PHYSICAL REVIEW A VOLUME 8, NUMBER 1 JULY 1973

Variational Principles for Single-Particle Expectation Values in the Hartree-Fock Approximation

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(Received 19 January 1973)

The formalism developed by the authors for the variational determination of the expectation value of single-particle operators $W = \Sigma_i W(\vec{r}_i)$ via Delves's principle in the Hartree approximation is extended here to the Hartree-Fock approximation by employing a Slater-determinant-type trial wave function and an appropriately antisymmetrized auxiliary function. A set of coupled integral-differential equations for the components of the auxiliary function are obtained by a subsidiary variational minimization of a functional involving the trial wave function, the auxiliary function, the Hamiltonian, and the operator W. Owing to the antisymmetric nature of both the trial and auxiliary functions, an exchange term involving the specific single-particle operator in question appears in these equations. Decoupling approximations are discussed and the equations solved exactly for single-particle operators that depend on the radial distance only. Employing a single-parameter appropriately antisymmetrized product of the 1*S* and 2*S* hydrogenic functions as the trial wave function, the formalism in this Hartree-Fock approximation is then applied to both the helium $2\,^3S$ and $2\,^1S$ isoelectronic sequences to obtain analytic expressions for the expectation value of the operators r^n, $n = 2, 1, -1$, and $\delta(\vec{r})$. The results of these calculations are observed to approximate closely the results of a 2300-parameter calculation due to Accad *et al.* and in the orthohelium case to be also equivalent to those due to Hartree-Fock.

I. INTRODUCTION

In two recent papers[1,2] (hereafter referred to as I and II) we have developed and applied[3,4] variational techniques for the calculation of single-particle expectation values employing a Hartree-type approximation for the wave function of the system. Since such an approximation is useful only in those systems in which exchange effects are of little importance, we present here an extension of our formalism by employing a Slater determinant as the approximate wave function of the system.

The variational determination of the expectation value of an arbitrary Hermitian operator W correct to second order[5] depends on two functions, a system trial wave function ψ_{0T} and an auxiliary function ψ_{1T} which is obtained via a subsidiary minimum principle.[6,7] This involves the variational minimization with respect to the auxiliary function ψ_{1T} of a functional M' containing ψ_{0T}, ψ_{1T}, the Hamiltonian, and the operator W whose expectation is to be determined, derived via a Green's-function expansion of the first-order perturbation correction to ψ_{0T} due to the perturbation W. Incorporating the Pauli exclusion principle by employing a Slater-determinant-type trial wave function ψ_{0T}, we minimize the functional $M'[\psi_{0T}, \psi_{1T}, H, W]$, subject to certain orthogonality constraints, with respect to the auxiliary function and obtain as in the Hartree approximation[2] a set of coupled integral-differential equations for the components of the auxiliary function. In this case, however, owing to the antisymmetric nature of both the trial and auxiliary functions, an exchange term involving the specific single-particle operator in question appears in the coupled integral-differential equations. Decoupling procedures are discussed and the method in this Hartree-Fock approximation is then applied to the simplest inequivalent two-electron system, viz., the triplet $2\,^3S$ state of the helium atom. Employing a single parameter appropriately antisymmetrized product of 1*S* and 2*S* hydrogenic wave functions as the trial wave function ψ_{0T}, analytic expressions for the expectation values of the single-particle operators r^n, $n = 2, 1$, and -1, and $\delta(\vec{r})$ are derived for the He $2\,^3S$ isoelectronic sequence and the results compared to those of an analytic Hartree-Fock calculation[8] and a 2300-parameter Hylleraas-type wave-function calculation due to Accad *et al.*[9] Finally, by again employing a single-parameter determinant of 1*S* and 2*S* hydrogenic functions as the trial wave function ψ_{0T}, the formalism is then applied to the singlet $2\,^1S$ state of the helium isoelectronic sequence to obtain analytic expressions for the expectation values for the same set of single-particle operators and the results again compared with those of the highly accurate values due to Accad *et al.*[9] The high accuracy of these results in comparison with the results of the many-parameter variational calculation suggests that the techniques developed here may prove useful in the calculation of expectation values of other interacting many-electron systems.

II. VARIATIONAL PRINCIPLE

According to Delves,[5] the expectation value of an arbitrary Hermitian operator W correct to second order is given by the functional

$$\langle W\rangle = \overline{W} + 2\,\mathrm{Re}\langle\psi_{1T}|H-E|\psi_{0T}\rangle\,, \tag{1}$$

where

$$\overline{W} = \langle\psi_{0T}|W|\psi_{0T}\rangle\,, \tag{2}$$

and ψ_{0T} and ψ_{1T} are the system trial wave function and auxiliary function, respectively. These functions are approximations to the exact functions ψ_0 and ψ_1 which satisfy the Schrödinger equation

$$H\psi_0 = E\psi_0 \tag{3}$$

and a subsidiary equation

$$(H-E)\psi_1 = (\overline{W}-W)\psi_0\,, \tag{4}$$

with E being the associated eigenenergy and H being the Hamiltonian of the system. Equation (4) is analogous to the expression in perturbation theory for the energy correction to first order and we may thus interpret ψ_1 as being a perturbational correction to ψ_0 due to the perturbation W. Having assumed a parametrized ψ_{0T} with the parameters being determined by various criteria such as energy minimization or orthogonality conditions, we now derive 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 the variation of the functional

$$M'[\psi_{0T},\psi_{1T},H,W] = \langle\psi_{1T}|H-\mathcal{E}|\psi_{1T}\rangle + \langle\psi_{1T}|W-\overline{W}|\psi_{0T}\rangle + \langle\psi_{0T}|W-\overline{W}|\psi_{1T}\rangle + N\,, \tag{5}$$

where $\mathcal{E}$ may be taken as $\mathcal{E} = \langle\psi_{0T}|H|\psi_{0T}\rangle$, and either

$$N = -\langle\psi_{1T}|H-\mathcal{E}|\psi_{0T}\rangle\langle\psi_{0T}|\psi_{1T}\rangle - \langle\psi_{1T}|\psi_{0T}\rangle\langle\psi_{0T}|H-\mathcal{E}|\psi_{1T}\rangle \tag{6}$$

or $N=0$ and M' is evaluated subject to

$$\langle\psi_{1T}|\psi_{0T}\rangle = 0 \tag{7}$$

in the latter case.

Since the exact functions ψ_0 and ψ_1 are orthogonal[10] to one another, we consider the variation of the functional M' subject to the orthogonality constraint of Eq. (7). The functional M' is thus given by

$$M'[\psi_{0T},\psi_{1T},H,W] = \langle\psi_{1T}|H-\mathcal{E}|\psi_{1T}\rangle + \langle\psi_{1T}|W|\psi_{0T}\rangle + \langle\psi_{0T}|W|\psi_{1T}\rangle\,. \tag{8}$$

As the trial wave function for the N-particle system we choose a Slater determinant of single-particle states:

$$\psi_{0T} = (N!)^{1/2}A\,|\psi_H\rangle\,, \tag{9}$$

where

$$|\psi_H\rangle = \prod_i \phi_i(\vec{x}_i),\quad x=\vec{r},\zeta \tag{10}$$

and $\vec{r}$ and ζ are the configuration space and spin variables, respectively. The single-particle states $\phi_i(\vec{x}_i)$ are chosen to be orthogonal to one another:

$$\langle\phi_i(\vec{x})|\phi_j(\vec{x})\rangle = \delta_{ij} \tag{11}$$

and to be a product of an orbital function $\psi_i(\vec{r}_i)$, and a spin function $\chi_i(\zeta_i)$:

$$\phi_i(\vec{x}_i) = \psi_i(\vec{r}_i)\chi_i(\zeta_i)\,, \tag{12}$$

where the spin function χ_i may be either α or β corresponding to S_z (the z component of the spin angular momentum) being plus or minus $\frac{1}{2}\hbar$.

