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Correlation Effects in Atoms. II. Angular Correlations between Electrons*

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The variational-perturbation method is applied to the study of angular correlations between electrons in the helium atom. We compare the relative merits of various basis functions for calculating the correlation energies. Starting from the hydrogenic and Hartree-Fock Hamiltonians as zeroth-order approximations, we have performed detailed numerical calculations on the ground state of helium. Very accurate results are obtained with a set of basis functions intermediate between the Hylleraas and the "configuration-interaction" types of trial functions. The perturbation theory of the $(1s\,2s)^1S_0$ and $(1s\,2s)^3S_1$ states is also investigated.

I. INTRODUCTION

In carrying out variational calculations on the two-electron system, trial functions depending explicitly on the interelectronic separation $u=r_{12}$ have proved by far the most accurate. This type of trial function, proposed first by Hylleraas,[1] has given extremely precise answers[2,3] when used in the context of the Rayleigh-Ritz method for the total energy of the ground state. More recently, it has also been shown[4] that the Hylleraas basis set of trial functions gives very good results in the framework of the variational-perturbation method, starting from a hydrogenic Hamiltonian as zeroth-order approximation.

However, there are certain problems in the study of atomic structure which are not readily answered in the Hylleraas formalism. In this work we will be interested in precisely such a problem, namely, that of determining the distribution of the correlation energy among the various relative partial waves occuring in the wave function of the system. Questions relating to this problem[5]—in particular the rate of convergence of the expansion of the energy in relative partial waves and the difficulties associated with obtaining reliable values for the contribution from relative partial waves with high angular momentum—have been of interest ever since the development of the configuration-interaction approach[6] to the study of many-electron atoms.

Perhaps an even more important consideration concerning the variational-perturbation method, which we shall use throughout this paper, is how to extend variational techniques to many-electron systems. If one elects to proceed via perturbation theory, which strikes us as being the most reasonable approach, then the natural zeroth-order starting point is the Hartree-Fock Hamiltonian and *not* the simple hydrogenic Hamiltonian nor even the Hartree Hamiltonian. These last two Hamiltonians are indeed "simple," because if one chooses them as zeroth-order approximations all the matrix elements which must be computed in variational-perturbation theory involve only straightforward closed-form expressions, even with the Hylleraas basis function. However, when dealing with the Hartree-Fock Hamiltonian, as was done in paper I,[7]

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[1] E. A. Hylleraas, Z. Physik **54**, 347 (1929); **65**, 209 (1930).

[2] C. L. Pekeris, Phys. Rev. **115**, 1216 (1959).

[3] C. Schwartz, Phys. Rev. **128**, 1146 (1962).

[4] C. W. Scherr and R. E. Knight, Phys. Rev. **128**, 2675 (1963); Rev. Mod. Phys. **35**, 436 (1963).

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

[6] See, for example, J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960), Vol. II, Chap. 18.

[7] 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. (8a), the first term should be $-\langle\chi_2|H_0-E_0|\chi_2\rangle$ and in Eq. (9b) the last term should read $-2E_2\langle\chi_2{}^t|\varphi_0\rangle$.

the computation of matrix elements of the nonlocal exchange potentials between basis functions involving increasing powers of the interelectronic coordinate becomes a very arduous problem. Therefore, in order to extend the usefulness of variational-perturbation theory to more complicated systems, it is desireable to look for a more tractable set of basis functions. Ideally, one would like to find a type of trial function intermediate between the Hylleraas form and the configuration-interaction type, thereby retaining the simplicity of the latter but still obtaining sufficiently accurate results. We have thus explored in this work some alternatives to the Hylleraas basis, with particular attention to a basis "intermediate" between the Hylleraas and the configuration-interaction types.

