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## Variational Principles for Single-Particle Expectation Values in the Hartree Approximation\*

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The application of Delves's variational principle for the calculation of the expectation value of single-particle operators  $W$  is investigated in the Hartree approximation. In this approximation the auxiliary function is taken to be of the form  $\psi_{1T} = \sum_i f_i(\mathbf{r}_i) \psi_{0T}$ , where  $\psi_{0T}$  is the trial ground-state wave function. For a given  $\psi_{0T}$ , a set of coupled integrodifferential equations satisfied by the  $f_i(\mathbf{r}_i)$  is derived by minimizing an auxiliary functional containing  $\psi_{0T}$ ,  $\psi_{1T}$ ,  $W$ , and the Hamiltonian of the system. The resulting equations are uncoupled in two different approximations each valid for one- and two-particle systems and are compared to those employed by others and to those previously suggested by us on the basis of certain self-consistency considerations. The uncoupled equations are solved exactly for single-particle operators that depend on the radial distance only. The utility of the technique is demonstrated by showing that for a model hydrogen-atom problem it leads to highly accurate results for the electron density at the origin and the Fourier transform of the electron density even when the calculation of these quantities employing  $\psi_{0T}$  alone is substantially in error. The results of applying the technique to the helium atom for the calculation of  $\langle r^n \rangle$ ,  $n = -2, -1, 1, 2$ , and the electron density at the origin employing an energy-minimized product of hydrogenic wave functions for  $\psi_{0T}$  are reviewed and compared with those of Pekeris and found to have an accuracy equivalent to a numerical Hartree-Fock calculation. Finally, the decoupling approximations are extended to systems containing more than two particles.

### I. INTRODUCTION AND CONCLUSIONS

The use of the Rayleigh-Ritz variational principle<sup>1</sup> with a many-parameter wave function for the determination of the ground-state energy of a quantum-mechanical system has two important characteristics. First of all, the calculated ener-

gy always overestimates the exact ground-state energy of the assumed Hamiltonian and thus enables us to determine which of two calculations for the energy is more accurate. Second, if the trial wave function is in error by  $O(\delta)$ , the calculated energy is in error by only  $O(\delta^2)$  which leads to the result that good estimates of the en-

ergy can be obtained by employing wave functions which can be substantially different from the exact wave function.

However, if one employs the resulting wave function to calculate expectation values of observables other than the energy the results have in general an error of  $O(\delta)$  of unknown sign. In the past few years considerable progress has been made in overcoming these two difficulties.

Techniques have been developed<sup>2,3</sup> for the rigorous calculation of upper and lower bounds for the expectation value of a Hermitian operator for a system described by a given Hamiltonian. While these methods are indispensable for determining which of two calculations is more accurate, the results are not in error by  $O(\delta^2)$  and thus require trial wave functions which closely approximate the exact ground state or else the bounds may be substantially different from the exact result and thus not very useful. Since our ability to calculate accurate wave functions for systems containing interacting particles decreases as the number of particles increases, these techniques can be expected to have less utility for many particle systems.

On the other hand, variational principles for the calculation of expectation values have been developed<sup>4,5</sup> which yield results correct to second order with an error of unknown sign. Although these methods do not provide a rigorous bound the results are usually more accurate than those obtained by simply calculating the expectations with the trial wave function.

These variational methods generally employ two functions,  $\psi_{0T}$ , the approximate ground-state wave function, and  $\psi_{1T}$ , which is an approximation to a function  $\psi_1$  satisfying a certain differential equation discussed in Sec. II. The parameters in a  $\psi_{0T}$  of a given form can be determined by minimizing the energy, but it is generally not possible to determine the parameters in a  $\psi_{1T}$  of a given form by making the variational estimate of the expectation value stationary with respect to their variation. This is due to the property that this estimate does not provide a bound and hence its extremum is generally a saddle point which is difficult to find numerically.<sup>5</sup> Moreover, there may be several such extrema and it is not clear which one is physically significant. This problem has been circumvented by constructing a functional involving the trial wave function  $\psi_{0T}$ , the auxiliary function  $\psi_{1T}$ , the Hamiltonian, and the operator representing the observable in question which when minimized leads to the best estimate of  $\psi_{1T}$  for a given  $\psi_{0T}$ .<sup>5,6</sup> This technique has previously been employed to calculate the best  $\psi_{1T}$  in terms of both linear and nonlinear variational parameters.<sup>6</sup> In Sec. II we minimize the functional for single-particle operators by varia-

tion of the auxiliary function  $\psi_{1T}$  having assumed  $\psi_{0T}$  to be a Hartree product of single-particle states, and we derive a set of coupled differential equations for the elements of  $\psi_{1T}$  in terms of the elements of  $\psi_{0T}$  without the introduction of any additional parameters to describe  $\psi_{1T}$ . In a certain approximation the equations are uncoupled and shown to be equivalent to those employed by others.<sup>7,8</sup> The equations are also uncoupled in a second approximation for one and two particle systems which leads to equations previously suggested on the basis of certain self-consistency considerations.<sup>9</sup>

In Sec. III the accuracy of the method in the two decoupling approximations is investigated for the model hydrogen-atom problem employing for  $\psi_{0T}$  an approximate hydrogenic-type wave function with  $Z = Z_1$  instead of  $Z = 1$ . Both the electron density at the origin  $\rho(0)$  and the elastic form factor  $F(\vec{k})$  are considered. We find that for  $\rho(0)$  the second decoupling approximation yields an error of approximately one-half that given by the first decoupling approximation and is, for example, within 0.3% of the exact result when the expectation value computed directly using the approximate wave function is in error by 13%. The results for the coherent form factor are still more impressive. We find that for a 10% error in the value of the parameter  $Z_1$  ( $Z_1 = 1.1$ ) the results of employing the second decoupling approximation yields a maximum error of only 2.5% for all values of momentum transfer  $\vec{k}$  and closely approximates the exact results for large  $\vec{k}$ , while the first decoupling approximation yields an error of about 6% for large  $\vec{k}$  compared to the more than 40% error in the approximate form factor in this region.