The antisymmetrizer A is defined as[11]

$$A = \frac{1}{N!}\sum_P (-1)^p P\,, \tag{13}$$

where P is the permutation operator and p is the parity of the permutation. The permutation operator P is a unitary operator,

$$PP^\dagger = P^\dagger P = 1 \tag{14}$$

and the antisymmetrizer A is a Hermitian operator,

$$A = A^\dagger \quad \text{satisfying}\quad A^2 = A\,. \tag{15}$$

For a system composed of identical particles,

$$[P,H] = 0\,, \tag{16}$$

and thus, from Eq. (13)

$$[A,H] = 0\,. \tag{17}$$

If, as in I and II, we restrict ourselves to operators which may be written as a sum of single-particle operators,

$$W(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N) = \sum_i W(\vec{r}_i)\,; \tag{18}$$

then the antisymmetrizer must commute with W:

$$[A,W] = 0\,. \tag{19}$$

The choice of the form of the auxiliary function ψ_{1T} is again governed by the interpretation given to it as a perturbational correction to ψ_{0T} due to the perturbation W. Thus our choice of an antisymmetrized single-particle product for ψ_{0T} leads to nonvanishing matrix elements for the perturbation only if we choose ψ_{1T} to be of the form

$$\psi_{1T} = (N!)^{1/2} A \left| \sum_j f_j(\vec{r}_j)\psi_H \right\rangle . \tag{20}$$

Including the orthogonality constraint of ψ_{1T} to ψ_{0T} by the introduction of a Lagrange multiplier λ, we may as in II obtain the differential equations for the individual $f_j(\vec{r}_j)$ by minimizing the real function

$$M = M' - \lambda\langle\psi_{1T}|\psi_{0T}\rangle - \lambda^*\langle\psi_{0T}|\psi_{1T}\rangle \tag{21}$$

for arbitrary variations in the $f_j(\vec{r}_j)$. The variational minimization leads to

$$\delta M = 0 = N!\left\langle \sum_j \delta f_j(\vec{r}_j)\psi_H \middle| A^\dagger(H-\mathcal{E})A\left(\sum_k f_k(\vec{r}_k)\psi_H\right) + A^\dagger(W-\lambda)A\psi_H \right\rangle + \text{c.c.}, \tag{22}$$

which on use of Eqs. (15), (17), and (19) may be written

$$N!\sum_j \left\langle \delta f_j(\vec{r}_j)\psi_H \middle| (H-\mathcal{E})A\left(\sum_k f_k(\vec{r}_k)\psi_H\right) + (W-\lambda)A\psi_H \right\rangle + \text{c.c.} = 0 . \tag{23}$$

As in the Hartree case, since the $\delta f_j(\vec{r}_j)$ are all independent, Eq. (23) is satisfied for each particle, provided

$$N!\left\langle \psi_H \middle| (H-\mathcal{E})A\left(\sum_k f_k(\vec{r}_k)\psi_H\right) + (W-\lambda)A\psi_H \right\rangle_j' = 0, \quad j = 1, \ldots, N \tag{24}$$

where the symbol $\langle\ \rangle_j'$ means integrate over all variables except the jth.

The Lagrange multiplier may be determined by integrating Eq. (24) over the jth variable, which gives the N identical equations:

$$\lambda = \overline{W} + \langle\psi_{0T}|H-\mathcal{E}|\psi_{1T}\rangle \tag{25}$$

or since $\langle\psi_{1T}|\psi_{0T}\rangle = 0$,

$$\lambda = \overline{W} + \Delta , \tag{26}$$

where

$$\Delta = \langle\psi_{0T}|H|\psi_{1T}\rangle = \left\langle \psi_H \middle| HA \middle| \sum_k f_k(\vec{r}_k)\psi_H \right\rangle . \tag{27}$$

Performing the indicated integration for each term of Eq. (24) we have

$$\begin{aligned} N!\langle\psi_H|WA|\psi_H\rangle_j' &\equiv \sum_P (-1)^p \langle\psi_H|WP|\psi_H\rangle_j' \\ &= \sum_i{}' [\langle\phi_i(\vec{x}_i)|W(\vec{r}_i)|\phi_i(\vec{x}_i)\rangle\, \phi_j^*(\vec{x}_j)\phi_j(\vec{x}_j) \\ &\quad - \langle\phi_i(\vec{x}_i)|W(\vec{r}_i)|\phi_j(\vec{x}_i)\rangle\, \phi_j^*(\vec{x}_j)\phi_i(\vec{x}_j)] \\ &\quad + \phi_j^*(\vec{x}_j)W(\vec{r}_j)\phi_j(\vec{x}_j) . \end{aligned} \tag{28}$$

Since the operator W is by hypothesis only spatially dependent, the first matrix element on the right-hand side of Eq. (28) is simply

$$\langle\phi_i(\vec{x}_i)|W(\vec{r}_i)|\phi_i(\vec{x}_i)\rangle = \langle\psi_i(\vec{r}_i)|W(\vec{r}_i)|\psi_i(\vec{r}_i)\rangle \equiv \overline{W}_i \tag{29}$$

as integration over spin space gives unity. The second matrix element on the right-hand side of Eq. (28) is the exchange integral for each operator $W(\vec{r}_i)$. This term arises strictly as a consequence of the inclusion of the Pauli principle and exists only if $\phi_i(\vec{x}_i)$ and $\phi_j(\vec{x}_j)$ have the same spin functions whether they be α or β. We may therefore write the exchange term as

$$\begin{aligned} &\sum_i{}' \langle\phi_i(\vec{x}_i)|W(\vec{r}_i)|\phi_j(\vec{x}_i)\rangle\phi_j^*(\vec{x}_j)\phi_i(\vec{x}_j) \\ &\quad = \sum_{\substack{i \\ \text{spin}\, i\, =\, \text{spin}\, j}}{}' \langle\psi_i(\vec{r}_i)|W(\vec{r}_i)|\psi_j\rangle(\vec{r}_i)\phi_j^*(\vec{x}_j)\phi_i(\vec{x}_j) . \end{aligned} \tag{30}$$

Equation (28) is then

$$\begin{aligned} N!\langle\psi_H|WA|\psi_H\rangle_j' &= \sum_i{}' \overline{W}_i\, \phi_j^*(\vec{x}_j)\phi_j(\vec{x}_j) \\ &\quad - \sum_{\substack{i \\ \text{spin}\, i\, =\, \text{spin}\, j}}{}' \langle\psi_i(\vec{r}_i)|W(\vec{r}_i)|\psi_j(\vec{r}_i)\rangle\, \phi_j^*(\vec{x}_j)\phi_i(\vec{x}_j) \\ &\quad + \phi_j^*(\vec{x}_j)W(\vec{r}_j)\phi_j(\vec{x}_j) . \end{aligned} \tag{31}$$

Employing the Hermiticity of A and the unitarity of P we find that the next term in Eq. (24) is simply

$$N!\langle\psi_H|\lambda A|\psi_H\rangle_j' = \lambda\phi_j^*(\vec{x}_j)\phi_j(\vec{x}_j) . \tag{32}$$

Finally, defining $\psi_H' \equiv \psi_H/\phi_j(\vec{x}_j)$ we have for the remaining term in Eq. (24)

$$\begin{aligned} N!\left\langle \psi_H \middle| (H-\mathcal{E})A \middle| \sum_k f_k(\vec{r}_k)\psi_H \right\rangle_j' &= N!\phi_j^*(\vec{x}_j)\left\langle \psi_H' \middle| (H-\mathcal{E})A \middle| \sum_k{}' f_k(\vec{r}_k)\psi_H \right\rangle_j' \\ &\quad + N!\phi_j^*(\vec{x}_j)\langle\psi_H'|(H-\mathcal{E})A|f_j(\vec{r}_j)\psi_H\rangle_j' . \end{aligned} \tag{33}$$