In order to illustrate the main relevant considerations, we present the results of our calculations on three problems. In Sec. II we study the second-order energy of the ground state of helium, starting from a hydrogenic Hamiltonian, and using various forms of the first-order wave function of perturbation theory. Section II is devoted to the calculation of the second- and third-order energies of the $(1s2s)^1S_0$ and $(1s2s)^3S_1$ excited states of helium, again using the interelectronic interaction as a perturbation. Finally, in Sec. III, we calculate the correlation energy in the helium ground state through fifth order in perturbation theory and using the Hartree and the Hartree-Fock Hamiltonians as starting points.

II. SECOND-ORDER ENERGY FOR THE GROUND STATE OF HELIUM

Let us consider the Schrödinger equation for the helium atom:

$$H\Psi=E\Psi\,, \tag{1}$$

where, in atomic units,[8]

$$H=-\tfrac{1}{2}\nabla_1^2-\tfrac{1}{2}\nabla_2^2-2/r_1-2/r_2+1/r_{12}\,. \tag{2}$$

We start from the zeroth-order equation

$$H_0\psi_0=E_0\psi_0\,, \tag{3}$$

where H_0 is the hydrogenic Hamiltonian

$$H_0=-\tfrac{1}{2}\nabla_1^2-\tfrac{1}{2}\nabla_2^2-2/r_1-2/r_2 \tag{4}$$

with the zeroth-order ground-state eigenvalue $E_0=-4.0$ a.u. (atomic units) and the corresponding eigenfunction

$$\psi_0(r_1,r_2)=(8/\pi)e^{-2(r_1+r_2)}\,. \tag{5}$$

The perturbation H_1 is defined as

$$H_1=H-H_0=1/r_{12}\,. \tag{6}$$

If we expand

$$\Psi=\sum_{n=0}^{\infty}\psi_n\,, \tag{7a}$$

and

$$E=\sum_{n=0}^{\infty}E_n\,, \tag{7b}$$

we get, for the first-order wave function ψ_1, the equation

$$(H_0-E_0)\psi_1+(H_1-E_1)\psi_0=0\,, \tag{8}$$

and thus

$$E_1=\langle\psi_0|H_1|\psi_0\rangle\,, \tag{9a}$$

and

$$E_2=\langle\psi_0|H_1-E_1|\psi_1\rangle=-\langle\psi_1|H_0-E_0|\psi_1\rangle\,. \tag{9b}$$

The first-order energy E_1 is readily evaluated with the result $E_1=1.25$ a.u. In order to calculate E_2 we note that Eq. (8) for ψ_1 may be obtained by varying the functional

$$F_1[\psi_1^t]=\langle\psi_1^t|H_0-E_0|\psi_1^t\rangle+2\langle\psi_1^t|H_1-E_1|\psi_0\rangle\,, \tag{10}$$

which, because of the completeness of the eigenfunctions of H_0, gives a *minimum* principle for E_2.

We now turn to our choice of trial function ψ_1^t. As a compromise between the Hylleraas type of basis functions and the configuration-interaction methods, we use a trial function of the form[5]

$$\psi_1^t(\mathbf{r}_1,\mathbf{r}_2)=\sum_{l,m,n}C_{lmn}\psi_{lmn}(\mathbf{r}_1,\mathbf{r}_2)$$

$$\equiv\frac{1}{4\pi}\sum_{l,m,n}C_{lmn}r_>^m r_<^n e^{-\frac{1}{2}\alpha r_>}e^{-\frac{1}{2}\beta r_<}P_l(\cos\theta_{12})\,, \tag{11}$$

where $r_>$ and $r_<$ denote, respectively, the larger and the smaller of r_1 and r_2. As noted by Schwartz,[5] functions of the type (11) are correlated in their radial part and are likely to facilitate a great deal the calculation of higher-l components of E_2. For reasons of convenience, the quantities α and β were both set equal to 4.0. Since the variational expression (10) for E_2 actually decouples into a sequence of minimum principles for each relative partial wave, we can deal with a single partial wave at a time, thereby working with relatively small matrices when solving the system of linear equations which result from Eq. (10).

