Variational principles for the determination of single-particle density matrices*

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A variational formalism for the determination of the spinless single-particle density matrix $\gamma(\vec{r}, \vec{r}')$ for an interacting many-particle system, correct to second order, is developed. The method is based on variational principles for determining single-particle expectation values, correct to second order, without requiring highly accurate wave functions in order to represent the interacting system. The expectation value of the operator $X = Y + iZ$, where $Y = (1/2)\sum_j [W(\vec{r}_j)T_j(\vec{a}) + W(\vec{r}_j)T_j(-\vec{a})]$, $Z = -(i/2)\sum_j [W(\vec{r}_j)T_j(\vec{a}) - W(\vec{r}_j)T_j(-\vec{a})]$, $W(\vec{r}_j) = \delta(\vec{r}_j - \vec{r})$, $T_j(\vec{a})$ is a translation operator, and $\vec{a} = \vec{r}' - \vec{r}$, is the reduced single-particle density matrix. For a given choice of a Slater-determinant-type trial wave function it is shown that the density matrix may be obtained from the charge density of the system where the latter too is determined via the same formalism to second order as the expectation value of the operator W employing the same system trial wave function. The applicability of the technique is then demonstrated by showing that for the model hydrogen-atom problem it leads to highly accurate results for the momentum density and the Compton profile in the impulse approximation, and that the virial theorem is closely satisfied, even when the calculations of the various properties employing an approximate trial wave function alone are substantially in error.

I. INTRODUCTION

In this paper we present a formalism for the variational determination of the reduced single-particle density matrix for an interacting many-particle system without requiring the use of accurate wave functions to describe the system. Thus a fair approximation to the system wave function leads to accurate results for the single-particle density matrix since the variational method ensures that first-order errors in the system trial wave function produce only second-order errors in the density matrix. It will be shown that in order to obtain the single-particle density matrix within this framework a knowledge is required of the charge density or, equivalently, its cosine Fourier transform for spherically symmetric systems, the latter quantities also being determined correctly to second order via the same general formalism with the use of the same system trial wave function.

With a knowledge of the N-particle wave function it is possible to determine single-particle expectation values for spatially dependent operators from the particle density in configuration space $\rho(\vec{r})$ and expectation values of momentum-dependent operators from the particle density in momentum space $\rho(\vec{k})$. The expectation values will then, of course, be correct to the same order as that of the wave function employed, and hence one would require accurate wave functions for determining these expectation values.

A most useful and common method for obtaining the wave function for a system is by use of the variational principle for the energy.[1] This prin-

ciple, in addition to producing only second-order errors in the energy, is a minimum principle and thus highly amenable to numerical computation. However, the results for the expectations of other observables of interest would be accurate only to the same order as that of the wave function itself.

Recently, variational methods based on the Delves-Schwartz[2-4] variational principle have been developed[5-7] by the authors for the determination of the expectation value of single-particle operators $W = \sum_i W(\vec{r}_i)$ correct to second order, and the methods were applied[7-9] to atomic systems. These variational principles, rather than being minimum principles, have stationary points which are generally saddle points. They depend upon a parameterized Slater-determinant–type function as the choice for the system trial wave function ψ_{0T} and an auxiliary function ψ_{1T} which is obtained via a subsidiary but minimum principle.[10,4] The subsidiary functional contains ψ_{0T}, ψ_{1T}, the Hamiltonian of the system, and the operator W whose expectation is to be determined. Thus variational minimization of the subsidiary functional with respect to the auxiliary function leads to an equation for the auxiliary function. Therefore the expectation value is dependent upon the property of interest in addition to requiring no further parameters other than those employed in the initial choice of the system trial wave function. With a reasonable approximation to the trial wave function it is possible to use these methods to determine the particle density $\rho(\vec{r})$, which is the expectation value of the operator $W = \sum_i \delta(\vec{r}_i - \vec{r})$, or equivalently, for spherically symmetric systems, the cosine Fourier transform of the charge

density or form factor which is simply the expectation value of $U = \sum_i \cos(\vec{k} \cdot \vec{r}_i)$.

Another quantity from which both the particle density and momentum density may be obtained is the generalized reduced single-particle density matrix $\gamma_\zeta(\vec{r}\zeta, \vec{r}'\zeta')$ defined[11] as

$$\gamma_\zeta(\vec{r}\zeta, \vec{r}'\zeta') = N \sum_{\zeta_2 \cdots \zeta_N} \int \psi^*(\vec{r}\zeta, \vec{r}_2\zeta_2, \ldots, \vec{r}_N\zeta_N)$$
$$\times \psi(\vec{r}'\zeta', \vec{r}_2\zeta_2, \ldots, \vec{r}_N\zeta_N) d\vec{r}_2, \ldots, d\vec{r}_N,$$

$$\text{(1)}$$

where ζ is the spin coordinate, and whose spinless form $\gamma(\vec{r}, \vec{r}')$ is

$$\gamma(\vec{r}, \vec{r}') = \sum_\zeta \gamma_\zeta(\vec{r}\zeta, \vec{r}'\zeta). \qquad (2)$$

The density is now the diagonal matrix element of $\gamma(\vec{r}, \vec{r}')$, i.e.,

$$\rho(\vec{r}) = \gamma(\vec{r}, \vec{r}), \qquad (3)$$

and the momentum density is given by the relationship

$$\rho(\vec{k}) = (2\pi)^{-3} \int e^{i\vec{k}\cdot\vec{r}} \gamma(\vec{r}, \vec{r}') e^{-i\vec{k}\cdot\vec{r}'} d\vec{r} \, d\vec{r}', \qquad (4)$$

where $\vec{p} = \hbar\vec{k}$ $(\hbar = 1)$.

