^2}{n} d\mathbf{r} \tag{13}$$

and this is true for both Kohn-Sham and Hartree-Fock theory. For the two cases we find from Eqs. (1) and (2),

$$T_c[n] = T[n] - T_w[n] \tag{14}$$

and

$$T_c^{\rm HF}[n_{\rm HF}] = 0 . \tag{15}$$

For the two-electron case we also have

$$T_w[n_{\rm HF}] = T^{\rm HF}[n_{\rm HF}] \tag{16}$$

so that Eq. (14) may be written

$$\begin{aligned} T_c[n] &= \{T[n] - T^{\rm HF}[n_{\rm HF}]\} \\ &\quad - \{T_w[n] - T_w[n] - T_w[n_{\rm HF}]\} \\ &= -E_c(\text{conventional}) - \{T_w[n] - T_w[n_{\rm HF}]\} \\ &= -E_c(\text{conventional}) - \{T_s[n] - T_s[n_{\rm HF}]\} \end{aligned} \tag{17}$$

where E_c (conventional) is the conventional quantum-chemical correlation energy, equal to the negative of the first term on the first line by the vivial theorem. (The density-functional quantity $T_c[n]$ obeys no such simple virial relation.) The second term, expected to be small, represents a correction to the formula, approximate at best,

$$T_c[n] \sim -E_c(\text{ conventional }) . \tag{18}$$

B. Numerical results

The calculation of $T_s[n]$ and $T_s^{\rm HF}[n_{\rm HF}] \equiv T^{\rm HF}[n_{\rm HF}]$ for any two-electron species is straightforward. One calculates $T_w[n]$ using Eq. (13) from Hartree-Fock and exact densities, and $T_c[n]$ from Eq. (14). In Table I are given results for the atomic species H^- through F^{7+}. Hartree-Fock wave functions were taken from Clementi and Roetti [9]. Accurate wave functions were taken from Thakkar and Smith [10].

Included in Table I are the conventional correlation energies,

$$\begin{aligned} E_c(\text{conventional}) &= E(\text{accurate}) - E^{\rm HF} \\ &= -(T[n] - T^{\rm HF}[n_{\rm HF}]) . \end{aligned} \tag{19}$$

Note the differences between $-E_c$ (conventional) and T_c, in accord with Eq. (17). Note the agreement with the inequalities of Eq. (5).

TABLE I. Values of T_s and T_c for two-electron atomic species (a.u.). (Results obtained for Ne^{8+}, Na^{9+}, and Mg^{10+} were also computed, but omitted for the reason indicated in the discussion just below Table VIII in Ref. [10]. We thank Professor Thakkar for discussion of this point.)

Species	$T[n]$[a]	$T^{\rm HF}[n_{\rm HF}]$[b]	$T_s[n]$[c]	$T_c[n]$[d]	$-E_c$ (conventional)[e]
H^-	0.5278	0.4879	0.4998	0.0280	0.0398
He	2.9037	2.8617	2.8671	0.0366	0.0420
Li^+	7.2799	7.2372	7.4411	0.0388	0.0435
Be^{2+}	13.6556	13.6112	13.6141	0.0415	0.0443
B^{3+}	22.0310	21.9868	21.9885	0.0424	0.0447
C^{4+}	32.4062	32.3610	32.3631	0.0432	0.0450
N^{5+}	44.7814	44.7365	44.7381	0.0434	0.0453
O^{6+}	59.1566	59.1120	59.1126	0.0440	0.0454
F^{7+}	75.5317	75.4841	75.4871	0.0446	0.0456

[a] Accurate kinetic energies from Ref. [10].

[b] Hartree-Fock kinetic energies from Ref. [9]. By Eqs. (13) and (15) of text, this also is $T_s[n_{\rm HF}]$.

[c] Equation (13) of text with accurate densities.

[d] Equation (14) of text. The corresponding Hartree-Fock values are zero by Eq. (15).

[e] Quantum-chemical correlation energy of Eq. (19) of text.