In Sec. IV the results of the two decoupling approximations as applied to the ground state of the helium isoelectronic sequence for the determination of the expectation values of the operators  $r^n$ ,  $n = -2, -1, 1, 2$ , and the electron density at the origin are briefly reviewed. A more detailed discussion is given in Ref. 9 (hereafter referred to as I). Here the trial wave function  $\psi_{0T}$  is taken as a simple product of energy-optimized hydrogenic functions and it is found that the second decoupling approximation yields expectation values with an accuracy comparable to a Hartree-Fock calculation and always leads to more accurate expectation values than does the first decoupling approximation except for  $n = -1$  in which case the results are the same. A discussion of the analytic calculation of the coherent form factor for the ground state of the helium isoelectronic sequence is given in the following paper.

Finally, in Sec. V we give a discussion of the decoupling procedure for a system composed of more than two particles in this Hartree approximation.

## II. VARIATIONAL PRINCIPLE

Consider the functional

$$\langle W \rangle = \bar{W} + 2 \operatorname{Re} \langle \psi_{1T} | H - E | \psi_{0T} \rangle \quad (1)$$

with

$$\bar{W} = \langle \psi_{0T} | W | \psi_{0T} \rangle, \quad (2)$$

where  $W$  is an arbitrary Hermitian operator and  $E$  the energy eigenvalue of the Hamiltonian:

$$H\psi_0 = E\psi_0. \quad (3)$$

Then if  $\psi_{0T} = \psi_0$ ,

$$\langle W \rangle = \bar{W}_E = \langle \psi_0 | W | \psi_0 \rangle, \quad (4)$$

where  $\bar{W}_E$  is the exact expectation value of the operator  $W$  independent of the choice of the auxiliary function  $\psi_{1T}$ . Furthermore, Delves<sup>4</sup> has shown that if  $\psi_{0T}$  differs from  $\psi_0$  by  $O(\delta)$  and  $\psi_{1T}$  differs from  $\psi_1$  by  $O(\delta_1)$ , where  $\psi_1$  satisfies

$$(H - E)\psi_1 = (\bar{W}_E - W)\psi_0, \quad (5)$$

then it follows directly from the Hermiticity of  $H$  that  $\langle W \rangle$  differs from  $\bar{W}_E$  by  $O(\delta^2, \delta\delta_1)$ , whereas  $\bar{W}$  differs from  $\bar{W}_E$  by  $O(\delta)$ .

The trial wave function  $\psi_{0T}$  may be taken as one containing parameters chosen to minimize the energy. The use of Eq. (1) therefore depends on our ability to determine a good approximation to  $\psi_1$ . For a given  $\psi_{0T}$ , Eq. (5) suggests we determine the auxiliary function  $\psi_{1T}$  from

$$(H - E)\psi_{1T} = (\bar{W} - W)\psi_{0T}. \quad (6)$$

However, if this equation were solved exactly we immediately obtain from Eq. (1)

$$\langle W \rangle = \bar{W},$$

which is still in error by  $O(\delta)$ .

The problem of finding a technique for the determination of the auxiliary function  $\psi_{1T}$  for a given  $\psi_{0T}$  and  $W$  has been considered by both Delves<sup>6</sup> and Aranoff and Percus.<sup>5</sup> According to them the auxiliary function may be obtained by minimization of a certain functional  $M'$  involving  $\psi_{1T}$ ,  $\psi_{0T}$ , the Hamiltonian  $H$ , and the operator  $W$  whose expectation is to be determined. However, in all these techniques, the choice for the auxiliary function is strictly arbitrary and there is no systematic procedure for the determination of  $\psi_{1T}$  once the trial wave function  $\psi_{0T}$  for a particular system has been chosen. Considering the functional  $M'[\psi_{0T}, \psi_{1T}, H, W]$  in the form given by Aranoff and Percus,<sup>5</sup> we wish to derive a systematic method for the determination of  $\psi_{1T}$  having assumed a  $\psi_{0T}$ . By this method  $\psi_{1T}$  will be found to be dependent on the operator whose expectation value is being determined and independent of any further parameters other than those involved in the initial choice for the trial

wave function  $\psi_{0T}$ . The functional  $M'$  is given by

$$M'[\psi_{0T}, \psi_{1T}, H, W] = \langle \psi_{1T} | H - \mathcal{E} | \psi_{1T} \rangle + \langle \psi_{1T} | W | \psi_{0T} \rangle + \langle \psi_{0T} | W | \psi_{1T} \rangle \quad (7)$$

subject to the orthogonality condition

$$\langle \psi_{1T} | \psi_{0T} \rangle = 0. \quad (8)$$

This requirement is certainly satisfied by the exact  $\psi_1$  and  $\psi_0$  if we interpret<sup>10</sup>  $\psi_1$  [from Eq. (5)] as being a perturbational correction to  $\psi_0$  due to the perturbation  $W$ . Here

$$H_0\psi_{0T} = \mathcal{E}\psi_{0T},$$

where  $H_0$  is some approximate Hamiltonian.

If, with the above interpretation for  $\psi_1$ , we choose a Hartree product of single-particle states for the trial wave function  $\psi_{0T}$ ,

$$\psi_{0T} = \prod_i \phi_i(\vec{r}_i), \quad (9)$$

with

$$\langle \phi_i | \phi_j \rangle = \delta_{ij},$$

then from first-order perturbation theory the only states coupled to  $\psi_{0T}$  by the single-particle operator

$$W(\vec{r}_1, \dots, \vec{r}_N) = \sum_i W(\vec{r}_i)$$

are those states with only one single-particle wave function different from those in  $\psi_{0T}$ . Hence, for the auxiliary function we choose the form<sup>7,9</sup>

$$\psi_{1T} = \sum_j f_j(\vec{r}_j)\psi_{0T}. \quad (10)$$

Including the orthogonality constraint of Eq. (8) by the introduction of a Lagrange multiplier  $\lambda$ , we can obtain the appropriate differential equations for the individual  $f_j(\vec{r}_j)$  by minimizing the real function

$$M = M' - \lambda \langle \psi_{1T} | \psi_{0T} \rangle - \lambda^* \langle \psi_{0T} | \psi_{1T} \rangle$$

for arbitrary variations in the  $f_j(\vec{r}_j)$ . The result of the variational minimization is

$$\sum_j \langle \delta f_j(\vec{r}_j)\psi_{0T} | (H - \mathcal{E}) \sum_k f_k(\vec{r}_k)\psi_{0T} + (W - \lambda)\psi_{0T} \rangle + \text{c. c.} = 0. \quad (11)$$