The primary advantage of the single-particle density matrix is that for an N-particle system it enables one to obtain all single-particle expectation values including the charge density $\rho(\vec{r})$ and momentum density $\rho(\vec{k})$. However, implicit in its very definition is the requirement of an accurate wave function for the N-body system if accurate expectations are to be obtained. This is precisely the quantity that one does not know. Here again, as in the determination of single-particle expectation values, what is required are variational methods whereby the single-particle density matrix may be obtained correct to second order if wave functions that are correct to first order are employed. Such a method is described in Secs. II–IV. This approach is thus quite different from the usual orbital approximation methods discussed extensively in the McWeeny[12] review article or the operator formulation[13] of the single-particle density matrix based on its interpretation as the kernel of an integral operator, or the methods whereby the ground-state properties of an N-interacting-particle system are obtained by making a variational calculation using the density matrices themselves as variational functions.[14] The latter methods require guaranteeing that the density matrices used in the variational calculations are derivable from some physically sensible N-particle wave function or, equivalently, that they represent a real N-particle system together with necessary and

sufficient conditions for such representability.[14,15] What is required within the present formalism is simply an initial choice of an appropriately antisymmetrized product of single-particle states as the trial wave function for the system in addition to a correct choice of a complex sum of Hermitian operators whose expectation value is the reduced single-particle density matrix.

After a brief description of the variational method in Sec. II, the formalism in a Hartree-type approximation in which the trial wave function is assumed to be a Hartree product of single-particle states is discussed in Sec. III. In Sec. IV the formalism is extended to exchange-dependent systems in a Hartree-Fock–type approximation. A discussion of the relationship of the present work to the N-representability problem is then given. Finally the technique is illustrated in Sec. V by applying it to the model hydrogen-atom problem and demonstrating that it leads to highly accurate results for various properties involving the particle density and momentum density even when the calculation employing the trial wave function ψ_{0T} alone is substantially in error.

II. VARIATIONAL METHOD

The variational methods for the determination of single-particle expectation values referred to in the Introduction may be used to determine the reduced single-particle density matrix for a system composed of N identical particles if we consider the operator

$$Y = \sum_i Y_i = \sum_i W(\vec{r}_i) T_i(\vec{a}), \qquad (5)$$

where

$$W(\vec{r}_i) = \delta(\vec{r}_i - \vec{r}), \qquad (6)$$

and where $T_i(\vec{a})$ is a translation operator such that

$$T_i(\vec{a})\psi(\vec{r}_1, \ldots, \vec{r}_i, \ldots, \vec{r}_N) = \psi(\vec{r}_1, \ldots, \vec{r}_i + \vec{a}, \ldots, \vec{r}_N).$$

$$\text{(7)}$$

The expectation value of Y is then

$$\overline{Y} = \gamma(\vec{r}, \vec{r} + \vec{a}). \qquad (8)$$

If we now let $\vec{a} = \vec{r}' - \vec{r}$, then

$$\overline{Y} = \gamma(\vec{r}, \vec{r}'), \qquad (9)$$

which is the reduced single-particle density matrix. In exactly the same manner the general single-particle density matrix $\gamma_\zeta(\vec{r}, \zeta; \vec{r}', \zeta')$, where ζ is the spin coordinate, may be obtained from the normalized many-particle wave function

$\psi(\vec{r}_1 \zeta_1, \ldots, \vec{r}_N \zeta_N)$ as the expectation value of the operator

$$Y = \sum_i W(\vec{r}_i) T_i(\vec{a}) P_i , \qquad (10)$$

where $P_i(\zeta, \zeta')$ is a projection operator which projects out the appropriate spin component.

Now according to the Delves-Schwartz[2,3] variational principle, the expectation value of an arbitrary Hermitian operator X, correct to second order, is given by the functional

$$\langle X \rangle = \overline{X} + 2 \operatorname{Re} \langle \psi_{1T} | H - E | \psi_{0T} \rangle , \qquad (11)$$

where

$$\overline{X} = \langle \psi_{0T} | X | \psi_{0T} \rangle , \qquad (12)$$

and ψ_{0T} and ψ_{1T} are the system trial wave function and an auxiliary function, respectively. The trial wave function ψ_{0T} is an approximation to the exact wave function ψ_0 which satisfies the Schrödinger equation

$$H\psi_0 = E\psi_0 , \qquad (13)$$

with E being the associated eigenenergy and H the Hamiltonian of the system.

Having assumed a parameterized ψ_{0T} with the parameters being determined by various criteria such as energy minimization or orthogonality constraints it is possible to derive[5-7] a systematic procedure for the determination of the auxiliary function ψ_{1T}, involving the same set of parameters, by employing a subsidiary minimum principle. This involves variational minimization of the functional

$$M'[\psi_{0T}, \psi_{1T}, H, X] = \langle \psi_{1T} | H - \mathscr{E} | \psi_{1T} \rangle$$
$$+ \langle \psi_{1T} | X | \psi_{0T} \rangle + \langle \psi_{0T} | X | \psi_{1T} \rangle , \qquad (14)$$

subject to the orthogonality constraint

$$\langle \psi_{1T} | \psi_{0T} \rangle = 0 , \qquad (15)$$

and where $\mathscr{E}$ is defined as $\mathscr{E} = \langle \psi_{0T} | H | \psi_{0T} \rangle$.

