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Correlation Effects in Atoms. III. Four-Electron Systems*

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The binding energy of the ground state of four-electron systems is investigated in the framework of Hartree-Fock perturbation theory. First, we show that the original problem can be decoupled into a series of helium-like equations describing pair correlation between electrons. Then, the variational-perturbation method is applied to each of these equations through fifth order in energy. We have obtained for the correlation energies the values $E_{\rm corr}$ (Be) $= -0.0925$ atomic units (a.u.) and $E_{\rm corr}(\rm B^+) = -0.1096$ a.u. The experimental numbers are $E_{\rm corr}{}^{\rm exp}$ (Be) $= -0.0944$ a.u. and $E_{\rm corr}{}^{\rm exp}$ $(\rm B^+) = -0.1116$ a.u.

I. INTRODUCTION

THE quantum mechanics of one- and two-electron systems can be said to be understood in complete detail,[1] with the possible exception of very small relativistic effects. However, attempts to extend the methods which have been so successful in dealing with these simplest of systems have proven to be difficult. In this paper, we wish to investigate, starting from first principles, the binding energies and wave functions of four-electron systems. Recently, a great deal of work has been done on three- and four-electron atoms,[2–7] and there are several approaches which have provided some useful insight into these problems. We shall comment on some of these approaches in what follows.

Certainly the most comprehensive attack on the many-electron problem is the Hartree-Fock method, which replaces the true many-body problem by a series of one-body problems in which each particle moves in a self-consistently determined potential generated by all the other particles. For many systems, and in particular for the four-electron atoms and ions, the Hartree-Fock equations have been solved and give accurate approximations to atomic wave functions and binding energies. In our case, since the Hartree-Fock energies and wave functions are known, the problem comes down to finding the relevant corrections to the energies and wave functions. We define

$$E_{\rm corr} = E_{\rm tot} - E_{\rm HF}\,,$$

$$\Psi_{\rm corr} = \Psi_{\rm tot} - \Psi_{\rm HF}\,,$$

where $E_{\rm tot}$ and $\Psi_{\rm tot}$ are, respectively, the total *nonrelativistic* energy and wave function, whereas $E_{\rm HF}$ and $\Psi_{\rm HF}$ are the Hartree-Fock energy and wave function of the system considered.

Since $E_{\rm tot}$ as defined above is not directly accessible to experiment, we have estimated it as follows: We take the extremely accurate calculations of Pekeris[8] to provide us with the nonrelativistic energy of the two electron core ($1s$-$1s$) corresponding to the four-electron system in question, and then use the experimental ionization potentials to obtain the binding energies of the outer two electrons. We estimated the relativistic corrections to the experimental binding energies in the manner suggested by Watson,[2] i.e., by using a simple Dirac-type relation for the energy. For Be and $\rm B^+$, in which we are interested in this paper, these relativistic corrections are less than 1% of the correlation energy, and therefore the precision with which they are estimated is not of great importance for our purposes. Thus, we believe that the values

$$E_{\rm corr}{}^{\rm exp}({\rm Be}) = -0.0944 \text{ a.u.}\,,$$

$$E_{\rm corr}{}^{\rm exp}({\rm B^+}) = -0.1116 \text{ a.u.}\,,$$

are very accurate estimates of the correlation energies for these two systems.[9] It seems unlikely that the correct nonrelativistic value could differ by more than 0.5% from these numbers. It is these "experimental" results that we wish to understand in a reasonably straightforward manner.

II. DERIVATION OF THE BASIC EQUATIONS

Since the Hartree-Fock wave functions give an excellent approximation to atomic energies, it seems reasonable to apply the Rayleigh-Schrödinger perturbation theory to our four-electron system, starting from the Hartree-Fock Hamiltonian as zeroth-order approximation. We begin by establishing some notation. We define the operators $T(\mathbf{r})$ and $V_i(\mathbf{r})$ by

$$T(\mathbf{r})f(\mathbf{r}) \equiv -\tfrac{1}{2}\nabla^2 f(\mathbf{r}) - (Z/r)f(\mathbf{r})\,, \tag{1a}$$

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[9] Thoughout this paper we will mean by a.u. atomic units, in which the reduced mass of the electron is set equal to one.

$$V_i(\mathbf{r})f(\mathbf{r})\equiv\int\phi_i^*(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_i(\mathbf{r}')d\mathbf{r}'f(\mathbf{r})$$

$$-\int\phi_i^*(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}f(\mathbf{r}')d\mathbf{r}'\phi_i(\mathbf{r})\,,\quad\text{(1b)}$$

where Z is the nuclear charge of the system considered, and ϕ_i is a Hartree-Fock single-particle orbital. The subscript i refers to a complete collection of one-particle quantum numbers, including spin. For our specific four-electron problem, we further define

$$\mathcal{V}(\mathbf{r})=V_{1s\uparrow}(\mathbf{r})+V_{1s\downarrow}(\mathbf{r})+V_{2s\uparrow}(\mathbf{r})+V_{2s\downarrow}(\mathbf{r})\,.\quad(2)$$

In a more general case $\mathcal{V}(\mathbf{r})$ would be a sum of operators V_i with i ranging over all filled Hartree-Fock orbitals. The spinor wave functions $\phi_{1s\uparrow}$, $\phi_{1s\downarrow}$, $\phi_{2s\uparrow}$, and $\phi_{2s\downarrow}$, whose existence is implied in our above definitions, are the solutions to four coupled equations, namely,

$$[T(\mathbf{r})+\mathcal{V}(\mathbf{r})]\phi_i(\mathbf{r})=\epsilon_i\phi_i(\mathbf{r})\,,(i=1s\uparrow,1s\downarrow,2s\uparrow,2s\downarrow)\,.\quad(3)$$

Because we are dealing with systems having all angular momentum shells filled, the space parts of $\phi_{1s\uparrow}$ and $\phi_{1s\downarrow}$ are the same, i.e.,

$$\phi_{1s\uparrow}=\phi_{1s}\alpha$$

and

$$\phi_{1s\downarrow}=\phi_{1s}\beta\,,$$

where ϕ_{1s} is a function of space variables only, and α and β are spinors representing spin up and spin down, respectively. Similarly,

$$\phi_{2s\uparrow}=\phi_{2s}\alpha$$

and

$$\phi_{2s\uparrow}=\phi_{2s}\beta\,.$$

A simple computation using Eq. (3) gives then the following two coupled integro-differential equations for ϕ_{1s} and ϕ_{2s}:

$$[T(\mathbf{r})+V_{1s}{}^d(\mathbf{r})+2V_{2s}{}^d(\mathbf{r})-V_{2s}{}^e(\mathbf{r})]\phi_{1s}(\mathbf{r})=\epsilon_{1s}\phi_{1s}(\mathbf{r})\,,\quad\text{(4a)}$$

$$[T(\mathbf{r})+V_{2s}{}^d(\mathbf{r})+2V_{1s}{}^d(\mathbf{r})-V_{1s}{}^e(\mathbf{r})]\phi_{2s}(\mathbf{r})=\epsilon_{2s}\phi_{2s}(\mathbf{r})\,.\quad\text{(4b)}$$

Here we have defined the spin-independent operators

$$V_{1s}{}^d(\mathbf{r})=\int\phi_{1s}^*(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_{1s}(\mathbf{r}')d\mathbf{r}'\,,\quad\text{(5a)}$$

$$V_{1s}{}^e(\mathbf{r})f(\mathbf{r})=\int\phi_{1s}^*(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}f(\mathbf{r}')d\mathbf{r}'\phi_{1s}(\mathbf{r})\,,\quad\text{(5b)}$$

with similar definitions for $V_{2s}{}^d(\mathbf{r})$ and $V_{2s}{}^e(\mathbf{r})$. The quantities ϵ_{1s} and ϵ_{2s} introduced in Eqs. (4a) and (4b) are such that $\epsilon_{1s}=\epsilon_{1s\uparrow}=\epsilon_{1s\downarrow}$ and $\epsilon_{2s}=\epsilon_{2s\uparrow}=\epsilon_{2s\downarrow}$. The object ϕ_{1s} is the eigenfunction corresponding to the lowest possible eigenvalue of Eq. (4a), whereas ϕ_{2s} is the eigenfunction corresponding to the lowest eigenvalue of Eq. (4b) which also satisfies the requirement $(\phi_{1s}|\phi_{2s})=0$. For such equations, Roothaan *et al.*[10] have given very accurate solutions in a convenient analytic form. We will use their functions, both for Be and B^+, throughout this work. Table I lists the relevant expectation values, where we have used the following definitions:

TABLE I. The values of important Hartree-Fock matrix elements (in a.u.).

	Be	B^+
$(1s\|T\|1s)$	−7.94206	−12.44114
$(2s\|T\|2s)$	−1.58939	− 2.73667
V_{1s1s}	+2.27293	+ 2.89618
V_{1s2s}	+0.48107	+ 0.70260
V_{2s2s}	+0.34346	+ 0.50380
V_{ex}	+0.02536	+ 0.04614
ϵ_{1s}	−4.73235	− 8.18590
ϵ_{2s}	−0.30915	− 0.87381

$$V_{1s1s}=\int|\phi_{1s}(\mathbf{r})|^2|\phi_{1s}(\mathbf{r}')|^2\frac{1}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'\,,\quad\text{(6a)}$$

$$V_{1s2s}=\int|\phi_{1s}(\mathbf{r})|^2|\phi_{2s}(\mathbf{r}')|^2\frac{1}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'\,,\quad\text{(6b)}$$

$$V_{2s2s}=\int|\phi_{2s}(\mathbf{r})|^2|\phi_{2s}(\mathbf{r}')|^2\frac{1}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'\,,\quad\text{(6c)}$$

$$V_{\text{ex}}=\int\phi_{1s}^*(\mathbf{r})\phi_{1s}^*(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_{2s}(\mathbf{r})\phi_{2s}(\mathbf{r}')d\mathbf{r}d\mathbf{r}'\,.\quad\text{(6d)}$$

Using these definitions, we see from Eqs. (4a) and (4b) that

$$\epsilon_{1s}=\langle 1s|T|1s\rangle+V_{1s1s}+2V_{1s2s}-V_{\text{ex}}\,,\quad\text{(7a)}$$

$$\epsilon_{2s}=\langle 2s|T|2s\rangle+V_{2s2s}+2V_{1s2s}-V_{\text{ex}}\,.\quad\text{(7b)}$$

With this notation established, we may write the total Hamiltonian for the system as

$$H=H_0+H_1\,,$$

where

$$H_0=H_{\text{HF}}(\mathbf{r}_1)+H_{\text{HF}}(\mathbf{r}_2)+H_{\text{HF}}(\mathbf{r}_3)+H_{\text{HF}}(\mathbf{r}_4)\,,\quad\text{(8a)}$$

and

$$H_1=\sum_{i>j}\frac{1}{r_{ij}}-\mathcal{V}(\mathbf{r}_1)-\mathcal{V}(\mathbf{r}_2)-\mathcal{V}(\mathbf{r}_3)-\mathcal{V}(\mathbf{r}_4)\,.\quad\text{(8b)}$$

The operator $H_{\text{HF}}(\mathbf{r})$ is the single-particle Hartree-Fock Hamiltonian

$$H_{\text{HF}}(\mathbf{r})=T(\mathbf{r})+\mathcal{V}(\mathbf{r})\,.$$

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[10] C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Rev. Mod. Phys. 32, 186 (1960).

The generalization to more than four electrons is obvious. The equation

$$H_0\psi_0 = E_0\psi_0 \tag{9}$$

has as its lowest eigenvalue (in the Hilbert space of totally antisymmetric functions)

$$E_0 = 2\epsilon_{1s} + 2\epsilon_{2s}, \tag{10}$$

with the corresponding normalized spinor eigenfunction

$$\psi_0(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4) = [1/\sqrt{(24)}] \times \mathcal{A}[\phi_{1s\uparrow}(\mathbf{r}_1)\phi_{1s\downarrow}(\mathbf{r}_2)\phi_{2s\uparrow}(\mathbf{r}_3)\phi_{2s\downarrow}(\mathbf{r}_4)], \tag{11}$$

where $\mathcal{A}$ denotes the operation of antisymmetrization in all coordinates. The quantities ψ_0 and E_0 being known, we look for the solution to

$$H\Psi = E\Psi$$

in the form

$$\Psi = \sum_{n=0}^{\infty} \psi_n, \tag{12a}$$

$$E = \sum_{n=0}^{\infty} E_n. \tag{12b}$$

This leads to the equations

$$(H_0 - E_0)\psi_1 + (H_1 - E_1)\psi_0 = 0, \tag{13a}$$

$$(H_0 - E_0)\psi_n + H_1\psi_{n-1} - \sum_{m=1}^{n-1} E_m\psi_{n-m} - E_n\psi_0 = 0 \quad (n \geqslant 2), \tag{13b}$$

and, therefore, we have[11]

$$E_1 = \langle\psi_0|H_1|\psi_0\rangle, \tag{14a}$$

$$E_2 = \langle\psi_0|H_1 - E_1|\psi_1\rangle = -\langle\psi_1|H_0 - E_0|\psi_1\rangle, \tag{14b}$$

$$E_3 = \langle\psi_1|H_1 - E_1|\psi_1\rangle - 2E_2\langle\psi_0|\psi_1\rangle, \tag{14c}$$

$$E_4 = -\langle\psi_2|H_0 - E_0|\psi_2\rangle - E_2\langle\psi_1|\psi_1\rangle - 2E_3\langle\psi_0|\psi_1\rangle, \tag{14d}$$

$$E_5 = \langle\psi_2|H_1 - E_1|\psi_2\rangle - 2E_2\langle\psi_1|\psi_2\rangle - E_3\langle\psi_1|\psi_1\rangle - 2E_3\langle\psi_0|\psi_2\rangle - 2E_4\langle\psi_0|\psi_1\rangle. \tag{14e}$$

The expression (14a) for E_1 is readily evaluated using Roothaan's functions for ϕ_{1s} and ϕ_{2s} in Eq. (11). We have

$$E_1 = -V_{1s1s} - 4V_{1s2s} - V_{2s2s} + 2V_{\mathrm{ex}}. \tag{15}$$

The sum $E_{\mathrm{HF}} = E_0 + E_1$ is what is usually referred to as the Hartree-Fock energy. For Be, $E_{\mathrm{HF}}(\mathrm{Be}) = -14.5730$ a.u., while for B$^+$, $E_{\mathrm{HF}}(\mathrm{B}^+) = -24.2376$ a.u.

We now proceed to the calculation of E_2, given by Eq. (14b) and therefore we have to solve Eq. (13a) for ψ_1. In BJI,[11] Eq. (13a) was solved for He in the case where ψ_0 is the ground-state solution to the Hartree-Fock equation. It was also noted there that this equation could be derived from a variational principle[1] based on the expression

$$F_1[\psi_1^t] = \langle\psi_1^t|H_0 - E_0|\psi_1^t\rangle + 2\langle\psi_1^t|H_1 - E_1|\psi_0\rangle, \tag{16}$$

where ψ_1^t is a (real) trial function. Varying $F_1[\psi_1^t]$ with respect to ψ_1^t, one obtains Eq. (13a) for the function ψ_1, which makes $F_1[\psi_1^t]$ stationary. If we are dealing with the ground state of a system, which is the case in this paper, it is easy to show using the completeness of the eigenfunctions of H_0 that we actually have a minimum principle, i.e., $F_1[\psi_1^t]$ takes on its smallest possible value for $\psi_1^t = \psi_1$, where ψ_1 satisfies Eq. (13a). This smallest value is just the expression (14b) for E_2. Because of the form of Eq. (13a) it is clear that we can always pick ψ_1 orthogonal to ψ_0. Throughout this paper we will constrain ψ_1 to satisfy this orthogonality condition. With this convention, E_2 is given simply by

$$E_2 = \langle\psi_0|H_1|\psi_1\rangle. \tag{17}$$

One would like to build a trial wave function ψ_1^t with a number of variable parameters in it, compute $F_1[\psi_1^t]$, and then vary the parameters to get a minimum. In BJI, this was done for helium, and good results were obtained for E_2. It might be thought that helium is a poor precedent to cite in this paper, since the possibility of many-electron overlap integrals, of the type already encountered in the study of lithium by James and Coolidge,[12] would seem to make this a prohibitively difficult program to carry out for Be. However, we will show that in fact we can reduce the problem of solving Eq. (13a) to a decoupled collection of two-electron problems, so that the techniques of BJI can be employed.