Equation (24) for each particle may thus be rewritten

$$\sum_i{}' \overline{W}_i \, \phi_j^*(\vec{x}_j)\phi_j(\vec{x}_j) - \sum_{\substack{i \\ \text{spin } i = \text{spin } j}}{}' \langle \psi_i(\vec{r}_i) | W(\vec{r}_i) | \psi_j(\vec{r}_i) \rangle \, \phi_j^*(\vec{x}_j)\phi_i(\vec{x}_j) + \phi_j^*(\vec{x}_j)[W(\vec{r}_j) - \lambda]\,\phi_j(\vec{x}_j)$$

$$+ N!\,\phi_j^*(\vec{x}_j)\left\langle \psi_H' \left| (H - \mathcal{E})A \right| \sum_k{}' f_k(\vec{r}_k)\psi_H \right\rangle_j' + N!\,\phi_j^*(\vec{x}_j)\langle \psi_H' | (H - \mathcal{E})A \,| f_j(\vec{r}_j)\psi_H \rangle_j' = 0 . \quad (34)$$

Again using the property of Hermiticity of the antisymmetrizer and the unitarity of the permutation operator it is easily seen that since the operator W is only spatially dependent,

$$\overline{W} = \sum_i \overline{W}_i \quad (35)$$

therefore

$$\lambda = \sum_i \overline{W}_i + \Delta .$$

On substituting the above value of λ and dividing by $\phi_j^*(\vec{x}_j)$, Eq. (34) reduces to

$$[W(\vec{r}_j) - \overline{W}_j - \Delta]\,\phi_j(\vec{x}_j) - \sum_{\substack{i \\ \text{spin } i = \text{spin } j}}{}' \langle \psi_i(\vec{r}_i) | W(\vec{r}_i) | \psi_j(\vec{r}_i) \rangle \, \phi_i(\vec{x}_j)$$

$$+ N!\left\langle \psi_H' \left| (H - \mathcal{E})A \right| \sum_k{}' f_k(\vec{r}_k)\psi_H \right\rangle_j' + N!\langle \psi_H' | (H - \mathcal{E})A \,| f_j(\vec{r}_j)\psi_H \rangle_j' = 0 . \quad (36)$$

Since the antisymmetrizer commutes with the Hamiltonian, we may write the last term of Eq. (36) as

$$N!\langle \psi_H' | (H - \mathcal{E})A \,| f_j(\vec{r}_j)\psi_H \rangle_j' = N!\langle \psi_H' | A^\dagger (H - \mathcal{E}) | \psi_H' \rangle_j' f_j(\vec{r}_j)\psi_j(\vec{r}_j)\chi_j(\zeta_j) . \quad (37)$$

Writing the nonrelativistic Hamiltonian as

$$H = \sum_i -\nabla_i^{\,2} + V(\vec{r}_1, \ldots, \vec{r}_N), \quad (38)$$

Eq. (37) reduces to

$$N!\langle \psi_H' | A^\dagger (H - \mathcal{E}) | \psi_H' \rangle_j' f_j(\vec{r}_j)\psi_j(\vec{r}_j)\chi_j(\zeta_j) = N![-\psi_j(\vec{r}_j)\nabla_j^2 f_j(\vec{r}_j) - 2\vec{\nabla}_j f_j(\vec{r}_j)\cdot\vec{\nabla}_j\psi_j(\vec{r}_j) - f_j(\vec{r}_j)\nabla_j^2\psi_j(\vec{r}_j)]$$

$$\times \chi_j(\zeta_j)\langle \psi_H' | A^\dagger | \psi_H' \rangle_j' + N!\left\langle \psi_H' \left| A^\dagger \left(\sum_i{}' \nabla_i^{\,2} + V\right) \right| \psi_H' \right\rangle_j' f_j(\vec{r}_j)\psi_j(\vec{r}_j)\chi_j(\zeta_j),$$

and since $N!\langle \psi_H' | A^\dagger | \psi_H' \rangle_j' = 1$, Eq. (37) further reduces to

$$N!\langle \psi_H' | A^\dagger (H - \mathcal{E}) | \psi_H' \rangle_j' f_j(\vec{r}_j)\psi_j(\vec{r}_j)\chi_j(\zeta_j) = [-\psi_j(\vec{r}_j)\nabla_j^2 f_j(\vec{r}_j) - 2\vec{\nabla}_j f_j(\vec{r}_j)\cdot\vec{\nabla}_j\psi_j(\vec{r}_j)]\,\chi_j(\zeta_j)$$

$$+ N! f_j(\vec{r}_j)\langle \psi_H' | A^\dagger (H - \mathcal{E}) | \psi_H' \rangle_j' \,\psi_j(\vec{r}_j)\chi_j(\zeta_j) . \quad (39)$$

The argument as in II, that only the real part of $f_j(\vec{r}_j)$ contributes to the correction to $\overline{W}$, remains unchanged so that on using $f_j = f_j^*$ we obtain on adding the last term of Eq. (39) to the next-to-last term of Eq. (36)

$$N!\left\langle \psi_H' \left| (H - \mathcal{E})A \right| \sum_k{}' f_k(\vec{r}_k)\psi_H \right\rangle_j'$$

$$+ N! f_j(\vec{r}_j)\langle \psi_H' | A^\dagger (H - \mathcal{E}) | \psi_H' \rangle_j' \,\phi_j(\vec{x}_j)$$

$$= N!\left\langle \sum_k f_k(\vec{r}_k)\psi_H' \left| (H - \mathcal{E})A \right| \psi_H' \right\rangle_j' \psi_j(\vec{r}_j)\chi_j(\zeta_j) . \quad (40)$$

Equation (36) may therefore be written

$$[W(\vec{r}_j) - \overline{W}_j - \Delta]\,\psi_j(\vec{r}_j)\chi_j(\zeta_j)$$

$$- \sum_{\substack{i \\ \text{spin } i = \text{spin } j}}{}' \langle \psi_i(\vec{r}_i) | W(\vec{r}_i) | \psi_j(\vec{r}_i) \rangle \, \phi_i(\vec{x}_j)$$

$$+ [-\psi_j(\vec{r}_j)\nabla_j^2 f_j(\vec{r}_j) - 2\vec{\nabla}_j f_j(\vec{r}_j)\cdot\vec{\nabla}_j\psi_j(\vec{r}_j)]\,\chi_j(\zeta_j)$$

$$+ N!\left\langle \sum_k f_k(\vec{r}_k)\psi_H' \left| (H - \mathcal{E})A \right| \psi_H' \right\rangle_j' \psi_j(\vec{r}_j)\chi_j(\zeta_j) = 0 . \quad (41)$$

We may now divide out the spin function $\chi_j(\zeta_j)$ in each term. Note that since for the exchange term to exist, spin i = spin j, the spin function of the ϕ_i must be the same as in all the other terms. The coupled integral-differential equation for the $f_j(\vec{r}_j)$ in the Hartree-Fock approximation is thus

$$
\begin{aligned}
&[W(\vec{r}_j)-\overline{W}_j-\Delta]\,\psi_j(\vec{r}_j)\\
&\quad-\sum_{\substack{i\\ \mathrm{spin}\,i\,=\,\mathrm{spin}\,j}}{}' \langle\psi_i(\vec{r}_i)|W(\vec{r}_i)|\psi_j(\vec{r}_i)\rangle\,\psi_i(\vec{r}_j)\\
&\quad-\psi_j(\vec{r}_j)\nabla_j^2 f_j(\vec{r}_j)-2\vec{\nabla}_j f_j(\vec{r}_j)\cdot\vec{\nabla}_j\psi_j(\vec{r}_j)\\
&\quad+N!\left\langle\sum_k f_k(\vec{r}_k)\psi_H'\,\middle|\,(H-\mathcal{E})A\,\middle|\,\psi_H'\right\rangle_j'\psi_j(\vec{r}_j)=0\,. \qquad (42)
\end{aligned}
$$

The above equation is similar in form to that derived in the Hartree approximation except for the presence of the exchange term and the fact that appropriately antisymmetrized trial wave functions have to be employed in dealing with the coupling term. The coupled equation may also be derived on the basis of the self-consistency argument discussed in I. In order to obtain the single-particle equations we now uncouple Eq. (42) in the two different approximations.

