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Correlation Effects in Atoms. I. Helium*

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The variational-perturbation method has been applied to the study of correlation effects in the helium atom. Starting from the Hartree-Fock Hamiltonian as zeroth-order approximation, we have evaluated the correlation energy through fifth order in perturbation theory. With a ten-parameter trial wave function we get $E_{\text{corr}} = -0.0419$ atomic units, which differs from the exact value by 0.4% and shows the rapid convergence of this type of Hartree-Fock perturbation theory. Comparison is also made with similar calculations using Hartree or hydrogenic Hamiltonians as starting points.

I. INTRODUCTION

THE problem of finding systematic ways to improve on the central field approximation has been of long-standing interest in atomic physics. In particular, the Hartree-Fock method provides an excellent zeroth-order approximation to atomic wave functions and binding energies, from which one would like to find a reasonably simple way of obtaining the next corrections to the energies and the wave functions. These corrections are usually called *correlation effects*, i.e., correlation energies and correlation corrections to wave functions. The purpose of this paper is to pave the way for a discussion of a technique which we hope will be of use in going beyond the Hartree-Fock method.

We choose the helium atom as a starting point because in this particular atom extensive theoretical investigations have been carried out, both "exact" computations¹⁻³ and perturbation-theory calculations⁴⁻⁶ having

been done with very high accuracy. Another reason for the choice of helium is that, in discussing many-electron atoms in a forthcoming paper, we will find it possible to reduce the problem to a series of two-body problems, each of which can be solved in principle by the method of this paper.

In Sec. II, we briefly describe the variational-perturbation method we have used to evaluate the correlation effects in helium. Section III is devoted to the presentation and the discussion of the results. It is shown that, using Hartree-Fock wave functions given by Roothaan *et al.*⁷ together with a ten-parameter trial wave function through fifth order in perturbation theory, the correlation energy is obtained to within 0.4% accuracy.⁸ We also discuss the convergence of the Hartree-Fock perturbation theory and compare our results with those obtained by using Hartree or hydrogenic Hamiltonians as starting points.

II. THE METHOD

Let us consider the Schrödinger equation for the helium atom,

$$H\Psi = E\Psi, \quad (1)$$

where, in atomic units (a.u.),⁸

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - 2/r_1 - 2/r_2 + r_{12}^{-1}. \quad (2)$$

We wish to discuss the possibility of solving this equation

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¹ H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic Press Inc., New York, 1957).

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

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

⁴ A. Dalgarno, *Proc. Roy. Soc. (London)* **A251**, 282 (1959).

⁵ A. Dalgarno and J. M. McNamee, *Proc. Phys. Soc. (London)* **77**, 673 (1961). See also L. C. Allen, *Phys. Rev.* **118**, 167 (1960) and S. Kaneko, *J. Phys. Soc. Japan* **14**, 1600 (1959).

⁶ C. W. Scherr and R. E. Knight, *Rev. Mod. Phys.* **35**, 436 (1963). See also A. W. Weiss and J. B. Martin, *Phys. Rev.* **132**, 2118 (1963).

⁷ C. C. J. Roothaan, L. M. Sachs and A. W. Weiss, *Rev. Mod. Phys.* **32**, 186 (1960).

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

tion starting from the zeroth-order equation

$$H_0\varphi_0 = E_0\varphi_0, \quad (3)$$

where H_0 is the Hartree-Fock Hamiltonian

$$H_0 = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - (2/r_1) - (2/r_2) + 2V_d(\mathbf{r}_1) - V_e(\mathbf{r}_1) + 2V_d(\mathbf{r}_2) - V_e(\mathbf{r}_2). \quad (4a)$$

The spin dependence has been removed by assuming that H_0 acts on a symmetric space function times a singlet spin function. In the expression (4a), the quantity V_d is the "direct" Hartree-Fock potential, defined by

$$V_d(\mathbf{x}) = \int \varphi_0^*(\mathbf{y}) \frac{1}{|\mathbf{x}-\mathbf{y}|} \varphi_0(\mathbf{y}) d\mathbf{y}, \quad (4b)$$

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

$$V_e(\mathbf{x})f(\mathbf{x}) = \varphi_0(\mathbf{x}) \int \varphi_0^*(\mathbf{y}) \frac{1}{|\mathbf{x}-\mathbf{y}|} f(\mathbf{y}) d\mathbf{y}. \quad (4c)$$

The perturbation H_1 is thus defined as

$$H_1 = H - H_0, \quad (5a)$$

which gives

$$H_1 = \frac{1}{r_{12}} - 2V_d(\mathbf{r}_1) + V_e(\mathbf{r}_1) - 2V_d(\mathbf{r}_2) + V_e(\mathbf{r}_2). \quad (5b)$$

As we shall see, for our purposes it is particularly convenient to use an analytic form for the Hartree-Fock functions similar to those which have been derived by Roothaan *et al.*⁷ We are interested only in the ground-state energy and wave function, both of which are known to very high accuracy in helium for the Hartree-Fock equation⁷ and for the exact Schrödinger equation.²⁻³