However, the operator Y given by Eq. (5) is not Hermitian. Moreover, since $\gamma(\vec{r}, \vec{r}')$ is in general complex, there exists no Hermitian operator whose expectation value yields $\gamma(\vec{r}, \vec{r}')$. Consider, however, the Hermitian operator

$$Y = \sum_i Y_i = \frac{1}{2} \sum_i [W(\vec{r}_i) T_i(\vec{a}) + W(\vec{r}_i') T_i(-\vec{a})] , \qquad (16)$$

with W and $\vec{a}$ defined as before.

Then

$$\overline{Y} = \tfrac{1}{2} [\gamma(\vec{r}, \vec{r}') + \gamma(\vec{r}', \vec{r})] ,$$

and since

$$\gamma(\vec{r}', \vec{r}) = \gamma^*(\vec{r}, \vec{r}') ,$$

then

$$\overline{Y} = \operatorname{Re} \gamma(\vec{r}, \vec{r}') . \qquad (17)$$

Similarly the expectation value of the Hermitian operator Z defined as

$$Z = -\frac{i}{2} \sum_i [W(\vec{r}_i) T_i(\vec{a}) - W(\vec{r}_i') T_i(-\vec{a})] \qquad (18)$$

is

$$\overline{Z} = -\frac{i}{2} [\gamma(\vec{r}, \vec{r}') - \gamma(\vec{r}', \vec{r})]$$
$$= \operatorname{Im} \gamma(\vec{r}, \vec{r}') . \qquad (19)$$

Thus

$$\gamma(\vec{r}, \vec{r}') = \overline{Y} + i\overline{Z} , \qquad (20)$$

so we require the calculation of expectation values of two Hermitian operators to obtain the single-particle density matrix.

III. HARTREE APPROXIMATION

In the Hartree approximation we assume the trial wave function to be a product of orthonormal single-particle states, i.e., $\psi_{0T} = \prod_i \phi_i(\vec{r}_i)$, and ψ_{1T} to be of the form $\psi_{1T} = \sum_j f_j(\vec{r}_j)\psi_{0T}$, the choice of the form being governed by perturbational considerations.[6] Then variational minimization of the functional M' with respect to the auxiliary function, subject to the orthogonality constraint of Eq. (15), leads to a set of coupled integral-differential equations for the components $f_j(\vec{r}_j)$ of the auxiliary function. This set of coupled equations[6] for the operator Y is

$$[Y - \overline{Y}_j - \Delta]\phi_j(\vec{r}_j) - \phi_j^2(\vec{r}_j)\nabla_j^2 f_j(\vec{r}_j) - 2\vec{\nabla}_j f_j(\vec{r}_j) \cdot \vec{\nabla}_j \phi_j(\vec{r}_j)$$
$$+ \left\langle \sum_k f_k(\vec{r}_k)\psi_{0T}' \middle| H - \mathscr{E} \middle| \psi_{0T}' \right\rangle_j' \phi_j(\vec{r}_j) = 0 , \qquad (21)$$

where

$$\overline{Y}_j = \langle \phi_j(\vec{r}_j) | Y_j | \phi_j(\vec{r}_j) \rangle ,$$
$$\psi_{0T}' = \psi_{0T}/\phi_j(\vec{r}_j) , \qquad (22)$$
$$\Delta = \left\langle \psi_{0T} \middle| H \middle| \sum_k f_k(\vec{r}_k)\psi_{0T} \right\rangle ,$$

and where the symbol $\langle \cdots \rangle_j'$ means integration over all variables except the variable $\vec{r}_j$. The components of the auxiliary function $f_j(\vec{r}_j)$ are then obtained by decoupling the equation in two different approximations. Similar equations obtain for the determination of the function ψ_{1T} associated with the expectation value of the operator Z.

A. First decoupling approximation

In this approximation[6] the coupling term is re-
placed by its value averaged over $\phi_j(\vec{r}_j)$. In this
case Eq. (21) reduces to

$$\nabla_j^2 f_{jY}(\vec{r}_j) + 2\vec{\nabla}_j f_{jY}(\vec{r}_j) \cdot \frac{\vec{\nabla}_j \phi_j(\vec{r}_j)}{\phi_j(\vec{r}_j)}$$

$$= \frac{1}{\phi_j(\vec{r}_j)} \left[Y(\vec{r}_j) - \overline{Y}_j \right] \phi_j(\vec{r}_j)$$

$$= \frac{1}{2} \left(\frac{\phi_j(\vec{r}+\vec{a})}{\phi_j(\vec{r})} \delta(\vec{r}_j - \vec{r}) - \overline{Y}_j^{(1)} + \frac{\phi_j(\vec{r}'-\vec{a})}{\phi_j(\vec{r}')} \right.$$

$$\left. \times \delta(\vec{r}_j - \vec{r}') - \overline{Y}_j^{(2)} \right), \tag{23}$$

with $\overline{Y}_j^{(1)}$ and $\overline{Y}_j^{(2)}$ the expectation value of each of
the terms in $Y(\vec{r}_j)$ and where the additional sub-
script Y in the f_j's is used to indicate that solu-
tion of the above equation leads to components of
the auxiliary function for the operator Y. The solu-
tion of Eq. (23) to within a constant is

$$f_{jY}(\vec{r}_j) = \frac{1}{2} \left(f_{jW}(\vec{r}_j, \vec{r}) \frac{\phi_j(\vec{r}+\vec{a})}{\phi_j(\vec{r})} \right.$$

$$\left. + f_{jW}(\vec{r}_j, \vec{r}') \frac{\phi_j(\vec{r}'-\vec{a})}{\phi_j(\vec{r}')} \right), \tag{24}$$