1. *First Decoupling Approximation*

In this approximation, as in the Hartree case, for an N-particle system, we replace the coupling term by its value averaged over $\phi_j(\vec{r}_j)$, i.e., by

$$
N!\left\langle\sum_k f_k(\vec{r}_k)\psi_H\,\middle|\,A^\dagger(H-\mathcal{E})\,\middle|\,\psi_H\right\rangle\psi_j(\vec{r}_j)\equiv\Delta\psi_j(\vec{r}_j)\,.
$$

Therefore Eq. (42) is

$$
\begin{aligned}
&\nabla_j^2 f_j(\vec{r}_j)+2\vec{\nabla}_j f_j(\vec{r}_j)\cdot\frac{\vec{\nabla}_j\psi_j(\vec{r}_j)}{\psi_j(\vec{r}_j)}\\
&\quad=\frac{1}{\psi_j(\vec{r}_j)}\left(W(\vec{r}_j)-\overline{W}_j-\frac{S(\vec{r}_j)}{\psi_j(\vec{r}_j)}\right)\psi_j(\vec{r}_j), \qquad (43)
\end{aligned}
$$

where $S(\vec{r}_j)$ is the exchange term

$$
S(\vec{r}_j)=\sum_{\substack{i\\ \mathrm{spin}\,i\,=\,\mathrm{spin}\,j}}{}' \langle\psi_i(\vec{r}_i)|W(\vec{r}_i)|\psi_j(\vec{r}_i)\rangle\,\psi_i(\vec{r}_j)\,. \qquad (44)
$$

Equation (43), of course, includes the case of both differential and nondifferential operators W. The second-order differential equation [Eq. (43)] may be solved exactly for radially dependent operators of the form

$$
W(\vec{r}_i)=W(r_i) \qquad (45)
$$

if we choose $\psi_i(\vec{r}_i)$ and $f_i(\vec{r}_i)$ to be of the form

$$
\psi_i(\vec{r}_i)=\psi_i(r_i)Y_l^m(\theta_i,\phi_i) \qquad (46)
$$

and

$$
f_i(\vec{r}_i)=f_i(r_i), \qquad (47)
$$

respectively, so that the auxiliary function is now defined as

$$
\psi_{1T}=(N!)^{1/2}A\left|\sum_j f_j(r_j)\psi_H\right\rangle. \qquad (48)
$$

The solution to Eq. (43) is

$$
f_j(r_j)=\int^{r_j}\frac{g_j(r)}{r^2}\,dr+C_1, \qquad (49)
$$

where

$$
g_j(r)=\frac{1}{\psi_j^2(r)}\int^{r}r'^2\psi_j^2(r')\left(W(r')-\overline{W}_j-\frac{S(r')}{\psi_j(r')}\right)dr'+C_2\,. \qquad (50)
$$

The constant of integration C_2 is chosen on the basis of the perturbative interpretation given to the auxiliary function and is determined by requiring that ψ_{1T} vanish at infinity. The constant C_1 is chosen to orthogonalize ψ_{1T} to ψ_{0T} in order to eliminate the unknown energy E of the system from Eq. (1). The expectation value $\langle W\rangle_0$ of the operator W may then be obtained by substituting the ψ_{1T} of Eq. (48) into Eq. (1).

2. *Second Decoupling Approximation*

The treatment of the coupling term in the second decoupling approximation is also similar to that discussed in the Hartree case. For two-particle systems we initially neglect the coupling term. The coupled integral-differential equation [Eq. (42)] therefore reduces to

$$
\nabla_j^2 f_j(\vec{r}_j)+2\vec{\nabla}_j f_j(\vec{r}_j)\cdot\frac{\vec{\nabla}_j\psi_j(\vec{r}_j)}{\psi_j(\vec{r}_j)}=\frac{1}{\psi_j(\vec{r}_j)}\left(W(\vec{r}_j)-\overline{W}_j-\frac{\langle W\rangle-\overline{W}}{2}-\frac{S(\vec{r}_j)}{\psi_j(\vec{r}_j)}\right)\psi_j(\vec{r}_j), \qquad (51)
$$

which for nondifferential operators has the solution

$$
f_j(\vec{r}_j)=f_j^0(\vec{r}_j)-\tfrac{1}{2}(\langle W\rangle-\overline{W})f_j^1(\vec{r}_j), \qquad (52)
$$

where $f_j^0(\vec{r}_j)$ and $f_j^1(\vec{r}_j)$ satisfy the second-order differential equations

$$
\nabla_j^2 f_j^0(\vec{r}_j)+2\vec{\nabla}_j f_j^0(\vec{r}_j)\cdot\frac{\vec{\nabla}_j\psi_j(\vec{r}_j)}{\psi_j(\vec{r}_j)}=W(\vec{r}_j)-\overline{W}_j-\frac{S(\vec{r}_j)}{\psi_j(\vec{r}_j)} \qquad (53)
$$

and

$$
\nabla_j^2 f_j^1(\vec{r}_j)+2\vec{\nabla}_j f_j^1(\vec{r}_j)\cdot\frac{\vec{\nabla}_j\psi_j(\vec{r}_j)}{\psi_j(\vec{r}_j)}=1, \qquad (54)
$$

respectively. For the same choice of the form of W, ψ_{0T}, and f as in Eqs. (45)–(47), the solutions to Eqs. (53) and (54) are

$$f_j^0(r_j) = \int^{r_j} \frac{g_j^0(r)}{r^2}\, dr + C_1 \tag{55}$$

and

$$f_j^1(r_j) = \int^{r_j} \frac{g_j^1(r)}{r^2}\, dr + B_1 , \tag{56}$$

where

$$g_j^0(r) = \frac{1}{\psi_j^2(r)} \int^{r} r'^2 \psi_j^2(r') \left(W(r') - \overline{W}_j - \frac{S(r')}{\psi_j(r')} \right) dr' + C_2 \tag{57}$$

and

$$g_j^1(r) = \frac{1}{\psi_j^2(r)} \int^{r} r'^2 \psi_j(r')\, dr' + B_2 , \tag{58}$$

where the constants of integration C_1, C_2, B_1, and B_2 are again obtained by the same considerations as discussed earlier. The auxiliary function is therefore

$$\psi_{1T} = \psi_{1T}^0 - \tfrac{1}{2}(\langle W\rangle - \overline{W})\psi_{1T}^1 , \tag{59}$$

where

$$\psi_{1T}^0 = (N!)^{1/2} A \left| \sum_j f_j^0(r_j)\psi_H \right\rangle \tag{60}$$

and

$$\psi_{1T}^1 = (N!)^{1/2} A \left| \sum_j f_j^1(r_j)\psi_H \right\rangle , \tag{61}$$

so that on substitution of ψ_{1T} into (1) we obtain the expectation value $\langle W\rangle$ for two-particle systems in the second decoupling approximation to be

$$\langle W\rangle = \overline{W} + \frac{2\,\mathrm{Re}\langle \psi_{1T}^0 | H - E | \psi_{0T}\rangle}{1 + \mathrm{Re}\langle \psi_{1T}^1 | H - E | \psi_{0T}\rangle} . \tag{62}$$

Equation (62) is similar to Eq. (38) of II with the exception that the auxiliary function ψ_{1T}^0 now incorporates exchange terms involving the operator W. As in I and II ψ_{1T}^1 is again independent of W and thus the denominator expression of (62) remains the same for all operators. In addition, the arguments developed in II for dealing with the coupling term for a many-particle system ($N \geq 2$) in the second decoupling approximation are equally valid in the Hartree-Fock case, so that for a system of N interacting particles we may in general write the denominator of Eq. (62) as $[1 + (2/N)\mathrm{Re}\langle \psi_{1T}^1 | H - E | \psi_{0T}\rangle]$. Finally, although the solution to the differential equation [Eq. (54)] may be singular at the origin, the Hamiltonian never operates on the auxiliary function ψ_{1T}^1 and all that is required of the singularities in ψ_{1T}^1 are that they be integrable.