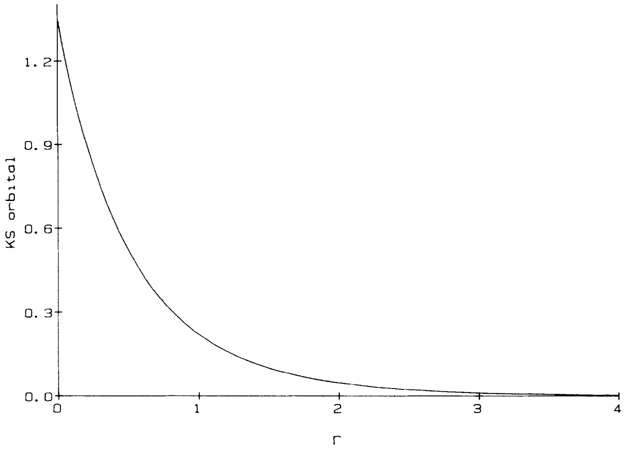

FIG. 1. Kohn-Sham orbital for He. The density is the accurate density. Atomic units.

The Kohn-Sham and Hartree-Fock orbitals for these systems are very similar but not identical. The Kohn-Sham orbital is displayed in Fig. 1 for the atom He. Note that the Kohn-Sham and Hartree-Fock orbitals necessarily have different long-range exponential decay constants, the first governed by the exact ionization potential, the second by the Koopmans theorem approximate ionization potential of Hartree-Fock theory.

Values of T_c for H^-, He, Li^+, and Be^{2+} were obtained less directly by Almbladh and Pedroza [2]: 0.8, 1.0, 1.1, and 1.1 eV, respectively. Our values should be more accurate.

III. FOUR-ELECTRON SYSTEMS

A. Theory

We consider a four-electron species in a singlet ground state, such as, for example the atom Be. The Hartree-Fock or Kohn-Sham determinant will have two doubly occupied orbitals, say $\phi_1(\mathbf{r})$ and $\phi_2(\mathbf{r})$. Again the problem is to carry out the procedure implied by Eq. (3), for the Hartree-Fock density n_{HF} and the accurate density n. The procedure is the same in both cases.

The determinant is invariant to unitary transformation. This permits us to write the two orbitals in the polar, circulant form [11,12]

$$\begin{aligned} \phi_1(\mathbf{r}) &= \sqrt{n(\mathbf{r})/4}\exp[i\theta(\mathbf{r})] \ , \\ \phi_2(\mathbf{r}) &= \sqrt{n(\mathbf{r})/4}\exp[-i\theta(\mathbf{r})] \ , \end{aligned} \tag{20}$$

where $\theta(\mathbf{r})$ is an arbitrary real function of $\mathbf{r}$. With this choice, Eq. (7) again becomes

$$T_s = T_w + \tfrac{1}{2}\int n(\mathbf{r})|\nabla\theta(\mathbf{r})|^2 d\mathbf{r} \ , \tag{21}$$

where T_w is given by Eq. (6). Again we must minimize T_s with respect to $\theta(\mathbf{r})$, but this time we have the additional orthogonality constraint,

$$\int \phi_1(\mathbf{r})\phi_2^*(\mathbf{r})d\mathbf{r} = 0 \ . \tag{22}$$

This complex constraint is equivalent to the two real constraints,

$$\int n(\mathbf{r})\cos[2\theta(\mathbf{r})]d\mathbf{r} = 0 \ , \tag{23}$$

$$\int n(\mathbf{r})\sin[2\theta(\mathbf{r})]d\mathbf{r} = 0 \ . \tag{24}$$

We attach Lagrange multipliers μ_1 and μ_2 to Eqs. (23) and (24) and proceed to carry out the minimization with respect to $\theta(\mathbf{r})$, at constant $n(\mathbf{r})$ as required by Eq. (3). We find

$$\frac{\delta}{\delta\theta}\left[\frac{1}{2}\int n|\nabla\theta|^2 d\mathbf{r} + \frac{\mu_1}{2}\int n\cos(2\theta)d\mathbf{r} + \frac{\mu_2}{2}\int n\sin(2\theta)d\mathbf{r}\right] = 0 \ , \tag{25}$$

from which we infer a differential equation for $\theta(\mathbf{r})$,

$$\nabla^2\theta(\mathbf{r}) + \nabla\theta(\mathbf{r})\cdot\frac{\nabla n(\mathbf{r})}{n(\mathbf{r})} = A\sin 2[\theta(\mathbf{r})-\theta^*] \ , \tag{26}$$

where

$$\begin{aligned} A &= -\frac{1}{(\mu_1^2+\mu_2^2)^{1/2}} \ , \\ \theta^* &= \tfrac{1}{2}\cos^{-1}[\mu_1/(\mu_1^2+\mu_2^2)^{1/2}] \ . \end{aligned} \tag{27}$$