We now state briefly the equations of perturbation theory which we shall utilize. If we write

$$\Psi = \varphi_0 + \chi_1 + \chi_2 + \cdots, \quad (6a)$$

and

$$E = E_0 + E_1 + E_2 + \cdots, \quad (6b)$$

where each term is imagined to be of successively higher order in some small parameter. Then, using Eqs. (1), (3), and (5), one gets the following relations:

$$(H_0 - E_0)\varphi_0 = 0, \quad (7a)$$

$$(H_0 - E_0)\chi_1 + (H_1 - E_1)\varphi_0 = 0, \quad (7b)$$

$$(H_0 - E_0)\chi_n + H_1\chi_{n-1} - \sum_{m=1}^{n-1} E_m\chi_{n-m} - E_n\varphi_0 = 0 \quad (n \geq 2). \quad (7c)$$

We assume that we are given some solution of the homogeneous equation (7a), and we solve the remaining inhomogeneous equations by a variational method. First,

we get from (7a), (7b), and (7c)

$$E_1 = \langle \varphi_0 | H_1 | \varphi_0 \rangle, \quad (8a)$$

$$E_2 = \langle \varphi_0 | H_1 - E_1 | \chi_1 \rangle = -\langle \chi_1 | H_0 - E_0 | \chi_1 \rangle, \quad (8b)$$

$$E_3 = \langle \chi_1 | H_1 - E_1 | \chi_1 \rangle - 2E_2 \langle \varphi_0 | \chi_1 \rangle, \quad (8c)$$

$$E_4 = -\langle \chi_2 | H_0 - E_0 | \chi_1 \rangle - E_2 \langle \chi_1 | \chi_1 \rangle - 2E_3 \langle \varphi_0 | \chi_1 \rangle, \quad (8d)$$

$$E_5 = \langle \chi_2 | H_1 - E_1 | \chi_2 \rangle - 2E_2 \langle \chi_1 | \chi_2 \rangle - E_3 \langle \chi_1 | \chi_1 \rangle - 2E_3 \langle \varphi_0 | \chi_2 \rangle - 2E_4 \langle \varphi_0 | \chi_1 \rangle. \quad (8e)$$

We define

$$E_{\text{corr}} = \sum_{i=2}^{\infty} E_i. \quad (8f)$$

The equations for χ_1 and χ_2 may be obtained by varying the functionals⁹

$$F_1[\chi_1^t] = \langle \chi_1^t | H_0 - E_0 | \chi_1^t \rangle + 2\langle \chi_1^t | H_1 - E_1 | \varphi_0 \rangle \quad (9a)$$

and

$$F_2[\chi_2^t] = \langle \chi_2^t | H_0 - E_0 | \chi_2^t \rangle + 2\langle \chi_2^t | H_1 - E_1 | \chi_1 \rangle - E_2 \langle \chi_2^t | \varphi_0 \rangle, \quad (9b)$$

where χ_1^t and χ_2^t denote the trial functions to be varied. Note that in Eq. (9b) χ_1 is assumed to be given and is not varied. If the expressions F_1 and F_2 are evaluated at the stationary solutions χ_1 and χ_2 , respectively, then

$$F_1[\chi_1] = -\langle \chi_1 | H_0 - E_0 | \chi_1 \rangle, \quad (10a)$$

and

$$F_2[\chi_2] = -\langle \chi_2 | H_0 - E_0 | \chi_2 \rangle. \quad (10b)$$

By comparison with Eq. (8a), one sees that $F_1[\chi_1]$ gives directly a variational principle for E_2 . Besides, in the form (10a), it is clear that E_2 must always be negative for the ground state. Furthermore, the expression $F_2[\chi_2]$ gives just the value of E_4 apart from terms independent of χ_2 , so that we also have a variational principle for E_4 .

The method of solving for χ_1 and χ_2 is now clear. We write a trial solution of the form

$$\chi_1^t = \sum_{i=1}^n C_i^1 \psi_i(r_1, r_2, r_{12}, k), \quad (11a)$$

$$\chi_2^t = \sum_{i=1}^n C_i^2 \psi_i(r_1, r_2, r_{12}, k'). \quad (11b)$$

With these functions, we calculate $F_1[\chi_1^t]$ and $F_2[\chi_2^t]$ and regard the quantities $\{C_1^1, C_2^1, \dots; k\}$ and $\{C_1^2, C_2^2, \dots; k'\}$ as parameters being varied in order to minimize the functionals F_1 and F_2 . This reduces the problem to one of matrix inversions. For the functions ψ_i we have used a set of twelve functions corresponding

⁹ For a discussion on the choice of functionals, see for example A. Dalgarno, *Advan. Phys.* **11**, 281 (1962) and references cited there.