III. APPLICATION TO 2 ^3S HELIUM ISOELECTRONIC SEQUENCE

In this section we apply the above procedure to the simplest inequivalent two-electron atomic system, viz., the excited $2\,^3S$ state of the helium atom. The requirement of the subsidiary condition[12] that the eigenfunction of the excited state be orthogonal to the eigenfunction of the ground state is automatically satisfied in this problem since the total spin S has different values for both states. Thus for this lowest state of orthohelium we employ a single-parameter antisymmetric product of the 1S and 2S hydrogenic wave functions as the trial wave function ψ_{0T}, i.e.,

$$\psi_1(r_1) = \frac{Z_1^{3/2}}{(\pi)^{1/2}} e^{-Z_1 r_1} ,$$

$$\psi_2(r_2) = \frac{Z_1^{3/2}}{2(2\pi)^{1/2}} (1 - \tfrac{1}{2} Z_1 r_2) e^{-Z_1 r_2/2} .$$

Since we are using hydrogenic-type functions, the choice of a single parameter ψ_{0T} (rather than at least a two-parameter trial wave function to describe the inner and outer electrons) is dictated by the requirement of orthogonality of the single-particle states to one another [see Eq. (11)]. The value for the parameter Z_1 may be obtained as in the case of the ground-state calculation by either the energy-minimization condition, in which case $Z_1 = Z - 0.1503$, or by treating it as a variational parameter in $\langle W\rangle$. The choice of different screening parameters for different physical properties has been previously discussed by others.[7,13]

The analytic expressions for the expectations values of the operators r^n, $n = 2$, 1, and -1, and $\delta(\vec{r})$ in the two decoupling approximations are presented in Appendix A.

In Table I we present the results of (i) a 2300-parameter wave-function treatment due to Accad *et al.*[9]; (ii) an eight-parameter analytic Hartree-Fock calculation due to Carlton[8]; (iii) $\overline{W}$ employing the trial wave function ψ_{0T} for the value of Z_1 which minimizes the energy ($Z_1 = Z - 0.1503$); (iv) the results[14] $\langle W\rangle_0$ of the first decoupling approximation with $Z_1 = Z - 0.1503$; (v) the results $\langle W\rangle$ of the second decoupling approximation with $Z_1 = Z - 0.1503$; (vi) the results $\langle W\rangle_{0e}$ of the first decoupling approximation for the Z_1 value obtained by extremizing the analytic expression $\langle W\rangle_0$ with respect to Z_1; and finally (vii) the results $\langle W\rangle_e$ of the second decoupling approximation for the Z_1 which extremizes $\langle W\rangle$.

With the exception of the results for the operator r^{-1}, trends similar to those of the ground-state calculation[10] are observed in the results for $\langle W\rangle_{0e}$ and $\langle W\rangle_e$. For the exterior of the atom these are again the best results, with $\langle W\rangle_e$ being superior to

TABLE I. Expectation values of the operators r^n, $n = 2$, 1, and -1, and $\delta(\vec{r})$ for the $2\,^3S$ helium isoelectronic sequence. Here

$$\left.\begin{aligned}\overline{W} &= \int \psi_{0T} W \psi_{0T} d\tau\,,\\ \langle W\rangle_0 &= \overline{W} + 2\,\mathrm{Re}\int \psi_{1T}^{0}(H-E)\psi_{0T} d\tau\,,\\ \langle W\rangle &= \overline{W} + 2\,\mathrm{Re}\int \psi_{1T}^{0}(H-E)\psi_{0T} d\tau / [1 + \mathrm{Re}\int \psi_{1T}^{1}(H-E)\psi_{0T} d\tau]\end{aligned}\right\}\ \text{for the } Z_1 \text{ value which minimizes the energy.}$$

$\langle W\rangle_{0e}$ and $\langle W\rangle_e$ are the expectations for the Z_1 value obtained by extremizing $\langle W(Z_1)\rangle_0$ and $\langle W(Z_1)\rangle$.

		Operator			
Calculation	Z	r^2	r	r^{-1}	$\delta(\vec{r})$
Accad *et al.*[a]	2	22.928	5.1010	2.3093	2.6408
Hartree-Fock[b]		23.093	5.1185	2.3087	...
$\overline{W}$		13.153	4.0548	2.3121	2.2661
$\langle W\rangle_0$		18.196	4.6897	2.3121	2.5881
$\langle W\rangle$		17.589	4.6133	2.3121	2.5496
$\langle W\rangle_{0e}$		20.131	4.8076	2.3121	2.6039
$\langle W\rangle_e$		22.930	4.9511	2.3097	2.5483
Accad *et al.*	3	7.5472	2.9878	...	9.1276
$\overline{W}$		5.5415	2.6319	3.5621	8.2867
$\langle W\rangle_0$		6.9204	2.8994	3.5621	9.0516
$\langle W\rangle$		6.8080	2.8776	3.5621	8.9892
$\langle W\rangle_{0e}$		7.2277	2.9296	3.5621	9.0754
$\langle W\rangle_e$		7.4558	2.9556	3.5605	8.9879
Accad *et al.*	4	3.7636	2.1273	...	21.926
$\overline{W}$		3.0365	1.9482	4.8121	20.430
$\langle W\rangle_0$		3.5958	2.0948	4.8121	21.826
$\langle W\rangle$		3.5613	2.0858	4.8121	21.740
$\langle W\rangle_{0e}$		3.6838	2.1067	4.8121	21.858
$\langle W\rangle_e$		3.7366	2.1159	4.8109	21.738
Accad *et al.*	5	2.2558	1.6543	...	43.184
$\overline{W}$		1.9133	1.5465	6.0621	40.845
$\langle W\rangle_0$		2.1931	1.6389	6.0621	43.060
$\langle W\rangle$		2.1792	1.6343	0.0621	42.950
$\langle W\rangle_{0e}$		2.2271	1.6447	6.0621	43.100
$\langle W\rangle_e$		2.2454	1.6489	6.0611	42.949
Accad *et al.*	6	1.5030	1.3541	...	75.050
$\overline{W}$		1.3151	1.2821	7.3121	71.679
$\langle W\rangle_0$		1.4745	1.3456	7.3121	74.903
$\langle W\rangle$		1.4679	1.3430	7.3121	74.769
$\langle W\rangle_{0e}$		1.4903	1.3489	7.3121	74.951
$\langle W\rangle_e$		1.4982	1.3512	7.3113	74.767
Accad *et al.*	7	1.0732	1.1464	...	119.67
$\overline{W}$		0.9591	1.0949	8.5621	115.08
$\langle W\rangle_0$		1.0584	1.1412	8.5621	119.50
$\langle W\rangle$		1.0549	1.1396	8.5621	119.34
$\langle W\rangle_{0e}$		1.0667	1.1433	8.5621	119.56
$\langle W\rangle_e$		1.0707	1.1447	8.5614	119.34
Accad *et al.*	8	0.804 70	0.994 10	...	179.20
$\overline{W}$		0.730 32	0.955 46	9.8121	173.20
$\langle W\rangle_0$		0.796 29	0.990 71	9.8121	179.01
$\langle W\rangle$		0.794 23	0.989 61	9.8121	178.83
$\langle W\rangle_{0e}$		0.801 04	0.992 06	9.8121	179.07
$\langle W\rangle_e$		0.803 27	0.992 94	9.8115	178.82

[a] See Ref. 9.