and similarly the solution to the differential equa-
tion for the operator Z is

$$f_{jZ}(\vec{r}_j) = -\frac{i}{2} \left[f_{jW}(\vec{r}_j, \vec{r}) \frac{\phi_j(\vec{r}+\vec{a})}{\phi_j(\vec{r})} \right.$$

$$\left. - f_{jW}(\vec{r}_j, \vec{r}') \frac{\phi_j(\vec{r}'-\vec{a})}{\phi_j(\vec{r}')} \right], \tag{25}$$

where $f_{jW}(\vec{r}_j, \vec{r})$ is a solution to the equation

$$\nabla_j^2 f_{jW}(\vec{r}_j, \vec{r}) + 2\vec{\nabla}_j f_{jW}(\vec{r}_j, \vec{r}) \cdot \frac{\vec{\nabla}_j \phi_j(\vec{r}_j)}{\phi_j(\vec{r}_j)} = W(\vec{r}_j, \vec{r}) - \overline{W}_j \tag{26}$$

with $W(\vec{r}_j, \vec{r})$ defined as in Eq. (6). However Eq.
(26) is precisely the equation that would have to be
solved if one were calculating the components of
the auxiliary function for the correction term to
a first-order calculation of the charge density via
this formalism.[6] Furthermore, as pointed out in
Ref. 7, the first constant of integration in the solu-
tion of an equation such as Eq. (26) for any arbi-
trary operator W, is governed by the perturbative
consideration that the auxiliary function vanish at
infinity. The second constant of integration is
chosen so as to orthogonalize the auxiliary func-
tion to the trial wave function thus eliminating the
requirement of the energy E of the system. This
latter process, however, is equivalent to replacing
E with the average value of the Hamiltonian taken
with respect to the trial wave function ψ_{0T}. Thus
all that is required in order to obtain a well-
defined component $f_{jY}(\vec{r}_j)$ for the operator Y is to
derive the appropriate component $f_{jW}(\vec{r}_j, \vec{r})$ for
the operator W.

With the definition of the auxiliary function given
above and employing Eqs. (24) and (25) we can
now calculate the correction terms to $\overline{Y}$ and $\overline{Z}$ by
substituting into Eq. (11) to obtain

$$\gamma(\vec{r}, \vec{r}') = \langle Y \rangle + i \langle Z \rangle$$

$$= \sum_j \phi_j^*(\vec{r}) \phi_j(\vec{r}')$$

$$+ \sum_j \left(\phi_j^*(\vec{r}) \frac{I_j(\vec{r}')}{\phi_j^*(\vec{r}')} + \phi_j(\vec{r}') \frac{I_j^*(\vec{r})}{\phi_j(\vec{r})} \right), \tag{27}$$

where

$$I_j(\vec{r}) = \langle f_{jW}(\vec{r}_j, \vec{r}) \psi_{0T} | H - \mathcal{E} | \psi_{0T} \rangle, \tag{28}$$

and where we have used $\vec{a} = \vec{r}' - \vec{r}$,

$$\text{Re}\chi + i\,\text{Re}\,i\chi = \chi^*$$

$$\text{Re}\chi - i\,\text{Re}\,i\chi = \chi.$$

Note, however, that the integral given by Eq. (28)
is the integral required in order to obtain the
charge density correct to second order. Thus, in
order to obtain the single-particle density matrix
correct to second order within this formalism it
is only necessary to calculate the charge density
correct to second order.

For spherically symmetric atomic systems it
has been observed[8] that it is easier to obtain the
cosine Fourier transform of the charge density
rather than the density itself by this method. In
other words it is easier to calculate the correc-
tion term with an auxiliary function obtained for
the operator

$$U(\vec{r}_1, \ldots, \vec{r}_N, \vec{k}) = \sum_j U(\vec{r}_j, \vec{k}) = \sum_j \cos(\vec{k} \cdot \vec{r}_j) \tag{29}$$

rather than that obtained for the operator
$W = \sum_i \delta(\vec{r}_i - \vec{r})$. From the previous discussion it
follows that the components $f_{jU}(\vec{r}_j, \vec{k})$ of the auxil-
iary function for the operator U in the first de-
coupling approximation must satisfy the equation

$$\nabla_j^2 f_{jU}(\vec{r}_j, \vec{k}) + 2\vec{\nabla}_j f_{jU}(\vec{r}_j, \vec{k}) \cdot \frac{\vec{\nabla}_j \phi_j(\vec{r}_j)}{\phi_j(\vec{r}_j)}$$

$$= \cos\vec{k} \cdot \vec{r}_j - \overline{U}_j. \tag{30}$$

From Eq. (30) it can easily be shown that $f_{jW}(\vec{r}_j, \vec{r})$
is the inverse cosine Fourier transform of the
$f_{jU}(\vec{r}_j, \vec{k})$. This implies that in the general expres-
sion (27) for $\gamma(\vec{r}, \vec{r}')$ we replace $I_j(\vec{r})$ by the cosine

Fourier transform $J_j(\vec{r})$ of the contribution of the jth particle to the correction term for the form factor $F_j(\vec{k})$ of the system, i.e., by

$$J_j(\vec{r}) = (1/8\pi^3) \int F_j(\vec{k}) \cos\vec{k}\cdot\vec{r}\, d\vec{k}, \qquad (31)$$

where

$$F_j(\vec{k}) = \langle f_{jU}(\vec{r}_j, \vec{k})\psi_{0T}|H - \mathcal{S}|\psi_{0T}\rangle. \qquad (32)$$

Thus we see that in order to obtain the reduced single-particle density matrix in those cases where it is less convenient to obtain the charge density we first need to calculate the form factor for the system correct to second order via the variational method.