to all terms through cubic order of the form¹⁰

$$\psi_i = (1/4\pi)e^{-\frac{1}{2}ks} s^l t^m u^n, \quad (12)$$

where $s=r_1+r_2$, $t=r_1-r_2$, $u=r_{12}$ and where k (or similarly k') is a scale factor. Thus, we have to form the matrices

$$M_{ij} = \langle \psi_i | -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 | \psi_j \rangle, \quad (13a)$$

$$L_{ij} = \langle \psi_i | \frac{1}{r_1} + \frac{1}{r_2} | \psi_j \rangle, \quad (13b)$$

$$L'_{ij} = \langle \psi_i | \frac{1}{r_{12}} | \psi_j \rangle, \quad (13c)$$

$$Z_{ij} = \langle \psi_i | V_d | \psi_j \rangle, \quad (13d)$$

$$E_{ij} = \langle \psi_i | V_e | \psi_j \rangle, \quad (13e)$$

$$N_{ij} = \langle \psi_i | \psi_j \rangle, \quad (13f)$$

and the column vectors

$$R_i = \langle \psi_i | \varphi_{\text{HF}} \rangle, \quad (14a)$$

$$S_i = \langle \psi_i | \frac{1}{r_{12}} | \varphi_{\text{HF}} \rangle, \quad (14b)$$

$$T_i = \langle \psi_i | V_d | \varphi_{\text{HF}} \rangle, \quad (14c)$$

where our zeroth-order wave function φ_0 is the Hartree-Fock wave function and

$$\varphi_{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2) = \varphi_0(\mathbf{r}_1)\varphi_0(\mathbf{r}_2). \quad (15)$$

We have taken $\varphi_0(\mathbf{r})$ to be given analytically by a function of the form

$$\varphi_0(\mathbf{r}) = \frac{1}{(4\pi)^{1/2}} \sum_{i=1}^N a_i r^{n_i} e^{-\gamma_i r}. \quad (16)$$

Roothaan *et al.*⁷ have given wave functions of the form (16) with N up to 12. Because of the lengthy numerical aspects of the calculation, we fitted the Roothaan's function by least squares to a sum of two functions with optimized exponents (i.e., a normalized function of three variable parameters). We find

$$\varphi_0(\mathbf{r}) = (4\pi)^{-1/2} (2.60505e^{-1.41r} + 2.08144e^{-2.61r}). \quad (17)$$

This function gives values of E_0 and E_1 which agree with those calculated with Roothaan's twelve-parameter function to a few parts in 10^4 . Moreover, much of the calculation of the correlation energy was done with a very accurate four-term Roothaan wave function and the results did not differ significantly from those obtained with our two-term function (17).

We now proceed to the calculation of the quantities appearing in Eqs. (13) and (14). For completeness, we list in Appendix I the general expressions for an element of the matrices M , L , L' , and N , i.e., we give formulas for

$$M_{lmn}^{\lambda\mu\nu} = \frac{1}{16\pi^2} \int e^{-\frac{1}{2}s} s^l t^m u^n (-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2) e^{-\frac{1}{2}s} s^\lambda t^\mu u^\nu d\mathbf{r}_1 d\mathbf{r}_2, \quad (18a)$$

$$L_{lmn}^{\lambda\mu\nu} = \frac{1}{16\pi^2} \int e^{-\frac{1}{2}s} s^l t^m u^n \left(\frac{1}{r_1} + \frac{1}{r_2} \right) e^{-\frac{1}{2}s} s^\lambda t^\mu u^\nu d\mathbf{r}_1 d\mathbf{r}_2, \quad (18b)$$

$$L'_{lmn}^{\lambda\mu\nu} = \frac{1}{16\pi^2} \int e^{-\frac{1}{2}s} s^l t^m u^n \frac{1}{r_{12}} e^{-\frac{1}{2}s} s^\lambda t^\mu u^\nu d\mathbf{r}_1 d\mathbf{r}_2, \quad (18c)$$

$$N_{lmn}^{\lambda\mu\nu} = \frac{1}{16\pi^2} \int e^{-\frac{1}{2}s} s^l t^m u^n e^{-\frac{1}{2}s} s^\lambda t^\mu u^\nu d\mathbf{r}_1 d\mathbf{r}_2. \quad (18d)$$

The expressions for Z , E , R , S , and T are somewhat more tedious. We get

$$Z_{ij} = \frac{1}{4\pi} \sum_{l,m} a_l a_m \int \int \int \psi_i(\mathbf{r}_1, \mathbf{r}_2) \psi_j(\mathbf{r}_1, \mathbf{r}_2) r_3^{n_l+n_m} e^{-(\gamma_l+\gamma_m)r_3} \frac{1}{r_{13}} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3, \quad (19a)$$

$$E_{ij} = \frac{1}{4\pi} \sum_{l,m} a_l a_m \int \int \int \psi_i(\mathbf{r}_1, \mathbf{r}_2) \psi_j(\mathbf{r}_2, \mathbf{r}_3) r_1^{n_l} r_3^{n_m} e^{-\gamma_l r_1} e^{-\gamma_m r_3} \frac{1}{r_{13}} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3, \quad (19b)$$

$$R_i = \frac{1}{4\pi} \sum_{l,m} a_l a_m \int \int \psi_i(\mathbf{r}_1, \mathbf{r}_2) r_1^{n_l} r_2^{n_m} e^{-\gamma_l r_1} e^{-\gamma_m r_2} d\mathbf{r}_1 d\mathbf{r}_2, \quad (19c)$$

¹⁰ E. A. Hylleraas, Z. Physik 54, 347 (1929); 65, 209 (1930).