[b] See Ref. 8.

$\langle W\rangle_{0e}$ as before. The expectations $\langle r^2\rangle_e$ and $\langle r\rangle_e$ for He are only in error by 0.009% and 2.9%, respectively, as compared to errors of 12.2% and 5.7% in $\langle r^2\rangle_{0e}$ and $\langle r\rangle_{0e}$. The improvement over the results of the first-order terms are quite substantial since $\overline{W}(W = r^2$ and $r)$ are in error by 42.7% and 21.5%, respectively. As was the case for the ground-state calculation, the results for $\langle\delta(\vec{r})\rangle_{0e}$ are better than those of $\langle\delta(\vec{r})\rangle_e$, the errors being 1.4% and 3.5%, respectively.

$\overline{W}(W = \delta(\vec{r}))$ in this instance is in error by 24.2%. The expectation $\langle r^{-1}\rangle_e$ in this case is slightly better than $\langle r^{-1}\rangle_{0e}$, whereas for the ground-state calculation the reverse was true. It is interesting to note that the value for the screening parameter Z_1 obtained by extremizing $\langle r^{-1}\rangle$, is slightly higher ($Z_1 = 1.7299$) than the energy-minimized value for the ground-state calculation[10] ($Z_1 = 1.6875$) and slightly lower for the excited-state calculation ($Z_1 = 1.8196$ as compared to the energy-minimized value of 1.8497). The trend therefore seems to be that for powers of $r < -1$ and $\delta(\vec{r})$, $\langle W\rangle_{0e}$ is superior to $\langle W\rangle_e$, the opposite being true for powers of $r \geqslant 1$. The fact that these results are also equivalent to those of the Hartree-Fock calculation are again easily understood on the basis of the Brillouin-Moller-Plesset theorem.[16]

For the energy-minimized Z_1 results it is observed that the results of the first decoupling approximation are superior to those of the second decoupling approximation $\langle W\rangle$ for all operators except r^{-1} in which case they are equivalent. As in the ground-state calculation, the results for $\langle r^{-1}\rangle_0$, $\langle r^{-1}\rangle$, and $\langle r^{-1}\rangle_{0e}$ all reduce to the value of $\overline{W}$. The accuracy of this result (an error of 0.17%) is due to the fact that the energy-minimized trial wave function employed in either case satisfies the virial theorem so that $\overline{W}$ is automatically correct to second order,[17] thereby leading to the vanishing of the correction term to $\overline{W}$. Finally, we note that with the exception of the results for $\langle r^2\rangle_e$ for which the error for Li^+ increases to 1.2% and then decreases for each increase in the atomic number, the results of all the other expectations improve for each heavier element of the isoelectronic sequence as expected.

IV. APPLICATION TO 2 ^1S HELIUM ISOELECTRONIC SEQUENCE

In this section we apply the procedure of Sec. II to the excited 2 ^1S state of the helium isoelectronic sequence. As in the orthohelium case we employ a single-determinant-type trial wave function where the spatial parts are again assumed to be the $1S$ and $2S$ hydrogenic functions with the same parameter. This approximation is rather severe since the trial wave function is then not an eigenket of S^2, the square of the total spin operator $\vec{S} = \vec{S}_1 + \vec{S}_2$. And this is reflected in the errors of the first-order expectation values being large. An appropriate approximate wave function ψ_{0T} would of course be one represented by a linear combination of determinants. The extension of our formalism to include configuration-interaction-type trial wave functions is currently being investigated. The motivation for the present set of calculations, however, is twofold. Firstly, with this choice for the trial wave function we note that the expressions for the first-order expectation values $\overline{W}$ remain unchanged for both the ortho- and parahelium states. The "exact" results,[9] however, especially for the exterior of the atom for the expectations of operators such as r^2 and r are quite different for the two states. It is of interest, therefore, to determine how well the formalism distinguishes between these states and to what extent the error of the first-order term for the 2 ^1S state is made up by the addition of the correction terms to $\overline{W}$ with this similar choice of trial wave function. As it turns out the results are surprisingly accurate. Secondly, since in the 2 ^1S state of parahelium the electrons have opposite spin, there are no exchange terms present in the differential equations for the components of the auxiliary function and thus the expressions for the f_i's are the same as those obtained in Sec. III but in this case without the exchange components. The absence of the exchange terms together with the orthogonality of the spin functions thus leads to the elimination of a number of matrix elements thereby simplifying the calculations considerably. The analytic expressions for the expectation values of the operators r^n, $n = 2, 1$, and -1, and $\delta(\vec{r})$ in the two decoupling approximations are presented in Appendix B.

The final consideration in this calculation concerns the choice for the value of the parameter Z_1 employed in the trial wave function ψ_{0T}.[7,13] In this case the subsidiary condition of orthogonality of the excited-state wave function to the ground-state function is not automatically satisfied as for the 2 ^3S state. This subsidiary requirement thus leads to a first choice for the parameter as being $Z_1 = Z - \frac{5}{16}$, which value ensures the orthogonality of the approximate excited-state wave function to the approximate ground-state function. A second criterion for determining Z_1 is the energy-minimization condition. For this condition $Z_1 = Z - \frac{68}{405}$. And finally one may treat the parameter Z_1 as a variational parameter and employ the value of Z_1 obtained by extremizing the analytic expressions for the expectation values in both decoupling approximations.

TABLE II. Expectation values of the operators r^n, $n = 2$, 1, and -1 and $\delta(\vec{r})$ for the $2\,^1S$ helium isoelectronic sequence.

Calculation	Z	Operator r^2	 r	 r^{-1}	 $\delta(\vec{r})$
Accad *et al*.[a]	2	32.1782	5.9461	···	2.6189
(a) W		15.8025	4.4444	2.1094	1.7208
$\langle W\rangle_0$		22.1142	5.0962	2.2901	2.4535
$\langle W\rangle$		22.8316	5.1702	2.3107	2.5367
(b) W		13.4065	4.0937	2.2901	2.2022
$\langle W\rangle_0$		20.4548	4.9697	2.2901	2.5443
$\langle W\rangle$		19.5743	4.8602	2.2901	2.5016
$\langle W\rangle_{0e}$		24.6733	5.2081	2.2901	2.5624
$\langle W\rangle_e$		29.2931	5.4010	2.2864	2.4920
Accad *et al*.	3	9.3902	3.2884	···	9.0376
(a) W		6.2304	2.7907	3.3594	6.9510
$\langle W\rangle_0$		7.7929	3.0476	3.5401	8.8093
$\langle W\rangle$		7.8999	3.0652	3.5525	8.9365
(b) W		5.6104	2.6482	3.5401	8.1344
$\langle W\rangle_0$		7.5186	3.0148	3.5401	8.9521
$\langle W\rangle$		7.3572	2.9838	3.5401	8.8830
$\langle W\rangle_{0e}$		8.1451	3.0737	3.5401	8.9798
$\langle W\rangle_e$		8.4508	3.1060	3.5377	8.8695
Accad *et al*.	4	4.4156	2.2795	···	21.722
(a) W		3.3094	2.0339	4.6094	17.956
$\langle W\rangle_0$		3.9143	2.1704	4.7901	21.454
$\langle W\rangle$		3.9439	2.1771	4.7990	21.625
(b) W		3.0644	1.9572	4.7901	20.152
$\langle W\rangle_0$		3.8346	2.1574	4.7901	21.649
$\langle W\rangle$		3.7854	2.1446	4.7901	21.553
$\langle W\rangle_{0e}$		4.0086	2.1802	4.7901	21.686
$\langle W\rangle_e$		4.0750	2.1910	4.7883	21.536
Accad *et al*.	5	2.5576	1.7459	···	42.823
(a) W		2.0480	1.6000	5.8594	36.883
$\langle W\rangle_0$		2.3425	1.6845	6.0401	42.536
$\langle W\rangle$		2.3537	1.6877	6.0470	42.752
(b) W		1.9273	1.5521	6.0401	40.403
$\langle W\rangle_0$		2.3114	1.6780	6.0401	42.783
$\langle W\rangle$		2.2917	1.6715	6.0401	42.661
$\langle W\rangle_{0e}$		2.3776	1.6892	6.0401	42.830
$\langle W\rangle_e$		2.3998	1.6941	6.0387	42.640
Accad *et al*.	6	1.6666	1.4152	···	74.485
(a) W		1.3911	1.3187	7.1094	65.882
$\langle W\rangle_0$		1.5560	1.3761	7.2901	74.204
$\langle W\rangle$		1.5611	1.3778	7.2958	74.464
(b) W		1.3230	1.2860	7.2901	71.036
$\langle W\rangle_0$		1.5415	1.3724	7.2901	74.503
$\langle W\rangle$		1.5321	1.3687	7.2901	74.354
$\langle W\rangle_{0e}$		1.5719	1.3787	7.2901	74.560
$\langle W\rangle_e$		1.5814	1.3813	7.2889	74.329
Accad *et al*.	7	1.1716	1.1900	···	118.86
(a) W		1.0062	1.1215	8.3594	107.10
$\langle W\rangle_0$		1.1076	1.1630	8.5401	118.61
$\langle W\rangle$		1.1103	1.1641	8.5449	118.91
(b) W		0.9641	1.0978	8.5401	114.20
$\langle W\rangle_0$		1.0100	1.1608	8.5401	118.96
$\langle W\rangle$		1.0950	1.1584	8.5401	118.78
$\langle W\rangle_{0e}$		1.1158	1.1646	8.5401	119.02
$\langle W\rangle_e$		1.1205	1.1661	8.5391	118.75