Since electron-pair correlations are expected to dominate the problem, it seems reasonable to take our trial function to be of the following form:

$$\begin{aligned}\psi_1^t(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4) = \mathcal{S}[&\chi_{1s\uparrow1s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)\phi_{2s\uparrow}(\mathbf{r}_3)\phi_{2s\downarrow}(\mathbf{r}_4)\\ &+\chi_{1s\uparrow2s\uparrow}(\mathbf{r}_1,\mathbf{r}_3)\phi_{1s\downarrow}(\mathbf{r}_2)\phi_{2s\downarrow}(\mathbf{r}_4)\\ &+\chi_{1s\uparrow2s\downarrow}(\mathbf{r}_1,\mathbf{r}_4)\phi_{1s\downarrow}(\mathbf{r}_2)\phi_{2s\uparrow}(\mathbf{r}_3)\\ &+\chi_{1s\downarrow2s\uparrow}(\mathbf{r}_2,\mathbf{r}_3)\phi_{1s\uparrow}(\mathbf{r}_1)\phi_{2s\downarrow}(\mathbf{r}_4)\\ &+\chi_{1s\downarrow2s\downarrow}(\mathbf{r}_2,\mathbf{r}_4)\phi_{1s\uparrow}(\mathbf{r}_1)\phi_{2s\uparrow}(\mathbf{r}_3)\\ &+\chi_{2s\uparrow2s\downarrow}(\mathbf{r}_3,\mathbf{r}_4)\phi_{1s\uparrow}(\mathbf{r}_1)\phi_{1s\downarrow}(\mathbf{r}_2)]/\sqrt{(12)},\end{aligned} \tag{18}$$

where the χ_{ij} are totally antisymmetric in the space and spin coordinates. The operator $\mathcal{S}$ denotes the linear combination of all 12 symmetric permutations on $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_3$, and $\mathbf{r}_4$. The function $\psi_1^t(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4)$ is then totally antisymmetric. In fact, what we are doing here is adding to the Hartree-Fock solution ψ_0 a function ψ_1^t containing all possible terms in which electrons with quantum numbers i and j correlate through some function χ_{ij}, while all the other electrons stay in their unperturbed Hartree-Fock orbitals.

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[11] F. W. Byron, Jr., and C. J. Joachain, Phys. Rev. **146**, 1 (1966), to be referred hereafter as BJI. In this paper the following misprints should be corrected: in Eq. (8d), the first term should be $-\langle\chi_2|H_0-E_0|\chi_2\rangle$ and in Eq. (9b) the last term should read $-2E_2\langle\chi_2^t|\varphi_0\rangle$.

[12] H. M. James and A. S. Coolidge, Phys. Rev. **49**, 688 (1936).

Now, let us consider the functions χ_{ij}. Because of the operator $\mathcal{S}$, it is clear that χ_{ij} cannot contain any components of $\phi_k(k\neq i,j)$. Indeed, if it did, such a component would vanish upon applying $\mathcal{S}$, since χ_{ij} is antisymmetric. Thus, without loss of generality, we may take[13]

$$\langle\chi_{ij}(\mathbf{r},\mathbf{r}')\,|\,\phi_k(\mathbf{r})\rangle=\langle\chi_{ij}(\mathbf{r},\mathbf{r}')\,|\,\phi_k(\mathbf{r}')\rangle=0 \qquad (19)$$

for $k\neq i,\ j$.

Finally, we anticipate here that χ_{ij} contains no components of ϕ_i or ϕ_j. This will be shown at the end of this section. Thus, we conclude that the χ_{ij} contain no components of any of the filled Hartree-Fock orbitals. This is one way of looking at the success of the Hartree-Fock model of the atom. Precisely those intermediate states that one would expect to contribute predominantly to ψ_1 (and hence to E_2 and E_3) do not occur either because of the Pauli principle [see Eq. (19)] or because of the particular form of the Hartree-Fock potentials (ϕ_i, ϕ_j orthogonal to χ_{ij}), as we shall see below.

Knowing that χ_{ij} is orthogonal to all the filled single-particle Hartree-Fock orbitals, we can easily derive the basic equations for the χ_{ij}. Returning to our expression for $F_1[\psi_1{}^t]$ [see Eq. (16)], we find for the first term[14]

$$\langle\psi_1{}^t|\,H_0-E_0\,|\psi_1{}^t\rangle=\sum_{i,j}{}'\,\langle\chi_{ij}(\mathbf{r},\mathbf{r}')\,|\,H_{\mathrm{HF}}(\mathbf{r})+H_{\mathrm{HF}}(\mathbf{r}')-\epsilon_i-\epsilon_j\,|\,\chi_{ij}(\mathbf{r},\mathbf{r}')\rangle, \qquad (20)$$

where we have used the fact that H_{HF} contains only *one-body* operators. For example, if one tried to obtain such a result for the expectation value of the total Hamiltonian H between two functions having the same form as our $\psi_1{}^t$, the presence of terms like $r_{12}{}^{-1}$ would prevent this decoupling from occurring (i.e., there are more than just pair-correlation effects in atoms).

The second term in $F_1[\psi_1{}^t]$ [see Eq. (16)] is $2\langle\psi_0|H_1-E_1|\psi_1{}^t\rangle$. Although this expression does contain terms of the type $r_{12}{}^{-1}$, $\psi_1{}^t$ occurs only on one side of the inner product. A simple calculation using Eq. (15) and the orthogonality properties of the χ_{ij} yields the result

$$\langle\psi_0|\,H_1-E_1\,|\psi_1{}^t\rangle=\sum_{i,j}{}'\,\langle\tfrac{1}{2}\sqrt{2}[\phi_i(\mathbf{r})\phi_j(\mathbf{r}')-\phi_i(\mathbf{r}')\phi_j(\mathbf{r})]\,|\,(1/|\mathbf{r}-\mathbf{r}'|)-V_i(\mathbf{r})-V_j(\mathbf{r})-V_i(\mathbf{r}')-V_j(\mathbf{r}')-\epsilon_{ij}{}^{(1)}\,|\,\chi_{ij}(\mathbf{r},\mathbf{r}')\rangle, \qquad (21)$$

where we have defined

$$\epsilon_{1s\uparrow1s\downarrow}{}^{(1)}=-V_{1s1s}, \qquad (22a)$$

$$\epsilon_{1s\uparrow2s\uparrow}{}^{(1)}=\epsilon_{1s\downarrow2s\downarrow}{}^{(1)}=-V_{1s2s}+V_{\mathrm{ex}}, \qquad (22b)$$

$$\epsilon_{1s\uparrow2s\downarrow}{}^{(1)}=\epsilon_{1s\downarrow2s\uparrow}{}^{(1)}=-V_{1s2s}, \qquad (22c)$$

$$\epsilon_{2s\uparrow2s\downarrow}{}^{(1)}=-V_{2s2s}. \qquad (22d)$$

Note that

$$E_1=\sum_{i,j}{}'\,\epsilon_{ij}{}^{(1)}. \qquad (22e)$$

Thus, collecting Eqs. (20) and (21), we obtain for $F_1[\psi_1{}^t]$

$$F_1[\psi_1{}^t]=\sum_{i,j}{}'\,\{\langle\chi_{ij}(\mathbf{r},\mathbf{r}')\,|\,H_{\mathrm{HF}}(\mathbf{r})+H_{\mathrm{HF}}(\mathbf{r}')-\epsilon_i-\epsilon_j\,|\,\chi_{ij}(\mathbf{r},\mathbf{r}')\rangle+2\langle\tfrac{1}{2}\sqrt{2}[\phi_i(\mathbf{r})\phi_j(\mathbf{r}')-\phi_i(\mathbf{r}')\phi_j(\mathbf{r})]\,|\,(1/|\mathbf{r}-\mathbf{r}'|)-V_i(\mathbf{r})-V_j(\mathbf{r})-V_i(\mathbf{r}')-V_j(\mathbf{r}')-\epsilon_{ij}{}^{(1)}\,|\,\chi_{ij}(\mathbf{r},\mathbf{r}')\rangle\}. \qquad (23)$$

We now vary the χ_{ij} independently and obtain the basic equations for our problem:

$$[H_{\mathrm{HF}}(\mathbf{r})+H_{\mathrm{HF}}(\mathbf{r}')-\epsilon_i-\epsilon_j]\chi_{ij}(\mathbf{r},\mathbf{r}')=-[(1/|\mathbf{r}-\mathbf{r}'|)-V_i(\mathbf{r})-V_j(\mathbf{r})-V_i(\mathbf{r}')-V_j(\mathbf{r}')-\epsilon_{ij}{}^{(1)}]\tfrac{1}{2}\sqrt{2}\times[\phi_i(\mathbf{r})\phi_j(\mathbf{r}')-\phi_i(\mathbf{r}')\phi_j(\mathbf{r})]. \qquad (24)$$

Thus, the problem of obtaining ψ_1 reduces to a matter of solving a collection of decoupled two-body problems of the type discussed in BJI. The value of $F_1[\psi_1{}^t]$ at the minimizing values of the χ_{ij} obtained from Eq. (24) is just

$$E_2=\sum_{i,j}{}'\,\epsilon_{ij}{}^{(2)}, \qquad (25a)$$

where

$$\epsilon_{ij}{}^{(2)}=\langle\chi_{ij}(\mathbf{r},\mathbf{r}')\,|\,(1/|\mathbf{r}-\mathbf{r}'|)-V_i(\mathbf{r})-V_j(\mathbf{r})-V_i(\mathbf{r}')-V_j(\mathbf{r}')-\epsilon_{ij}{}^{(1)}\,|\,\tfrac{1}{2}\sqrt{2}[\phi_i(\mathbf{r})\phi_j(\mathbf{r}')-\phi_i(\mathbf{r}')\phi_j(\mathbf{r})]\rangle. \qquad (25b)$$

Returning to our pair equation [Eq. (24)], we note that if we take the inner product of the right-hand side of this equation by $\phi_i(\mathbf{r})\phi_j(\mathbf{r}')$ [or by $\phi_i(\mathbf{r}')\phi_j(\mathbf{r})$] we get zero because of the definitions (1b) of the potentials V_i and (22a)–(22d) for $\epsilon_{ij}{}^{(1)}$. Thus our equation is well posed since, due to the Hermiticity of H_{HF}, the inner product of the left-hand side of Eq. (24) with $\phi_i(\mathbf{r})\phi_j(\mathbf{r}')$ [or $\phi_i(\mathbf{r}')\phi_j(\mathbf{r})$] also vanishes. Let us agree to choose the indeterminate inner product $\langle\phi_i\phi_j|\chi_{ij}\rangle$ to vanish. In solving the pair equations variationally, we will constrain our functions χ_{ij} to satisfy this condition. Now,

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[13] Throughout this paper, we extend the definition of inner products to expressions of the form

$$\langle f(x,y)\,|\,g(y)\rangle\equiv\int f^*(x,y)g(y)dy,$$

i.e., such an "inner product" is actually a function of x.

[14] We use the notation $\sum_{ij}{}'$ to denote a sum on all *distinct pairs* of indices.

because of the special properties of the Hartree-Fock potentials, if we multiply the right-hand side of Eq. (24) by just, say, $\phi_i(\mathbf{r}')$ and integrate over all space, this integral is identically zero (integration implies, as usual, summation over the appropriate spin indices). Integrating the left-hand side of the equation after multiplying by $\phi_i(\mathbf{r}')$ and using the Hermiticity of H_{HF}, we get the equation

$$[H_{\mathrm{HF}}(\mathbf{r})-\epsilon_j]\langle\phi_i(\mathbf{r}')\,|\,\chi_{ij}(\mathbf{r},\mathbf{r}')\rangle=0,$$

which tells us that

$$\langle\phi_i(\mathbf{r}')\,|\,\chi_{ij}(\mathbf{r},\mathbf{r}')\rangle=a\phi_j(\mathbf{r}),$$

where a is some constant. Now, taking the inner product of both sides by $\phi_j(\mathbf{r})$, we get

$$\langle\phi_i(\mathbf{r}')\phi_j(\mathbf{r})\,|\,\chi_{ij}(\mathbf{r},\mathbf{r}')\rangle=a.$$

But we have also

$$\langle\phi_i(\mathbf{r}')\phi_j(\mathbf{r})\,|\,\chi_{ij}(\mathbf{r}',\mathbf{r})\rangle=-a$$

because χ_{ij} is antisymmetric. Since we have already decided to choose this inner product to be zero, we conclude that $a=0$, so that

$$\langle\phi_i(\mathbf{r}')\,|\,\chi_{ij}(\mathbf{r},\mathbf{r}')\rangle=0, \qquad (26\text{a})$$

and similarly,

$$\langle\phi_j(\mathbf{r}')\,|\,\chi_{ij}(\mathbf{r},\mathbf{r}')\rangle=0. \qquad (26\text{b})$$

Hence χ_{ij} contains no components of ϕ_i or ϕ_j, as we claimed above. Note also that the orthogonality properties of the χ_{ij} guarantee that $\langle\psi_0|\psi_1\rangle=0$.

One might be tempted to object that although we have succeeded in obtaining a simple set of equations for ψ_1, we have not taken $\psi_1{}^t$ to be of the most general form possible, and therefore the true E_2 for the four-electron system might be lower than the E_2 which we would obtain from our Eq. (24) and Eqs. (25a) and (25b). However, if we substitute into the basic equation [Eq. (13a)] the expression (18) for $\psi_1{}^t$ and make use of the fact that the χ_{ij} satisfy Eq. (24), a simple calculation shows that the basic equation of first-order wave-function perturbation theory [Eq. (13a)] is actually satisfied exactly. Thus we have found the solution (unique if $\langle\psi_0|\psi_1\rangle=0$) for the first-order wave function.

In concluding this section we note that our above discussion is not at all restricted to four-electron systems, and Eq. (24) which we have derived for the χ_{ij} applies to atoms with any number of electrons. In Sec. III we point out in what ways the practical matter of actually solving the equations for the χ_{ij} is expedited by having a four-electron ground state (or more generally, an atom with all angular momentum shells filled).