$$S_i = \frac{1}{4\pi} \sum_{l,m} a_l a_m \int \int \psi_i(\mathbf{r}_1, \mathbf{r}_2) r_1^{n_l} r_2^{n_m} e^{-\gamma l r_1} e^{-\gamma m r_2} \frac{1}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2, \quad (19d)$$

$$T_i = \frac{1}{16\pi^2} \sum_{j,k,l,m} a_j a_k a_l a_m \int \int \int \psi_i(\mathbf{r}_1, \mathbf{r}_2) r_1^{n_j} r_2^{n_k} r_3^{n_l + n_m} e^{-\gamma j r_1} e^{-\gamma k r_2} e^{-(\gamma l + \gamma m) r_3} \frac{1}{r_{13}} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3. \quad (19e)$$

In Appendix II, we sketch briefly how to express the elements of Z , R , S , and T in terms of a few basic integrals. The only serious difficulty—from the points of view of both the algebra and the amount of computational labor involved—lies in the calculation of the elements of the exchange matrix E . This is discussed in Appendix III. Thus, having the elements of the matrices M , L , L' , Z , E , and N , as well as those of the column vectors R , S , and T , we can now write our expression for F_1 [Eq. (9a)] in matrix notation as

$$F_1 = \sum_{i,j} (M_{ij} - 2L_{ij} + 4Z_{ij} - 2E_{ij} - E_0 N_{ij}) C_i^1 C_j^1 - 2 \sum_i (E_1 R_i + 2T_i - S_i) C_i^1. \quad (20)$$

Varying the C_i^1 , we obtain the system of linear equations

$$\sum_j (M_{ij} - 2L_{ij} + 4Z_{ij} - 2E_{ij} - E_0 N_{ij}) C_j^1 = E_1 R_i + 2T_i - S_i, \quad (21)$$

which is solved by matrix inversion. Similar considerations apply to F_2 and the solution for χ_2 . Once $\{C_i^1\}$ and $\{C_i^2\}$ are obtained then E_2 through E_5 may all be expressed in matrix notation, and are readily evaluated. For example,

$$E_3 = \sum_{ij} (L_{ij}' - 4Z_{ij} + 2E_{ij} - E_1 N_{ij}) C_i^1 C_j^1 - 2E_2 \sum_i R_i C_i^1. \quad (22)$$

III. RESULTS AND DISCUSSION

Table I gives the second- and third-order energies E_2 and E_3 as functions of the number of parameters in the trial function χ_1 , which we varied from one to ten. The two remaining cubic terms are omitted since in similar calculations (see below) they were found to contribute negligibly and also because they increase considerably

TABLE I. Second- and third-order perturbation energy in helium as the number of basis functions in the trial function increases.

Number of terms	Hartree-Fock		Hartree		Hydrogenic E_2
	E_2	E_3	E_2	E_3	
1	-0.025361	-0.003550	-0.033376	0.004400	-0.134826
2	-0.029392	-0.004139	-0.038491	0.004827	-0.146133
3	-0.032770	-0.005001	-0.042860	0.004628	-0.146133
4	-0.034452	-0.005438	-0.045220	0.004747	-0.153503
5	-0.035558	-0.004509	-0.045579	0.004916	-0.156394
6	-0.036852	-0.003647	-0.047134	0.006570	-0.156603
7	-0.036986	-0.003432	-0.047160	0.006626	-0.156627
8	-0.037158	-0.003349	-0.047517	0.007088	-0.156702
9	-0.037164	-0.003298	-0.047545	0.007073	-0.157151
10	-0.037190	-0.003461	-0.047927	0.007059	-0.157151
11			-0.047969	0.007011	-0.157380
12			-0.048041	0.007133	-0.157441

the computational labor in handling the elements of the exchange matrix. The terms in the trial function are added in the obvious order suggested by Table II. For

TABLE II. Sequence of basis functions used in the trial functions.

i	(l,m,n)	i	(l,m,n)
1	(0,0,1)	7	(2,0,1)
2	(1,0,0)	8	(3,0,0)
3	(2,0,0)	9	(0,2,1)
4	(0,2,0)	10	(1,2,0)
5	(0,0,2)	11	(1,0,2)
6	(1,0,1)	12	(0,0,3)

comparison, we show the values of E_2 and E_3 calculated using for H_0 the Hartree Hamiltonian

$$H_0 = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + V_d(\mathbf{r}_1) + V_d(\mathbf{r}_2). \quad (23)$$

Here, in the absence of any exchange matrix, the calculation was carried out using a twelve-parameter trial wave function, thus keeping all the cubic terms in it. We also show the values of E_2 obtained by starting from the simple hydrogenic Hamiltonian

$$H_0 = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2}. \quad (24)$$

Figure 1 shows a comparison of the zeroth-order wave function for the Hartree-Fock (or Hartree) case and for the hydrogenic case. Recall that in the Hartree-Fock (or Hartree) framework we have $E_0 + E_1 = -2.86167$ a.u. whereas starting from hydrogenic wave functions one gets $E_0 + E_1 = -2.750$ a.u. The value of the scale

TABLE III. Fourth- and fifth-order perturbation energy in helium as the number of basis functions in the trial function increases.