TABLE II *(Continued)*

Calculation	Z	Operator r^2	r	r^{-1}	$\delta(\vec{r})$
Accad *et al*.	8	0.868 43	1.0267	⋯	178.10
(a) $\overline{W}$		0.761 45	0.9756	9.6094	162.69
(a) $\langle W\rangle_0$		0.828 21	1.0070	9.7901	177.89
(a) $\langle W\rangle$		0.829 74	1.0077	9.7943	178.24
(b) $\overline{W}$		0.733 59	0.9576	9.7901	172.04
(b) $\langle W\rangle_0$		0.823 81	1.0055	9.7901	178.30
(b) $\langle W\rangle$		0.820 90	1.0040	9.7901	178.09
$\langle W\rangle_{0e}$		0.832 87	1.0081	9.7901	178.37
$\langle W\rangle_e$		0.835 45	1.0091	9.7892	178.06

[a] See Ref. 9. The sets (a) and (b) correspond to the results with $Z_1=Z-\frac{5}{16}$ and $Z_1=Z-\frac{68}{405}$, respectively. $\langle W\rangle_{0e}$ and $\langle W\rangle_e$ are the expectations obtained by extremizing the expressions for $\langle W\rangle_0$ and $\langle W\rangle$, respectively, with respect to the parameter Z_1.

Together with the results due to Accad *et al.*[9] we present in Table II our results for $\overline{W}$, $\langle W\rangle_0$, and $\langle W\rangle$ for $Z_1=Z-\frac{5}{16}$ and $Z_1=Z-\frac{68}{405}$ [designated by the brackets (a) and (b), respectively] and the results $\langle W\rangle_{0e}$ and $\langle W\rangle_e$ obtained by extremizing the expressions for $\langle W\rangle_0$ and $\langle W\rangle$ with respect to the parameter Z_1.

With the exception of the operator r^{-1} for which the results of Accad *et al.* are unavailable, it is observed that the results for $\langle W\rangle$ are superior to those of $\langle W\rangle_0$ for the Z_1 obtained via the orthogonality requirement and is slightly less accurate than $\langle W\rangle_0$ for the energy minimized value of Z_1. It is also interesting to note that a better result for $\langle\delta(\vec{r})\rangle_0$ is obtained with the choice of Z_1 which minimizes the energy and which thus leads to a good approximate wave function in the region of greatest interaction, viz., the interior of the atom, than with the Z_1 obtained via the orthogonality constraint. In this case the error for helium is only 2.8%. As was the case for both the ground state and the $2\,^3S$ state, the results $\langle W\rangle_e$ are observed to be better than those of $\langle W\rangle_{0e}$ for the exterior of the atom, the reverse being true for the deep interior. Here for He the errors in the first-order terms $\overline{W}(W=r^2$ and r with $Z_1=Z-\frac{68}{405})$ of 58% and 31%, respectively, are reduced to errors of 9% in both $\langle r^2\rangle_e$ and $\langle r\rangle_e$ and an error of 34% in $\overline{W}(W=\delta(\vec{r}))$ is reduced to an error of 2% in $\langle\delta(\vec{r})\rangle_{0e}$. As may be observed from the analytic expressions for the expectation value of the operator r^{-1}, the correction term to $\overline{W}$ again vanishes for the energy-minimized value of Z_1. This is again due to the fact that the trial wave function ψ_{0T} satisfies the virial theorem and consequently r^{-1} is automatically correct to second order. Also the results of the first decoupling approximation for $Z_1=Z-\frac{5}{16}$ reduce to the results obtained by energy minimization. On the basis of the accuracy of the results for $\langle r^{-1}\rangle$ for both the ground and $2\,^3S$ excited state it is reasonable to assume that the results presented here for the $2\,^1S$ state for the expectation value of r^{-1} is a close approximation to the exact result. And finally, the results for all the expectation values are observed to improve with each increase in the atomic number as should be the case.

Although it is not clear at present why one or the other of the decoupling approximations leads to better results for a particular property, it is observed that no matter which decoupling approximation is used or what criterion for obtaining the parameter value is employed, the results closely approximate the "exact" results and are in every instance a significant improvement over the first-order results of $\overline{W}$.

ACKNOWLEDGMENT

One of us (J. B. K.) gratefully acknowledges the hospitality of the Aspen Center for Theoretical Physics where some of this work was completed during August 1972.

APPENDIX A

In the following subsections we present the analytic expressions for the expectation values of the operators r^n, $n=2$, 1, and -1 and $\delta(\vec{r})$ in the second decoupling approximation $\langle W\rangle$ for the helium $2\,^3S$ isoelectronic sequence together with the corresponding functions $f_i^0(r_i)$ and $f_i^1(r_i)$ of the auxiliary functions ψ_{1T}^0 and ψ_{1T}^1. The constants C_1 and C_2 in the expressions for the f's are chosen so as to orthogonalize ψ_{1T}^0 and ψ_{1T}^1 to ψ_{0T}. The first terms on the right-hand side in the equations for $\langle W\rangle$ as usual correspond to $\overline{W}$ and the second to the correction terms. The results of the first decoupling approximation $\langle W\rangle_0$ are obtained by setting the factor B to unity in these equations.

