Correlation in the Ground State of He Atom

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It is possible to reproduce the entire results of Pekeris et al. of different atomic parameters for the He atom by introducing (ll) type correlation in a self consistent variation perturbation procedure using the Hartree-Fock (HF) wavefunction as the zero-order wavefunction.

1. Introduction

Electron correlation has been recognised as a major problem in the theory of atomic structure for a long time. The definition of the correlation energy as

$$E_{\text{Corr}} = E_{\text{Exact}} - E_{\text{HF}} \tag{1}$$

was first given by Löwdin [1]. Since then several different approaches to the correlation problem have been studied [2–7]. These approaches, like the Hylleraas type expansion using inter-particle coordinates explicitly in the wavefunction [3], configuration interaction (CI) [4], manybody perturbation theory (MBPT) [5], multiconfiguration HF theory (MCHF) [6], and numerical methods [7] are much more laborious and computationally difficult than the conventional HF calculation. The present method introduces correlation through a correction of the unperturbed HF wavefunction. It thus differs from the above methods and is similar to the many electron theory (MET) [8]. This similarity is only superficial because the procedure of arriving at the correlation function is altogether different.

Wavefunctions obtained by the HF approximation enjoy immense popularity for their applicability in many cases. In this approximation each electron moves within the average field of the other electrons. This effectively means more freedom for the electrons to come near to each other than they actually possess, because within that field the motion is independent of the motions of the other electrons. In a number of communications [9–10] the present authors developed a selfconsistent variation perturbation procedure to take into account the correlation in the He atom starting with the HF wavefunction as the zero-order wavefunction. There the effect of correlation is introduced through a correction of the unperturbed HF orbitals. In the present paper we make ourearlier method more compact and general by introducing the (ll) type of correlation for different values of l in successive stages.

2. Theory

For a two particle system the Hamiltonian in a.u. may be written as

$$H = -\tfrac{1}{2}[\nabla_1^2 + \nabla_2^2] - Z\left[\frac{1}{r_1} + \frac{1}{r_2}\right] + \frac{1}{r_{12}}. \tag{2}$$

The expansion for $1/r_{12}$, where r_{12} is the inter electronic distance, gives rise to a combination of spherical harmonics $L(l)$, where

$$L(l) = \sum_{m=-l}^{m=+l} (-1)^m Y_l^m(1)\, Y_l^m(2)\,. \tag{3}$$

$L(l)$ projects the required angular symmetry out of the doubly excited configuration for different values of l and thus ensures the appropriate angular symmetry of the correction. Ψ_0 and E_0 are the ground state HF determinantal wavefunction and the energy, respectively. In Ψ_0 each of the spin-orbitals is assumed to be the product of a function of coordinates ψ_0 and a function of α or β of spin. The HF determinantal wavefunction for the He atom may be written as

$$\Psi_0 = \frac{1}{\sqrt{2!}} \begin{vmatrix} \psi_0(1)\alpha(1) & \psi_0(2)\alpha(2) \\ \psi_0(1)\beta(1) & \psi_0(2)\beta(2) \end{vmatrix}. \tag{4}$$

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On simplification Ψ_0 reduces to

$$\Psi_0 = \frac{1}{\sqrt{2!}}\,\chi(1,2)\,[\alpha(1)\,\beta(2) - \alpha(2)\,\beta(1)]\,, \tag{5}$$

where

$$\chi(1,2) = \psi_0(1)\,\psi_0(2)\,, \tag{6}$$

ψ_0 is represented by

$$\psi_0(k) = \sum_i a_i(k)\, r_k^{n_i}\, e^{-\xi_i r_k}\, Y_0^0(k)\,. \tag{7}$$

Therefore

$$\chi(1,2) = \sum_{i,j} A_{ij}\, r_1^{n_i} r_2^{n_j}\, e^{-\xi_i r_1 - \xi_j r_2}\, Y_0^0(1)\, Y_0^0(2)\,, \tag{8}$$

where

$$A_{ij} = a_i(1)\, a_j(2) \tag{9}$$

are the coefficients of the zero-order correlated wavefunction Ψ_0. The corrected wavefunction, considering the correlation due to the $1/r_{12}$ term, may be written as