B. Second decoupling approximation

For one- and two-particle systems in this second approximation[6] we decouple Eq. (21) by treating the coupling term as a perturbation and initially neglecting it. We then have to solve the equation

$$\nabla_j^2 f_{jY}(\vec{r}_j) + 2\vec{\nabla}_j f_{jY}(\vec{r}_j) \cdot \frac{\vec{\nabla}_j \phi_j(\vec{r}_j)}{\phi_j(\vec{r}_j)}$$
$$= \frac{1}{\phi_j(\vec{r}_j)} \left[Y(\vec{r}_j) - \overline{Y}_j - \frac{\langle Y\rangle - \overline{Y}}{2} \right]\phi_j(\vec{r}_j), \quad (33)$$

whose solution is

$$f_{jY}(\vec{r}_j) = f_{jY}^0(\vec{r}_j) - \frac{\langle Y\rangle - \overline{Y}}{2} f_j^1(\vec{r}_j), \qquad (34)$$

where the $f_{jY}^0(\vec{r}_j)$ and $f_j^1(\vec{r}_j)$ satisfy, respectively, the differential equations

$$\nabla_j^2 f_{jY}^0(\vec{r}_j) + 2\vec{\nabla}_j f_{jY}^0(\vec{r}_j) \cdot \frac{\vec{\nabla}_j \phi_j(\vec{r}_j)}{\phi_j(\vec{r}_j)}$$
$$= \frac{1}{\phi_j(\vec{r}_j)} [Y(\vec{r}_j) - \overline{Y}_j]\, \phi_j(\vec{r}_j) \quad (35)$$

and

$$\nabla_j^2 f_j^1(\vec{r}_j) + 2\vec{\nabla}_j f_j^1(\vec{r}_j) \cdot \frac{\vec{\nabla}_j \phi_j(\vec{r}_j)}{\phi_j(\vec{r}_j)} = 1. \qquad (36)$$

Similar equations arise for the operator Z. The functional $\gamma(\vec{r}, \vec{r}')$ in this approximation is then given as

$$\gamma(\vec{r}, \vec{r}') = \overline{Y} + i\overline{Z} + \frac{2\operatorname{Re}\langle\psi_{1T(Y)}^0|H - \mathcal{S}|\psi_{0T}\rangle + i2\operatorname{Re}\langle\psi_{1T(Z)}^0|H - \mathcal{S}|\psi_{0T}\rangle}{1 + \operatorname{Re}\langle\psi_{1T}^1|H - \mathcal{S}|\psi_{0T}\rangle}, \qquad (37)$$

where the auxiliary functions ψ_{1T}^0 and ψ_{1T}^1 for the operators Y and Z are defined as

$$\psi_{1T(Y,Z)}^0 = \sum_j f_{jY,Z}^0(\vec{r}_j)\psi_{0T} \quad \text{and} \quad \psi_{1T}^1 = \sum_j f_j'(\vec{r}_j)\psi_{0T}. \qquad (38)$$

Equation (35) for the components $f_{jY}^0(\vec{r}_j)$ of the auxiliary function $\psi_{1T(Y)}^0$ is the same as that of Eq. (23) of the first decoupling approximation. Hence the arguments in Sec. III A for the determination of $\gamma(\vec{r}, \vec{r}')$ from either the charge density or the form factor are thus equally applicable in this approximation for the calculation of the numerator in the correction term to $(\overline{Y} + i\overline{Z})$ of the functional $\gamma(\vec{r}, \vec{r}')$ of Eq. (37). The denominator in the correction term however remains the same for all operators since the auxiliary function ψ_{1T}^1 is independent of the operator whose expectation is being determined.[6]

For many-particle systems in this second decoupling approximation one cannot neglect the coupling term since its contribution to the integral-differential equation increases with the number of particles. Various methods for approximating the coupling term are discussed in Ref. 6, the net result of these approximations being to replace the denominator in the correction term for $\gamma(\vec{r}, \vec{r}')$ by $1 + (2/N)\operatorname{Re}\langle\psi_{1T}^1|H - \mathcal{S}|\psi_{0T}\rangle$ for an N-particle system.

IV. HARTREE-FOCK APPROXIMATION

As in the Hartree case we begin our discussion of the variational method in the Hartree-Fock approximation by considering the expectation value of the operator Y of Eq. (5). In the Hartree-Fock approximation for the determination of $\gamma(\vec{r}, \vec{r}')$ we use a Slater determinant of single-particle states as the system trial wave function, i.e., $\psi_{0T} = \sqrt{N!} A|\psi_H\rangle$; $\psi_H = \prod_i \phi_i(\vec{x}_i)$; $\vec{x} = \vec{r}, \zeta$, and A is the antisymmetrizer.[16] The auxiliary function too is appropriately antisymmetrized in this approximation: $\psi_{1T} = \sqrt{N!} A|\sum_j f_j(\vec{r}_j)\psi_H\rangle$. Using the property of commutivity of the antisymmetrizer with both the Hamiltonian, and the operators Y, and Z

$$[A, H] = 0, \quad [A, Y] = 0, \quad \text{and}\ [A, Z] = 0, \qquad (39)$$

variational minimization of the functional M' leads, as in the Hartree case, to a coupled integral-differential equation for the components $f_j(\vec{r}_j)$ of the auxiliary function.[7] The difference between this equation and that derived in the Hartree approximation is the presence of an exchange term involving the specific operator whose expectation is to be determined. The expression for the exchange term for the operator Y is

$$S_Y(\vec{r}_j) = \underset{\text{spin}\,i\,=\,\text{spin}\,j}{\sum_i}{}' \langle \phi_i(\vec{r}_i)|Y(\vec{r}_i)|\phi_j(\vec{r}_i)\rangle \phi_i(\vec{r}_j). \qquad (40)$$