Finally, since the addition of a constant to $\theta(\mathbf{r})$ does not change the original Slater determinant, we may set $\theta^*=0$, obtaining

$$\nabla^2\theta(\mathbf{r}) + \nabla\theta(\mathbf{r})\cdot\frac{\nabla n(\mathbf{r})}{n(\mathbf{r})} = A\sin[2\theta(\mathbf{r})] \ . \tag{28}$$

This equation may be found in a paper by Harriman [13]. It has also been derived and variously discussed by Aryasetiawan and Stott [3] and by March and co-workers [4,14,15]. It is the zero-electron repulsion special case of an equation of Nyden and Parr [12]. Apparently, however, no previous authors have derived this equation from the constrained-search procedure of Eq. (3).

Assume spherical symmetric $n(\mathbf{r})=n(r)$, for the ground state of Be. Then $\theta(\mathbf{r})=\theta(r)$. For well behavedness of $\theta(r)$ we may require

$$\theta(\infty) = -\pi/2 \ , \quad \theta'(\infty) = 0 \ , \tag{29}$$

and

$$\theta'(0) = 0 \ . \tag{30}$$

For a given density $n(r)$ we then accomplish the solution of Eq. (28) as follows. Guess a value of A. Numerically integrate Eq. (28) inward from some large r, assuming Eq. (29), testing the resultant solution as to whether both Eqs. (22) and (30) are satisfied. Repeat with new values of A until the solution is found. In our actual calculation, for accurate density Eqs. (23) and (24) reached 7.6×10^{-5} and 1.7×10^{-5}, respectively, corresponding to an overlap between ϕ_1 and ϕ_2 of about 7.7×10^{-5}. For HF density, we have a similar situation.

B. Calculation of T_s, T_c, and orbitals for Be

Table II gives calculated results for the various kinetic energies for the ground state of Be. We have proceeded

TABLE II. Values of T_s and T_c for the atom Be (a.u.). (Hartree-Fock density from Ref. [9], accurate density from Ref. [16].)

Accurate kinetic energy $T[n]$	14.6669
Hartree-Fock kinetic energy $T^{\rm HF}[n_{\rm HF}]$	14.5730
Accurate Kohn-Sham kinetic energy $T_s[n]$	14.5932
Hartree-Fock-Kohn-Sham kinetic energy $T_s[n_{\rm HF}]$	14.5720
Density-functional kinetic-energy contribution to the exchange-correlation energy $T_c[n]$	0.0737
Kinetic-energy contribution to conventional correlation energy $-E_c$ (conventional)	0.0939

as described above for the Hartree-Fock density determined from the Hartree-Fock wave function of Clementi and Roetti [9], and then again for the accurate density determined from the accurate wave function of Esqvivel and Bunge [16] (which gives 99.5% of the conventional correlation energy).

Note that $T_s[n_{\rm HF}]$ is smaller than $T^{\rm HF}[n_{\rm HF}]$, as required by Eq. (5). Their difference, 0.0010, is just the small correction term of Eq. (20). The Hartree-Fock-Kohn-Sham orbitals are only slightly different from the Hartree-Fock orbitals. The total electron densities are identical in the two cases, but $\theta(r)$ is not quite the same. Table III shows that the difference between these two $\theta(r)$ is hardly discernible. In Sec. V we make a special proposal to capitalize on this result. In Table III we also tabulate the accurate and HF densities for some r, so that one can reproduce the HF, HF-KS, and Kohn-Sham orbitals (see below).