III. REDUCTION OF THE PAIR EQUATIONS

We now want to factor out the spin dependence from the pair equations. Let us begin by writing down the six pair equations for the four-electron problem. Using Eq. (24), we get

$$[H_{\mathrm{HF}}(\mathbf{r}_1)+H_{\mathrm{HF}}(\mathbf{r}_2)-2\epsilon_{1s}]\chi_{1s\uparrow1s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)$$
$$=-[1/r_{12}-V_{1s\uparrow}(\mathbf{r}_1)-V_{1s\downarrow}(\mathbf{r}_1)-V_{1s\uparrow}(\mathbf{r}_2)-V_{1s\downarrow}(\mathbf{r}_2)-\epsilon_{1s\uparrow1s\downarrow}{}^{(1)}]\tfrac{1}{2}\sqrt{2}[\phi_{1s\uparrow}(\mathbf{r}_1)\phi_{1s\downarrow}(\mathbf{r}_2)-\phi_{1s\uparrow}(\mathbf{r}_2)\phi_{1s\downarrow}(\mathbf{r}_1)] \qquad (27\text{a})$$

$$[H_{\mathrm{HF}}(\mathbf{r}_1)+H_{\mathrm{HF}}(\mathbf{r}_2)-\epsilon_{1s}-\epsilon_{2s}]\chi_{1s\uparrow2s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)$$
$$=-[1/r_{12}-V_{1s\uparrow}(\mathbf{r}_1)-V_{2s\downarrow}(\mathbf{r}_1)-V_{1s\uparrow}(\mathbf{r}_2)-V_{2s\downarrow}(\mathbf{r}_2)-\epsilon_{1s\uparrow2s\downarrow}{}^{(1)}]\tfrac{1}{2}\sqrt{2}[\phi_{1s\uparrow}(\mathbf{r}_1)\phi_{2s\downarrow}(\mathbf{r}_2)-\phi_{1s\uparrow}(\mathbf{r}_2)\phi_{2s\downarrow}(\mathbf{r}_1)] \qquad (27\text{b})$$

$$[H_{\mathrm{HF}}(\mathbf{r}_1)+H_{\mathrm{HF}}(\mathbf{r}_2)-\epsilon_{1s}-\epsilon_{2s}]\chi_{1s\uparrow2s\uparrow}(\mathbf{r}_1,\mathbf{r}_2)$$
$$=-[1/r_{12}-V_{1s\uparrow}(\mathbf{r}_1)-V_{2s\uparrow}(\mathbf{r}_1)-V_{1s\uparrow}(\mathbf{r}_2)-V_{2s\uparrow}(\mathbf{r}_2)-\epsilon_{1s\uparrow2s\uparrow}{}^{(1)}]\tfrac{1}{2}\sqrt{2}[\phi_{1s\uparrow}(\mathbf{r}_1)\phi_{2s\uparrow}(\mathbf{r}_2)-\phi_{1s\uparrow}(\mathbf{r}_2)\phi_{2s\uparrow}(\mathbf{r}_1)], \qquad (27\text{c})$$

$$[H_{\mathrm{HF}}(\mathbf{r}_1)+H_{\mathrm{HF}}(\mathbf{r}_2)-\epsilon_{1s}-\epsilon_{2s}]\chi_{1s\downarrow2s\uparrow}(\mathbf{r}_1,\mathbf{r}_2)$$
$$=-[1/r_{12}-V_{1s\downarrow}(\mathbf{r}_1)-V_{2s\uparrow}(\mathbf{r}_1)-V_{1s\downarrow}(\mathbf{r}_2)-V_{2s\uparrow}(\mathbf{r}_2)-\epsilon_{1s\downarrow2s\uparrow}{}^{(1)}]\tfrac{1}{2}\sqrt{2}[\phi_{1s\downarrow}(\mathbf{r}_1)\phi_{2s\uparrow}(\mathbf{r}_2)-\phi_{1s\downarrow}(\mathbf{r}_2)\phi_{2s\uparrow}(\mathbf{r}_1)], \qquad (27\text{d})$$

$$[H_{\mathrm{HF}}(\mathbf{r}_1)+H_{\mathrm{HF}}(\mathbf{r}_2)-\epsilon_{1s}-\epsilon_{2s}]\chi_{1s\downarrow2s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)$$
$$=-[1/r_{12}-V_{1s\downarrow}(\mathbf{r}_1)-V_{2s\downarrow}(\mathbf{r}_1)-V_{1s\downarrow}(\mathbf{r}_2)-V_{2s\downarrow}(\mathbf{r}_2)-\epsilon_{1s\downarrow2s\downarrow}{}^{(1)}]\tfrac{1}{2}\sqrt{2}[\phi_{1s\downarrow}(\mathbf{r}_1)\phi_{2s\downarrow}(\mathbf{r}_2)-\phi_{1s\downarrow}(\mathbf{r}_2)\phi_{2s\downarrow}(\mathbf{r}_1)], \qquad (27\text{e})$$

$$[H_{\mathrm{HF}}(\mathbf{r}_1)+H_{\mathrm{HF}}(\mathbf{r}_2)-2\epsilon_{2s}]\chi_{2s\uparrow2s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)$$
$$=-[1/r_{12}-V_{2s\uparrow}(\mathbf{r}_1)-V_{2s\downarrow}(\mathbf{r}_1)-V_{2s\uparrow}(\mathbf{r}_2)-V_{2s\downarrow}(\mathbf{r}_2)-\epsilon_{2s\uparrow2s\downarrow}{}^{(1)}]\tfrac{1}{2}\sqrt{2}[\phi_{2s\uparrow}(\mathbf{r}_1)\phi_{2s\downarrow}(\mathbf{r}_2)-\phi_{2s\uparrow}(\mathbf{r}_2)\phi_{2s\downarrow}(\mathbf{r}_1)]. \qquad (27\text{f})$$

Before proceeding further let us note that these rather messy equations have a very simple physical interpretation. Each equation is precisely what would arise if one performed first-order wave-function perturbation theory on a particular two-body reduced Hamiltonian. For example, Eq. (27a) is obtained from the reduced Hamiltonian H_{red} given by

$$H_{\mathrm{red}}=T(\mathbf{r}_1)+T(\mathbf{r}_2)+1/r_{12}+V_{2s\uparrow}(\mathbf{r}_1)+V_{2s\downarrow}(\mathbf{r}_1)+V_{2s\uparrow}(\mathbf{r}_2)+V_{2s\downarrow}(\mathbf{r}_2) \qquad (28)$$

starting from a zero-order wave function given by

$$\phi_0=\tfrac{1}{2}\sqrt{2}[\phi_{1s\uparrow}(\mathbf{r}_1)\phi_{1s\downarrow}(\mathbf{r}_2)-\phi_{1s\uparrow}(\mathbf{r}_2)\phi_{1s\downarrow}(\mathbf{r}_1)].$$

The same reasoning applies to any pair. This is just the Hamiltonian for two particles moving in a central Coulomb potential of charge Z, interacting through the true electron-electron interaction, but seeing also an "average potential" (nonlocal because of exchange) due to the two $2s$ electrons. Unfortunately, because of the interelectronic interactions, this reduced two-body Hamiltonian is not valid to all orders in perturbation theory. If it were, one might envision solving the whole problem by tackling each two-body Hamiltonian of the type given in Eq. (28) by the Rayleigh-Ritz method, employed so successfully in helium by Hylleraas and others.[8,15] Even this program would not be without serious difficulties, however, since in trying to solve the $2s$-$2s$ pair problem one would be looking for a very highly excited state of the two-body Hamiltonian.

Returning to our problem of reducing Eqs. (27a)–(27f), we note that the functions χ_{ij} can be written in general as

$$\chi(\mathbf{r}_1,\mathbf{r}_2)=f(\mathbf{r}_1,\mathbf{r}_2)\Phi_s(1,2)+g(\mathbf{r}_1,\mathbf{r}_2)\Phi_t(1,2),$$

where f and g are functions of position alone, f being a symmetric function and g being antisymmetric. The objects Φ_s and Φ_t are spin-wave functions of total spin equal to zero and one, respectively. Now, for the ground state of the four-electron problem, the space parts of $\phi_{1s\uparrow}$ and $\phi_{1s\downarrow}$ are the same, as are the space parts of $\phi_{2s\uparrow}$ and $\phi_{2s\downarrow}$. For this reason, we find that

$$\begin{aligned}[H_{\mathrm{HF}}(\mathbf{r}_1)+H_{\mathrm{HF}}(\mathbf{r}_2)]\chi(\mathbf{r}_1,\mathbf{r}_2)=[\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)f(\mathbf{r}_1,\mathbf{r}_2)]\Phi_s(1,2)&\\ +[\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)g((\mathbf{r}_1,\mathbf{r}_2)]\Phi_t(1,2),&\qquad(29)\end{aligned}$$

where $\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)$ is an operator, symmetric under the interchange of $\mathbf{r}_1$ and $\mathbf{r}_2$, which acts only on space variables;

$$\begin{aligned}\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)=T(\mathbf{r}_1)+T(\mathbf{r}_2)+2V_{1s}{}^d(\mathbf{r}_1)+2V_{2s}{}^d(\mathbf{r}_1)&\\ +2V_{1s}{}^d(\mathbf{r}_2)+2V_{2s}{}^d(\mathbf{r}_2)-V_{1s}{}^e(\mathbf{r}_1)&\\ -V_{2s}{}^e(\mathbf{r}_1)-V_{1s}{}^e(\mathbf{r}_2)-V_{2s}{}^e(\mathbf{r}_2).&\qquad(30)\end{aligned}$$

With these results in hand, the reduction of the basic pair equations is straightforward. For the inner-shell correlation functions $\chi_{1s\uparrow1s\downarrow}$ and $\chi_{2s\uparrow2s\downarrow}$, the reduction is particularly simple, since the right-hand side of Eqs. (27a) and (27f) has a pure singlet spin dependence. Hence, we write

$$\chi_{1s\uparrow1s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)=f(\mathbf{r}_1,\mathbf{r}_2)\tfrac{1}{2}\sqrt{2}[\alpha(1)\beta(2)-\alpha(2)\beta(1)],\qquad(31a)$$

$$\chi_{2s\uparrow2s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)=g(\mathbf{r}_1,\mathbf{r}_2)\tfrac{1}{2}\sqrt{2}[\alpha(1)\beta(2)-\alpha(2)\beta(1)].\qquad(31b)$$

Then from Eqs. (27a) and (27f) we obtain

$$\begin{aligned}[\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)-2\epsilon_{1s}]f(\mathbf{r}_1,\mathbf{r}_2)=-[1/r_{12}-V_{1s}{}^d(\mathbf{r}_1)&\\ -V_{1s}{}^d(\mathbf{r}_2)-\epsilon_{1s\uparrow1s\downarrow}{}^{(1)}]\phi_{1s}(\mathbf{r}_1)\phi_{1s}(\mathbf{r}_2),&\qquad(32)\end{aligned}$$

$$\begin{aligned}[\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)-2\epsilon_{2s}]g(\mathbf{r}_1,\mathbf{r}_2)=-[1/r_{12}-V_{2s}{}^d(\mathbf{r}_1)&\\ -V_{2s}{}^d(\mathbf{r}_2)-\epsilon_{2s\uparrow2s\downarrow}{}^{(1)}]\phi_{2s}(\mathbf{r}_1)\phi_{2s}(\mathbf{r}_2).&\qquad(33)\end{aligned}$$

Remember that in solving these equations we must constrain $f(\mathbf{r}_1,\mathbf{r}_2)$ to contain no components of ϕ_{2s}, and $g(\mathbf{r}_1,\mathbf{r}_2)$ must be constrained to contain no components of ϕ_{1s}. In addition, if we require that

$$\langle\phi_{1s}\phi_{1s}|f\rangle=\langle\phi_{2s}\phi_{2s}|g\rangle=0,\qquad(34)$$

then, automatically, $f(\mathbf{r}_1,\mathbf{r}_2)$ will contain no components of ϕ_{1s} and $g(\mathbf{r}_1,\mathbf{r}_2)$ will contain no components of ϕ_{2s}.

In the case of the inter-shell correlation functions, we first note that apart from reversal of spin, Eqs. (27b) and (27d) are equivalent; i.e., we can use the same space function for both equations. The same remark applies to Eqs. (27c) and (27e). In what follows, we will discuss only Eqs. (27b) and (27c). For Eq. (27c), the right-hand side is a pure triplet spin function, so we can write

$$\chi_{1s\uparrow2s\uparrow}(\mathbf{r}_1,\mathbf{r}_2)=h_{1,1}(\mathbf{r}_1,\mathbf{r}_2)\alpha(1)\alpha(2),\qquad(35a)$$

and similarly, from Eq. (27e),

$$\chi_{1s\downarrow2s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)=h_{1,1}(\mathbf{r}_1,\mathbf{r}_2)\beta(1)\beta(2),\qquad(35b)$$

where the subscripts in the function $h_{1,1}$ indicate that we consider a triplet state with total spin $S=1$ and $M_s=\pm1$. A simple calculation yields for $h_{1,1}$ the equation

$$\begin{aligned}[\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)-\epsilon_{1s}-\epsilon_{2s}]h_{1,1}(\mathbf{r}_1,\mathbf{r}_2)=-[1/r_{12}-V_{1s}{}^d(\mathbf{r}_1)&\\ -V_{2s}{}^d(\mathbf{r}_1)-V_{1s}{}^d(\mathbf{r}_2)-V_{2s}{}^d(\mathbf{r}_2)+V_{1s}{}^e(\mathbf{r}_1)+V_{2s}{}^e(\mathbf{r}_1)&\\ +V_{1s}{}^e(\mathbf{r}_2)+V_{2s}{}^e(\mathbf{r}_2)-\epsilon_{1s\uparrow2s\uparrow}{}^{(1)}]\tfrac{1}{2}\sqrt{2}&\\ \times[\phi_{1s}(\mathbf{r}_1)\phi_{2s}(\mathbf{r}_2)-\phi_{1s}(\mathbf{r}_2)\phi_{2s}(\mathbf{r}_1)].&\qquad(36)\end{aligned}$$

Clearly, because of (35a) and (35b) we have

$$\epsilon_{1s\uparrow2s\uparrow}{}^{(2)}=\epsilon_{1s\downarrow2s\downarrow}{}^{(2)}.$$

Finally, we consider Eq. (27b) for $\chi_{1s\uparrow2s\downarrow}$. In this case, the right-hand side of Eq. (27b) has a combination of singlet ($S=0$, $M_s=0$) and triplet ($S=1$, $M_s=0$) spin dependence, so that we write

$$\begin{aligned}\chi_{1s\uparrow2s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)=h_{1,0}(\mathbf{r}_1,\mathbf{r}_2)\tfrac{1}{2}\sqrt{2}[\alpha(1)\beta(2)+\alpha(2)\beta(1)]&\\ +h_{0,0}(\mathbf{r}_1,\mathbf{r}_2)\tfrac{1}{2}\sqrt{2}[\alpha(1)\beta(2)-\alpha(2)\beta(1)],&\qquad(37a)\end{aligned}$$

and similarly from Eq. (27d)

$$\begin{aligned}\chi_{1s\downarrow2s\uparrow}(\mathbf{r}_1,\mathbf{r}_2)=h_{1,0}(\mathbf{r}_1,\mathbf{r}_2)\tfrac{1}{2}\sqrt{2}[\beta(1)\alpha(2)+\beta(2)\alpha(1)]&\\ +h_{0,0}(\mathbf{r}_1,\mathbf{r}_2)\tfrac{1}{2}\sqrt{2}[\beta(1)\alpha(2)-\beta(2)\alpha(1)],&\qquad(37b)\end{aligned}$$

where $h_{1,0}$ is an antisymmetric function and $h_{0,0}$ a symmetric one. A straightforward computation yields

$$\begin{aligned}[\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)-\epsilon_{1s}-\epsilon_{2s}]h_{1,0}(\mathbf{r}_1,\mathbf{r}_2)=-\tfrac{1}{2}[1/r_{12}-\epsilon_{1s\uparrow2s\downarrow}{}^{(1)}]&\\ \times[\phi_{1s}(\mathbf{r}_1)\phi_{2s}(\mathbf{r}_2)-\phi_{1s}(\mathbf{r}_2)\phi_{2s}(\mathbf{r}_1)]&\\ +\tfrac{1}{2}[V_{2s}{}^d(\mathbf{r}_1)+V_{1s}{}^d(\mathbf{r}_2)]\phi_{1s}(\mathbf{r}_1)\phi_{2s}(\mathbf{r}_2)&\\ -\tfrac{1}{2}[V_{1s}{}^d(\mathbf{r}_1)+V_{2s}{}^d(\mathbf{r}_2)]\phi_{1s}(\mathbf{r}_2)\phi_{2s}(\mathbf{r}_1),&\qquad(38)\end{aligned}$$

and

$$\begin{aligned}[\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)-\epsilon_{1s}-\epsilon_{2s}]h_{0,0}(\mathbf{r}_1,\mathbf{r}_2)=-\tfrac{1}{2}[1/r_{12}-\epsilon_{1s\uparrow2s\downarrow}{}^{(1)}]&\\ \times[\phi_{1s}(\mathbf{r}_1)\phi_{2s}(\mathbf{r}_2)+\phi_{1s}(\mathbf{r}_2)\phi_{2s}(\mathbf{r}_1)]&\\ +\tfrac{1}{2}[V_{2s}{}^d(\mathbf{r}_1)+V_{1s}{}^d(\mathbf{r}_2)]\phi_{1s}(\mathbf{r}_1)\phi_{2s}(\mathbf{r}_2)&\\ +\tfrac{1}{2}[V_{1s}{}^d(\mathbf{r}_1)+V_{2s}{}^d(\mathbf{r}_2)]\phi_{1s}(\mathbf{r}_2)\phi_{2s}(\mathbf{r}_1).&\qquad(39)\end{aligned}$$

It is apparent from Eqs. (37a) and (37b) that $\epsilon_{1s\uparrow2s\downarrow}{}^{(2)}=\epsilon_{1s\downarrow2s\uparrow}{}^{(2)}$. Apart from a statistical over-all factor $2^{-1/2}$, the difference between Eqs. (36) and (38) is a matter of constraints. We note that Eq. (36) needs no constraints because of the spin factors which multiply

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[15] E. A. Hylleraas, Z. Physik 54, 347 (1929).