Since the  $\delta f_j(\vec{r}_j)$  are all independent, Eq. (11) will be satisfied for each particle provided

$$\langle \psi_{0T} | (H - \mathcal{E}) \sum_k f_k(\vec{r}_k)\psi_{0T} + (W - \lambda)\psi_{0T} \rangle'_j = 0, \quad j = 1, 2, \dots, N \quad (12)$$

where the symbol  $\langle \rangle'_j$  means integration over all variables except the variable  $\vec{r}_j$ . Integration of Eq. (12) over  $\vec{r}_j$  leads to the  $N$  identical equations for the Lagrange multiplier  $\lambda$ :

$$\lambda = \bar{W} + \langle \psi_{0T} | H - \mathcal{E} | \sum_k f_k(\vec{r}_k)\psi_{0T} \rangle,$$

which on employing the orthogonality constraint may be written as

$$\lambda = \bar{W} + \Delta, \quad (13)$$

where

$$\Delta = \langle \psi_{0T} | H | \sum_k f_k(\vec{r}_k) \psi_{0T} \rangle. \quad (14)$$

Equation (12) thus represents  $N$  coupled differential equations satisfied by the  $f_j(\vec{r}_j)$ . Performing the indicated integrations for each term in Eq. (12) we have

$$\langle \psi_{0T} | W | \psi_{0T} \rangle'_j = \sum'_i \bar{W}_i \phi_j^*(\vec{r}_i) \phi_j(\vec{r}_i) + \phi_j^*(\vec{r}_j) W(\vec{r}_j) \phi_j(\vec{r}_j), \quad (15)$$

where the primed sum implies that the term  $i=j$  is excluded and where

$$\bar{W}_i = \int \phi_i^*(\vec{r}_i) W(\vec{r}_i) \phi_i(\vec{r}_i) d\vec{r}_i \quad (16)$$

and

$$\begin{aligned} \langle \psi_{0T} | H - \mathcal{E} | \sum_k f_k \psi_{0T} \rangle'_j \\ = \phi_j^*(\vec{r}_j) \langle \psi_{0T} | H - \mathcal{E} | \sum'_k f_k(\vec{r}_k) \psi_{0T} \rangle'_j \phi_j(\vec{r}_j) \\ + \phi_j^*(\vec{r}_j) \langle \psi_{0T} | H - \mathcal{E} | \psi_{0T} \rangle'_j f_j(\vec{r}_j) \phi_j(\vec{r}_j), \end{aligned} \quad (17)$$

where  $\psi_{0T}' = \psi_{0T} / \phi_j(\vec{r}_j)$ . And finally

$$\lambda \langle \psi_{0T} | \psi_{0T} \rangle'_j = \lambda \phi_j^*(\vec{r}_j) \phi_j(\vec{r}_j). \quad (18)$$

Equation (12) for each particle may thus be re-written as

$$\begin{aligned} \sum'_i \bar{W}_i \phi_j^*(\vec{r}_i) \phi_j(\vec{r}_i) + \phi_j^*(\vec{r}_j) [W(\vec{r}_j) - \lambda] \phi_j(\vec{r}_j) \\ + \phi_j^*(\vec{r}_j) \langle \psi_{0T} | H - \mathcal{E} | \sum'_k f_k(\vec{r}_k) \psi_{0T} \rangle'_j \phi_j(\vec{r}_j) \\ + \phi_j^*(\vec{r}_j) \langle \psi_{0T} | H - \mathcal{E} | \psi_{0T} \rangle'_j f_j(\vec{r}_j) \phi_j(\vec{r}_j) = 0. \end{aligned} \quad (19)$$

Substituting the value of  $\lambda$  derived above,

$$\lambda = \bar{W} + \Delta = \sum_i \bar{W}_i + \Delta,$$

into Eq. (19) and then dividing the equation by  $\phi_j^*(\vec{r}_j)$  yields

$$\begin{aligned} [W(\vec{r}_j) - \bar{W}_j - \Delta] \phi_j(\vec{r}_j) \\ + \langle \psi_{0T} | H - \mathcal{E} | \sum'_k f_k(\vec{r}_k) \psi_{0T} \rangle'_j \phi_j(\vec{r}_j) \\ + \langle \psi_{0T} | H - \mathcal{E} | \psi_{0T} \rangle'_j f_j(\vec{r}_j) \phi_j(\vec{r}_j) = 0. \end{aligned} \quad (20)$$

Now assuming a nonrelativistic Hamiltonian of the form

$$H = -\sum_i \nabla_i^2 + V(\vec{r}_1, \dots, \vec{r}_N),$$

the last term of Eq. (20) may be expanded as

$$\langle \psi_{0T} | H - \mathcal{E} | \psi_{0T} \rangle'_j f_j(\vec{r}_j) \phi_j(\vec{r}_j)$$

$$\begin{aligned} = -\phi_j(\vec{r}_j) \nabla_j^2 f_j(\vec{r}_j) - 2\vec{\nabla}_j \phi_j(\vec{r}_j) \cdot \vec{\nabla}_j f_j(\vec{r}_j) \\ + f_j(\vec{r}_j) \langle \psi_{0T} | H - \mathcal{E} | \psi_{0T} \rangle'_j \phi_j(\vec{r}_j). \end{aligned} \quad (21)$$