Note that the fully correlated density gives a Kohn-Sham $T_s[n]$ that is significantly larger than $T_s[n_{\rm HF}]$. This inequality may be generally true, but it does not follow from the rigorous inequalities of Eq. (5).

The $T_c[n]$ we obtain, 0.0737 a.u., compares favorably with the value obtained by Almbladh and Pedroza by another method, 2.01 eV. This is quite different from the conventional quantum-chemical $-E_c$(conventional)$=$ 0.0939 [2], but as we have seen, there is no reason to expect the two quantities to be the same.

In terms of the atomic orbitals ϕ_1 and ϕ_2 as written in Eq. (20), the conventional canonical orbitals for Be are

TABLE III. The accurate, HF densities and phases factor $\theta(r)$ for Hartree-Fock, Hartree-Fock-Kohn-Sham, and Kohn-Sham orbitals and in Be.

r (a.u.)	$n_{\rm HF}$	n	$\theta_{\rm HF}$[a]	$\theta_{\rm HFKS}$[b]	$\theta_{\rm KS}$[c]
0.0960	16.5520	16.5415	0.1780	0.1872	0.1960
0.2160	6.5576	6.5472	0.1670	0.1749	0.1829
0.3060	3.3591	3.3154	0.1498	0.1561	0.1628
0.4260	1.3591	1.3589	0.1088	0.1120	0.1160
0.5160	0.7023	0.7039	0.0584	0.0593	0.0601
0.6060	0.3674	0.3696	−0.0155	−0.0165	−0.0199
0.7260	0.1610	0.1633	−0.1624	−0.1645	−0.1748
0.9060	0.0576	0.0597	−0.5009	−0.4996	−0.5185
1.0260	0.0372	0.0391	−0.7687	−0.7625	−0.7816
1.2060	0.0275	0.0295	−1.1053	−1.0933	−1.1070
1.3260	0.0252	0.0265	−1.2556	−1.2423	−1.2523
1.4160	0.0240	0.0252	−1.3354	−1.3221	−1.3306
1.5060	0.0229	0.0240	−1.3943	−1.3816	−1.3879
1.6260	0.0213	0.0223	−1.4450	−1.4382	−1.4429
1.7160	0.0200	0.0209	−1.4788	−1.4686	−1.4723
1.8060	0.0187	0.0194	−1.5007	−1.4916	−1.4946
1.9260	0.0169	0.0175	−1.5216	−1.5140	−1.5162
2.1060	0.0142	0.0147	−1.5415	−1.5358	−1.5373
2.4060	0.0103	0.0105	−1.5581	−1.5548	−1.5555
2.8260	0.0062	0.0062	−1.5666	−1.5652	−1.5655
3.1260	0.0042	0.0041	−1.5689	−1.5681	−1.5682
3.5160	0.0025	0.0024	−1.5701	−1.5698	−1.5698
3.8160	0.0016	0.0015	−1.5705	−1.5703	−1.5703
4.0860	0.0011	0.0010	−1.5707	−1.5706	−1.5706
4.4760	0.0007	0.0006	−1.5707	−1.5708	−1.5708

[a] Evaluated by transforming Hartree-Fock orbitals of Ref. [9] to the form of Eq. (20).

[b] Calculated by solving Eq. (28) with $n_{\rm HF}(r)$ taken from the Hartree-Fock wave function of Ref. [9].

[c] Calculated by solving Eq. (28) with $n(r)$ taken from the accurate wave function of Ref. [16].

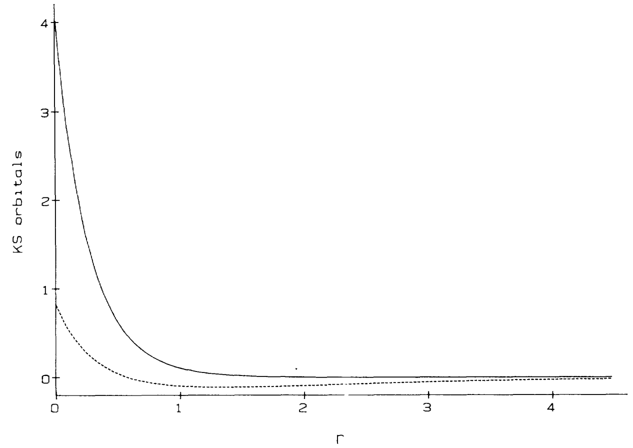

FIG. 2. Kohn-Sham orbitals for the accurate density of Atomic units. Be, where the solid curve is $1s(r)$ and the dashed curve is $2s(r)$. Atomic units.