In performing the variational calculations, we chose two types of trial functions of the general class (11). In case I, negative powers of m in Eq. (11) were allowed in a wave function containing 30 terms (in each partial wave) satisfying $-1\leqslant m+n\leqslant 4$. In case II, no negative powers were allowed in the trial function, and we used a 36-term function (in each partial wave), including all terms satisfying $m+n\leqslant 7$. In both cases we included all contributions coming from partial waves through $l=20$. Asymptotically, one expects[5] for large l that $E_2(l)$, the contribution to E_2 from each partial wave, is given by

$$E_2(l)=-(45/256)l^{-4}\ \text{a.u.}, \tag{12}$$

which would predict, for example, a value of $E_2(10)=-1.76\times10^{-5}$, which is 28% larger in magnitude than

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[8] We neglect the mass-polarization term and use twice the reduced-mass rydberg as unit of energy.

TABLE I. The contribution of the various partial waves to the second-order energy (in a.u.) of the ground state of helium in hydrogenic perturbation theory. The three cases correspond to the three choices of trial function discussed in the text.

l	$E_2(l)$ (case I)	$E_2(l)$ (case II)	$E_2(l)$ (case III)
0	−0.125334	−0.125320	−0.125031
1	−0.026495	−0.026475	−0.025903
2	−0.003906	−0.003893	−0.003531
3	−0.001077	−0.001070	−0.000874
4	−0.000405	−0.000401	−0.000292
5	−0.000183	−0.000182	−0.000118
6	−0.000094	−0.000094	−0.000055
7	−0.000053	−0.000053	−0.000028
8	−0.000032	−0.000032	−0.000015
9	−0.000021	−0.000020	−0.000009
10	−0.000014	−0.000014	−0.000006
$\geqslant 11$	−0.000042	−0.000041	−0.000013
Total	−0.157656	−0.157595	−0.155873

the value $E_2(10)=-1.38\times10^{-5}$ a.u. found in our calculation. For $l=20$ we find $E_2(20)=-0.944\times10^{-6}$ a.u., whereas the asymptotic formula (12) gives $E_2(20)=-1.10\times10^{-6}$ a.u., which is 16% larger in magnitude than our variational result. Thus, as l increases the calculated value of $E_2(l)$ gets slowly closer to the predicted asymptotic value. Notice, however, that the ratios $E_2(l)/E_2(l+1)$ approach much more rapidly their asymptotic value of $[(l+1)/1]^4$. The results through $l=10$ are given in Table I. We also include in this table the contributions of all higher partial waves obtained by actually calculating the terms from $l=11$ to $l=20$ and using the asymptotic form (12) to extrapolate the remainder.[8a]

For comparison we also list in Table I the results of a calculation done with a trial function of the "configuration-interaction" type (case III):

$$\psi_1{}^t(\mathbf{r}_1,\mathbf{r}_2)=\frac{1}{4\pi}\sum_{l,m,n}C_{lmn}(r_1{}^m r_2{}^n+r_1{}^n r_2{}^m)e^{-2(r_1+r_2)}\times P_l(\cos\theta_{12}). \qquad (13)$$

We used 20 terms in each relative partial wave, i.e., all terms such that $m+n\leqslant7$. Table I shows how poor these results are (recall that we have a minimum principle for each partial wave) when compared with those obtained using a trial function given by Eq. (11). This is particularly obvious for the higher partial waves. Nevertheless, these values are more accurate than those obtained by Schwartz[5] using a trial function with 30 parameters. The reason for this fact is that Schwartz insisted on the restriction $m\geqslant l$, $n\geqslant l$ in Eq. (13), which indeed must be satisfied by the *exact* first-order wave function, as may easily be seen by considering the expression for ψ_1 in the form of a sum over the complete set of eigenfunctions belonging to H_0. Thus we have an example of the fact that building a trial function to have some particular property of the exact wave function does not necessarily yield an improved result for the variational energy.