Furthermore it is clear that if the  $\phi_i(\vec{r}_i)$  satisfy single-particle equations of the form

$$H_i \phi_i(\vec{r}_i) = [-\nabla_i^2 + v_i(\vec{r}_i)] \phi_i(\vec{r}_i) = \epsilon_i \phi_i(\vec{r}_i),$$

then the second term of Eq. (1) may be written as

$$\begin{aligned} 2 \operatorname{Re} \langle \psi_{1T} | H - \sum_i H_i | \psi_{0T} \rangle \\ = 2 \operatorname{Re} \sum_j \int f_j^*(\vec{r}_j) \psi_{0T}^* U(\vec{r}_1, \dots, \vec{r}_N) \psi_{0T} d\tau, \end{aligned}$$

where  $U(\vec{r}_1, \dots, \vec{r}_N)$  is a real function. Thus only the real part of the  $f_j(\vec{r}_j)$  contributes to the correction to  $\bar{W}$  and we can, without any loss of generality, consider only real  $f_j(\vec{r}_j)$ . Substituting Eq. (21) into Eq. (20) and using  $f_j = f_j^*$ , we obtain

$$\begin{aligned} [W(\vec{r}_j) - \bar{W}_j - \Delta] \phi_j(\vec{r}_j) \\ - \phi_j(\vec{r}_j) \nabla_j^2 f_j(\vec{r}_j) - 2\vec{\nabla}_j \phi_j(\vec{r}_j) \cdot \vec{\nabla}_j f_j(\vec{r}_j) \\ + \langle \sum_k f_k(\vec{r}_k) \psi_{0T} | H - \mathcal{E} | \psi_{0T} \rangle'_j \phi_j(\vec{r}_j) = 0. \end{aligned} \quad (22)$$

Equation (22) represents the coupled integrodifferential equation for the  $f_j(\vec{r}_j)$  which we now proceed to decouple in two different approximations.

#### First Decoupling Approximation

In this approximation we replace the coupling term by its value averaged over  $\phi_j(\vec{r}_j)$ , i. e., by

$$\langle \sum_k f_k(\vec{r}_k) \psi_{0T} | H - \mathcal{E} | \psi_{0T} \rangle \phi_j(\vec{r}_j) \equiv \Delta \phi_j(\vec{r}_j),$$

where we have used Eqs. (8) and (20) and  $f_j(\vec{r}_j)$  as real. Therefore, in this approximation Eq. (22) becomes

$$\begin{aligned} \nabla_j^2 f_j(\vec{r}_j) + 2\vec{\nabla}_j \phi_j(\vec{r}_j) \cdot [\vec{\nabla}_j \phi_j(\vec{r}_j) / \phi_j(\vec{r}_j)] \\ = [\phi_j(\vec{r}_j)]^{-1} [W(\vec{r}_j) - \bar{W}_j] \phi_j(\vec{r}_j), \end{aligned} \quad (23)$$

which includes the case where  $W(\vec{r}_j)$  may be a differential operator. Equation (23) is essentially the same as that employed elsewhere<sup>7,8</sup> but was previously obtained as the approximation to an equation which, if solved exactly, would yield no correction to  $\bar{W}$ .

If for the case of nondifferential radially dependent single-particle operators of the form

$$W(\vec{r}_i) = W(r_i) \quad (24)$$

we choose our single-particle wave functions  $\phi_i(\vec{r}_i)$  to be

$$\phi_i(\vec{r}_i) = \phi_i(r_i) Y_l^m(\theta_i, \phi_i), \quad (25)$$

then owing to the orthogonality of the spherical

harmonics the only states that are coupled to the original state by the perturbation  $W$  are those single-particle states having the same angular dependence as the original state, and thus we seek

$$f_j(r_j) = \int^{r_j} [r_j'^2 \phi_j^2(r_j')]^{-1} \left\{ \int_0^{r_j'} r_j''^2 \phi_j^2(r_j'') [W(r_j'') - \bar{W}_j] dr_j'' \right\} dr_j' + C, \quad (27)$$

where the constant  $C$  may be chosen to orthogonalize the auxiliary function which is now defined as

$$\psi_{1T} = \sum_j f_j(r_j) \psi_{0T} \quad (28)$$

to the trial wave function  $\psi_{0T}$ . This then eliminates the generally unknown quantities  $E$  and  $\mathcal{E}$ . The expectation value of the operator  $W$  (to be designated in this approximation as  $\langle W \rangle_0$ ) may now be obtained via Eq. (1).

#### Second Decoupling Approximation

In this second approximation, for one- and two-particle systems, we treat the coupling term as a perturbation and initially neglect it. By employing the orthogonality of  $\psi_{1T}$  to  $\psi_{0T}$ , the reality of the function  $f_j(\vec{r}_j)$  and Eq. (1), we may rewrite Eq. (22) as

$$\nabla_j^2 f_j(\vec{r}_j) + 2\vec{\nabla}_j f_j(\vec{r}_j) \cdot [\vec{\nabla}_j \phi_j(\vec{r}_j) / \phi_j(\vec{r}_j)]$$

$$f_j^0(r_j) = \int^{r_j} [r_j'^2 \phi_j^2(r_j')]^{-1} \left\{ \int_0^{r_j'} r_j''^2 \phi_j^2(r_j'') [W(r_j'') - \bar{W}_j] dr_j'' \right\} dr_j' + C_1 \quad (33)$$

and

$$f_j^1(r_j) = \int^{r_j} [r_j'^2 \phi_j^2(r_j')]^{-1} \left[ \int_0^{r_j'} r_j''^2 \phi_j^2(r_j'') dr_j'' \right] dr_j' + C_2, \quad (34)$$

where  $C_1$  and  $C_2$  are arbitrary constants of integration. The auxiliary function is therefore

$$\begin{aligned} \psi_{1T} &= \sum_j f_j(r_j) \psi_{0T} \\ &= \sum_j [f_j^0(r_j) - \frac{1}{2}(\langle W \rangle - \bar{W}) f_j^1(r_j)] \psi_{0T} \\ &= \psi_{1T}^0 - \frac{1}{2}(\langle W \rangle - \bar{W}) \psi_{1T}^1, \end{aligned} \quad (35)$$