$$
\begin{aligned}
1s(\mathbf{r}) &= \frac{\phi_1+\phi_2}{\sqrt{2}} = \sqrt{n(\mathbf{r})/2}\cos\theta(\mathbf{r}) \ , \\
2s(\mathbf{r}) &= \frac{\phi_1-\phi_2}{\sqrt{2}i} = \sqrt{n(\mathbf{r})/2}\sin\theta(\mathbf{r}) \ .
\end{aligned}
\tag{31}
$$

From the data of Table III one can reproduce and compare the Hartree-Fock, Hartree-Fock-Kohn-Sham, and the Kohn-Sham 1s and 2s orbitals for Be. While the three sets of orbitals are qualitatively similar, they are in fact significantly different. Note that $1s(\mathbf{r})$ is nodeless, while $2s(\mathbf{r})$ has one node. In Fig. 2 we plotted these two orbitals for the accurate density of Be.

C. Pauli potential for Be

From Eqs. (9) and (21) we can proceed to determine the Pauli potential for Be. We first obtain

$$
v_p(\mathbf{r}) = \tfrac{1}{2}|\nabla\theta(\mathbf{r})|^2 + \int \frac{\delta T_s(\mathbf{r}')}{\delta n(\mathbf{r})} d\mathbf{r}' \ . \tag{32}
$$

But Eqs. (25) and (28) give

$$
\frac{\delta T_s(\mathbf{r})}{\delta\theta(\mathbf{r})} = -An(\mathbf{r})\sin 2\theta(\mathbf{r}) \tag{33}
$$

while functional differentiation of Eq. (23) gives

$$
\int n(\mathbf{r}')\sin 2\theta(\mathbf{r}')\frac{\delta\theta(\mathbf{r}')}{\delta n(\mathbf{r})} d\mathbf{r}' = \frac{\cos 2\theta(\mathbf{r})}{2} \ . \tag{34}
$$

Consequently,

$$
\begin{aligned}
v_p(\mathbf{r}) &= \tfrac{1}{2}|\nabla\theta(\mathbf{r})|^2 - \frac{A}{2}\cos 2\theta(\mathbf{r}) \\
&= \tfrac{1}{2}|\nabla\theta(\mathbf{r})|^2 - A\cos^2\theta(\mathbf{r}) + \tfrac{1}{2}A \ .
\end{aligned}
\tag{35}
$$

The Hartree-Fock and Kohn-Sham v_p for Be are compared in Fig. 3. There is little difference between them. Equation (35) may be found in Ref. [18].

We may rewrite Eq. (8) as

$$
\frac{\delta T_s[n]}{\delta n} = v_w + v_p \ , \tag{36}
$$

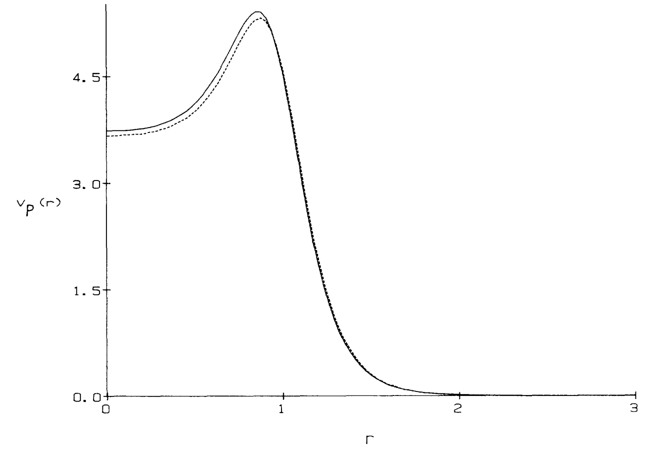

FIG. 3. Pauli potentials for the accurate and HF densities of Be, where the solid curve is for accurate density and the dashed curve is for HF density. Atomic units.