$h_{1,1}$ in Eq. (35a), i.e., $\chi_{1s\uparrow 2s\uparrow}$ is automatically orthogonal to $\phi_{1s\downarrow}$ and $\phi_{2s\downarrow}$ because of spin considerations. This is further reflected in Eq. (36), where the form of the right-hand side guarantees that $h_{1,1}$ will contain no components of ϕ_{1s} or ϕ_{2s}. On the contrary, in solving Eq. (38) we must constrain $h_{1,0}$ to contain no components of ϕ_{1s} or ϕ_{2s} (or, alternatively, we must constrain $\chi_{1s\uparrow 2s\downarrow}$ to contain no components of $\phi_{1s\downarrow}$ or $\phi_{2s\uparrow}$) even though the form of Eq. (27c) guarantees that $\chi_{1s\uparrow 2s\downarrow}$ will contain no components of $\phi_{1s\uparrow}$ or $\phi_{2s\downarrow}$. Once the appropriate constraints are applied, it can be shown that Eqs. (36) and (38) turn out to be the same. Therefore, we can omit Eq. (38) in what follows, since on the subspace of the two-particle Hilbert space on which $h_{1,0}$ is different from zero it is equal to a constant multiple of $h_{1,1}$. Finally, in solving Eq. (39), we have to constrain $h_{0,0}$ to contain no components of ϕ_{1s} or ϕ_{2s}.

Thus, we see that the problem comes down to solving Eqs. (32), (33), (36), and (39), the relevant constraints discussed above being taken into account. We now proceed to the solution of these equations.

IV. SOLUTION OF THE PAIR EQUATIONS

We propose to carry out the solution of the reduced Eqs. (32), (33), (36), and (39) by the variational method discussed in BJI. Each of these equations has the form

$$\mathcal{P}\rho=-Q\phi\,, \tag{40}$$

where $\mathcal{P}$ and Q are given Hermitian operators, ρ is any of the unknown functions f, g, $h_{1,1}$, $h_{1,0}$, or $h_{0,0}$ defined in Sec. III, and ϕ is a given function. Equation (40) can be derived from the variational expression

$$\epsilon^{(2)}[\rho^t]=\langle\rho^t|\mathcal{P}|\rho^t\rangle+2\langle\rho^t|Q|\phi\rangle\,, \tag{41}$$

where we have used the notation $\epsilon^{(2)}[\rho^t]$ because of the fact that each of the variational expressions from which are derived Eqs. (32), (33), (36), (38), and (39) can actually be shown to be a *minimum principle* for the appropriate $\epsilon_{ij}{}^{(2)}$ referred to in Eq. (25b). We emphasize that the existence of a *minimum* principle for all of the $\epsilon_{ij}{}^{(2)}$ is directly linked to the constraints imposed upon the functions f, g, $h_{1,1}$, $h_{1,0}$, and $h_{0,0}$, because the constraints project out of the relevant first-order trial function all components of those states which have lower-zero-order energy than the state in question.

Before proceeding to the solutions it is necessary to decide on a good choice of trial function for ρ^t. In BJI, we used for helium the Hylleraas-type function

$$\rho(s,t,u)=\frac{1}{4\pi}e^{-\frac{1}{2}ks}\sum_{l,m,n}C_{lmn}s^l t^m u^n\,, \tag{42}$$

where $s=r_1+r_2$, $t=r_1-r_2$, $u=r_{12}$, and k is a scale parameter roughly equal to twice the effective charge seen by the two electrons. It is well known from the work of Hylleraas and others[8,15] in the two-electron systems that this set of trial functions is a very good one, and in BJI we found that with a small number of terms in Eq. (42) we could get within 0.5% of the helium correlation energy. However, these functions suffer from one grave defect when applied to a Hartree-Fock–type problem: Because of the existence of the nonlocal exchange potential there occur certain integrals[16] in the variational expression which cannot be done in closed form. This difficulty arises because of the use of the variable $u=r_{12}$ in Eq. (42). As one includes higher and higher powers of u, these intergrals require progressively more complicated infinite sums in their evaluation. Now, in BJI it was found that with only 10 parameters in Eq. (42), i.e., only terms linear and quadratic in u, a very good value for the correlation energy could be obtained. Clearly, we expect the same to be the case in our four-electron system for the calculation of the 1*s*-1*s* correlation energy, which should be particularly amenable to the treatment of BJI. Indeed, the effective central charge seen by the inner two 1*s* electrons is close to $Z=4$, as opposed to just $Z=2$ in helium. In fact, we employed this method in calculating the 1*s*-1*s* correlation energy and achieved satisfactory results. However, the 2*s*-2*s* correlation energy poses a more serious problem. Here we are dealing with a rather loosely bound *excited* two-body state, and we may anticipate that a wave function with only 10 parameters, even of the Hylleraas type, might not be able to represent adequately such a diffuse structure. In actual calculations of the 2*s*-2*s* correlation energy, just such difficulties were encountered.

At the opposite pole from the Hylleraas-type function is a trial function which is of the "configuration-mixing" type:

$$\rho_{\pm}(r_1,\mathbf{r}_2,\cos\theta_{12})=\frac{1}{4\pi}\sum_{l,m,n}C_{lmn}(r_1{}^m r_2{}^n+r_1{}^n r_2{}^m)$$
$$\times(e^{-\frac{1}{2}\alpha r_1}e^{-\frac{1}{2}\beta r_2}\pm e^{-\frac{1}{2}\alpha r_2}e^{-\frac{1}{2}\beta r_1})P_l(\cos\theta_{12})\,, \tag{43}$$

where the choice of the plus sign or of the minus sign gives us a symmetric or antisymmetric function of the space variables. This function, too, has several drawbacks. Calculations by Watson[2] and Weiss[3] utilizing the configuration-mixing method have been able at best to get within 7% of the Be correlation energy. Schwartz[17] has pointed out that one pays dearly for the omission of terms in r_{12}, which is in some sense the optimal way of including the angular part of the correlation function. It turns out that the expansion in Legendre polynomials is rather slowly convergent, and the difficulty of getting accurate values for the contribution of the higher terms in $P_l(\cos\rho_{12})$ grows rapidly as l increases.

On the other hand, these functions have some attractive features. All the integrals in the variational princi-

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[16] These are the integrals referred to as $g(l,m,n,\alpha,\beta,\gamma,a,b)$ with a and b odd in Appendix III of BJI (Ref. 11).

[17] C. Schwartz, Phys. Rev. **126**, 1015 (1962).

ple are easy to perform, and the constraint requirements on ρ can be seen to be purely on the function of r_1 and r_2 multiplying the relative s-wave ($l=0$) term in ρ. Perhaps more important from the computational point of view is the fact that the problem for a particular ρ decouples into a series of relative partial-wave problems, i.e., we can write

$$\epsilon_{ij}^{(2)}=\sum_{l=0}^{\infty}\epsilon_{ij}^{(2)}(l)\,,$$

and obtain trivially minimum principles for each $\epsilon_{ij}^{(2)}(l)$. Also it seems reasonable to suppose that functions of the type (43) might do very nicely in trying to calculate *inter-shell* correlations, since the difficulty in helium, as noted by Schwartz,[17] comes primarily from the problem of representing adequately the cusp behavior of the correlation function at $r_1=r_2$. For inter-shell correlations, we expect the region $r_1=r_2$ to be considerably less important than it would be for inner-shell correlations, where the pair of electrons overlap maximally. We have verified that this is the case in helium, where we have investigated successfully in this way the perturbation theory of the $(1s2s)$ $^1S_0$ and the $(1s2s)$ $^3S_1$ states.[18] Therefore, in the case of the four-electron system, we have used trial functions of the type (43) for the inter-shell correlation functions $h_{0,0}(\mathbf{r}_1,\mathbf{r}_2)$ and $h_{1,1}(\mathbf{r}_1,\mathbf{r}_2)$.

Going back to the *inner-shell* correlations, we note that there exists a type of function which retains much of the simplicity of the configuration-mixing type (43), but nevertheless manages to give some cusplike behavior at $r_1=r_2$, namely,

$$\rho(r_>,r_<,\cos\theta_{12})=\frac{1}{4\pi}\sum_{l,m,n}C_{lmn}r_>^{\,m}r_<^{\,n}e^{-(\alpha/2)r_>}e^{-(\beta/2)r_<}\times P_l(\cos\theta_{12})\,,\tag{44}$$

where $r_>$ denotes the greater and $r_<$ the lesser of r_1 and r_2. Using functions of this type in helium, we were able to get extremely accurate results for the ground-state correlation energy.[18] Therefore, we used the $(r_>r_<)$ basis to calculate the inner-shell correlation functions $f(\mathbf{r}_1,\mathbf{r}_2)$ and $g(\mathbf{r}_1,\mathbf{r}_2)$ in the four-electron system.

To summarize, let us write out our trial functions for the four different cases:

$$f(\mathbf{r}_1,\mathbf{r}_2)=\sum_l F^{(l)}(r_1,r_2)P_l(\cos\theta_{12})\,,\tag{45a}$$

$$g(\mathbf{r}_1,\mathbf{r}_2)=\sum_l G^{(l)}(r_1,r_2)P_l(\cos\theta_{12})\,,\tag{45b}$$

$$h_{1,1}(\mathbf{r}_1,\mathbf{r}_2)=\sum_l H_{1,1}^{(l)}(r_1,r_2)P_l(\cos\theta_{12})\,,\tag{45c}$$

$$h_{0,0}(\mathbf{r}_1,\mathbf{r}_2)=\sum_l H_{0,0}^{(l)}(r_1,r_2)P_l(\cos\theta_{12})\,,\tag{45d}$$

where

$$F^{(l)}(r_1,r_2)=\sum_{m,n}A_{mn}^{(l)}r_>^{\,m}r_<^{\,n}e^{-\frac{1}{2}\alpha r_>}e^{-\frac{1}{2}\beta r_<}\,,\tag{46a}$$

$$G^{(l)}(r_1,r_2)=\sum_{m,n}B_{mn}^{(l)}r_>^{\,m}r_<^{\,n}e^{-\frac{1}{2}\alpha' r_>}e^{-\beta' r_<}\,,\tag{46b}$$

$$H_{1,1}^{(l)}(r_1,r_2)=\sum_{m,n}C_{mn}^{(l)}(r_1^{\,m}r_2^{\,n}+r_1^{\,n}r_2^{\,m})\times(e^{-\frac{1}{2}ar_1}e^{-\frac{1}{2}br_2}-e^{-\frac{1}{2}ar_2}e^{-\frac{1}{2}br_1})\,,\tag{46c}$$

$$H_{0,0}^{(l)}(r_1,r_2)=\sum_{m,n}D_{mn}^{(l)}(r_1^{\,m}r_2^{\,n}+r_1^{\,n}r_2^{\,m})\times(e^{-\frac{1}{2}a'r_1}e^{-\frac{1}{2}b'r_2}+e^{-\frac{1}{2}a'r_2}e^{-\frac{1}{2}b'r_1})\,.\tag{46d}$$

As we remarked before, the constraints all refer to the form of the relative s-wave ($l=0$) correlation functions. The simplest constraints, i.e.,

$$\langle\phi_{1s}\phi_{1s}|F^{(0)}\rangle=0\,,\tag{47a}$$

$$\langle\phi_{2s}\phi_{2s}|G^{(0)}\rangle=0\,,\tag{47b}$$

$$\langle\phi_{1s}\phi_{2s}|H_{1,1}^{(0)}\rangle=0\,,\tag{47c}$$

$$\langle\phi_{1s}\phi_{2s}|H_{0,0}^{(0)}\rangle=0\,,\tag{47d}$$

are easily disposed of by the use of Lagrange multipliers. However, for $F^{(0)}$, we must also require that our trial function contain no components of ϕ_{2s}. Thus, instead of taking $F^{(0)}$ as trial function in the $l=0$ partial wave, we shall use

$$\tilde{F}^{(0)}(r_1,r_2)=F^{(0)}(r_1,r_2)-\phi_{2s}(r_1)\langle\phi_{2s}(r_3)|F^{(0)}(r_3,r_2)\rangle-\phi_{2s}(r_2)\langle\phi_{2s}(r_3)|F^{(0)}(r_1,r_3)\rangle+\phi_{2s}(r_1)\phi_{2s}(r_2)\langle\phi_{2s}\phi_{2s}|F^{(0)}\rangle\,.\tag{48a}$$

Similarly, instead of $G^{(0)}$, we use

$$\tilde{G}^{(0)}(r_1,r_2)=G^{(0)}(r_1,r_2)-\phi_{1s}(r_1)\langle\phi_{1s}(r_3)|G^{(0)}(r_3,r_2)\rangle-\phi_{1s}(r_2)\langle\phi_{1s}(r_3)|G^{(0)}(r_1,r_3)\rangle+\phi_{1s}(r_1)\phi_{1s}(r_2)\langle\phi_{1s}\phi_{1s}|G^{(0)}\rangle\,.\tag{48b}$$

For the inter-shell correlation functions, we have a more complicated expression to guarantee that no components of either ϕ_{1s} or ϕ_{2s} are present in $H_{0,0}^{(0)}$. Thus we define

$$\begin{aligned}\tilde{H}_{0,0}^{(0)}(r_1,r_2)=H_{0,0}^{(0)}(r_1,r_2)&-\phi_{1s}(r_1)\langle\phi_{1s}(r_3)|H_{0,0}^{(0)}(r_3,r_2)\rangle-\phi_{1s}(r_2)\langle\phi_{1s}(r_3)|H_{0,0}^{(0)}(r_1,r_3)\rangle+\phi_{1s}(r_1)\phi_{1s}(r_2)\\&\times\langle\phi_{1s}\phi_{1s}|H_{0,0}^{(0)}\rangle-\phi_{2s}(r_1)\langle\phi_{2s}(r_3)|H_{0,0}^{(0)}(r_3,r_2)\rangle-\phi_{2s}(r_2)\langle\phi_{2s}(r_3)|H_{0,0}^{(0)}(r_1,r_3)\rangle\\&+\phi_{2s}(r_1)\phi_{2s}(r_2)\langle\phi_{2s}\phi_{2s}|H_{0,0}^{(0)}\rangle\,,\end{aligned}\tag{48c}$$

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[18] F. W. Byron, Jr., and C. J. Joachain, preceding paper, Phys. Rev. **157**, 1 (1967), to be referred to as BJII.

where we have omitted two terms in $\phi_{1s}(r_1)\phi_{2s}(r_2)$ and $\phi_{1s}(r_2)\phi_{2s}(r_1)$ which are unnecessary if $H_{0,0}^{(0)}$ already satisfies Eq. (47d).