where we define

$$\psi_{1T}^0 = \sum_j f_j^0(r_j) \psi_{0T}, \quad (36)$$

$$\psi_{1T}^1 = \sum_j f_j^1(r_j) \psi_{0T}. \quad (37)$$

The auxiliary function may now be substituted into Eq. (1) and solved for  $\langle W \rangle$  to obtain

solutions to Eq. (23) of the form

$$f_j(\vec{r}_j) = f_j(r_j). \quad (26)$$

The solution to Eq. (23) is thus

$$= [\phi_j(\vec{r}_j)]^{-1} [W(\vec{r}_j) - \bar{W}_j - \frac{1}{2}(\langle W \rangle - \bar{W})] \phi_j(\vec{r}_j). \quad (29)$$

For nondifferential single-particle operators the solution to Eq. (29) is

$$f_j(\vec{r}_j) = f_j^0(\vec{r}_j) - \frac{1}{2}(\langle W \rangle - \bar{W}) f_j^1(\vec{r}_j), \quad (30)$$

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

$$\nabla_j^2 f_j^0(\vec{r}_j) + 2\vec{\nabla}_j f_j^0(\vec{r}_j) \cdot [\vec{\nabla}_j \phi_j(\vec{r}_j) / \phi_j(\vec{r}_j)] = W(\vec{r}_j) - \bar{W}_j \quad (31)$$

and

$$\nabla_j^2 f_j^1(\vec{r}_j) + 2\vec{\nabla}_j f_j^1(\vec{r}_j) \cdot [\vec{\nabla}_j \phi_j(\vec{r}_j) / \phi_j(\vec{r}_j)] = 1. \quad (32)$$

If we again restrict ourselves to radially dependent operators of the form of Eq. (24) and to single-particle wave functions as given by Eq. (25), then following the same argument as above,  $f_j(\vec{r}_j) = f_j(r_j)$ , and the solutions to Eqs. (31) and (32) are

$$\langle W \rangle = \bar{W} + \frac{2\text{Re} \langle \psi_{1T}^0 | H - E | \psi_{0T} \rangle}{1 + \text{Re} \langle \psi_{1T}^1 | H - E | \psi_{0T} \rangle}. \quad (38)$$

This is, of course, the same expression for  $\langle W \rangle$  as obtained through the self-consistency considerations of I. The integration constants  $C_1$  and  $C_2$  may be chosen to orthogonalize the functions  $\psi_{1T}^0$  and  $\psi_{1T}^1$  to  $\psi_{0T}$ . Also, since the function  $f_j^1(\vec{r}_j)$  is independent of the operator whose expectation value is being sought, the denominator in the correction term to  $\bar{W}$  in Eq. (38) is the same for all operators.

We note therefore that the expectation value of any operator  $W = \sum_i W(r_i)$  calculated by the analytical method in both decoupling approximations is very much a function of the specific property of

interest and the only parameters required in the calculation are those involved in the description of the trial wave function  $\psi_{0T}$ . Finally we note again that since the error in  $\langle W \rangle$  is  $O(\delta^2, \delta\delta_1)$ , where  $\psi_{1T}$  is in error by  $O(\delta_1)$ , then even if we carried out our procedure without making any approximation in calculating  $\psi_{1T}$  for a given  $\psi_{0T}$ , the results would be in error by  $O(\delta^2)$ .

### III. APPLICATION OF TECHNIQUE TO HYDROGEN ATOM

In order to illustrate the application of the technique and demonstrate its utility we now apply the analytical method to the model hydrogen-atom problem for the determination of the electron density at the origin  $\rho(0)$  and the coherent form factor  $F(k)$ . We write the Hamiltonian in atomic units as

$$H = -\nabla^2 - 2/r$$

and for both cases we assume our trial wave function to be of hydrogenic form with a variable parameter  $Z_1$ , i. e.,

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

#### Electron Density at Origin

The electron density at the origin  $\rho(0)$  is the expectation value of the operator  $W = \delta(\vec{r})$ . The analytic expressions for the components of  $\langle W \rangle_0$  and  $\langle W \rangle$  (the expectation values in the first and second decoupling approximations) are

$$\bar{W} = Z_1^3/\pi,$$

$$\langle \psi_{1T}^0 | H | \psi_{0T} \rangle = -(3/2\pi) Z_1 (Z_1 - 1)^2,$$

$$[1 + \langle \psi_{1T}^1 | H | \psi_{0T} \rangle] = 1 + \frac{3}{2} - 3/2Z_1.$$

(Note that the correction term to  $\bar{W}$  for  $\langle W \rangle_0$  is the same as the numerator expression in the correction term to  $\bar{W}$  of  $\langle W \rangle$ .)

When  $\psi_{0T}$  is the exact wave function (i. e., when  $Z_1 = 1$ ) the correction terms to both  $\langle W \rangle_0$  and  $\langle W \rangle$  vanish and the result reduces to the exact value  $\bar{W}_E = 1/\pi$ . In order to study the two decoupling approximations for the determination of expectation values we plot in Fig. 1 the variation of  $\bar{W}$ ,  $\langle W \rangle_0$ ,  $\langle W \rangle$ , and the energy  $\mathcal{E} = \langle \psi_{0T} | H | \psi_{0T} \rangle$  as a function of the variational parameter  $Z_1$ . As may be observed the results for both  $\langle W \rangle_0$  and  $\langle W \rangle$ , being correct to second order, are substantial improvements over the results of the first-order approximation and for a given  $Z_1$  are essentially as accurate as the average energy  $\mathcal{E}$ . We note for example that a 1% error in  $Z_1$  leads to a 3% error in  $\bar{W}$ , whereas  $\langle W \rangle$  is exact to four significant figures. A 6% error in  $Z_1$ , on the other hand, leads to only a 0.5% error in  $\langle W \rangle$  but to a 16% error in  $\bar{W}$ . The error in  $\langle W \rangle_0$  is, however, usually double the error in  $\langle W \rangle$ . For the last example quoted the

error in  $\langle W \rangle_0$  is 1.2%. Thus over the large range of  $Z_1$ , when  $\psi_{0T}$  is significantly different from the exact wave function, the second decoupling approximation leads to better results than the first and tends to make the expectation value more insensitive to variations in  $Z_1$ .