where

$$
v_w \equiv \frac{1}{8}\frac{|\nabla n|^2}{n^2} - \frac{1}{4}\frac{\nabla^2 n}{n} \ . \tag{37}
$$

It is interesting to compare the magnitudes of v_w and v_p as functions of $\mathbf{r}$. This is done in Fig. 4 for the Kohn-Sham description of Be. For either small r or large r, as first suggested by Herring and Chopra [6], v_w dominates. In the medium r region, on the other hand, v_w and v_p have comparable magnitudes. Note that v_w is greater than zero for medium r.

For the ground state the Kohn-Sham effective potential v_{KS} that enters Eq. (10) above satisfies the identity [1,17]

$$
\mu = v_{\mathrm{KS}}(\mathbf{r}) + \frac{\delta T_s[n]}{\delta n(\mathbf{r})} \ , \tag{38}
$$

$$
\mu = v_{\mathrm{KS}}(\mathbf{r}) + v_w(\mathbf{r}) + v_p(\mathbf{r}) \ , \tag{39}
$$

where μ is the chemical potential of the system. One should beware, however, of taking Eq. (39) as defining

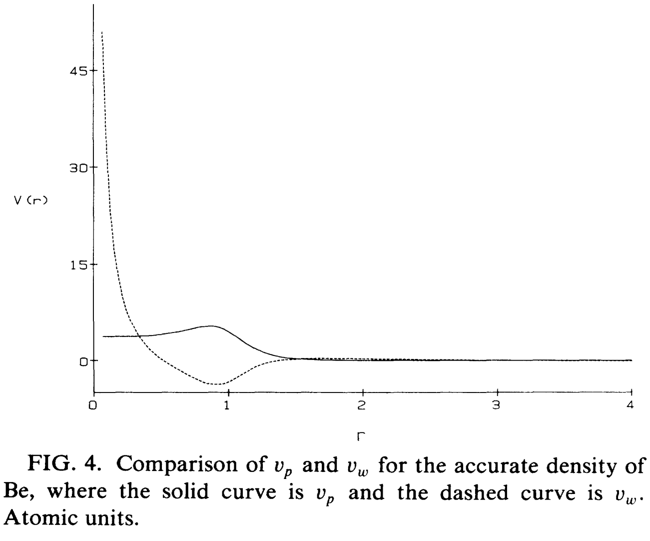

FIG. 4. Comparison of v_p and v_w for the accurate density of Be, where the solid curve is v_p and the dashed curve is v_w. Atomic units.

equation for $v_{\mathrm{KS}}(\mathbf{r})$ in a variational procedure for determining $n(\mathbf{r})$. This will fail, because this equation is an identity at the solution point.

IV. GENERAL CASE

The determination of $T_s[n]$ for the general case is a problem of much interest on which there already has been substantial progress, especially by March and coworkers [4,14,15,18]. Below we describe two methods. The first is simply a special case of a procedure given some time ago by Nyden and Parr and coincides more or less a less with the strategy being employed by March. The second is ours.

A. Method in which all orbitals are expressed in semipolar form

Following Nyden and Parr [12], we write each and every orbital in the trial determinants being used in the constrained search of Eq. (3) in the "semipolar" form

$$\phi_j(\mathbf{r})=\sqrt{n(\mathbf{r})/N}\,\exp[i\theta_j(\mathbf{r})]\ . \tag{40}$$

The "phase factor" θ_j here may have imaginary as well as real parts (although the imaginary parts will generally be small [11]). Orthogonality requires the conditions

$$\int n(\mathbf{r})\exp\{i[\theta_j^*(\mathbf{r})-\theta_k(\mathbf{r})]\}d\mathbf{r}=\delta_{jk}N\ . \tag{41}$$

In this representation, the kinetic energy is given by a simple generalization of Eq. (21), namely,

$$T_s=T_w+\tfrac{1}{2}\sum_j\int n(\mathbf{r})|\nabla\theta_j(\mathbf{r})|^2 d\mathbf{r}\ . \tag{42}$$

Minimizing this with respect to the θ_j, for fixed $n(\mathbf{r})$, subject to the constraints of Eq. (41), then gives a set of simultaneous equations generalizing Eq. (26). The left side of the equation for θ_j is just $\nabla^2\theta_j+\nabla\theta_j\cdot\nabla n(\mathbf{r})/n(\mathbf{r})$; the right side is just a linear combination of trigonometric functions with coefficients that are Lagrange multipliers for the Eqs. (41). One solves these equations.