With this in hand, we substitute our various trial functions into the variational expression for E_2, Eq. (16), compute the inner products, and vary the parameters to obtain a minimum. As shown above, the problem breaks up into separate variational problems for the $\epsilon_{ij}^{(2)}$, which in turn split up into still smaller variational problems for the $\epsilon_{ij}^{(2)}(l)$, the energies contributed by each relative partial wave. In practice, we determined reasonable values of the nonlinear parameters $(\alpha,\beta,\alpha',\beta',a,b,a',b')$ in Eqs. (46a)–(46d) by physical considerations connected with effective charges. Thus, our variational expression is a quadratic form in the linear parameters $A_{mn}^{(l)}$, $B_{mn}^{(l)}$, $C_{mn}^{(l)}$, and $D_{mn}^{(l)}$ of Eqs. (46a)–(46d), so that, as in BJI our problem reduces to one of matrix inversion. With the parameters determined in such a way that they minimize the variational expression $F_1[\psi_1^t]$ [Eq. (16)], it is a simple matter to calculate the various $\epsilon_{ij}^{(2)}$ from Eq. (25b). All the integrals appearing in the calculation can be written in terms of finite sums of the basic integrals $V(l,m,\alpha,\beta)$ and $W(l,m,n,\alpha,\beta,\gamma)$ discussed in BJI. These integrals can in turn be written as finite sums of factorials and powers or, more conveniently, may be evaluated by the use of recursion relations.[12] The most complicated expressions encountered are those involved in computing the matrix elements of the exchange potentials V_i^e [see Eq. (5b)]. These actually involve significant computational labor in each relative partial wave.

V. THE SECOND-ORDER ENERGY

In this section we want to discuss the contributions of the various pairs to E_2.

A. 1s-1s Correlations

For the 1s-1s case, we used 21 terms in Eq. (46a) for each relative partial wave; i.e., we allowed $m+n$ to take on all possible positive values up to $m+n=5$. We evaluated explicitly all terms through $l=6$ in the relative partial-wave expansion (45a). The contribution of the higher partial waves to $\epsilon_{1s\uparrow 1s\downarrow}^{(2)}$ was estimated by extrapolation, using the fact that it drops off like l^{-4} for large l.[17] This asymptotic behavior seems to set in quite rapidly after $l=4$. The results are shown in Table II. The most interesting feature concerns the relative s-wave contribution $\epsilon_{1s\uparrow 1s\downarrow}^{(2)}(0)$. In doing perturbation calculations for the ground state of helium starting from a hydrogenic Hamiltonian, one finds a very large relative s-wave contribution,[18] but here, because of the Hartree-Fock potentials the size of the relative s-wave contribution is reduced until it is actually significantly smaller than the relative p-wave contribution. Beyond the relative p wave, the terms $\epsilon_{1s\uparrow 1s\downarrow}^{(2)}(l)$ drop off quite rapidly. The same phenomenon occurs in doing Hartree-Fock perturbation theory in helium and is discussed in BJII.

TABLE II. The contribution of each relative partial wave to the $1s\uparrow 1s\downarrow$ correlation energy in second order (in a.u.).

l	$\epsilon_{1s\uparrow 1s\downarrow}^{(2)}$ Be	$\epsilon_{1s\uparrow 1s\downarrow}^{(2)}$ B$^+$
0	−0.01236	−0.01197
1	−0.02242	−0.02317
2	−0.00352	−0.00360
3	−0.00099	−0.00101
4	−0.00038	−0.00038
5	−0.00017	−0.00017
6	−0.00009	−0.00009
$\geqslant 7$	−0.00015	−0.00016
Total	−0.04008	−0.04055

Another interesting point about the relative s-wave contribution is how it is effected by the constraint which prevents any components of ϕ_{2s} from appearing in $\tilde{F}^{(0)}(r_1,r_2)$ [Eq. (48a)]. This constraint must clearly increase $\epsilon_{1s\uparrow 1s\downarrow}^{(2)}(0)$, as may easily be seen by writing

$$\epsilon_{1s\uparrow 1s\downarrow}^{(2)}(0)=\sum_{m\neq 1s,n\neq 1s}\frac{|\langle\phi_{1s}(r_1)\phi_{1s}(r_2)|1/r_{12}|\tfrac{1}{2}\sqrt{2}[\phi_m(r_1)\phi_n(r_2)+\phi_m(r_2)\phi_n(r_1)]\rangle|^2}{2\epsilon_{1s}-\epsilon_m-\epsilon_n}, \tag{49}$$

where the sum runs only over terms in which both m and n refer to s states. If we apply the constraint that no ϕ_{2s} components appear in the 1s-1s correlation function, then in the above sum we must exclude all states in which *either* m or n is equal to 2s. Since ϵ_{1s} is the lowest single-particle energy, we see that the removal of ϕ_{2s} components will remove terms from Eq. (49) with negative energy denominators, thus increasing $\epsilon_{1s\uparrow 1s\downarrow}^{(2)}(0)$. The restriction $m\neq 1s$, $n\neq 1s$ is guaranteed by the form of Eq. (32) for $f(\mathbf{r}_1,\mathbf{r}_2)$. This essentially is the reason that $\epsilon_{1s\uparrow 1s\downarrow}^{(2)}(0)$ is so much larger in hydrogenic than in Hartree-Fock perturbation theory: In first order, the potentials in the Hartree-Fock case act as projection operators to annihilate any component of ϕ_{1s}. Similar remarks apply, *mutatis mutandis*, to the functions g, $h_{1,1}$, and $h_{0,0}$.

If we neglect the constraint imposed in Eq. (48a) and just compute $\epsilon_{1s\uparrow 1s\downarrow}^{(2)}(0)$, including the ϕ_{2s} components, we find for Be, a value which is 0.00152 a.u. lower than the number given in Table II, whereas for B$^+$, the value is 0.00204 a.u. lower. This is in accordance with our above discussion. It turns out that this is essentially the only difference between the 1s-1s correlation energy in Be and in Be^{++} or in B$^+$ and in B^{3+}. Thus, the outer two electrons in Be and B^+ make themselves felt in the $1s$-$1s$ correlation energy *only through the exclusion principle*, not through the electrostatic forces which they exert on the $1s$ electrons.

B. Inter-shell Correlations

To evaluate the inter-shell correlations, we used 20 parameters in Eqs. (46c) and (46d) for $H_{1,1}^{(l)}$ and $H_{0,0}^{(l)}$, thereby including all terms in the sum with $m+n\leq 7$. Partial-wave contributions through $l=3$ were calculated, and the remaining terms were estimated by extrapolation. We expect the values of $\epsilon_{1s\uparrow 2s\uparrow}^{(2)}$ and $\epsilon_{1s\uparrow 2s\downarrow}^{(2)}$ to be small because of the small overlap between the $1s$-shell and $2s$-shell wave functions. Tables III and IV show the results for these two cases. For the relative s-wave contribution to $\epsilon_{1s\uparrow 2s\uparrow}^{(2)}$, the choice of the Hartree-Fock potential, plus the fact that the space function $h_{1,1}(\mathbf{r}_1,\mathbf{r}_2)$, being antisymmetric, already vanishes at $r_1=r_2$, serves to reduce the s-wave contribution to insignificance. The fact that the Hartree-Fock function does not vanish properly when $\mathbf{r}_i=\mathbf{r}_j$ can be thought of as giving rise to the correlation effects which we are studying. Of course, the singularity of the Coulomb potential at $\mathbf{r}_i=\mathbf{r}_j$ means that two electrons cannot come arbitrarily close together. For pairs in which both electrons have the same z component of spin, the exclusion principle forces the pair function to be zero at $\mathbf{r}_i=\mathbf{r}_j$, which works in the direction required by the Coulomb force. For this reason, we expect $\epsilon_{1s\uparrow 2s\uparrow}^{(2)}$ to be smaller than $\epsilon_{1s\uparrow 2s\downarrow}^{(2)}$, and we see in Tables III and IV that this is indeed the case, although the difference is only about a factor of 2. Note also that $\epsilon_{1s\uparrow 2s\downarrow}^{(2)}$ contains a contribution from the space-symmetric function $h_{1,1}$ as well as from the space-antisymmetric function $h_{0,0}$, the latter one yielding $\frac{1}{2}\epsilon_{1s\uparrow 2s\uparrow}^{(2)}(l)$ in each partial wave, as pointed out above. Thus, in fact, the *total* contribution of all antisymmetric functions to the inter-shell correlation energy is not significantly smaller than the total arising from all symmetric functions. Only in the s wave is the reduction due to antisymmetry striking. Thus, it is possible to be misled by choosing a "simple" variational function to estimate the relative sizes of the antisymmetric and symmetric contributions,[19] since there is a good chance that the "simple" function will be purely relative s wave in character. Even in the symmetric case, the bulk of the correlation energy comes from relative partial waves with $l\geq 1$.

TABLE III. The contribution of each relative partial wave to the $1s\uparrow 2s\uparrow$ correlation energy in second order (in a.u.).

l	$\epsilon_{1s\uparrow 2s\uparrow}^{(2)}$ Be	B^+
0	−0.000009	−0.000014
1	−0.000645	−0.000887
2	−0.000041	−0.000059
3	−0.000005	−0.000008
⩾4	−0.000001	−0.000001
Total	−0.000701	−0.000969

TABLE IV. The contribution of each relative partial wave to the $1s\uparrow 2s\downarrow$ correlation energy in second order (in a.u.).

l	$\epsilon_{1s\uparrow 2s\downarrow}^{(2)}$ Be	B^+
0	−0.000380	−0.000576
1	−0.001065	−0.001571
2	−0.000108	−0.000167
3	−0.000022	−0.000035
⩾4	−0.000012	−0.000015
Total	−0.001587	−0.002364

C. 2s-2s Correlations

For the $2s$-$2s$ shell we used the same type of trial function (with the same number of parameters) as was employed in the $1s$-$1s$ calculation. Looking at Table V for the $\epsilon_{2s\uparrow 2s\downarrow}^{(2)}(l)$, we see immediately how different the effects in this shell are from those in the $1s$-$1s$ case. The contribution of the $l=1$ partial wave strongly dominates all the other terms, being an order of magnitude larger than the $l=0$ contribution and a factor of six larger than the $l=2$ contribution. The reason for this is easily seen. In the $2s$-$2s$ case, there is a nearby $2p$-$2p$ state which is expected to have a very large mixing with the $2s$-$2s$ state in second-order perturbation theory because of the smallness of the energy denominator associated with it. (Recall that states like $2s$-$2p$ cannot mix because we have an over-all s state). There is no analogous state in the $1s$-$1s$ case (or $1s$-$2s$ case), so the two shells display very great qualitative as well as quantitative differences. If the above interpretation is correct, we would expect the p-wave dominance effect to be much more pronounced in B^+, where the stronger central field should cause the $2s$-$2s$ and $2p$-$2p$ states to be even more nearly degenerate. Clearly, when electron-electron interactions become "com-

TABLE V. The contribution of each relative partial wave to the $2s\uparrow 2s\downarrow$ correlation energy in second order (in a.u.).

l	$\epsilon_{2s\uparrow 2s\downarrow}^{(2)}$ Be	B^+
0	−0.00235	−0.00245
1	−0.02213	−0.03020
2	−0.00382	−0.00449
3	−0.00118	−0.00133
4	−0.00048	−0.00052
5	−0.00022	−0.00024
6	−0.00012	−0.00013
⩾7	−0.00020	−0.00022
Total	−0.03050	−0.03958

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[19] W. R. Conkie, Can. J. Phys. 43, 102 (1965).

TABLE VI. The contribution of each electronic pair to the total second-order correlation energy (in a.u.).

Electronic pair	$\epsilon_{ij}^{(2)}$ Be	B$^+$
$1s\uparrow 1s\downarrow$	−0.04008	−0.04055
$1s\uparrow 2s\uparrow$	−0.00070	−0.00097
$1s\uparrow 2s\downarrow$	−0.00159	−0.00237
$1s\downarrow 2s\uparrow$	−0.00159	−0.00237
$1s\downarrow 2s\downarrow$	−0.00070	−0.00097
$2s\uparrow 2s\downarrow$	−0.03050	−0.03958
Total	−0.07516	−0.08681

pletely negligible" those states would be precisely degenerate if we neglect very small relativistic effects. When we look at B$^+$ in Table V, we find that this is indeed the case. In closing our discussion of the $2s$-$2s$ shell we remark that for $\epsilon_{2s\uparrow 2s\downarrow}^{(2)}(0)$ the subtraction of the $1s$ orbitals gives only a very small effect, changing $\epsilon_{2s\uparrow 2s\downarrow}^{(2)}(0)$ by about 2%.

Table VI summarizes our results for E_2. (Note that by our discussion in Sec. IV. $\epsilon_{1s\uparrow 2s\uparrow}^{(2)}=\epsilon_{1s\downarrow 2s\downarrow}^{(2)}$ and $\epsilon_{1s\uparrow 2s\downarrow}^{(2)}=\epsilon_{1s\downarrow 2s\uparrow}^{(2)}$.) We find the total values

$$E_2(\text{Be})=-0.0752\text{ a.u.},\qquad E_2(\text{B}^+)=-0.0868\text{ a.u.},\tag{50}$$

which is about 80% of the correlation energy. We believe that these are very accurate values of E_2, probably not differing from the exact E_2 by more than one or two in the third significant figure. We should emphasize that these numbers are "exact" in the sense that no approximation other than the use of a finite number of parameters in our trial function has been made in obtaining them.

VI. THE THIRD-ORDER ENERGY

With the function ψ_1 calculated, it is a simple matter to evaluate the third-order energy E_3 via the relation

$$E_3=\langle\psi_1|H_1-E_1|\psi_1\rangle.\tag{51}$$

Using Eq. (18), together with the fact that $\mathcal{S}$ is a projection operator, this expression can be written as a sum of 36 terms of which six have the following typical form:

$$\epsilon_{1s\uparrow 1s\downarrow}^{(3)}=\langle[\chi_{1s\uparrow 1s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)\phi_{2s\uparrow}(\mathbf{r}_3)\phi_{2s\downarrow}(\mathbf{r}_4)]|H_1-E_1|\mathcal{S}[\chi_{1s\uparrow 1s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)\phi_{2s\uparrow}(\mathbf{r}_3)\phi_{2s\downarrow}(\mathbf{r}_4)]\rangle.\tag{52}$$

These terms we will refer to as "diagonal," or direct, terms. The remaining ones, which we call "off-diagonal" terms, have typically the form

$$\epsilon_{1s\uparrow 1s\downarrow;1s\uparrow 2s\downarrow}^{(3)}=\langle[\chi_{1s\uparrow 1s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)\phi_{2s\uparrow}(\mathbf{r}_3)\phi_{2s\downarrow}(\mathbf{r}_4)]|H_1-E_1|\mathcal{S}[\chi_{1s\uparrow 2s\downarrow}(\mathbf{r}_1,\mathbf{r}_4)\phi_{1s\downarrow}(\mathbf{r}_2)\phi_{2s\uparrow}(\mathbf{r}_3)]\rangle.\tag{53}$$

Let us focus our attention on terms of the type of Eq. (52). Among the 12 terms which, because of the action of the operator $\mathcal{S}$, appear in Eq. (52), we first look explicitly at

$$\begin{aligned}\langle\chi_{1s\downarrow 1s\uparrow}(\mathbf{r}_1,\mathbf{r}_2)\phi_{2s\uparrow}(\mathbf{r}_3)\phi_{2s\downarrow}(\mathbf{r}_4)|&\frac{1}{r_{12}}+\frac{1}{r_{13}}+\frac{1}{r_{14}}+\frac{1}{r_{23}}+\frac{1}{r_{24}}+\frac{1}{r_{34}}-\mathcal{V}(\mathbf{r}_1)-\mathcal{V}(\mathbf{r}_2)\\&-\mathcal{V}(\mathbf{r}_3)-\mathcal{V}(\mathbf{r}_4)-E_1|\chi_{1s\uparrow 1s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)\phi_{2s\uparrow}(\mathbf{r}_3)\phi_{2s\downarrow}(\mathbf{r}_4)\rangle.\end{aligned}\tag{54}$$