The coupled equation is again decoupled in the two different approximations discussed earlier. Typically in the first decoupling approximation one has to solve the differential equation

$$\nabla_j^2 f_{jY}(\vec{r}_j) + 2\vec{\nabla}_j f_{jY}(\vec{r}_j) \cdot \frac{\vec{\nabla}_j \phi_j(\vec{r}_j)}{\phi_j(\vec{r}_j)}$$

$$= \frac{1}{\phi_j(\vec{r}_j)} \left(Y(\vec{r}_j) - \overline{Y}_j - \frac{S_Y(\vec{r}_j)}{\phi_j(\vec{r}_j)} \right) \phi_j(\vec{r}_j) \quad (41)$$

for the components $f_{jY}(\vec{r}_j)$ of the auxiliary function. However the exchange term $S_Y(\vec{r}_j)$ for the operator Y is related to the exchange term $S_W(\vec{r}_j)$ for the operator $W = \delta(\vec{r}_j - \vec{r})$ by

$$S_Y(\vec{r}_j) = S_W(\vec{r}_j, \vec{r}) \frac{\phi_j(\vec{r} + \vec{a})}{\phi_j(\vec{r})} + S_W(\vec{r}_j, \vec{r}') \frac{\phi_j(\vec{r}' - \vec{a})}{\phi_j(\vec{r}')},$$

$$(42)$$

where

$$S_W(\vec{r}_j, \vec{r}) = \sum_i{}' \langle \phi_i(\vec{r}_i) | \delta(\vec{r}_i - \vec{r}) | \phi_j(\vec{r}_i) \rangle \phi_i(\vec{r}_j).$$

$$\text{spin}i = \text{spin}j$$

$$(43)$$

The solution to Eq. (41) and the appropriate differential equation for the operator Z to within a constant are

$$f_{jY}(\vec{r}_j) = \frac{1}{2} \left(f_{jW}(\vec{r}_j, \vec{r}) \frac{\phi_j(\vec{r} + \vec{a})}{\phi_j(\vec{r})} \right.$$

$$\left. + f_{jW}(\vec{r}_j, \vec{r}') \frac{\phi_j(\vec{r}' - \vec{a})}{\phi_j(\vec{r}')} \right) \quad (44)$$

and

$$f_{jZ}(\vec{r}_j) = -\frac{i}{2} \left(f_{jW}(\vec{r}_j, \vec{r}) \frac{\phi_j(\vec{r} + \vec{a})}{\phi_j(\vec{r})} \right.$$

$$\left. - f_{jW}(\vec{r}_j, \vec{r}') \frac{\phi_j(\vec{r}' - \vec{a})}{\phi_j(\vec{r}')} \right), \quad (45)$$

where $f_{jW}(\vec{r}_j, \vec{r})$ is a solution of the equation

$$\nabla_j^2 f_{jW}(\vec{r}_j) + 2\vec{\nabla}_j f_{jW}(\vec{r}_j) \cdot \frac{\vec{\nabla}_j \phi_j(\vec{r}_j)}{\phi_j(\vec{r}_j)}$$

$$= \delta(\vec{r}_j - \vec{r}) - \overline{W}_j - S_W(\vec{r}_j). \quad (46)$$

This is the equation that must be solved if one wishes to obtain the charge density of an exchange-dependent system via the variational method. The functional form of $\gamma(\vec{r}, \vec{r}')$ in the Hartree-Fock approximation is thus the same as that of the Hartree case given by Eq. (27) except that in this instance the integral $I_j(\vec{r})$ is given as

$$I_j(\vec{r}) = \sum_P (-1)^p \langle f_{jW}(\vec{r}_j, \vec{r}) \psi_H | (H - \mathcal{E}) P | \psi_H \rangle, \quad (47)$$

where p is the parity of the permutation and P the permutation operator. Therefore, in this Hartree-

Fock approximation we again use the variational method to initially calculate either the charge density or its cosine Fourier transform for spherically symmetric systems; from it we obtain the single-particle density matrix. All that is required is an initial choice of a parameterized trial wave function ψ_{0T} which need not be a highly accurate representation of the exact wave function. Nor does it need to be correlated. The systematic calculation of the appropriate correction terms to the first-order expectations leads to results which are correct to second order.

Finally, when any approximate method of calculating a density matrix is proposed it is reasonable to inquire whether the result corresponds to exactly N particles, i.e., does $\int \gamma(\vec{r}, \vec{r}) d\vec{r} = N$, and, more generally, is the derived γ N representable, that is to say, is it derivable from some N-particle wave function? The answers to these questions are easily determined in the following way.