Number of terms	Hartree-Fock		Hartree	
	E_4	E_5	E_4	E_5
1	0.000689	+0.000013	-0.000438	-0.000111
2	0.000233	-0.000140	-0.000516	-0.000106
3	-0.000312	-0.000088	-0.000613	-0.000057
4	-0.000629	-0.000113	-0.000790	+0.000004
5	-0.000656	-0.000133	-0.000793	+0.000001
6	-0.000672	-0.000144	-0.001023	+0.000110
7	-0.000709	-0.000155	-0.001036	+0.000122
8	-0.000709	-0.000155	-0.001117	+0.000165
9	-0.000795	-0.000134	-0.001128	+0.000170
10	-0.001086	-0.000063	-0.001151	+0.000183
11			-0.001177	+0.000214
12			-0.001207	+0.000240

TABLE IV. Coefficients of the basis functions for the correlated wave functions. (The scale factors k and k' are such that $k=k'=3.72$.)

Coefficient	Hartree-Fock		Hartree	
	χ_1	χ_2	χ_1	χ_2
C_1/k	+1.924880	+0.294524	+2.166550	+0.270665 $\times 10^{-1}$
C_2/k	-0.314568 $\times 10^{-1}$	+0.682257 $\times 10^{-1}$	-0.110226	+0.214254
C_3/k^2	-0.104288 $\times 10^{-1}$	-0.124684 $\times 10^{-1}$	-0.950153 $\times 10^{-2}$	-0.677986 $\times 10^{-1}$
C_4/k^2	+0.685349 $\times 10^{-1}$	-0.446628 $\times 10^{-1}$	+0.319173 $\times 10^{-1}$	+0.311003 $\times 10^{-2}$
C_5/k^2	-0.148467	+0.551155 $\times 10^{-1}$	-0.183234	-0.142566 $\times 10^{-2}$
C_6/k^2	+0.515117 $\times 10^{-2}$	-0.267843 $\times 10^{-1}$	+0.648630 $\times 10^{-1}$	+0.711624 $\times 10^{-1}$
C_7/k^3	+0.106626 $\times 10^{-1}$	-0.295276 $\times 10^{-2}$	+0.125427 $\times 10^{-1}$	-0.207508 $\times 10^{-1}$
C_8/k^3	-0.665754 $\times 10^{-2}$	+0.347408 $\times 10^{-3}$	-0.928131 $\times 10^{-2}$	+0.812738 $\times 10^{-2}$
C_9/k^3	-0.421135 $\times 10^{-2}$	-0.671910 $\times 10^{-2}$	-0.130326 $\times 10^{-1}$	-0.132568 $\times 10^{-2}$
C_{10}/k^3	+0.410153 $\times 10^{-2}$	+0.137636 $\times 10^{-1}$	+0.179817 $\times 10^{-1}$	+0.349211 $\times 10^{-2}$
C_{11}/k^3			-0.114274 $\times 10^{-1}$	+0.179936 $\times 10^{-1}$
C_{12}/k^3			+0.108721 $\times 10^{-1}$	-0.692774 $\times 10^{-2}$

factor k for Table I is $k=3.72$, which gives the minimum energy E_2 for our trial function, although for such a number of parameters E_2 is a fairly insensitive function of k , changing by only 0.2% as k is varied from 3.36 to 3.72. Since there is no minimum principle for the third order energy E_3 , the successive values of E_3 do not decrease monotonically as they do for E_2 . It is also worth noting that although E_2 is quite different in the Hartree-Fock and Hartree methods, and moreover E_3 is even different in sign, the sum E_2+E_3 is very nearly the same in the two cases. Finally, it is interesting to remark that, starting from the hydrogenic Hamiltonian (24), the results we obtain for E_2 in the case of 2, 6, and 12 parameters, respectively, are in complete agreement with those given by Schwartz.¹¹

Table III gives the values of E_4 and E_5 in the Hartree-Fock and Hartree cases, as functions of the number of parameters in the trial function χ_2 . Here we use $k'=3.72$ for the value of the scale factor k' . This value is not optimal; we estimate that a somewhat smaller value of k' (around 3.30) would decrease E_4 by about 2%. Clearly, E_5 has not converged as completely as E_2 , E_3 , and E_4 . We estimate that E_2 , the dominant contribution will decrease by about 0.5% if the number of parameters in χ_1 were made very large. This would probably be the

most significant difference between our calculation and one done with a very extensive trial function. Thus, our final values for the Hartree-Fock case (with a 10-parameter trial function and within the accuracy of our calculation) are, in a.u.

$$E_2 = -0.0372,$$

$$E_3 = -0.0035,$$

$$E_4 = -0.0011,$$

$$E_5 = -0.0001.$$

This gives for the value of the correlation energy

$$E_{\text{corr}} = -0.0419 \text{ a.u.}$$

The corresponding values for the Hartree case (with a twelve-parameter trial function) are, in a.u.

$$E_2 = -0.0480,$$

$$E_3 = +0.0071,$$

$$E_4 = -0.0012,$$

$$E_5 = +0.0002,$$

giving thus also

$$E_{\text{corr}} = -0.0419 \text{ a.u.}$$

This result differs by 0.4% from the exact value of the correlation energy,

$$E_{\text{corr}}^{\text{exact}} = -0.04205 \text{ a.u.},$$

obtained by subtracting from the "exact" value of the total energy given by Pekeris² or Schwartz³ the value of the Hartree-Fock energy found by Roothaan *et al.*⁷

In Table IV we give the coefficients of the basis functions for our best trial functions χ_1 and χ_2 , both in the Hartree-Fock and in the Hartree cases.