Performing the integrations on the $\mathbf{r}_3$ and $\mathbf{r}_4$ variables, we get for this term

$$\langle\chi_{1s\uparrow 1s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)|1/r_{12}+2V_{2s}^{d}(\mathbf{r}_1)+2V_{2s}^{d}(\mathbf{r}_2)+V_{2s2s}-\mathcal{V}(\mathbf{r}_1)-\mathcal{V}(\mathbf{r}_2)-2V_{2s2s}-4V_{1s2s}-2V_{\text{ex}}-E_1|\chi_{1s\uparrow 1s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)\rangle,\tag{55}$$

where we have used the fact that

$$\langle\phi_{2s\uparrow}|\mathcal{V}|\phi_{2s\uparrow}\rangle=\langle\phi_{2s\downarrow}|\mathcal{V}|\phi_{2s\downarrow}\rangle=V_{2s2s}+2V_{1s2s}-V_{\text{ex}}.\tag{56}$$

The other nonvanishing terms in Eq. (52) contribute precisely the exchange terms which are necessary to reduce Eq. (52) to the form

$$\epsilon_{1s\uparrow 1s\downarrow}^{(3)}=\langle\chi_{1s\uparrow 1s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)|1/r_{12}-V_{1s\uparrow}(\mathbf{r}_1)-V_{1s\downarrow}(\mathbf{r}_1)-V_{1s\uparrow}(\mathbf{r}_2)-V_{1s\downarrow}(\mathbf{r}_2)-\epsilon_{1s\uparrow 1s\downarrow}^{(1)}|\chi_{1s\uparrow 1s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)\rangle.\tag{57}$$

Note that in obtaining this result we have used the fact that the expectation value of the sum $[r_{34}^{-1}-\mathcal{V}(\mathbf{r}_3)-\mathcal{V}(\mathbf{r}_4)]$ precisely cancels all of E_1 except $\epsilon_{1s\uparrow 1s\downarrow}^{(1)}$. A similar reduction can be carried out for the remaining diagonal terms. Thus, the six terms of the type of Eq. (52) have the form which we would expect if our two-body model discussed above (Eq. 28) were exact. However, there remain terms like the one written in Eq. (53), which prevent this two-body model from being exact beyond the calculation of E_2. Fortunately, it is easily seen by looking at Eq. (53) that the off-diagonal terms make very small contributions to E_3. Because of orthogonality, all one-body operators give no contribution, so that we get from Eq. (53).

$$\begin{aligned}\epsilon_{1s\uparrow 1s\downarrow;1s\uparrow 2s\downarrow}^{(3)}=\langle\chi_{1s\uparrow 1s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)\phi_{2s\uparrow}(\mathbf{r}_3)\phi_{2s\downarrow}(\mathbf{r}_4)|&1/r_{12}+1/r_{13}+1/r_{14}+1/r_{23}\\&+1/r_{24}+1/r_{34}|\mathcal{S}[\chi_{1s\uparrow 2s\downarrow}(\mathbf{r}_1,\mathbf{r}_4)\phi_{1s\downarrow}(\mathbf{r}_2)\phi_{2s\uparrow}(\mathbf{r}_3)]\rangle.\end{aligned}$$

Most of the terms in this inner product vanish, and after a simple calculation one finds

$$\begin{aligned}\epsilon_{1s\uparrow 1s\downarrow;1s\uparrow 2s\downarrow}{}^{(3)}=&2\langle\chi_{1s\uparrow 1s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)\phi_{2s\downarrow}(\mathbf{r}_4)\,|\,(1/r_{24})\,|\,\chi_{1s\uparrow 2s\downarrow}(\mathbf{r}_1,\mathbf{r}_4)\phi_{1s\downarrow}(\mathbf{r}_2)\rangle\\&-2\langle\chi_{1s\uparrow 1s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)\phi_{2s\downarrow}(\mathbf{r}_4)\,|\,(1/r_{24})\,|\,\chi_{1s\uparrow 2s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)\phi_{1s\downarrow}(\mathbf{r}_4)\rangle\\&-\langle\chi_{1s\uparrow 1s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)\,|\,\chi_{1s\uparrow 2s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)\rangle\langle\phi_{2s\uparrow}(\mathbf{r}_3)\phi_{2s\downarrow}(\mathbf{r}_4)\,|\,(1/r_{34})\,|\,\phi_{2s\uparrow}(\mathbf{r}_3)\phi_{1s\downarrow}(\mathbf{r}_4)\rangle.\end{aligned}\quad(58)$$

Expressions analogous to this one are readily obtained for all off-diagonal terms. Clearly, these terms are small compared to the direct terms, since they all involve expectation values of operators between orthogonal functions. We have made estimates of typical terms of the off-diagonal type and found that they are more than an order of magnitude smaller than the diagonal ones. On the basis of these estimates we consider it unlikely that the off-diagonal terms contribute more than 0.001 a.u. to the correlation energy, and in fact they probably contribute less than this amount. Therefore we will neglect them in what follows. It should be mentioned that with functions of the type we have used in calculating the χ_{ij}, it is possible, although tedious, to evaluate the off-diagonal contributions explicitly.

Thus, to obtain E_3, we need only evaluate inner products of the type written in Eq. (57). These are not diagonal with respect to the various partial waves (because of the presence of $r_{12}{}^{-1}$) and therefore the evaluation of the $\epsilon_{ij}{}^{(3)}$ is more complicated than was the calculation of the $\epsilon_{ij}{}^{(2)}$. However, this complication is an inessential one, and using the results of our calculation for the χ_{ij} we obtain the results listed in Table VII for the $\epsilon_{ij}{}^{(3)}$. Adding the six $\epsilon_{ij}{}^{(3)}$ together, we get

$$\begin{aligned}E_3(\mathrm{Be})&=-0.01029\text{ a.u.},\\E_3(\mathrm{B}^+)&=-0.01337\text{ a.u.}.\end{aligned}\quad(59)$$

In looking at the results displayed in Table VII, one is struck by the fact that $\epsilon_{2s\uparrow 2s\downarrow}{}^{(3)}$ is much larger than the other $\epsilon_{ij}{}^{(3)}$. Of course, we expect both $\epsilon_{1s\uparrow 1s\downarrow}{}^{(3)}$ and $\epsilon_{2s\uparrow 2s\downarrow}{}^{(3)}$ to be much larger than the contribution from inter-shell terms, but $\epsilon_{2s\uparrow 2s\downarrow}{}^{(3)}$ is more than three times larger than $\epsilon_{1s\uparrow 1s\downarrow}{}^{(3)}$, even though $\epsilon_{1s\uparrow 1s\downarrow}{}^{(2)}$ and $\epsilon_{2s\uparrow 2s\downarrow}{}^{(2)}$ differ only by 25%, with $\epsilon_{1s\uparrow 1s\downarrow}{}^{(2)}$ being even larger than $\epsilon_{2s\uparrow 2s\downarrow}{}^{(2)}$. The reason for this phenomenon is easily seen. The outer pair of 2*s* electrons is loosely bound, and we may expect that the convergence of perturbation theory for such a pair would be rather slow, compared, for example, with the very tightly bound pair of 1*s* electrons. In fact, we see from Tables VI and VII that the convergence of the perturbation expansion for the 1*s*-1*s* correlation energy is very rapid. In a similar manner, one also sees that the inter-shell correlation energies are also converging rapidly. However, it is clear that the results for $E_{\text{corr}}{}^{2s\text{-}2s}$, i.e., the 2*s*-2*s* correlation energy, are not converging rapidly, and it would certainly not be surprising if higher-order terms in perturbation theory made significant contributions to $E_{\text{corr}}{}^{2s\text{-}2s}$. We will consider this problem in Sec. VII.

TABLE VII. The contribution of each electronic pair to the total third-order correlation energy (in a.u.).

Electronic pair	$\epsilon_{ij}{}^{(3)}$ Be	B$^+$
$1s\uparrow 1s\downarrow$	−0.00210	−0.00174
$1s\uparrow 2s\uparrow$	−0.00011	−0.00012
$1s\uparrow 2s\downarrow$	−0.00022	−0.00027
$1s\downarrow 2s\uparrow$	−0.00022	−0.00027
$1s\downarrow 2s\downarrow$	−0.00011	−0.00012
$2s\uparrow 2s\downarrow$	−0.00753	−0.01085
Total	−0.01029	−0.01337

VII. HIGHER-ORDER EFFECTS

Our results so far are very satisfactory as far as the 1*s*-shell and inter-shell correlations are concerned. However, for Be the sum of E_2 and E_3 is equal to −0.0855 a.u., which is approximately 0.009 a.u. greater than the experimentally observed correlation energy. For B$^+$, $E_2+E_3=-0.100$ a.u., approximately 0.012 greater than the experimental correlation energy. On the basis of what appears to be a very rapid convergence of the 1*s*-1*s* and inter-shell contributions, we conclude that the discrepancy must be due to higher-order effects of pair correlations, primarily in the 2*s* shell and probably also to three- and four-body correlations. Thus, the question arises of how to describe higher-order effects. The inclusion of three- and four-body effects is beyond the scope of this paper, although, as we have already remarked, with ψ_1 determined exactly, it is possible to evaluate the off-diagonal contributions to E_3, thereby obtaining the lowest-order contribution to the three- and four-body effects.

In order to deal with higher-order effects, we simply move from our equation for ψ_1 to a similar equation for ψ_2 which is readily obtained from Eq. (13b), namely,

$$(H_0-E_0)\psi_2+(H_1-E_1)\psi_1-E_2\psi_0=0.\quad(60)$$

As noted in BJI, this equation can be derived from a variational expression

$$\begin{aligned}F_2[\psi_2{}^t]=\langle\psi_2{}^t|H_0-E_0|\psi_2{}^t\rangle+2\langle\psi_2{}^t|H_1-E_1|\psi_1\rangle\\-2E_2\langle\psi_2{}^t|\psi_0\rangle.\end{aligned}\quad(61)$$

Because we have already calculated ψ_1, it would appear reasonable to construct a function $\psi_2{}^t$ just as we did for $\psi_1{}^t$ and then form $F_2[\psi_2{}^t]$ which will yield ψ_2 upon variation of the parameters in $\psi_2{}^t$. With ψ_2 obtained we then find E_4 and E_5 by using Eqs. (14d) and (14e). Since we have chosen ψ_1 to be orthogonal to ψ_0 and since we are free to make the same choice for ψ_2 [because of the form of Eq. (60)], Eqs. (14d) and (14e) simplify to

$$E_4=-\langle\psi_2|H_0-E_0|\psi_2\rangle-E_2\langle\psi_1|\psi_1\rangle\,, \tag{62}$$

$$E_5=\langle\psi_2|H_1-E_1|\psi_2\rangle-2E_2\langle\psi_1|\psi_2\rangle-E_3\langle\psi_1|\psi_1\rangle\,. \tag{63}$$

Comparing Eqs. (60), (61), and (62) we see that the value taken on by F_2 when $\psi_2{}^t$ is equal to the true ψ_2 is just E_4, apart from a term in $\langle\psi_1|\psi_1\rangle$ which does not depend on ψ_2. Thus, Eq. (61) is a variational principle for E_4, and in fact it is easy to show that since we are dealing with a ground state we actually have a *minimum* principle for E_4.

However, we note that $F_2[\psi_2{}^t]$, because it contains the inner product $\langle\psi_2{}^t|H_1-E_1|\psi_1\rangle$, will not decouple exactly into a set of pair problems as did $F_1[\psi_1{}^t]$. This inner product is exactly of the form of the inner product occuring in the expression for E_3 [Eq. (51)], so since E_3 did not decouple exactly into a sum of $\epsilon_{ij}{}^{(3)}$, the term $\langle\psi_2{}^t|H_1-E_1|\psi_1\rangle$ will also not decouple in this manner. It should be noted that this is not the only reason that decoupling does not occur. Another, slightly more obscure, reason comes from the term $\langle\psi_2{}^t|H_0-E_0|\psi_2{}^t\rangle$. In discussing a similar term in $F_1[\psi_1{}^t]$ we concluded that it did decouple into a set of pair terms. This decoupling depended critically on the fact that the χ_{ij} contained no component of *any* filled Hartree-Fock orbital in ψ_0. However, for $\psi_2{}^t$, we will want to replace the χ_{ij} of Eq. (18) for $\psi_1{}^t$ with χ_{ij}', and although it will still be true, for example, that $\chi_{2s\uparrow2s\downarrow}'$ will contain no components of $\phi_{1s\uparrow}$ or $\phi_{1s\downarrow}$ because of the exclusion principle, nevertheless, components of $\phi_{2s\uparrow}$ and $\phi_{2s\downarrow}$ are no longer excluded because of the form of the equation for ψ_2 as they were in the case of ψ_1. This is again a consequence of the term $(H_1-E_1)\psi_1$ in the equation for ψ_2.

With these difficulties in mind, let us be guided by the physics of the situation. Since our work on E_2 and E_3 has shown that the contribution to the correlation energy from inter-shell correlations is small and is mostly exhausted by ψ_1, we conjecture that the dominant terms in ψ_2 are of the $1s$-$1s$ or $2s$-$2s$ correlation type. Thus we take our trial function $\psi_2{}^t$ to be of the form

$$\begin{aligned}\psi_2{}^t=[1/\surd(12)]\mathcal{S}[\chi_{1s\uparrow1s\downarrow}'(\mathbf{r}_1,\mathbf{r}_2)\phi_{2s\uparrow}(\mathbf{r}_3)\phi_{2s\downarrow}(\mathbf{r}_4)\\ +\phi_{1s\uparrow}(\mathbf{r}_1)\phi_{1s\downarrow}(\mathbf{r}_2)\chi_{2s\uparrow2s\downarrow}'(\mathbf{r}_3,\mathbf{r}_4)\\ +a\chi_{1s\uparrow1s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)\chi_{2s\uparrow2s\downarrow}(\mathbf{r}_3,\mathbf{r}_4)]\,,\end{aligned} \tag{64}$$

where $\chi_{1s\uparrow1s\downarrow}'$ and $\chi_{2s\uparrow2s\downarrow}'$ contain a large number of parameters to be varied, and a is also a variational parameter. The functions $\chi_{1s\uparrow1s\downarrow}$ and $\chi_{2s\uparrow2s\downarrow}$ are given in Sec. V. Note that in Eq. (64), because of the operator $\mathcal{S}$, $\chi_{2s\uparrow2s\downarrow}'$ can be taken to contain no components of $\phi_{1s\uparrow}$ on $\phi_{1s\downarrow}$. A similar comment applies to $\chi_{1s\uparrow1s\downarrow}'$.

Now, a term involving $\chi_{1s\uparrow1s\downarrow}'$ (or $\chi_{2s\uparrow2s\downarrow}'$) can be thought as arising in perturbation theory from two successive interactions between the $1s$ (or $2s$) electrons. Our assumption concerning the form of $\psi_2{}^t$ is essentially that terms in which there are two successive inter-shell interactions between the same electrons are unimportant. However, there is another type of term to be considered in second order, namely, an interaction within one pair followed by an interaction within a different pair. Situations in which the two pairs have an element in common correspond, roughly speaking, to triple correlations in which one electron is in a different shell than the other two. Contributions of this type are expected to be small compared to those coming from terms in which there are successive interactions between two electrons in the same shell. But in an atom with more than three electrons, there exists one more possibility, namely, an interaction within a pair of electrons followed by an interaction within another pair having no element in common with the first. Terms like this correspond to *disconnected* diagrams in perturbation theory. An example of this case is an interaction between the $1s$ electrons followed by an interaction between the $2s$ electrons. There are two other possibilities corresponding to inter-shell pairs which, because of the smallness of inter-shell effects, one expects to be negligible. Making a reasonably simple model of correlations, we assume that a term representing two independent correlations in different shells should arise in $\psi_2{}^t$ through a term proportional to the product $\chi_{1s\uparrow1s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)\times\chi_{2s\uparrow2s\downarrow}(\mathbf{r}_3,\mathbf{r}_4)$ of the appropriate first-order correlation functions. This explains the appearance of the last term on the right-hand side of Eq. (64).