The values of E_2 obtained with the two trial functions of the $(r_>,r_<)$ type are

$$E_2=-0.157656\text{ a.u.}\quad(\text{case I}), \qquad (14a)$$

and

$$E_2=-0.157595\text{ a.u.}\quad(\text{case II}). \qquad (14b)$$

We believe that the bulk of the uncertainty in our results (14a) and (14b) comes from inaccuracies in the relative partial waves with $l\geqslant5$. We note that the values (14a) and (14b) compare favorably with the most accurate calculations of Knight and Scherr,[4] who obtained with a trial function of the Hylleraas type:

$$E_2=-0.157666\text{ a.u.} \qquad (15)$$

Thus the trial function used in case I gives slightly better results than the one employed in case II, although both functions give very satisfactory answers. Of course, the Hylleraas-type function is clearly desirable if extreme accuracy is needed.

We also see in Table I that the results obtained by using a "configuration-mixing" type of trial function [case III, Eq. (13)] are accurate to only about 1%. However, in many cases extreme accuracy in E_2 is not needed, so that a trial function of the form (13) may be quite useful in these circumstances. For example, in calculating the correlation energies of four-electron systems,[9] the contributions arising from pairs of electrons which are not in the same shell are relatively small. Therefore, it is sufficient to calculate these contributions to only a few percent accuracy, so that a trial function of the form (13) is quite satisfactory for such a purpose. This is also illustrated in Sec. III, where we investigate the perturbation theory of the lowest-excited states of helium.

III. THE EXCITED STATES $(1s2s)^1S_0$ AND $(1s2s)^3S_1$

Since we are not working with a ground state, the functional (10) does *not* give a minimum principle for E_2 in the case of the first singlet excited state $(1s2s)^1S_0$. However, it is easy to show that, although there is no over-all minimum principle for E_2, we do have a minimum principle for all partial-wave contributions to E_2 with $l\geqslant1$. In the case of the first excited triplet state $(1s2s)^3S_1$, we recover a minimum principle for E_2

[8a] *Note added in proof.* Dr. C. Schwartz has informed us (private communication) that a more precise result than Eq. (12) is

$$E_2(l)=-(45/256)(l+\tfrac{1}{2})^{-4}[1-(5/4)(l+\tfrac{1}{2})^{-2}+\mathcal{O}(l^{-4})].$$

Using this result, one finds $E_2(5)=-1.84\times10^{-4}$ a.u., $E_2(10)=-1.43\times10^{-5}$ a.u., and $E_2(20)=-0.992\times10^{-6}$ a.u., in very good agreement with the calculations reported in the text. Using this asymptotic formula, we estimate that the total error made in calculating contributions from relative partial waves with $l\geqslant5$ is about -7.0×10^{-6} a.u. for case I.

[9] F. W. Byron, Jr., and C. J. Joachain, following paper, Phys. Rev. **157**, 7 (1967).

TABLE II. The contribution of the various partial waves to the second-order energy (in a.u.) of the $(1s2s)^1S_0$ and $(1s2s)^3S_1$ states of helium. The former state is designated by a superscript s, the latter by a superscript t.

l	$E_2^{(s)}(l)$ (a.u.)	$E_2^{(t)}(l)$ (a.u.)
0	−0.106335	−0.045316
1	−0.006239	−0.001898
2	−0.000816	−0.000137
3	−0.000199	−0.000020
4	−0.000066	−0.000004
5	−0.000027	−0.000001
⩾6	−0.000041	−0.000001
Total	−0.113723	−0.047377

because this $^3S_1$ state is the lowest one having total spin equal to unity.