Thus we see that the Hartree-Fock equation serves as a satisfactory starting point for a fairly rapidly convergent perturbation theory. Using terms through fifth order we get to within 0.4% of the total correlation energy. Scherr and Knight⁶ in their study of perturbation theory in helium starting from hydrogenic functions

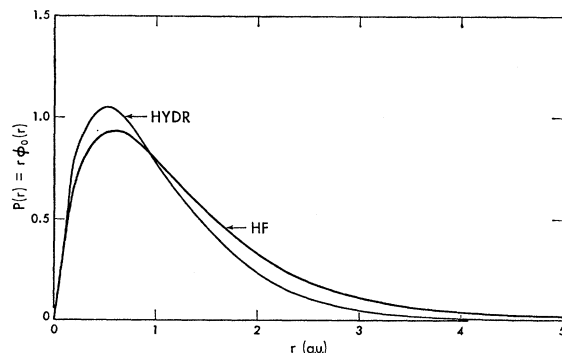


FIG. 1. Comparison of the radial functions $\rho(r) = r\phi_0(r)$, where $\phi_0(r)$ is either the Hartree-Fock (HF) or the hydrogenic (HYDR) ground-state radial wave function for the helium atom.

¹¹ C. Schwartz, Phys. Rev. **126**, 1015 (1962).

found that through E_5 they got (with a hundred-parameter trial wave function) $E_{\text{corr}} = -0.04200$, i.e., to within 0.1% of the correct answer. We believe that if we added more parameters to our trial functions our value for E_{corr} would be at least this accurate. However, as the complication of the problem increases rapidly with the number of parameters in the trial functions, and since our main interest lies in more complicated atoms

than helium, increasing the number of parameters in this case does not seem worthwhile.

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APPENDIX I

A straightforward but lengthy integration, making use of the variables s , t , u , gives for Eq. (18a) of the text

$$M_{lmn}^{\lambda\mu\nu} = \frac{1}{8} \left\{ \left[\frac{l\lambda + l\nu + n\lambda - n\mu - m\nu}{(m+\mu+1)(m+n+\mu+\nu+3)} - \frac{n\nu + l\nu + n\lambda}{(m+\mu+3)(m+n+\mu+\nu+3)} \right. \right. \\ + \frac{n\nu + n\mu + m\nu}{(m+\mu+1)(m+n+\mu+\nu+1)} + \frac{m\mu}{(m+\mu-1)(m+n+\mu+\nu+1)} - \frac{m\mu}{(m+\mu+1)(m+n+\mu+\nu+3)} \\ \left. - \frac{l\lambda}{(m+\mu+3)(m+n+\mu+\nu+5)} \right] (l+m+n+\lambda+\mu+\nu+3)! + \left[\frac{l+\lambda}{2(m+\mu+3)(m+n+\mu+\nu+5)} \right. \\ \left. - \frac{l+\lambda}{2(m+\mu+1)(m+n+\mu+\nu+3)} - \frac{n+\nu}{(m+\mu+1)(m+\mu+3)(m+n+\mu+\nu+3)} \right] (l+m+n+\lambda+\mu+\nu+4)! \\ \left. + \left[\frac{1}{4(m+\mu+1)(m+n+\mu+\nu+3)} - \frac{1}{4(m+\mu+3)(m+n+\mu+\nu+5)} \right] (l+m+n+\lambda+\mu+\nu+5)! \right\}, \quad (\text{I.1})$$

where all the variables are greater than or equal to zero. In the case $m=0$, $\mu=1$ or $m=1$, $\mu=0$ (a case which is not relevant in this work, because the symmetry of the wave function requires that only even powers of t appear) the term

$$\frac{m\mu}{(m+\mu-1)(m+n+\mu+\nu+1)}$$

is not well defined. In this special case it should be taken to be zero. The remaining integrals are easily done and give

$$L_{lmn}^{\lambda\mu\nu} = \frac{1}{2} \frac{(l+m+n+\lambda+\mu+\nu+4)!}{(m+\mu+1)(m+n+\mu+\nu+3)}, \quad (\text{I.2})$$

$$L'_{lmn}^{\lambda\mu\nu} = \frac{1}{8} \left[\frac{1}{(m+\mu+1)(m+n+\mu+\nu+2)} - \frac{1}{(m+\mu+3)(m+n+\mu+\nu+4)} \right] (l+m+n+\lambda+\mu+\nu+4)!, \quad (\text{I.3})$$

$$N_{lmn}^{\lambda\mu\nu} = \frac{1}{8} \left[\frac{1}{(m+\mu+1)(m+n+\mu+\nu+3)} - \frac{1}{(m+\mu+3)(m+n+\mu+\nu+5)} \right] (l+m+n+\lambda+\mu+\nu+5)!. \quad (\text{I.4})$$