$$\Phi = N[\Psi_0 + \partial\Psi]\,, \tag{10}$$

where N is the normalization constant. Keeping terms up to second order N is given by

$$N = 1 - \tfrac{1}{2}\langle\partial\Psi|\,\partial\Psi\rangle \tag{11}$$

and $\partial\Psi$ may be written as

$$\partial\Psi = \sum_{l=0}^{\infty} \partial\Psi_l\,. \tag{12}$$

$\partial\Psi_0, \partial\Psi_1, \ldots$ are the corrections due to correlation of specific configurations to the zero-order correlated wavefunction Ψ_0 for $l = 0, 1, \ldots$ of (3), respectively. The orthogonality condition is

$$\sum_l \langle\Psi_0|\,\partial\Psi_l\rangle = 0\,, \tag{13}$$

which reduces to

$$\langle\Psi_0|\,\partial\Psi_0\rangle = 0 \tag{14}$$

as in the present case the rest of the terms in (13) vanishes through the angular symmetry. This orthogonality condition is inserted in to the energy expression only in case $l = 0$. Now the total energy of the system, keeping terms up to second order, is given by

$$E = \langle\Phi|\,H\,|\Phi\rangle = [1 - \langle\partial\Psi|\,\partial\Psi\rangle]\,E_0 + 2\langle\Psi_0|\,H\,|\,\partial\Psi\rangle + \langle\partial\Psi|\,H\,|\,\partial\Psi\rangle\,. \tag{15}$$

The contribution of the effects of correlation to the energy is given by

$$\Delta E = -E_0\langle\partial\Psi|\,\partial\Psi\rangle + 2\langle\Psi_0|\,H\,|\,\partial\Psi\rangle + \langle\partial\Psi|\,H\,|\,\partial\Psi\rangle\,. \tag{16}$$

In the present method a systematic procedure for computing an accurate approximation of Φ is followed. Starting with $l = 0$ of (3), for each l the number of specific configurations in the sum increases until the change in energy ΔE is sufficiently small. Thus ΔE may be denoted as

$$\Delta E = \sum_{l=0}^{\infty} \Delta E_l\,, \tag{17}$$

where ΔE_l is the improvement in the energy for a given value of l. The value of l is increased until ΔE_l is sufficiently small. At each stage a new configuration is added to the approximation in an accumulative manner. ΔE_l is given by

$$\Delta E_l = -\Big[E_0 + \sum_{l=0}^{l} \Delta E_l - \Delta E_l\Big]\langle\partial\Psi_l|\,\partial\Psi_l\rangle + 2\Big\langle\partial\Psi_l\,|\,H\,|\,\Psi_0 + \sum_{l=0}^{l}\partial\Psi_l - \partial\Psi_l\Big\rangle + \langle\partial\Psi_l|\,H\,|\,\partial\Psi_l\rangle\,. \tag{18}$$

By taking proper care of the orthogonality condition (14) ΔE_l is optimized variationally. For this purpose, the analytic expressions chosen to represent $\partial\Psi_l$ are of the form

$$\partial\Psi_l = \sum_{i,j} C_{ij}(l)\, r_1^{n_{li}} r_2^{n_{lj}}\, e^{-\xi_i r_1 - \xi_j r_2}\, L(l') \cdot [\alpha(1)\,\beta(2) - \alpha(2)\,\beta(1)]\,. \tag{19}$$

The C's are variation parameters and differ for different values of l. The angular functions $L(l')$ are taken such that the symmetry required by (3) is always satisfied. Appropriate values of n_{li} are preassigned for different values of l. We use the same values of ξ_i as appearing in the zero-order correlated wavefunction. The energy optimization condition leads to a set of simultaneous linear equations in the C's which can be solved easily.

3. Results and Discussion

All the relevant results are condensed in Tables 1, 2, 3, and 4. The values of different quantities are given along with the most accepted values for comparison. The results clearly bring out the effects of correlation in successive stages. It may be con-

Table 1. Parameters for the wavefunctions.