With H_0 still given by Eq. (4), we have, for the space parts of the relevant zeroth-order wave functions,

$$\psi_0{}^s=(2/\pi)[e^{-(2r_1+r_2)}(1-r_2)+e^{-(r_1+2r_2)}(1-r_1)] \tag{16a}$$

and

$$\psi^t{}_0=(2/\pi)\,[e^{-(2r_1+r_2)}(1-r_2)-e^{-(r_1+2r_2)}(1-r_1)], \tag{16b}$$

where the superscripts s and t remind us that the wave functions (16a) and (16b) must be multiplied by singlet and triplet spin functions, respectively. The corresponding zeroth-order energy is $E_0{}^s=E_0{}^t=-2.50$ a.u. The first-order energy E_1 is easily obtained from Eq. (9a) with the results $E_1{}^s=(338/729)$ a.u.$=0.4636$ a.u. and $E_1{}^t=(274/729)$ a.u.$=0.3759$ a.u.

For the trial functions $\psi_1{}^s$ and $\psi_1{}^t$ to be inserted into the variational expression (10), we choose the following configuration-interaction forms:

$$\psi_1{}^s=\frac{1}{4\pi}\sum_{l,m,n} C_{lmn}{}^s(r_1{}^m r_2{}^n+r_1{}^n r_2{}^m)$$
$$\times[e^{-(\frac{1}{2}\alpha r_1+\frac{1}{2}\beta r_2)}+e^{-(\frac{1}{2}\beta r_1+\frac{1}{2}\alpha r_2)}]P_l(\cos\theta_{12}), \tag{17a}$$

and

$$\psi_1{}^t=\frac{1}{4\pi}\sum_{l,m,n} C_{lmn}{}^t(r_1{}^m r_2{}^n+r_1{}^n r_2{}^m)$$
$$\times[e^{-(\frac{1}{2}\alpha r_1+\frac{1}{2}\beta r_2)}-e^{-(\frac{1}{2}\beta r_1+\frac{1}{2}\alpha r_2)}]P_l(\cos\theta_{12}). \tag{17b}$$

The scale factors in the exponents were fixed at the obvious choice $\alpha=4.0$, $\beta=2.0$ without being varied. Using 30 parameters in each partial wave, we have calculated the contributions of terms through the $l=5$ partial wave.

The results are listed in Table II. In particular, it is worth noting how rapidly the values of $E_2{}^t(l)$ decrease with increasing l. This fact is in accordance with the conjecture of Schwartz[5] that the terms $E_2{}^t(l)$ should decrease like l^{-6} for large l, as compared with a decrease of the type l^{-4} for the terms $E_2{}^s(l)$. In fact, we find

$$E_2{}^s(4)/E_2{}^s(5)=2.49,\quad (5/4)^4=2.44, \tag{18a}$$

and

$$E_2{}^t(4)/E_2{}^t(5)=3.95,\quad (5/4)^6=3.82. \tag{18b}$$

Thus we see that even for quite small values of l the asymptotic behavior is fairly well obeyed as far as the ratios of successive terms is concerned. Using this fact, we have extrapolated the contribution from partial waves with $l\geqslant 6$. Our results for E_2 are then

$$E_2{}^s=-0.1137 \text{ a.u.} \tag{19a}$$

and

$$E_2{}^t=-0.0474 \text{ a.u.} \tag{19b}$$

As one should expect from symmetry considerations, the quantity $E_2{}^s$ is larger in magnitude than $E_2{}^t$.

With $\psi_1{}^s$ and $\psi_1{}^t$ calculated, it is a simple matter to evaluate the third-order energy, since

$$E_3=\langle\psi_1|H_1-E_1|\psi_1\rangle-2E_2\langle\psi_0|\psi_1\rangle. \tag{20}$$

We have obtained

$$E_3{}^s=0.0035 \text{ a.u.} \tag{21a}$$

and

$$E_3{}^t=-0.0025 \text{ a.u.} \tag{21b}$$

Therefore, we get, from Eqs. (19) and (21),

$$E_2{}^s+E_3{}^s=-0.1102 \text{ a.u.} \tag{22a}$$

and

$$E_2{}^t+E_3{}^t=-0.0499 \text{ a.u.} \tag{22b}$$

Now, defining

$$\Delta E=\sum_{n=2}^{\infty} E_n, \tag{23}$$

one can obtain "experimental" values of ΔE^s and ΔE^t by subtracting, respectively, the quantities $(E_0+E_1{}^s)$ or $(E_0+E_1{}^t)$ from the experimental value of the total energy of the $^1S_0$ and $^3S_1$ states considered. These experimental values are