In Fig. 1 we also plot the variation of the expectation value  $\langle W \rangle_{\text{iteration}}$  under a first iteration. By the iteration procedure we mean the determination of the auxiliary function by solution of the approximate coupled integrodifferential equation (22) in the second decoupling approximation, i. e., we solve the approximate equation

$$\psi_{0T} \nabla^2 f(r) + 2\vec{\nabla} f(r) \cdot \vec{\nabla} \psi_{0T} = [W(r) - \bar{W} - \frac{1}{2}(\langle W \rangle - \bar{W}) + f^{00}(r)(H - \mathcal{E})] \psi_{0T},$$

where  $f^{00}(r)$  satisfies the basic differential equation [Eq. (29)] of the second decoupling approximation. The analytic expression for  $\langle W \rangle_{\text{iteration}}$  in this case is

$$\langle W \rangle_{\text{iteration}} = \frac{Z_1^3}{\pi} - \frac{3}{\pi} \left[ \frac{Z_1^2(Z_1 - 1) + Z_1(Z_1 - 1)^2}{1 + \frac{3}{2}[(Z_1 - 1)/Z_1] + \frac{3}{2}[(Z_1 - 1)/Z_1]^2} \right]. \quad (39)$$

We note that the iteration procedure does not im-

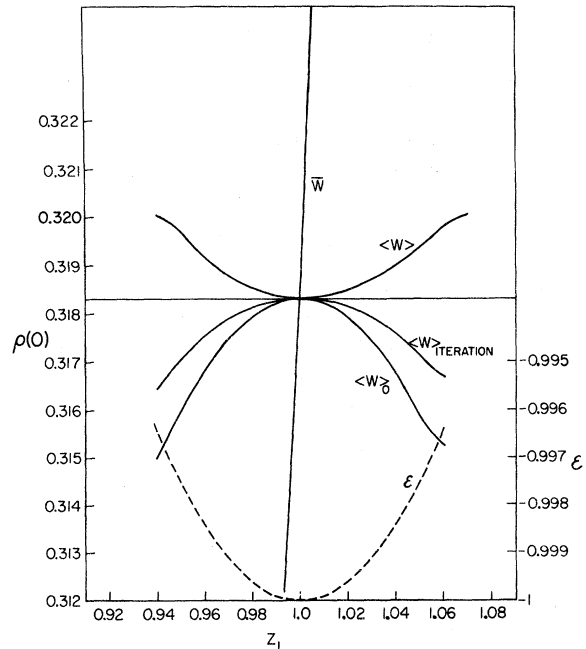


FIG. 1. Density at the origin  $\rho(0)$  and the energy  $\mathcal{E}$  for hydrogen vs the parameter  $Z_1$  assuming  $\psi_{0T} = (Z_1^{3/2}/\sqrt{\pi}) e^{-Z_1 r}$ . Here  $\bar{W} = (Z_1^3/\pi)$ ,  $\langle W \rangle_0$  and  $\langle W \rangle$  are the results for  $\rho(0)$  calculated using the first and second decoupling approximations, respectively, and  $\langle W \rangle_{\text{iteration}}$  is given by Eq. (39).

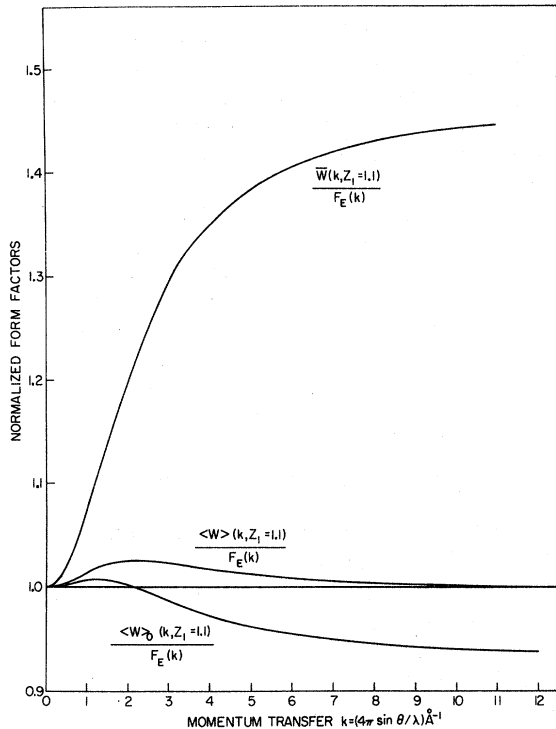


FIG. 2. Fourier transform of the electron density in hydrogen normalized with respect to the exact result  $F_E(k)$  vs the wave number  $k$  assuming  $\psi_{0T} = (Z_1^3/2\sqrt{\pi})e^{-Z_1 r}$ . Here  $\bar{W}(k, Z_1) = [16Z_1^4/(4Z_1^2 + k^2)^2]$ ,  $F_E(k) = [16/(4 + k^2)^2]$ , and  $\langle W(k, Z_1) \rangle_0$  and  $\langle W(k, Z_1) \rangle$  are the results for the Fourier transform using the first and second decoupling approximations, respectively.

prove substantially on the results of  $\langle W \rangle$ . This is not surprising in view of the fact that  $\langle W \rangle$  is already correct to second order and that all that Delves's principle guarantees is a second-order error even if the equation for  $f$  is solved exactly.