If we now insert our trial function (64) into the minimum principle (61) for E_4, we get

$$F_2[\psi_2{}^t]=A+2B-2E_2C\,, \tag{65a}$$

where we have defined

$$A=\langle\psi_2{}^t|H_0-E_0|\psi_2{}^t\rangle\,, \tag{65b}$$

$$B=\langle\psi_2{}^t|H_1-E_1|\psi_1\rangle\,, \tag{65c}$$

$$C=\langle\psi_2{}^t|\psi_0\rangle\,. \tag{65d}$$

The discussion of the term C is trivial. Since we may choose $\langle\psi_2|\psi_0\rangle=0$, we will consider our trial function $\psi_2{}^t$ to be orthogonal to ψ_0, or in terms of the functions $\chi_{1s\uparrow1s\downarrow}'$ and $\chi_{2s\uparrow2s\downarrow}'$, we will constrain them to satisfy

$$\langle\phi_{1s\uparrow}\phi_{1s\downarrow}|\chi_{1s\uparrow1s\downarrow}'\rangle=0 \tag{66a}$$

and

$$\langle\phi_{2s\uparrow}\phi_{2s\downarrow}|\chi_{2s\uparrow2s\downarrow}'\rangle=0\,. \tag{66b}$$

Thus the term C enters essentially as a Lagrange multiplier in our problem.

The term A is also straightforward. It breaks up into a simple sum of three terms. There will be no interference between the second-order correlation function terms and the term in $\chi_{1s\uparrow1s\downarrow}\chi_{2s\uparrow2s\downarrow}$ because both $\chi_{1s\uparrow1s\downarrow}$ and $\chi_{2s\uparrow2s\downarrow}$ are orthogonal to *all* Hartree-Fock orbitals (this is also why the term in $\chi_{1s\uparrow1s\downarrow}\chi_{2s\uparrow2s\downarrow}$ does not contribute to C.) There will be no interference between the two second-order correlation functions since all but two terms in the overlap expression vanish because $\langle\phi_{1s}|\phi_{2s}\rangle=0$ and the remaining two terms vanish because of the action of $H_0-\epsilon_0$. Thus, in a fairly straightforward manner we get

$$A=\langle\chi_{1s\uparrow1s\downarrow}'|H_{\mathrm{HF}}(\mathbf{r})+H_{\mathrm{HF}}(\mathbf{r}')-2\epsilon_{1s}|\chi_{1s\uparrow1s\downarrow}'\rangle+\langle\chi_{2s\uparrow2s\downarrow}'|H_{\mathrm{HF}}(\mathbf{r})+H_{\mathrm{HF}}(\mathbf{r}')-2\epsilon_{2s}|\chi_{2s\uparrow2s\downarrow}'\rangle$$
$$+a^2\langle\chi_{1s\uparrow1s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)\chi_{2s\uparrow2s\downarrow}(\mathbf{r}_3,\mathbf{r}_4)|H_0-E_0|\mathcal{S}[\chi_{1s\uparrow1s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)\chi_{2s\uparrow2s\downarrow}(\mathbf{r}_3,\mathbf{r}_4)]\rangle.\quad(67)$$

The term B poses the only significant problem in the evaluation of $F_2[\psi_2{}^t]$. On the right-hand side of the inner product [Eq. (65b)] ψ_1 is the sum of six first-order pair-correlation terms, and on the left-hand side we have a sum of three terms given by Eq. (64). The reduction of this expression will involve the neglect of certain terms, and therefore, since we neglect them in the variational principle (i.e., a functional), we are on less firm ground than when we neglect terms in a scalar like E_3. However, the 12 terms involving overlaps between inner-shell functions like $\chi_{1s\uparrow1s\downarrow}'$, $\chi_{1s\uparrow1s\downarrow}$, etc., and the inter-shell functions $\chi_{1s\uparrow2s\downarrow}$, etc., are expected to be extremely small, so that neglecting them is probably not a serious error. Thus we are left with six terms in B which should be considered carefully. The two direct terms between the inner-shell correlation functions reduce to

$$\langle\chi_{1s\uparrow1s\downarrow}'(\mathbf{r}_1,\mathbf{r}_2)|(1/r_{12})-V_{1s\uparrow}(\mathbf{r}_1)-V_{1s\downarrow}(\mathbf{r}_1)-V_{1s\uparrow}(\mathbf{r}_2)-V_{1s\downarrow}(\mathbf{r}_2)-\epsilon_{1s\uparrow1s\downarrow}{}^{(1)}|\chi_{1s\uparrow1s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)\rangle\quad(68\text{a})$$

and

$$\langle\chi_{2s\uparrow2s\downarrow}'(\mathbf{r}_3,\mathbf{r}_4)|(1/r_{34})-V_{2s\uparrow}(\mathbf{r}_3)-V_{2s\downarrow}(\mathbf{r}_3)-V_{2s\uparrow}(\mathbf{r}_4)-V_{2s\downarrow}(\mathbf{r}_4)-\epsilon_{2s\uparrow2s\downarrow}{}^{(1)}|\chi_{2s\uparrow2s\downarrow}(\mathbf{r}_3,\mathbf{r}_4)\rangle\quad(68\text{b})$$

after a simple calculation completely analogous to the evaluation of similar ("diagonal") terms in E_3.

Next we investigate the contributions involving overlaps between the two different inner-shell terms. These are

$$\langle\phi_{1s\uparrow}(\mathbf{r}_1)\phi_{1s\downarrow}(\mathbf{r}_2)\chi_{2s\uparrow2s\downarrow}'(\mathbf{r}_3,\mathbf{r}_4)|(1/r_{12})|\mathcal{S}[\chi_{1s\uparrow1s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)\phi_{2s\uparrow}(\mathbf{r}_3)\phi_{2s\downarrow}(\mathbf{r}_4)]\rangle\quad(69\text{a})$$

and

$$\langle\chi_{1s\uparrow1s\downarrow}'(\mathbf{r}_1,\mathbf{r}_2)\phi_{2s\uparrow}(\mathbf{r}_3)\phi_{2s\downarrow}(\mathbf{r}_4)|(1/r_{34})|\mathcal{S}[\phi_{1s\uparrow}(\mathbf{r}_1)\phi_{1s\downarrow}(\mathbf{r}_2)\chi_{2s\uparrow2s\downarrow}(\mathbf{r}_3,\mathbf{r}_4)]\rangle.\quad(69\text{b})$$

The two terms contributing to each of these expressions which do not involve overlaps between different shells are identically zero because of the constraint equations, Eqs. (66a) and (66b). Again, the remaining terms involve overlap integrals between different shells which we neglect. We note that except for one part of Eq. (69a) and also of Eq. (69b) which is very much smaller (by probably two orders of magnitude) than a typical term of B, the remaining terms which are discarded contribute only to the relative s-wave part of $\chi_{1s\uparrow1s\downarrow}'$ and $\chi_{2s\uparrow2s\downarrow}'$. We expect the s-wave contribution from $\chi_{2s\uparrow2s\downarrow}'$ to be very small by analogy with the s-wave contribution from $\chi_{2s\uparrow2s\downarrow}$ (see Table V), so that errors in this partial wave will be relatively unimportant.

Finally, the last contributions to B will come from the overlap of the term in $\chi_{1s\uparrow1s\downarrow}\chi_{2s\uparrow2s\downarrow}$ with the first-order, inner-shell correlation terms in ψ_1. These terms are

$$a\langle\chi_{1s\uparrow1s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)\chi_{2s\uparrow2s\downarrow}(\mathbf{r}_3,\mathbf{r}_4)|H_1-E_1|\mathcal{S}[\chi_{1s\uparrow1s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)\phi_{2s\uparrow}(\mathbf{r}_3)\phi_{2s\downarrow}(\mathbf{r}_4)]\quad(70\text{a})$$

and

$$a\langle\chi_{1s\uparrow1s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)\chi_{2s\uparrow2s\downarrow}(\mathbf{r}_3,\mathbf{r}_4)|H_1-E_1|\mathcal{S}[\phi_{1s\uparrow}(\mathbf{r}_1)\phi_{1s\downarrow}(\mathbf{r}_2)\chi_{2s\uparrow2s\downarrow}(\mathbf{r}_3,\mathbf{r}_4)]\rangle,\quad(70\text{b})$$

and they involve only functions which are not varied.

Combining the results expressed in Eqs. (68a), (68b), (70a), and (70b), we get for B

$$B=\langle\chi_{1s\uparrow1s\downarrow}'|(1/r_{12})-V_{1s\uparrow}(\mathbf{r}_1)-V_{1s\downarrow}(\mathbf{r}_1)-V_{1s\uparrow}(\mathbf{r}_2)-V_{1s\downarrow}(\mathbf{r}_2)-\epsilon_{1s\uparrow1s\downarrow}{}^{(1)}|\chi_{1s\uparrow1s\downarrow}\rangle$$
$$+\langle\chi_{2s\uparrow2s\downarrow}'|(1/r_{34})-V_{2s\uparrow}(\mathbf{r}_3)-V_{2s\downarrow}(\mathbf{r}_3)-V_{2s\uparrow}(\mathbf{r}_4)-V_{2s\downarrow}(\mathbf{r}_4)-\epsilon_{2s\uparrow2s\downarrow}{}^{(1)}|\chi_{2s\uparrow2s\downarrow}\rangle$$
$$+a\langle\chi_{1s\uparrow1s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)\chi_{2s\uparrow2s\downarrow}(\mathbf{r}_3,\mathbf{r}_4)|H_1-E_1|\mathcal{S}[\phi_{1s\uparrow}(\mathbf{r}_1)\phi_{1s\downarrow}(\mathbf{r}_2)\chi_{2s\uparrow2s\downarrow}(\mathbf{r}_3,\mathbf{r}_4)]\rangle$$
$$+a\langle\chi_{1s\uparrow1s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)\chi_{2s\uparrow2s\downarrow}(\mathbf{r}_3,\mathbf{r}_4)|H_1-E_1|\mathcal{S}[\chi_{1s\uparrow1s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)\phi_{2s\uparrow}(\mathbf{r}_3)\phi_{2s\downarrow}(\mathbf{r}_4)]\rangle.\quad(71)$$

Following Eq. (65a), we now combine Eq. (67) for A with Eq. (71) for B to obtain $F_2[\psi_2{}^t]$. We constrain $\chi_{1s\uparrow1s\downarrow}'$ and $\chi_{2s\uparrow2s\downarrow}'$ according to Eqs. (66a) and (66b) and vary $F_2[\psi_2{}^t]$ with respect to $\chi_{1s\uparrow1s\downarrow}'$, $\chi_{2s\uparrow2s\downarrow}'$, and a, so that we obtain the relations

$$[H_{\mathrm{HF}}(\mathbf{r}_1)+H_{\mathrm{HF}}(\mathbf{r}_2)-2\epsilon_{1s}]\chi_{1s\uparrow1s\downarrow}'(\mathbf{r}_1,\mathbf{r}_2)$$
$$+[(1/r_{12})-V_{1s\uparrow}(\mathbf{r}_1)-V_{1s\downarrow}(\mathbf{r}_1)-V_{1s\uparrow}(\mathbf{r}_2)-V_{1s\downarrow}(\mathbf{r}_2)-\epsilon_{1s\uparrow1s\downarrow}{}^{(1)}]\chi_{1s\uparrow1s\downarrow}=0,\quad(72\text{a})$$

$$[H_{\mathrm{HF}}(\mathbf{r}_3)+H_{\mathrm{HF}}(\mathbf{r}_4)-2\epsilon_{2s}]\chi_{2s\uparrow2s\downarrow}'+[(1/r_{34})-V_{2s\uparrow}(\mathbf{r}_3)-V_{2s\downarrow}(\mathbf{r}_3)-V_{2s\uparrow}(\mathbf{r}_4)-V_{2s\downarrow}(\mathbf{r}_4)-\epsilon_{2s\uparrow2s\downarrow}{}^{(1)}]\chi_{2s\uparrow2s\downarrow}=0,\quad(72\text{b})$$

$$a\langle\chi_{1s\uparrow1s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)\chi_{2s\uparrow2s\downarrow}(\mathbf{r}_3,\mathbf{r}_4)|H_0-E_0|\mathcal{S}[\chi_{1s\uparrow1s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)\chi_{2s\uparrow2s\downarrow}(\mathbf{r}_3,\mathbf{r}_4)]\rangle$$
$$+\langle\chi_{1s\uparrow1s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)\chi_{2s\uparrow2s\downarrow}(\mathbf{r}_3,\mathbf{r}_4)|H_1-E_1|\mathcal{S}[\phi_{1s\uparrow}(\mathbf{r}_1)\phi_{1s\downarrow}(\mathbf{r}_2)\chi_{2s\uparrow2s\downarrow}(\mathbf{r}_3,\mathbf{r}_4)]\rangle$$
$$+\langle\chi_{1s\uparrow1s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)\chi_{2s\uparrow2s\downarrow}(\mathbf{r}_3,\mathbf{r}_4)|H_1-E_1)|\mathcal{S}[\chi_{1s\uparrow1s\downarrow}(\mathbf{r}_1,\mathbf{r}_2)\phi_{2s\uparrow}(\mathbf{r}_3)\phi_{2s\downarrow}(\mathbf{r}_4)]\rangle.\quad(72\text{c})$$

We make our usual approximation concerning the neglect of integrals involving overlaps between different shells. Hence, we can easily reduce Eq. (72c) to the form

$$-2a[\epsilon_{1s\uparrow1s\downarrow}^{(2)}\langle\chi_{1s\uparrow1s\downarrow}|\chi_{2s\uparrow2s\downarrow}\rangle+\epsilon_{2s\uparrow2s\downarrow}^{(2)}\langle\chi_{1s\uparrow1s\downarrow}|\chi_{1s\uparrow1s\downarrow}\rangle]$$
$$+\sqrt{2}[\epsilon_{1s\uparrow1s\downarrow}^{(2)}\langle\chi_{2s\uparrow2s\downarrow}|\chi_{2s\uparrow2s\downarrow}\rangle+\epsilon_{2s\uparrow2s\downarrow}^{(2)}\langle\chi_{1s\uparrow1s\downarrow}|\chi_{1s\uparrow1s\downarrow}\rangle]=0,$$

from which we conclude that $a=2^{-1/2}$.

Equations (72a) and (72b) are just the equations which we would get from a model Hamiltonian of the form of Eq. (28). They can be solved by the methods of BJI, which we have already used in solving for the first-order correlation functions. If we insert the solutions of Eqs. (72a) and (72b), along with the value $a=2^{-1/2}$, into Eq. (64), $\psi_2{}^t$ becomes the true second-order wave function which we will use in calculating E_4 and E_5. We thus see that when we come to second order in wave-function perturbation theory, our wave function is not strictly speaking what one would obtain from a simple-minded solution of the two-body model Hamiltonians of the type of Eq. (28). However, the terms which must be added are of a very simple and intuitively reasonable kind $(\chi_{1s\uparrow1s\downarrow}\chi_{2s\uparrow2s\downarrow})$ and they can also be obtained in a straightforward manner from the perturbation solutions to the pair equations. Another way of looking at these results is, of course, by examining ordinary perturbation theory in terms of sums over intermediate states and picking out subsums which can be argued to dominate in various orders. This approach lends strong support to the approximations made in this section.