$$\Delta E^s=-0.1096 \text{ a.u.} \tag{24a}$$

and

$$\Delta E^t=-0.0511 \text{ a.u.} \tag{24b}$$

Thus we see that with just E_2 and E_3 we are within a few percent of the total value of ΔE. Therefore, we conclude that a trial function of the configuration-interaction form (13) is sufficient to deal with intershell-type correlations between electrons, at least in those cases where an error of a few percent is not important.

IV. HARTREE-FOCK PERTURBATION CALCULATIONS

As a final example, we turn to Hartree-Fock perturbation theory in helium. Our starting point is the Hartree-Fock Hamiltonian

$$H_0=-\tfrac{1}{2}\nabla_1{}^2-\tfrac{1}{2}\nabla_2{}^2-2/r_1-2/r_2$$
$$+2V_d(\mathbf{r}_1)-V_e(\mathbf{r}_1)+2V_d(\mathbf{r}_2)-V_e(\mathbf{r}_2). \tag{25}$$

In this expression, V_d is the "direct" Hartree-Fock potential

$$V_d(\mathbf{r})=\int \phi_0^*(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_0(\mathbf{r}')d\mathbf{r}', \tag{26a}$$

whereas V_e is the "exchange" Hartree-Fock potential, which, acting on a given function $f(\mathbf{r})$, yields

$$V_e(\mathbf{r})f(\mathbf{r})=\int \phi_0^*(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}f(\mathbf{r}')d\mathbf{r}'\phi_0(\mathbf{r}). \tag{26b}$$

In the above definitions, the object $\phi_0(\mathbf{r})$ is the $1s$ single-particle Hartree-Fock orbital such that

$$\psi_0(\mathbf{r}_1,\mathbf{r}_2)=\phi_0(\mathbf{r}_1)\phi_0(\mathbf{r}_2), \tag{27}$$

where $\psi_0(\mathbf{r}_1,\mathbf{r}_2)$ is the ground-state eigenfunction of the Hartree-Fock Hamiltonian (25), yielding for the Hartree-Fock energy

$$E_{\mathrm{HF}}=E_0+E_1=-2.86167 \text{ a.u.} \tag{28}$$

In a previous work,[7] we started from the Hartree-Fock Hamiltonian (25) and evaluated the corrections to the Hartree-Fock energy (28) through fifth order in perturbation theory by using Hylleraas-type trial functions with ten parameters. In what follows, we want to re-do this calculation with trial functions of the form (11) containing 21 terms [i.e., $m+n\leqslant 5$ in Eq. (11)] for each partial wave and including the contributions from all partial waves through $l=6$. As in BJI, we determine the first-order wave function by using the variational expression (10) and the second-order wave function ψ_2 by varying the functional[7]

$$\begin{aligned}F_2[\psi_2{}^t]=\langle\psi_2{}^t|H_0-E_0|\psi_2{}^t\rangle\\ +2\langle\psi_2{}^t|H_1-E_1|\psi_1\rangle-2E_2\langle\psi_2{}^t|\psi_0\rangle.\end{aligned} \tag{29}$$

With the functions ψ_1 and ψ_2 determined variationally, the quantities E_2, E_3, E_4, and E_5 are readily evaluated by using the formulas (9b) and (20) together with

$$E_4=-\langle\psi_2|H_0-E_0|\psi_2\rangle-E_2\langle\psi_1|\psi_1\rangle-2E_3\langle\psi_0|\psi_1\rangle \tag{30a}$$

and

$$\begin{aligned}E_5=\langle\psi_2|H_1-E_1|\psi_2\rangle-2E_2\langle\psi_1|\psi_2\rangle-E_3\langle\psi_1|\psi_1\rangle\\ -2E_3\langle\psi_0|\psi_2\rangle-2E_4\langle\psi_0|\psi_1\rangle.\end{aligned} \tag{30b}$$