Ψ_0 [15]			(4-Parameter)	$\delta\Psi_{l=0}$	$\delta\Psi_{l=1}$	$\delta\Psi_{l=2}$	(8-Parameter)	$\delta\Psi_{l=0}$	$\delta\Psi_{l=1}$	$\delta\Psi_{l=2}$
ξ	n	c	ξ	n	n	n	ξ	n	n	n
1.4532	0	2.90957	1.4532	0	1	2	1.4532	0	1	2
2.7709	0	1.65883	2.7709	0	1	2	2.7709	0	1	2
4.1000	0	0.18580	4.1000	0	1	2	4.1000	0	1	2
0.5948	0	0.00346	0.5948	0	1	2	0.5948	0	1	2
							1.4532	1	2	3
							2.7709	1	2	3
							4.1000	1	2	3
							0.5948	1	2	3

Table 2. Values of the matrix elements $(1/M)\langle \boldsymbol{p}_1 \cdot \boldsymbol{p}_2 \rangle$ and $\langle \boldsymbol{r}_1 \cdot \boldsymbol{r}_2 \rangle$ for the ground state of He atom.

$l_{\max}$	$(1/M)\langle \boldsymbol{p}_1 \cdot \boldsymbol{p}_2 \rangle$ in cm^{-1}			$-\langle \boldsymbol{r}_1 \cdot \boldsymbol{r}_2 \rangle$ in a.u.		
	4 parameter	8 parameter	Pekeris [11]	4 parameter	8 parameter	Dalgarno [19]
0	0.0	0.0		0.0	0.0	
1	5.1404	5.1026		0.0695	0.0693	
2	4.9427	4.8990		0.0682	0.0680	
			4.785			0.0623

Table 3. Values of the correlation energy in a.u. for the ground state of He atom.

Method	$-\Delta E_{l=0}$	$-\Delta E_{l=1}$	$-\Delta E_{l=2}$	$-\sum_{l=0}^{l=2} \Delta E_l$	$-\Delta E$
Present					
4 Para	0.01700	0.02136	0.00248	0.04048	
8 para	0.01739	0.02151	0.00261	0.04151	
Weiss [16]	0.01728	0.02143	0.00219	0.04090	
Froese Fischer [7, 14, 17]	0.01731	0.02140	0.00212	0.04083	
Bunge [18]	0.01735	0.02148	0.00224	0.04107	
Sabelli [6]	0.01735				
Exact [11]					0.04205

cluded that it is possible to attain the non-relativistic limit of the total energy by introducing a number of (ll) type correlations and parameters starting with the HF wavefunction.

It is evident from Table 2 that the values of $(1/M)\langle \boldsymbol{p}_1 \cdot \boldsymbol{p}_2 \rangle$ (M denotes the nuclear mass) and $\langle \boldsymbol{r}_1 \cdot \boldsymbol{r}_2 \rangle$ are strongly dependent on the electron correlation, as these values tend to become more accurate [11] with higher values of l.

It is also very interesting to note that the values of the length and velocity form of the oscillator strength f for dipole transitions improve significantly from its initial values and attains a value recognised as the most accurate by Pekeris et al. [12]. It should be remembered that in calculating the oscillator strength we have neglected the correlation for the excited states [13].

The present method is quite general and can be extended to systems with a large number of electrons without much difficulty because of the simplicity of the approach as well as the availability of the unperturbed HF wavefunction.

Table 4. Values of matrix element $\langle r_1^n + r_2^n \rangle$ and oscillator strength for different dipole transitions for He atom in a.u. (with $l_{\max} = 2$).

	$\langle r_1^n + r_2^n \rangle$					Oscillator strength					
						1^1s-2^1p		1^1s-3^1p		1^1s-4^1p	
	$n = -2$	$n = -1$	$n = 0$	$n = 1$	$n = 2$	f_L	f_V	f_L	f_V	f_L	f_V
Present 4para	12.0170	3.3685	1.9999	1.8690	2.4222	0.2917	0.2624	0.0706	0.0699	0.0290	0.0288
Present 8para	11.9990	3.3667	1.9999	1.8709	2.4257	0.2777	0.2629	0.0743	0.0703	0.0306	0.0289
Accurate [12]						0.2761	0.2761	0.0740	0.0734	0.0300	0.0299
HF	11.9810	3.3731	2.0000	1.8554	2.3701	0.2596	0.2390	0.0696	0.0644	0.0289	0.0265

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