Having determined $\chi_{1s\uparrow1s\downarrow}'$ and $\chi_{2s\uparrow2s\downarrow}'$ by the variational method (we used trial functions of the same functional form as we employed in obtaining $\chi_{1s\uparrow1s\downarrow}$ and $\chi_{2s\uparrow2s\downarrow}$), we now evaluate E_4 and E_5. The first term in E_4 [see Eq. (62)] is $-\langle\psi_2|H_0-E_0|\psi_2\rangle$. In the same way in which we arrived at Eq. (67) for A, we find

$$-\langle\psi_2|H_0-E_0|\psi_2\rangle=-\langle\chi_{1s\uparrow1s\downarrow}'|H_{\mathrm{HF}}(\mathbf{r}_1)+H_{\mathrm{HF}}(\mathbf{r}_2)-2\epsilon_{1s}|\chi_{1s\uparrow1s\downarrow}'\rangle-\langle\chi_{2s\uparrow2s\downarrow}'|H_{\mathrm{HF}}(\mathbf{r}_3)+H_{\mathrm{HF}}(\mathbf{r}_4)-2\epsilon_{2s}|\chi_{2s\uparrow2s\downarrow}'\rangle$$
$$+\epsilon_{1s\uparrow1s\downarrow}^{(2)}\langle\chi_{2s\uparrow2s\downarrow}|\chi_{2s\uparrow2s\downarrow}\rangle+\epsilon_{2s\uparrow2s\downarrow}^{(2)}\langle\chi_{1s\uparrow1s\downarrow}|\chi_{1s\uparrow1s\downarrow}\rangle,$$

where we have reduced the term involving $\chi_{1s\uparrow1s\downarrow}\chi_{2s\uparrow2s\downarrow}$ in a manner similar to that used in solving Eq. (72c) for a. The second term in E_4 is $-E_2\langle\psi_1|\psi_1\rangle$, which we write as

$$-E_2\langle\psi_1|\psi_1\rangle=-(\epsilon_{1s\uparrow1s\downarrow}^{(2)}+\epsilon_{2s\uparrow2s\downarrow}^{(2)})[\langle\chi_{1s\uparrow1s\downarrow}|\chi_{1s\uparrow1s\downarrow}\rangle+\langle\chi_{2s\uparrow2s\downarrow}|\chi_{2s\uparrow2s\downarrow}\rangle]+\text{remainder}.$$

The terms appearing in the remainder are readily evaluated and are found to be very small compared with the term written out in detail. We neglect these terms since they are analogous to inter-shell terms and terms involving overlaps between different shells, which we have always neglected. An an example, for Be the omitted terms contribute 0.0002 a.u. to $E_2\langle\psi_1|\psi_1\rangle$, while the terms retained contribute 0.0021 a.u. The size of the neglected terms gives a rough idea of the order of magnitude of the overlap effects which we have neglected and which correspond in part to triple and quadruple correlations and in part to pair correlations between electrons in different shells. We see that the term $\chi_{1s\uparrow1s\downarrow}\chi_{2s\uparrow2s\downarrow}$ in ψ_2 has the effect of removing terms like $\epsilon_{1s\uparrow1s\downarrow}^{(2)}\langle\chi_{2s\uparrow2s\downarrow}|\chi_{2s\uparrow2s\downarrow}\rangle$ from the final expression for E_4, so that finally we have

$$E_4=\sum_{i,j}{}'\,\epsilon_{ij}^{(4)}, \tag{73a}$$

with

$$\epsilon_{ij}^{(4)}=-\langle\chi_{ij}'|H_{\mathrm{HF}}(\mathbf{r})+H_{\mathrm{HF}}(\mathbf{r}')-\epsilon_i-\epsilon_j|\chi_{ij}'\rangle-\epsilon_{ij}^{(2)}\langle\chi_{ij}|\chi_{ij}\rangle, \tag{73b}$$

which is just what we would have obtained if we had calculated the eigenvalue of the appropriate reduced Hamiltonian of the type of Eq. (28) through fourth order in energy. Entirely similar considerations show that, with the omission of terms of the type which we have been neglecting, E_5 may be written in a similar manner;

$$E_5=\sum_{i,j}{}'\,\epsilon_{ij}^{(5)}, \tag{74a}$$

with

$$\epsilon_{ij}^{(5)}=\langle\chi_{ij}'|(1/|\mathbf{r}-\mathbf{r}'|)-V_i(\mathbf{r})-V_j(\mathbf{r})-V_i(\mathbf{r}')-V_j(\mathbf{r}')-\epsilon_{ij}^{(1)}|\chi_{ij}'\rangle-2\epsilon_{ij}^{(2)}\langle\chi_{ij}|\chi_{ij}'\rangle-\epsilon_{ij}^{(3)}\langle\chi_{ij}|\chi_{ij}\rangle. \tag{74b}$$

Evaluating $\epsilon_{ij}^{(4)}$ and $\epsilon_{ij}^{(5)}$ for the inner-shell pairs which are of interest, we find for Be:

$\epsilon_{1s\uparrow1s\downarrow}^{(4)}=-0.00026$ a.u., $\epsilon_{2s\uparrow2s\downarrow}^{(4)}=-0.00478$ a.u.,
$\epsilon_{1s\uparrow1s\downarrow}^{(5)}=-0.00003$ a.u., $\epsilon_{2s\uparrow2s\downarrow}^{(5)}=-0.00201$ a.u..

For B$^+$ we get

$\epsilon_{1s\uparrow1s\downarrow}^{(4)}=-0.00018$ a.u., $\epsilon_{2s\uparrow2s\downarrow}^{(4)}=-0.00615$ a.u.,
$\epsilon_{1s\uparrow1s\downarrow}^{(5)}=-0.00002$ a.u., $\epsilon_{2s\uparrow2s\downarrow}^{(5)}=-0.00297$ a.u..

Table VIII summarizes the contributions of various orders of perturbation theory to the quantities $E_{\mathrm{corr}}{}^{1s\text{-}1s}$, $E_{\mathrm{corr}}{}^{1s\text{-}2s}$, and $E_{\mathrm{corr}}{}^{2s\text{-}2s}$ for Be, while Table IX lists the same quantities for B$^+$.

In calculating these results it is found that the s-wave contribution to $\epsilon_{2s\uparrow2s\downarrow}^{(4)}$ is smaller than the dominant p-wave term by about a factor of 20 or 30. Thus, even errors in the s wave of the order or magnitude of 50% are unimportant for our purposes. This

TABLE VIII. The contributions to $E_{\text{corr}}^{1s\text{-}1s}$, $E_{\text{corr}}^{1s\text{-}2s}$, and $E_{\text{corr}}^{2s\text{-}2s}$ from each order of perturbation theory for Be (in a.u.).

Order of perturbation theory	1*s*-1*s*	1*s*-2*s*	2*s*-2*s*
Second	−0.04008	−0.00458	−0.03050
Third	−0.00210	−0.00066	−0.00753
Fourth	−0.00026	···	−0.00478
Fifth	−0.00003	···	−0.00201
Total	−0.04247	−0.00524	−0.04482

TABLE IX. The contributions to $E_{\text{corr}}^{1s\text{-}1s}$, $E_{\text{corr}}^{1s\text{-}2s}$, and $E_{\text{corr}}^{2s\text{-}2s}$ from each order of perturbation theory for B^+ (in a.u.).

Order of perturbation theory	1*s*-1*s*	1*s*-2*s*	2*s*-2*s*
Second	−0.04055	−0.00668	−0.03958
Third	−0.00174	−0.00078	−0.01085
Fourth	−0.00018	···	−0.00615
Fifth	−0.00001	···	−0.00297
Total	−0.04248	−0.00746	−0.05955

strengthens the arguments made in reducing the quantity $F_2[\psi_2^t]$. It is also clear that the contributions of the 1*s* shell to E_4 and E_5 are insignificant. Thus for the accuracy needed we could have neglected the function $\chi_{1s\uparrow 1s\downarrow}'$ entirely, so that many of our overlap problems would not have existed. We have retained it to illustrate the typical difficulties which one would encounter in a more general situation. It is interesting to see the very significant effect of the term $\chi_{1s\uparrow 1s\downarrow}\chi_{2s\uparrow 2s\downarrow}$ in the trial function ψ_2^t. If we had omitted this term, we would have found values of E_4 20 to 30% smaller in magnitude than the results given in Tables VIII and IX. The effect would have been even more drastic in E_5, where the magnitude of the results presented in Tables VIII and IX would have been reduced by 35 to 50%. Had we omitted this term we would have found for the total correlation energy $E_{\text{corr}}^{\text{total}}(\text{Be}) = -0.0897$ a.u. and $E_{\text{corr}}^{\text{total}}(\text{B}^+) = -0.1071$ a.u., instead of the results given in Tables VIII and IX. These tables also illustrate the slow rate of convergence of the 2*s*-2*s* correlation energy. We see that the final values of $E_{\text{corr}}^{2s\text{-}2s}$ for Be and B^+ will probably be 0.001 to 0.002 a.u. lower than the values given by the tables. We did not pursue our calculation to higher orders, partly because the effects of three- and four-particle correlations will begin to compete seriously with pair correlations and partly because problems relating to loss of precision become more significant in solving for ψ_3.

VIII. CONCLUSIONS

Summarizing our final results in Be, we have

$$E_{\text{corr}}^{1s\text{-}1s}(\text{Be}) = -0.0425 \text{ a.u.},$$
$$E_{\text{corr}}^{1s\text{-}2s}(\text{Be}) = -0.0052 \text{ a.u.},$$
$$E_{\text{corr}}^{2s\text{-}2s}(\text{Be}) = -0.0448 \text{ a.u.},$$
$$E_{\text{corr}}^{\text{total}}(\text{Be}) = -0.0925 \text{ a.u.},$$

while for B^+ we have

$$E_{\text{corr}}^{1s\text{-}1s}(\text{B}^+) = -0.0425 \text{ a.u.},$$
$$E_{\text{corr}}^{1s\text{-}2s}(\text{B}^+) = -0.0075 \text{ a.u.},$$
$$E_{\text{corr}}^{2s\text{-}2s}(\text{B}^+) = -0.0596 \text{ a.u.},$$
$$E_{\text{corr}}^{\text{total}}(\text{B}^+) = -0.1096 \text{ a.u.},$$

Thus, our final results in both Be and B^+ are in good agreement with the experimental results:

$$E_{\text{corr}}^{\text{exp}}(\text{Be}) = -0.0944 \text{ a.u.},\qquad E_{\text{corr}}^{\text{exp}}(\text{B}^+) = -0.1116 \text{ a.u.}$$

There have been several investigations of the binding energy of Be in the past few years, and it is of interest to compare our results with those of other authors. Kelly[6] has used the Bethe-Goldstone version of perturbation theory and has obtained results which are in very close agreement with ours. He finds

$$E_{\text{corr}}^{1s\text{-}1s}(\text{Be}) = -0.0421 \text{ a.u.},$$
$$E_{\text{corr}}^{1s\text{-}2s}(\text{Be}) = -0.0050 \text{ a.u.},$$
$$E_{\text{corr}}^{2s\text{-}2s}(\text{Be}) = -0.0449 \text{ a.u.},$$
$$E_{\text{corr}}^{\text{total}}(\text{Be}) = -0.0920 \text{ a.u.}$$

We see that our result for the 1*s*-1*s* contribution is 1% lower than Kelly's, and for the 1*s*-2*s* contribution our result is 4% lower. The difference between our figures and those of Kelly in both these cases is about the same as the estimated numerical uncertainty in our results. In our case, one can see explicitly the very rapid convergence of perturbation theory which makes it seem very unlikely that the 1*s*-1*s* and 1*s*-2*s* correlation energies which we have calculated differ from the actual energies by more than the above stated uncertainties. In particular the results of Sinanoglu *et al.*,[7] $E_{\text{corr}}^{1s\text{-}1s} = -0.0440$ a.u. and $E_{\text{corr}}^{1s\text{-}2s} = -0.0065$ a.u., definitely disagree with our results. Sinanoglu's result for the 1*s*-1*s* shell is rather close to what we would have obtained if we had not removed the components of ϕ_{2s} from our trial function for $\chi_{1s\uparrow 1s\downarrow}$. In the case of the 2*s*-2*s* energy, Kelly's result and ours are essentially identical, although we can see from Table VIII that if we carried out pair model to higher orders we would probably obtain a result about 0.001 to 0.002 a.u. *lower* than the result we have found. Again, we are in disagreement with Sinanoglu, who finds $E_{\text{corr}}^{2s\text{-}2s} = -0.0438$ a.u. a result 2% *higher* than ours.

Basically, we feel that the close agreement between our work and that of Kelly, which are after all just two different approaches to perturbation theory, tends to suggest that the results presented here reflect faithfully the content of the lowest orders of perturbation theory. Furthermore, the rate of convergence of perturbation theory seems to be quite rapid for the 1*s*-1*s* and 1*s*-2*s* correlation energies, so that for them contributions from higher orders are in all probability not significant. The main uncertaintly in our results comes from the slow convergence of the 2*s*-2*s* contributions, but even here the indications are quite good that higher orders will contribute no more than -0.002 a.u. to our result.

Regarding B^+, there does not seem to be any theoretical work on this ion. We have included it here to point up some of the more interesting features of the four-body system. We see that the $1s$-$2s$ correlation energy increases by about 50% as we go from Be to B^+, which illustrates the physically reasonable fact that the intershell correlation energy depends critically on the distance between the shells in question. It is for this reason that we expect intershell effects to be much more important in systems with more than four electrons, where there in strong spacial overlap between the $2s$ and $2p$ shells. Also in B^+ we see a very large increase in the $2s$-$2s$ contribution to the correlation energy. This occurs because of the fact that the $2p$ state of the Hartree-Fock Hamiltonian gets progressively closer in energy to the $2s$ state as the central field becomes larger and larger, thus contributing smaller and smaller energy denominators in the sums over intermediates states occuring in perturbation theory. Also of interest is the great stability of the $1s$-$1s$ correlation energy, which is to be expected from similar studies of the two-body systems He, Li^+, Be^{++}, B^{3+}, etc.[20]

In closing this discussion, we emphasize again that the results obtained can be viewed in lowest order of perturbation theory as coming out of a simple two-body generalization of Hartree-Fock theory [see Eq. (28)], where each pair of particle is thought of as interacting though the true Coulomb potential, but also seeing an average potential due to the other electrons which remain in this approximation in their unperturbed Hartree-Fock orbitals. However, if we go higher in perturbation theory, correlations within disconnected pairs of electrons modify the perturbation wave functions in a significant way, although it is still possible to take these effects into account in a straightforward manner by using the pair-correlation functions already calculated in the two-body Hartree-Fock model. The effect of this change in the character of the *wave function* is just to give an expression for the perturbation theory *energy* which is precisely what one would obtain by applying the two-body model in a simple-minded way to compute the total energy.

We believe that the method described here can be extended in a trivial way to the lithium atom. There will be coupling between singlet and triplet parts of the two-body correlation functions in this case, but this is a minor complication. In calculating the correlation energy in lithium, one will also need analytic solutions to the true Hartree-Fock equations, i.e., solutions in which the $1s\uparrow$ orbital has a different space wave function than the $1s\downarrow$ orbital because the $2s$ shell is not closed. (Thus, $\chi_{1s\uparrow 1s\downarrow}$ will not be a pure singlet function as it was in Be and B^+.) Again, this represents an inessential complication. We believe that one should be able to get extremely accurate results in lithium by going through fifth order in energy. Extending this method into the $2p$ shell (boron, carbon, etc.) will entail some vector-coupling modifications, but, more important, the approximations concerning inter-shell effects ($2s$-$2p$) will have to be examined carefully. A further problem is that of determining the effect of approximate solutions to the Hartree-Fock equation in this method, since the solutions to the true Hartree-Fock equation, involving potentials which are not spherically symmetric, are not readily obtainable, except in very special cases (e.g., closed angular-momentum shells). This is probably the most serious difficulty which will occur in generalizing this method to more complicated systems.

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[20] C. C. J. Roothaan and A. W. Weiss, Rev. Mod. Phys. 32, 194 (1960).