It follows from Eq. (26) in the Hartree approximation and from Eq. (46) in the Hartree-Fock approximation that $\int f_{jW}(\vec{r}_j, \vec{r}) d\vec{r} = 0$ which implies

$$\int I_j(\vec{r}) d\vec{r} = 0. \quad (48)$$

Using this result and Eq. (27) we obtain $\int \gamma(\vec{r}, \vec{r}) d\vec{r} = N$ exactly. However, $\gamma(\vec{r}, \vec{r}')$ is not exactly N-representable as can be seen from the fact that Eq. (48) implies that ϕ_i is an eigenfunction of γ with eigenvalue $\lambda_i = 1$. Since there are N different ϕ_i this leads to $\sum_i \lambda_i = N$, which saturates the sum rule for an N-particle system.[17] Thus the sum of all other eigenvalues of γ must be zero which implies at least one negative eigenvalue (they all cannot be zero since otherwise $\gamma = \gamma_0$ where $\gamma_0 = \overline{Y} + i\overline{Z}$ which is impossible for a γ that is N representable.[17] However, the derived γ is N representable through $O(\delta)$ as can be seen from the fact that to $O(\delta)$ our result is equivalent to

$$\gamma(\vec{r}, \vec{r}') = \sum_i [\phi_i(\vec{r}) + P_i(\vec{r})]^*[\phi_i(\vec{r}') + P_i(\vec{r}')],$$

where $P_i(\vec{r}) \equiv I_i(\vec{r})/\phi_i^*(\vec{r})$, which corresponds to a wave function that is a Slater determinant with elements $[\phi_i(\vec{r}_i) + P_i(\vec{r}_i)]$. Our results in the first decoupling approximation therefore reduce to those of Hall et al.[18] for their choice of the set $\{\phi_i\}$, i.e., all ϕ_i are eigenfunctions of the same single-particle Hamiltonian. However, our results are more general than theirs because all we require of the set $\{\phi_i\}$, are that they be orthonormal which enables us, for example, to employ wave functions with different screening parameters for core and valence states which can significantly improve the accuracy of calculations of the density matrix

as it does when employing the variational principle for the energy.

V. APPLICATION TO THE MODEL HYDROGEN-ATOM PROBLEM

In order to illustrate the application of this technique and demonstrate its utility we now apply it to the model hydrogen-atom problem for the determination of (a) the Fourier transform of the electron density, (b) the electron density, (c) the single-particle density matrix, (d) the momentum density, and (e) the Compton profile in the impulse approximation.[19] Following these calculations we also discuss how well the virial theorem is satisfied within this formalism for this model problem.

We assume our trial wave function to be of hydrogenic form with a variable parameter Z_1, i.e.,

$$\psi_{0T} = (Z_1^{3/2}/\sqrt{\pi})e^{-Z_1 r}.$$

The results below are in the second decoupling approximation where the factor D is the denominator term of Eq. (37):

$$D = 1 + \langle \psi_{1T}^1 | H - \mathcal{E} | \psi_{0T} \rangle = \tfrac{5}{2} - 3/2Z_1.$$

If in these equations D is set equal to unity we obtain the results in the first decoupling approximation. The expressions for the various properties are written as a sum of the first-order expectation value plus the correction term, the form factor, charge density, and the density matrix being obtained as the expectations of the operators U, W and X, respectively. The expressions are as follows.

(a). Fourier transform of electron density:

$$F(k) = F_0(k) + F_1(k),$$

$$F_0(k) = 16Z_1^4/(k^2 + 4Z_1^2),$$

$$F_1(k) = -\frac{4(Z_1 - Z)}{D}\frac{16Z_1^3 k^2}{(k^2 + 4Z_1^2)^3}.$$

(b). Electron density:

$$\rho(r) = \rho_0(r) + \rho_1(r),$$

$$\rho_0(r) = (Z_1^3/\pi)e^{-2Z_1 r},$$

$$\rho_1(r) = -\frac{(Z_1 - Z)}{D}\frac{Z_1^2 e^{-2Z_1 r}}{\pi}(3 - 2Z_1 r).$$

(c). Single-particle density matrix:

$$\gamma(\vec{r}, \vec{r}') = \gamma_0(\vec{r}, \vec{r}') + \gamma_1(\vec{r}, \vec{r}'),$$

$$\gamma_0(\vec{r}, \vec{r}') = (Z_1^3/\pi)e^{-Z_1(r+r')},$$

$$\gamma_1(\vec{r}, \vec{r}') = -\frac{(Z_1 - Z)}{D}\frac{Z_1^2 e^{-Z_1(r+r')}}{\pi}[3 - Z_1(r + r')].$$

(d). Momentum density:

$$\rho(k) = \rho_0(k) + \rho_1(k),$$

$$\rho_0(k) = \frac{32Z_1^5 k^2}{\pi(k^2 + Z_1^2)^4},$$

$$\rho_1(k) = -\frac{(Z_1 - Z)}{D}\frac{32k^2 Z_1^4}{\pi(k^2 + Z_1^2)^4}\left(5 - \frac{8Z_1^2}{(k^2 + Z_1^2)}\right).$$

(e). Compton profile in impulse approximation (Ref. 19):

$$J(q) = \frac{1}{2}\int_{|q|}^{\infty}\frac{\rho(k)}{k}dk = J_0(q) + J_1(q),$$

$$J_0(q) = \frac{8Z_1^5}{3\pi(q^2 + Z_1^2)^3},$$

$$J_1(q) = -\frac{(Z_1 - Z)}{D}\frac{16Z_1^5}{\pi(q^2 + Z_1^2)^3}\left(\frac{5}{6} - \frac{Z_1^2}{(q^2 + Z_1^2)^4}\right).$$

(q is the projection of the electron momentum on the scattering vector.)

A plot of the variation of the form factors in the two decoupling approximations as compared to that of the first-order term for a 10% error in the variational parameter is given in Ref. 6. It was observed in Ref. 6 that addition of the correction term to $\overline{U}$ drastically improved the results. Typically errors of over 40% in $\overline{U}$ for large momentum transfer were reduced to errors of less than a percent. Over the low and medium momentum transfer ranges the results of the two decoupling approximations consistently reduced large errors in the first-order term to errors which were always less than $2\tfrac{1}{2}\%$. It is expected therefore that these improvements will be reflected in the results for the single-particle density matrix and hence the momentum density since these are obtained from the form factor.