#### Coherent Form Factor

The coherent form factor for a spherically symmetric system may be defined as the expectation value of the operator  $W = (\sin kr)/kr$ , where  $k$  is the magnitude of the momentum transfer. The elements of the expectation values  $\langle W \rangle_0$  and  $\langle W \rangle$  are

$$\bar{W} = 16Z_1^4/(4Z_1^2 + k^2)^2,$$

$$\int \psi_{1T}^0 (1/r) \psi_{0T} d\tau = -16Z_1^3 k^2 / (4Z_1^2 + k^2)^3.$$

(For details of the calculation, see the succeeding paper.<sup>11</sup>) As in the previous example

$$(1 + \langle \psi_{1T}^1 | H | \psi_{0T} \rangle) = 1 + \frac{3}{2} - 3/2Z_1$$

since the auxiliary function  $\psi_{1T}^1$  is independent of the operator whose expectation value is being determined. The exact form factor is

$$F_E(k) = 16/(4 + k^2)^2.$$

In Fig. 2 we plot the variation of the form factors normalized with respect to  $F_E(k)$  as a function of the momentum transfer for  $Z_1 = 1.1$ . We observe that over the entire range of momentum transfer the maximum error in  $\langle W \rangle$  is 2.5% at which value of momentum transfer  $\bar{W}$  is in error by 20%. For large values of  $k$  the results for  $\langle W \rangle$  converge towards the exact result, the error being only a few tenths of a percent, whereas the error in  $\langle W \rangle_0$  is about 6% and  $\bar{W}$  is in error by more than 40%. The convergence of  $\langle W \rangle$  towards and the divergence of  $\langle W \rangle_0$  from the exact result for large values of momentum transfer is also observed in the case of the ground state of the helium isoelectronic sequence.<sup>11</sup> There, even for small values of momentum transfer,  $\langle W \rangle$  is superior to  $\langle W \rangle_0$ . This behavior of convergence of  $\langle W \rangle$  towards the correct result for large momentum transfer thus leads to a highly accurate value for the derivative of the electron density at the origin.<sup>11</sup>

#### IV. APPLICATION TO GROUND STATE OF HELIUM ATOM

The fact that  $\langle W \rangle$  is essentially insensitive to the variations in the parameter  $Z_1$  and that the accuracy of the results is essentially unchanged by iteration in the model hydrogen-atom problem encourages one to attempt calculations for systems containing interacting electrons by employing simple products for  $\psi_{0T}$ . Any parameters appearing in the trial ground-state wave function can be determined by minimizing the energy. The constants of integration  $C_1$  and  $C_2$  in  $\psi_{1T}$  are then obtained by orthogonalization to  $\psi_{0T}$ . This has been done in I for the ground state of the helium isoelectronic sequence where we apply the above procedure employing an energy-minimized product of hydrogenic wave functions for the determination of the expectation values of the operators  $r_1^n + r_2^n$ ,  $n = -2, -1, 1, 2$ , and the electron density at the origin.

There we presented analytic results for  $\langle W \rangle$  of the second decoupling approximation for the expectation values of these operators together with those of (a)  $\bar{W}$  obtained employing the same trial wave function, (b)  $\langle W \rangle_0$  of the first decoupling approximation also using the same  $\psi_{0T}$ , (c) the Hartree-Fock results,<sup>12</sup> and finally (d) the "exact" results due to Pekeris,<sup>13</sup> employing a 1078-term Hylleraas variational wave function.

As is the case for the hydrogen atom the improvement of  $\langle W \rangle_0$  and  $\langle W \rangle$  over  $\bar{W}$  was always significant except for  $r^{-1}$  in which case they were equivalent and reduced to the value as given by  $\bar{W}$ . This is due to the fact that if one employs wave functions that satisfy the virial theorem, then the expectation value of the operator  $r^{-1}$  is automatically correct to second order for a first-order error in the wave function.<sup>14</sup> Since our energy-min-

imized trial wave function  $\psi_{0T}$  satisfies the virial theorem, the correction term to  $\bar{W}$  is zero, although for other values of the screening parameter, this would not be the case.<sup>9</sup> Moreover, excepting  $\langle r^{-1} \rangle$  the results for  $\langle W \rangle$  were consistently superior to those of  $\langle W \rangle_0$  for all operators. The least accurate of our results for  $\langle W \rangle$  was for  $\langle r^2 \rangle$  which was in error by 1% for He. For this operator  $\langle W \rangle_0$  is in error by 2.7%.

In addition our results for  $\langle W \rangle$  were essentially equivalent to and in fact, except for  $\langle r^2 \rangle$ , were slightly more accurate than those due to a Hartree-Fock calculation. This high accuracy of the Hartree-Fock calculation is a consequence of Brillouin's<sup>15</sup> theorem according to which the expectation values of single-particle operators for closed-shell systems employing Hartree-Fock wave functions are correct to second order. A more detailed discussion of the results for the entire isoelectronic sequence including the hydride ion is given in I where it is shown that for the one-electron operators considered above, the results for  $\langle W \rangle$  and those of a Hartree-Fock calculation have approximately the same accuracy for all elements of the isoelectronic sequence heavier than helium.

The fact that an entirely analytic calculation yields results as accurate as those given by a Hartree-Fock calculation suggests that the techniques developed here may be particularly useful in those cases where Hartree-Fock calculations are difficult and unavailable as in the cases of molecules and solids. For these cases, however, it is necessary to derive the appropriate equations for the  $f_i(\vec{r}_i)$  assuming an antisymmetric  $\psi_{0T}$ . We are currently investigating this problem.

#### V. DECOUPLING APPROXIMATIONS FOR MANY-PARTICLE SYSTEMS

For systems containing more than two identical particles, it is not possible to write an antisymmetric trial wave function  $\psi_{0T}$  as a product of single-particle position-dependent functions multiplied by a spinor, i. e., we require at least a Slater determinant of single-particle states. Nevertheless, for systems in which exchange effects can be neglected, the Hartree approximation can provide useful information.