B. Method involving the direct solution of SCF equations

We imagine the problem to be the problem of solving the Hartree-Fock problem for $\hat{H}=\hat{T}$, subject to the constraint $\sum_j|\psi_j|^2=n_0$, where n_0 is given. That is, if $n\equiv\sum_j|\psi_j|^2$, $n(\mathbf{r})-n_0(\mathbf{r})=0$ for all r. Or, $\int[n(\mathbf{r})-n_0(\mathbf{r})]^2 d\mathbf{r}=0$. Or,

$$\int\int\frac{[n(\mathbf{r})-n_0(\mathbf{r})][n(\mathbf{r}')-n_0(\mathbf{r}')]}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}'=0\ . \tag{43}$$

We associate a Lagrange multiplier λ with this constraint, and define

$$v(\mathbf{r})=\int\frac{n(\mathbf{r}')-n_0(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'\ . \tag{44}$$

Then the Hartree-Fock equation to be solved is

$$[-\tfrac{1}{2}\nabla^2+\lambda v(\mathbf{r})]\psi_j(\mathbf{r})=\varepsilon_j\psi_j(\mathbf{r})\ . \tag{45}$$

For a particular λ value, we solve these equations using a conventional method (e.g., basis sets) to give ψ_j^λ ε_j^λ, v^λ, n^λ, and the quantities

$$T_j^\lambda=\langle\psi_j^\lambda|-\tfrac{1}{2}\nabla^2|\psi_j^\lambda\rangle=\varepsilon_j^\lambda-\lambda\langle\psi_j^\lambda|v^\lambda|\psi_j^\lambda\rangle\ , \tag{46}$$

$$T_s^\lambda=\sum_j T_j^\lambda=\sum_j\varepsilon_j^\lambda-\lambda\langle n^\lambda v^\lambda\rangle\ . \tag{47}$$

We repeat for higher and higher λ values, finally obtaining

$$T_s=\lim_{\lambda\to\infty}T_s^\lambda=\lim_{\lambda\to\infty}\sum_j\varepsilon_j^\lambda-\lim_{\lambda\to\infty}[\lambda\langle n^\lambda v^\lambda\rangle]\ . \tag{48}$$

V. DISCUSSION

We are encouraged to believe that it will become possible to determine $T_s[n]$ systematically for any N-electron species. In this paper we have demonstrated how to do this for two and four-electron systems (and by implication for one- and three-electron systems) and have outlined how it can be achieved for $N>4$ as well. Our analysis generally conforms with work by Holas and March [18].

It should be mentioned, however, that the results we have obtained for Be differ in numerical detail from the results of Nagy and March [15]. This is due to an alternative (we believe faulty) treatment of the boundary conditions associated with Eq. (28) by those authors. Certain kinks in the Nagy-March plots do not appear in ours.

The major conclusions from our study are that Kohn-Sham orbitals differ very little from Hartree-Fock orbitals [19] and that Kohm-Sham-Hartree-Fock orbitals are almost identical with Hartree-Fock orbitals. This leads to a strong suggestion as to how to get an electronic wave function from an electron density. Namely, determine the Kohn-Sham orbitals by the Levy constrained search procedure of Eq. (3). We commend this particular idea to the community of x-ray crystallographers. There have been many studies on how to fit a density matrix to a density [20], but the simple suggestion we make here appears not to have been explicitly made previously. Kohn-Sham orbitals are very physical.

ACKNOWLEDGMENTS

The authors are grateful to the North Carolina Supercomputing Center for CPU time, to Dr. A Nagy for helpful correspondence, and to Dr. Zhongxiang Zhou and Dr. Yue Wang for useful advice. This research has been aided by a research grant from the National Science Foundation.

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