APPENDIX II

All of the integrals which are necessary for the calculation of Z , R , S , and T can be written in the following simple form

$$f_k(l, m, n, \alpha, \beta, \gamma) = \frac{1}{4} \int r_1^l r_2^m r_3^n e^{-\alpha r_1} e^{-\beta r_2} e^{-\gamma r_3} \frac{1}{r_{12}^k} dr_1 dr_2 dr_3 d(\cos\theta_{12}) d(\cos\theta_{13}). \quad (\text{II.1})$$

These integrals can be expressed as finite sums of two basic integrals which were defined originally by James and

Coolidge,¹² namely,

$$V(l, m, \alpha, \beta) = \int_0^\infty dx \int_x^\infty dy x^l e^{-\alpha x} y^m e^{-\beta y}, \quad (\text{II.2})$$

and

$$W(l, m, n, \alpha, \beta, \gamma) = \int_0^\infty dx \int_x^\infty dy \int_y^\infty dz x^l e^{-\alpha x} y^m e^{-\beta y} z^n e^{-\gamma z}. \quad (\text{II.3})$$

We first write the various quantities f_k in terms of the functions V and W and finally derive simple expressions for V and W .

It is clear that any integral with k even can immediately be reduced to a sum of integrals with $k=0$. An elementary integration gives

$$f_0(l, m, n, \alpha, \beta, \gamma) = \frac{m!}{\beta^{m+1}} [V(l, n-1, \alpha, \gamma) + V(n, l-1, \gamma, \alpha)]. \quad (\text{II.4})$$

When k is odd we find a more complicated relation:

$$\begin{aligned} f_k(l, m, n, \alpha, \beta, \gamma) = \sum_{j=1}^{k+2} \frac{(k+1)!}{j!(k+2-j)!} & [W(l-1+j, m+k+1-j, n-1, \alpha, \beta, \gamma) + W(m-1+j, l+k+1-j, n-1, \beta, \alpha, \gamma) \\ & + W(n, l-2+j, m+k+1-j, \gamma, \alpha, \beta) + W(l-1+j, n-1, m+k+1-j, \alpha, \gamma, \beta) \\ & + W(m-1+j, n, l+k-j, \beta, \gamma, \alpha) + W(n, m-1+j, l+k-j, \gamma, \beta, \alpha)], \quad (\text{II.5}) \end{aligned}$$

where the prime on the summation means that only odd k are to be included.

It is easy to obtain expressions for the functions V and W . For example, if $n \geq 0$, we get

$$V(m, n, \alpha, \beta) = \frac{n!}{(\alpha + \beta)^{m+1} \beta^{n+1}} \sum_{\nu=0}^n \frac{(m+\nu)!}{\nu!} \left(\frac{\beta}{\alpha + \beta} \right)^\nu. \quad (\text{II.6})$$

Similarly, if $n \geq 0$, the function $W(l, m, n, \alpha, \beta, \gamma)$ can be written as

$$W(l, m, n, \alpha, \beta, \gamma) = \frac{n!}{\gamma^{n+1}} \sum_{\nu=0}^n \frac{\gamma^\nu}{\nu!} V(l, m+\nu, \alpha, \beta + \gamma). \quad (\text{II.7})$$

Analogous expressions may be derived for $n < 0$. In actual calculations it is very convenient to make use of recursion relations of the type discussed by James and Coolidge.¹²

With these functions all the elements of Z , R , S , and T may be written explicitly. For example,

$$Z_{12} = \sum_{l, m} a_l a_m [f_1(3, 2, n_l + n_m + 2, k, k, \gamma_l + \gamma_m) + f_1(2, 3, n_l + n_m + 2, k, k, \gamma_l + \gamma_m)], \quad (\text{II.8})$$

$$Z_{5,12} = \sum_{l, m} a_l a_m f_5(2, 2, n_l + n_m + 2, k, k, \gamma_l + \gamma_m), \text{ etc.,}$$

where we use the same notation as in Eq. (19a).

APPENDIX III

In writing expressions for the elements of the exchange matrix

$$E_{ij} = \langle \psi_i | V_e | \psi_j \rangle, \quad (\text{III.1})$$

one encounters integrals of the following type, arising from the action of the exchange operator V_e :

$$g(l, m, n, \alpha, \beta, \gamma, a, b) = \frac{1}{8\pi} \int r_1^l r_2^m r_3^n e^{-\alpha r_1} e^{-\beta r_2} e^{-\gamma r_3} (1/r_{13}) r_{12}^a r_{23}^b dr_1 dr_2 dr_3 d(\cos\theta_{12}) d(\cos\theta_{23}) d\varphi_{13}. \quad (\text{III.2})$$

If a and b are odd, one cannot write an expression in closed form for this quantity. In this case, after expanding in