From our experience with the Hylleraas basis we used $\alpha=\beta=3.72$ for this calculation. For the Hartree-Fock function we used the four-parameter function of the form

$$\phi_0(r)=\sum_{i=1}^{4} a_i r^{n_i} e^{-\gamma_i r}, \tag{31}$$

where the numbers a_i, n_i, and γ_i are given by Roothaan *et al.*[10] In BJI we made use of a simple two-term analytic function for the $1s$ orbital, but because the trial function used in the present calculation contains higher powers of r_1 and r_2 than did the trial function of BJI, it was found that this simple Hartree-Fock function leads to errors in the evaluation of matrix elements which result in errors of about 1.5% in E_2. With these remarks made, the calculations are identical to those described in BJI except for the fact that the evaluation of the matrix elements (especially those of the exchange potential) is simplified considerably by the use of the $(r_>,r_<)$ basis. We illustrate this increase in computational simplicity by writing the expressions for the only two nontrivial matrix elements occurring in our calculation, namely $\langle\psi_{lmn}|V_d|\psi_{l'm'n'}\rangle$ and $\langle\psi_{lmn}|V_e|\psi_{l'm'n'}\rangle$. Thus we have

$$\begin{aligned}\langle\psi_{lmn}|V_d|\psi_{l'm'n'}\rangle=\frac{\delta_{ll'}}{2l+1}\sum_{i,j=1}^{4} a_ia_j[&2W(n+n'+2,\, m+m'+2,\, n_i+n_j+1,\, \beta,\, \alpha,\, \gamma_i+\gamma_j)\\ &+W(n+n'+2,\, n_i+n_j+1,\, m+m'+2,\, \beta,\, \gamma_i+\gamma_j,\, \alpha)+W(n_i+n_j+2,\, n+n'+1,\, m+m'+2,\, \gamma_i+\gamma_j,\, \beta,\, \alpha)\\ &+W(n_i+n_j+2,\, n+n'+2,\, m+m'+1,\, \gamma_i+\gamma_j,\, \beta,\, \alpha)+W(n+n'+2,\, n_i+n_j+2,\, m+m'+1,\, \beta,\, \gamma_i+\gamma_j,\, \alpha)],\end{aligned} \tag{32}$$

and

$$\begin{aligned}\langle\psi_{lmn}|V_e|\psi_{l'm'n'}\rangle=\frac{\delta_{ll'}}{(2l+1)^2}\sum_{i,j=1}^{4} a_ia_j[&W(l+n+n_i+2,\, m+n'+2,\, m'+n_j+1-l,\, \gamma_i+\tfrac{1}{2}\beta,\, \tfrac{1}{2}\alpha+\tfrac{1}{2}\beta,\, \gamma_j+\tfrac{1}{2}\alpha)\\ &+W(l+n+n_i+2,\, n'+n_j+1-l,\, m+m'+2,\, \gamma_i+\tfrac{1}{2}\beta,\, \gamma_j+\tfrac{1}{2}\beta,\, \alpha)\\ &+W(l+n'+n_j+2,\, n+n_i+1-l,\, m+m'+2,\, \gamma_j+\tfrac{1}{2}\beta,\, \gamma_i+\tfrac{1}{2}\beta,\, \alpha)\\ &+W(l+n'+n_j+2,\, m'+n+2,\, m+n_i+1-l,\, \gamma_j+\tfrac{1}{2}\beta,\, \tfrac{1}{2}\alpha+\tfrac{1}{2}\beta,\, \gamma_i+\tfrac{1}{2}\alpha)\\ &+W(n+n'+2,\, l+m'+n_j+2,\, m+n_i+1-l,\, \beta,\, \gamma_j+\tfrac{1}{2}\alpha,\, \gamma_i+\tfrac{1}{2}\alpha)\\ &+W(n+n'+2,\, l+m+n_i+2,\, m'+n_j+1-l,\, \beta,\, \gamma_i+\tfrac{1}{2}\alpha,\, \gamma_j+\tfrac{1}{2}\alpha)],\end{aligned} \tag{33}$$