For the denominator of Eq. (62) we have

$$f_1^1(r_1)=\frac{1}{4Z_1^3r_1}-\frac{r_1}{2Z_1}-\frac{1}{2Z_1^2}\ln r_1+C_1,$$

$$f_2^1(r_2)=\frac{4(1-Z_1r_2)}{Z_1^3r_2(2-Z_1r_2)}-\frac{r_2}{Z_1}-\frac{4}{Z_1^2}\ln r_2+C_2,$$

$$B^{-1}\equiv 1+\int \psi_{1T}^1(H-E)\psi_{0T}\,d\tau$$

$$=1+\frac{355}{81}\frac{Z_1-Z}{Z_1}$$

$$+\frac{2}{Z_1}\left(\frac{2605}{2916}-\frac{53}{81}\ln 3+\frac{296}{729}\ln 2\right).$$

a. $W=r_1^2+r_2^2$.

$$f_1^0(r_1)=-\frac{r_1^3}{6Z_1}-\frac{r_1^2}{2Z_1^2}+f_{1xc}^0(r_1)+C_1,$$

$$f_{1xc}^0(r_1)=-(2048/729Z_1^4)(1-\tfrac{1}{2}Z_1r_1)e^{Z_1r_1/2},$$

$$f_2^0(r_2)=-\frac{16}{Z_1^4(1-\frac{1}{2}Z_1r_2)}+\frac{8r_2}{Z_1^3}-\frac{3r_2^2}{Z_1^2}-\frac{r_2^3}{3Z_1}$$

$$+f_{2xc}+C_2,$$

$$f_{2xc}^0(r_2)=\frac{8192}{729Z_1^4}\frac{e^{-Z_1r_2/2}}{1-\frac{1}{2}Z_1r_2},$$

$$\langle W\rangle=\frac{45}{Z_1^2}+B\left(90\frac{Z_1-Z}{Z_1^3}+\frac{8049574}{729\times 243}\frac{1}{Z_1^3}\right).$$

Here, the $f_{ixc}^0(r_i)$ are the exchange contributions to the $f_i^0(r_i)$. The extremum of $\langle W\rangle_0$ occurs at

$$Z_1=Z-8049574/270\times 729\times 81.$$

b. $W=r_1+r_2$.

$$f_1^0(r_1)=-r_1^2/4Z_1+f_{1xc}^0(r_1)+C_1,$$

$$f_{1xc}^0(r_1)=-(64/243Z_1^3)(1-\tfrac{1}{2}Z_1r_1)e^{Z_1r_1/2},$$

$$f_2^0(r_2)=-\frac{r_2^2}{2Z_1}+\frac{r_2}{Z_1^2}\frac{2}{Z_1^3(1-\frac{1}{2}Z_1r_2)}+f_{2xc}^0(r_2)+C_2,$$

$$f_{2xc}^0(r_2)=\frac{512}{243}\frac{e^{-Z_1r_2/2}}{Z_1^3(1-\frac{1}{2}Z_1r_2)},$$

$$\langle W\rangle=\frac{15}{2Z_1}+B\left(\frac{15}{2}\frac{Z_1-Z}{Z_1^2}+\frac{4811}{1458}\frac{1}{Z_1^2}\right).$$

The extremum for $\langle W\rangle_0$ occurs at

$$Z_1=Z-4811/15\times 729.$$

c. $W=r_1^{-1}+r_2^{-1}$.

$$f_1^0(r_1)=\tfrac{1}{2}r_1+f_{1xc}^0(r_1)+C_1,$$

$$f_{1xc}^0(r_1)=(8/81Z_1)(1-\tfrac{1}{2}Z_1r_1)e^{Z_1r_1/2},$$

$$f_2^0(r_2)=\tfrac{1}{4}r_2+1/2Z_1(1-\tfrac{1}{2}Z_1r_2)+f_{2xc}^0(r_2)+C_2,$$

$$f_{2xc}^0(r_2)=-\frac{64}{81Z_1}\frac{e^{-Z_1r_2/2}}{(1-\frac{1}{2}Z_1r_2)},$$

$$\langle W\rangle=\tfrac{5}{4}Z_1+B[-\tfrac{5}{4}(Z_1-Z)-\tfrac{137}{729}].$$

In this case the expression for $\langle W\rangle_0$ is not a function of the variational parameter Z_1 and the result is the same as that obtained by the variational principle which minimizes the energy.

d. $W=\delta(\vec{r}_1)+\delta(\vec{r}_2)$.

$$f_1^0(r_1)=\frac{Z_1}{2\pi}(Z_1r_1+\ln r_1-1/2Z_1r_1)+f_{1xc}^0(r_1)+C_1,$$

$$f_{1xc}^0(r_1)=(Z_1/6\pi)(1-\tfrac{1}{2}Z_1r_2)e^{Z_1r_2/2},$$

$$f_2^0(r_2)=\frac{1}{\pi}\left(-\frac{1}{4r_2(1-\frac{1}{2}Z_1r_2)}+\frac{Z_1}{(1-\frac{1}{2}Z_1r_2)}\right.$$

$$\left.+\tfrac{1}{8}Z_1^2r_2+\tfrac{1}{2}Z_1\ln r_2\right)+f_{2xc}^0(r_2)+C_2,$$

$$f_{2xc}^0(r_2)=-\frac{4Z_1}{3\pi}\frac{e^{-Z_1r_2/2}}{(1-\frac{1}{2}Z_1r_2)},$$

$$\langle W\rangle=\frac{9Z_1^3}{8\pi}+B\left(-\frac{27}{8\pi}(Z_1-Z)Z_1^2\right.$$

$$\left.-\frac{Z_1^2}{\pi}\left(\tfrac{2201}{2187}-\tfrac{2549}{1458}\ln 3+\tfrac{1184}{729}\ln 2\right)\right).$$

The extremum of $\langle W\rangle_0$ occurs at

$$Z_1=Z-\tfrac{8}{27}\left(\tfrac{2201}{2187}-\tfrac{2549}{1458}\ln 3+\tfrac{1184}{729}\ln 2\right).$$

APPENDIX B

In the following subsections we present the analytic expressions in the second decoupling approximation for the expectation values of the operators r^n, $n=2$, 1, -1 and $\delta(\vec{r})$ for the helium $2\,{}^1S$ isoelectronic sequence. The results of the first decoupling approximation $\langle W\rangle_0$ are obtained by setting the factor B equal to unity.

The denominator expression in Eq. (62) is

$$B^{-1}=1+\int \psi_{1T}^1(H-E)\psi_{0T}\,d\tau$$

$$=1+3\frac{Z_1-Z}{Z_1}+\frac{2}{Z_1}\left(\tfrac{233}{324}-\tfrac{5}{9}\ln 3+\tfrac{32}{81}\ln 2\right).$$

a. $W=r_1^2+r_2^2$.

$$\langle W\rangle=\frac{45}{Z_1^2}+B\left(90\frac{Z_1-Z}{Z_1^3}+\frac{42614}{729}\frac{1}{Z_1^3}\right).$$

The extremum of $\langle W\rangle_0$ occurs at

$$Z_1=Z-42614/270\times 243.$$

b. $W=r_1+r_2$.

$$\langle W\rangle=\frac{15}{2Z_1}+B\left(\frac{15}{2}\frac{Z_1-Z}{Z_1^2}+\frac{2041}{486Z_1^2}\right).$$

In this case the extremum of $\langle W\rangle_0$ occurs at $Z_1=Z-2041/243\times 15$.

c. $W=r_1^{-1}+r_2^{-1}$.

$$\langle W\rangle = \tfrac{5}{4} Z_1 + B[-\tfrac{5}{4}(Z_1 - Z) - \tfrac{17}{81}].$$

Here again $\langle W\rangle_0$ is not a function of the variational parameter Z_1, and the result reduces to that obtained by the variational principle which minimizes the energy.

d. $W = \delta(\vec{r}_1) + \delta(\vec{r}_2)$.

$$\langle W\rangle = \frac{9Z_1^3}{8\pi} + B\left(-\frac{27}{8\pi}(Z_1 - Z)Z_1^2 - \frac{Z_1^2}{\pi}\left(\tfrac{79}{81} - \tfrac{269}{162}\ln 3 + \tfrac{128}{81}\ln 2\right)\right).$$

The extremum of $\langle W\rangle_0$ occurs at

$$Z_1 = Z - \tfrac{8}{27}\left(\tfrac{79}{81} - \tfrac{269}{162}\ln 3 + \tfrac{128}{81}\ln 2\right).$$

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*Supported in part by the Office of Naval Research under Contract No. N0014-67-A-0438-0011 during the summer of 1972 at the Polytechnic Institute of Brooklyn.

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