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

spherical harmonics, one obtains the general expression

$$\begin{aligned}
g(l, m, n, \alpha, \beta, \gamma, a, b) = & \sum_{\mathcal{E}=0}^{\infty} \sum_{N=0}^K \sum_{M=0}^{K-N} \sum_{L=0}^N \sum_{L'=\mathcal{E}'}^{\mathcal{E}+N-L} \sum_{\nu=0}^{K'} \sum_{\mu=0}^{K'-\nu} \sum_{\lambda=0}^{\nu} \sum_{L''=\mathcal{E}''}^{\mathcal{E}+\nu-\lambda} \begin{pmatrix} N-L & \mathcal{E} & L' \\ 0 & 0 & 0 \end{pmatrix}^2 \times \begin{pmatrix} \nu-\lambda & \mathcal{E} & L'' \\ 0 & 0 & 0 \end{pmatrix}^2 \\
& \times (-1)^{N+\nu} \frac{(2N-2L+1)(2\nu-2\lambda+1)K!K'(N-\frac{1}{2}L)!(\nu-\frac{1}{2}\lambda)!2^{2N+2\nu-L-\lambda}}{M!\mu!(\frac{1}{2}L)!(\frac{1}{2}\lambda)!(K-M-N)!(K'-\mu-\nu)!(2N-L+1)!(2\nu-\lambda+1)!} \\
& \times \{W(l+2M+N+\mathcal{E}+L', m+2K+2K'-2M-2\mu-N-\nu+L''-L-1, n+2\mu+\nu-\mathcal{E}-L''-2, \alpha, \beta, \gamma) \\
& + W(m+2K+2K'-2M-2\mu-N-\nu+L'+L', L+2M+N+\mathcal{E}-L'-1, n+2\mu+\nu-\mathcal{E}-L''-2, \beta, \alpha, \gamma) \\
& + W(n+2\mu+\nu+\mathcal{E}+L'', L+2M+N+L'-\mathcal{E}-1, m+2K+2K'-2M-2\mu-N-\nu-L-L''-2, \gamma, \alpha, \beta) \\
& + W(L+2M+N+L'+\mathcal{E}, n+2\mu+\nu-\mathcal{E}+L''-1, m+2K+2K'-2M-2\mu-N-\nu-L'-L''-2, \alpha, \gamma, \beta) \\
& + W(m+2K+2K'-2M-2\mu-N-\nu+L'+L'', n+2\mu+\nu+\mathcal{E}-L''-1, L+2M+N-\mathcal{E}-L'-2, \beta, \gamma, \alpha) \\
& + W(n+2\mu+\nu+\mathcal{E}+L'', m+2K+2K'-2M-2\mu-N-\nu-L''+L'-1, L+2M+\mu-\mathcal{E}-L'-2, \gamma, \beta, \alpha)\}, \quad (\text{III.3})
\end{aligned}$$

where

$$K = (a+1)/2, \quad (\text{III.4a})$$

$$K' = (b+1)/2, \quad (\text{III.4b})$$

$$\mathcal{E}' = |\mathcal{E} - (N-L)|, \quad (\text{III.4c})$$

$$\mathcal{E}'' = |\mathcal{E} - (\nu-\lambda)|, \quad (\text{III.4d})$$

and

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \quad (\text{III.4e})$$

is the standard $3j$ symbol.¹³ The primes on summations mean that the sum runs in steps of two. The function W is defined in Appendix II. In practice, the expression (III.3) will simplify considerably for particular values of a and b . In this work, because of the form of our trial wave function, only the case $a=b=1$ is needed (i.e., there was no term involving u^3 in our trial function). In that case, we get, explicitly,

$$\begin{aligned}
g(l, m, n, \alpha, \beta, \gamma, 1, 1) = & \sum_{J=0}^{\infty} \frac{1}{(2J+1)^2} \left\{ \sum_{I=0}^1 \sum_{K=0}^1 \frac{(2I-1)(2K-1)}{(2J-4I+3)(2J-4K+3)} \right. \\
& \times [W(m-2I-2K+2J+4, l+2I-1, n+2K-2J-2, \beta, \alpha, \gamma) \\
& + W(m-2I-2K+2J+4, n+2I-1, l+2K-2J-2, \beta, \gamma, \alpha) \\
& + W(l-2I+2J+2, m+2I-2K+1, n+2K-2J-2, \alpha, \beta, \gamma) \\
& + W(n-2I+2J+2, m+2I-2K+1, l+2K-2J-2, \gamma, \beta, \alpha) \\
& + W(n-2I+2J+2, l-2K+1, m+2I+2K-2J-2, \gamma, \alpha, \beta) \\
& \left. + W(l-2I+2J+2, n-2K+1, m+2I+2K-2J-2, \alpha, \gamma, \beta) \right\}. \quad (\text{III.5})
\end{aligned}$$

In practice, it was found that this sum converged very rapidly so that only the first three terms ($J=0, 1, 2$) were necessary for our purposes.

With the above notation a typical element of the exchange matrix involving the function g is

$$E_{11} = \sum_{l, m} a_l a_m g \left(n_l + 2, 2, n_m + 2, \frac{k}{2} + \gamma_l, k, \frac{k}{2} + \gamma_m \right). \quad (\text{III.6})$$

Other terms involving r_{12} on both sides of the exchange operator can be written similarly in terms of the functions g . All remaining terms of the matrix E can be written in terms of the functions discussed in Appendix II. It should be mentioned that in calculating the various functions g , one needs the expressions $W(l, m, n, \alpha, \beta, \gamma)$ of Appendix II for negative as well as positive values of n .

¹³ A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1957).