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

TABLE III. The contribution of the various partial waves to the second-order energy (in a.u.) of the helium ground state in Hartree-Fock and in Hartree perturbation theory.

l	$E_2(l)$ (Hartree-Fock)	$E_2(l)$ (Hartree)
0	−0.01347	−0.01798
1	−0.01894	−0.02475
2	−0.00317	−0.00365
3	−0.00092	−0.00100
4	−0.00035	−0.00038
5	−0.00016	−0.00017
6	−0.00008	−0.00009
$\geqslant 7$	−0.00015	−0.00015
Total	−0.03725	−0.04817

in terms of the basic integrals W originally defined by James and Coolidge[11] (see also Appendix II of BJI). To make the comparison with BJI complete, we have also done this calculation using the Hartree Hamiltonian

$$H_0=-\tfrac{1}{2}\nabla_1^2-\tfrac{1}{2}\nabla_2^2-2/r_1-2/r_2+V_d(\mathbf{r}_1)+V_d(\mathbf{r}_2) \qquad (34)$$

as our starting point.

The results for E_2 (in the Hartree-Fock and Hartree cases) are shown in Table III. The most striking point is the very large reduction in the magnitude of $E_2(0)$ due to the effect of the average self-consistent potential. In the Hartree case, all the contributions of higher-relative partial waves to E_2 are nearly equal to the corresponding contributions in the hydrogenic case (see Table I). In the Hartree-Fock case, the exchange potential has a significant effect on $E_2(0)$ and on $E_2(1)$, but even here we see that its importance decreases rapidly with increasing l, so that the partial-wave contributions in the Hartree and Hartree-Fock cases are nearly equal for $l>2$.

TABLE IV. The contribution through fifth order of perturbation theory to the correlation energy (in a.u.) of the helium ground state, both for the Hartree and Hartree-Fock zeroth-order Hamiltonians. The results of BJI are included for comparison.

	Hartree-Fock		Hartree	
Energy	This paper	BJI	This paper	BJI
E_2	−0.03725	−0.03719	−0.04817	−0.04804
E_3	−0.00377	−0.00346	+0.00717	+0.00713
E_4	−0.00085	−0.00109	−0.00129	−0.00121
E_5	−0.00016	−0.00006	+0.00026	+0.00024
Total	−0.04203	−0.04180	−0.04203	−0.04192

Table IV gives the quantities E_2, E_3, E_4, and E_5 for the Hartree and Hartree-Fock cases, both as calculated in the present work using the $(r_>,r_<)$ basis and as calculated in BJI using a Hylleraas set of basis functions. We see that for both the Hartree and Hartree-Fock cases we obtain for the correlation energy[7] (neglecting contributions from orders higher than fifth):

$$E_{\text{corr}}=-0.04203 \text{ a.u.}, \qquad (35)$$

compared with the value $E_{\text{corr}}=-0.0419$ a.u. found in BJI and the "exact" value $E_{\text{corr}}{}^{\text{exact}}=-0.04205$ a.u. We note that the present calculation represents an improvement over our preceding one, particularly in the computation of E_4 and E_5 for the Hartree-Fock case. This is not surprising, since in BJI the Hartree case was treated with a 12-parameter trial function, whereas in the Hartree-Fock case we used only a 10-parameter trial function. Note that the terms omitted in BJI for the Hartree-Fock case were those containing higher powers of the variable $u=r_{12}$. The inclusion of such terms induces considerable computational labor in calculating the matrix elements of the exchange potential. By choosing the basis functions (11), one circumvents nicely these difficulties. All the integrals can be done systematically in closed form and the only (low) cost of the improvement is the inclusion of more parameters in the trial function, which is a trivial matter when dealing with modern computing machines.

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