In Fig. 1 we plot the variation of the momentum densities in the different approximations again for $Z_1 = 1.1$ normalized with respect to the exact result. Here $\rho_{0N}(k)$, $\rho_N^0(k)$ and $\rho_N(k)$ are the results of the first-order, first and second decoupling approximations, respectively. At $k = 0$, a 25% error in $\rho_{0N}(k)$ is reduced to errors of 7% and 4.4% in $\rho_N(k)$ and $\rho_N^0(k)$, respectively. At $k = 2$, the error in the first-order term ρ_{0N} is 37% whereas the errors in ρ_N and ρ_N^0 are 2% and 2.5%. With increasing momentum the error in ρ_{0N} continues to increase rapidly. For $k = 3$, ρ_{0N} is in error by 48% whereas ρ_N is in error by only 0.16% and the error in ρ_N^0 has increased to 6.4%. We therefore observe that even with the use of a rather poor trial wave function the results obtained within this formalism are a significant improvement over the first-order calculation.

In Fig. 2 we plot the results for the normalized Compton profiles in the impulse approximation.
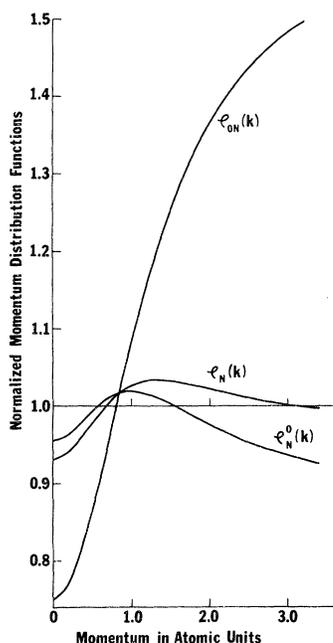
FIG. 1. Momentum distribution functions for hydrogen normalized with respect to the exact result assuming $\psi_{0T} = (Z_1^{3/2}/\sqrt{\pi})e^{-Z_1 r}$ with $Z_1 = 1.1$. Here $\rho_{0N}(k)$ are the first-order results and $\rho_N^0(k)$ and $\rho_N(k)$ the results in the first and second decoupling approximations, respectively.

Here J_{0N} is the first-order term, and J_N^0 and J_N the results in the first and second decoupling approximations. At $q = 0$, J_{0N} is in error by 9% whereas J_N is in error by 1% and J_N^0 is correct to seven significant figures. A 19% error in J_{0N} at $q = 1$ is reduced to errors of 1.3% and 1.1%, respectively, for J_N and J_N^0. The results of the second decoupling approximation J_N may be observed to be accurate over the entire range of q considered and are more accurate for larger values of q than the results of J_N^0, but in each case the addition of the correction term improves the first-order results rather significantly.

Finally with the expressions for the charge density and momentum density derived above we obtain the expectation values of the kinetic and potential energies in order to determine to what degree of accuracy the virial theorem is satisfied. The analytic expressions for the expectations of the operators $\langle T \rangle$ and $\langle \vec{r} \cdot \vec{\nabla} V \rangle$ in atomic units are
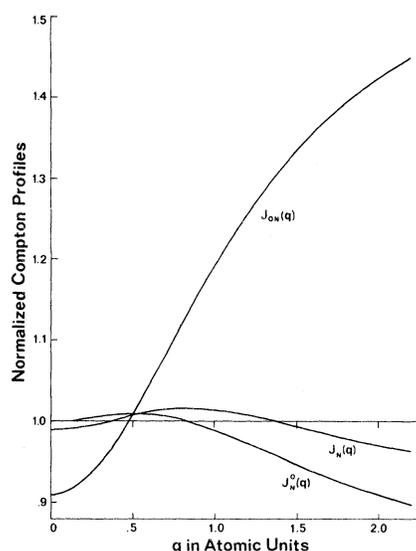
FIG. 2. Impulse-approximation Compton profiles for hydrogen normalized with respect to the exact result assuming $\psi_{0T} = (Z_1^{3/2}/\sqrt{\pi})e^{-Z_1 r}$ with $Z_1 = 1.1$. Here $J_{0N}(q)$, $J_N^0(q)$, and $J_N(q)$ are the first-order, first and second decoupling approximation results.

$$\tfrac{1}{2}\langle \vec{r} \cdot \nabla V \rangle = \langle r^{-1} \rangle = Z_1 - D^{-1}(Z_1 - Z)$$

and

$$\langle T \rangle = \langle k^2 \rangle = Z_1^2 - D^{-1} 2 Z_1 (Z_1 - Z),$$

where, as before, the results $\langle 0 \rangle$ are quoted in the second decoupling approximation, and where the first term corresponds to the first-order expectation value $\bar{0}$, and the second to the correction term. Setting D to unity gives the results in the first decoupling approximation $\langle 0 \rangle_0$.

For $Z_1 = 1.1$ the ratio of the first-order expectation values of T and $\tfrac{1}{2}\vec{r} \cdot \vec{\nabla} V$ is 1.1, whereas the ratios in the first and second decoupling approximations are $\langle T \rangle_0 / \tfrac{1}{2}\langle \vec{r} \cdot \vec{\nabla} V \rangle_0 = 0.9900$ and $\langle T \rangle / \tfrac{1}{2}\langle \vec{r} \cdot \vec{\nabla} V \rangle = 1.0043$, respectively. Thus even for substantial errors in the variational parameter the fact that the expectation values have been obtained correct to second order leads to the virial theorem being closely satisfied.

We are currently employing these techniques to accurately analytically calculate the single-particle density matrix for systems containing many interacting electrons.

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