We can again decouple Eq. (22) in two different ways. In the first decoupling approximation, we can replace the coupling term by its average value, in which case the entire formalism already given for this case in Sec. II is applicable, i. e., the average value of the coupling term exactly cancels  $\Delta$  in Eq. (22) and the  $f_j$  satisfy Eq. (23). We have seen, however, that application of the second decoupling approximation for one- and two-particle systems gives even better results. In the many-particle case, however, it is not possible to com-

pletely neglect the coupling term since its contribution to the integrodifferential equation tends to be of the same order of magnitude as  $\Delta$  which increases as the number of particles increases.

The coupling term in Eq. (22) for the determination of  $f_j$  can be written

$$\begin{aligned} \langle \sum_k f_k \psi'_{0T} | H - \mathcal{E} | \psi'_{0T} \rangle'_j \phi_j &= \langle \sum_{k \neq j} f_k \psi'_{0T} | \mathcal{H} - \mathcal{E} | \psi'_{0T} \rangle'_j \phi_j \\ &+ \langle \sum_{k \neq j} f_k \psi'_{0T} | H - \mathcal{H} | \psi'_{0T} \rangle'_j \phi_j \\ &+ f_j \langle \psi'_{0T} | H - \mathcal{E} | \psi'_{0T} \rangle'_j \phi_j, \quad (40) \end{aligned}$$

where  $\mathcal{H}$  is that part of the Hamiltonian  $H$  which does not involve the  $j$ th particle. The first term on the right-hand side is then a scalar multiple of  $\phi_j$  while the other terms are functions of  $\vec{r}_j$  multiplying  $\phi_j$ . In the spirit of the second decoupling approximation we neglect the latter terms and attempt to estimate the former. The precise value of this term will depend on our original choice of  $\psi_{0T}$ . We may, however, approximate it by considering two limiting cases. In the first we assume that the electron-electron interaction contributions to the correction term to  $\bar{W}$  of Eq. (1), i. e.,  $\langle \sum_k f_k \psi_{0T} | H - E | \psi_{0T} \rangle$ , are much larger than the contributions due to the single-particle operators in  $H$ . Now for a  $N$ -particle system, there are  $N(N-1)$  e-e terms, the average value of each one of these terms being (for  $N \geq 2$ )  $[N(N-1)]^{-1} \times \frac{1}{2}(\langle W \rangle - \bar{W})$ . The first term on the right-hand side of Eq. (40) is one involving  $(N-1)$  particles with  $(N-1)(N-2)$  electron-electron terms. Thus, assuming that the e-e contributions dominate, we have on the average

$$\begin{aligned} \langle \sum_{k \neq j} f_k \psi'_{0T} | \mathcal{H} - \mathcal{E} | \psi'_{0T} \rangle'_j \phi_j & \\ &\cong \left[ \frac{(N-1)(N-2)}{N(N-1)} \left( \frac{\langle W \rangle - \bar{W}}{2} \right) \right] \phi_j \\ &= [ (1 - 2/N) \frac{1}{2} (\langle W \rangle - \bar{W}) ] \phi_j. \quad (41) \end{aligned}$$

Using Eq. (41) as our first approximation to the right-hand side of Eq. (40) and substituting into Eq. (22) yields

$$\begin{aligned} \phi_j(\vec{r}_j) \nabla_j^2 f_j(\vec{r}_j) + 2 \vec{\nabla}_j f_j(\vec{r}_j) \cdot \vec{\nabla}_j \phi_j(\vec{r}_j) \\ = [ W(\vec{r}_j) - \bar{W}_j - (\langle W \rangle - \bar{W})/N ] \phi_j(\vec{r}_j), \quad (42) \end{aligned}$$

whose solution is

$$f_j(\vec{r}_j) = f_j^0(\vec{r}_j) - [ (\langle W \rangle - \bar{W})/N ] f_j^1(\vec{r}_j), \quad (43)$$

where  $f_j^0$  and  $f_j^1$  satisfy the second-order differential Eqs. (31) and (32). Employing this result for the  $f_j$  in the auxiliary function  $\psi_{1T}$  given by Eq. (35) and substituting  $\psi_{1T}$  into Eq. (1) and solving for  $\langle W \rangle$ , we obtain for  $N \geq 2$



$$\langle W \rangle = \bar{W} + \frac{2 \operatorname{Re} \langle \psi_{1T}^0 | H - E | \psi_{0T} \rangle}{1 + (2/N) \operatorname{Re} \langle \psi_{1T}^1 | H - E | \psi_{0T} \rangle}. \quad (44)$$

We note that for  $N=2$ , this expression reduces to the  $\langle W \rangle$  of the second decoupling approximation discussed in Sec. II as it must, since for  $N=2$  the contribution given by Eq. (41) is zero and we have neglected the other contributions to the coupling term.

If, on the other hand, we consider the possibility that the choice of  $\psi_{0T}$  leads to the result that the contribution of each e-e term is approximately equal to the contribution of each single-particle term in the first term of Eq. (40), we obtain

$$\left\langle \sum_{k \neq j} f_k \psi'_{0T} | \mathcal{H} - \mathcal{E} | \psi'_{0T} \right\rangle_j \phi_j \\ \approx \left( \frac{(N-1)^2}{N^2} \frac{\langle W \rangle - \bar{W}}{2} \right) \phi_j. \quad (45)$$

Employing the same procedure as above yields the result that the term  $2/N$  in Eq. (44) should be replaced by  $(2N-1)/N^2$ . Thus, in the limit of large  $N$  both results are identical. Furthermore, since both the first and second decoupling approximations yield results for  $\langle W \rangle$  correct to second order the additional term in the denominator of Eq. (44) will generally be small compared to 1 as is the case for both the model hydrogen- and helium-atom problems already discussed. Thus replacing  $(2N-1)/N^2$  by  $2/N$  for  $N \geq 2$  can change  $\langle W \rangle$  only slightly and we conclude that Eq. (44) is a good approximation in either case. Finally, since in any calculation employing a  $\psi_{0T}$  in the Hartree approximation, we expect the relative size of the e-e and single-particle contributions to be between the two extreme cases considered here, it appears reasonable to believe that Eq. (44) is a good approximation in any case.

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