

Correlation in the Ground State of He Atom

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Z. Naturforsch. **36a**, 272–275 (1981); received December 12, 1980

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

$$E_{\text{Corr}} = E_{\text{Exact}} - E_{\text{HF}} \quad (1)$$

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 our earlier 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

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

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

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

$L(l)$ 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

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

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On simplification Ψ_0 reduces to

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

where

$$\chi(1, 2) = \psi_0(1)\psi_0(2), \quad (6)$$

ψ_0 is represented by

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

Therefore

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

where

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

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

$$\Phi = N[\Psi_0 + \partial\Psi], \quad (10)$$

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

$$N = 1 - \frac{1}{2} \langle \partial\Psi | \partial\Psi \rangle \quad (11)$$

and $\partial\Psi$ may be written as

$$\partial\Psi = \sum_{l=0}^{\infty} \partial\Psi_l. \quad (12)$$

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

$$\sum_l \langle \Psi_0 | \partial\Psi_l \rangle = 0, \quad (13)$$

which reduces to

$$\langle \Psi_0 | \partial\Psi_0 \rangle = 0 \quad (14)$$

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

$$E = \langle \Phi | H | \Phi \rangle = [1 - \langle \partial\Psi | \partial\Psi \rangle] E_0 + 2 \langle \Psi_0 | H | \partial\Psi \rangle + \langle \partial\Psi | H | \partial\Psi \rangle. \quad (15)$$

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

$$\Delta E = -E_0 \langle \partial\Psi | \partial\Psi \rangle + 2 \langle \Psi_0 | H | \partial\Psi \rangle + \langle \partial\Psi | H | \partial\Psi \rangle. \quad (16)$$

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

$$\Delta E = \sum_{l=0}^{\infty} \Delta E_l, \quad (17)$$

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

$$\begin{aligned} \Delta E_l = & -[E_0 + \sum_{l=0}^l \Delta E_l - \Delta E_l] \langle \partial\Psi_l | \partial\Psi_l \rangle \\ & + 2 \langle \partial\Psi_l | H | \Psi_0 + \sum_{l=0}^l \partial\Psi_l - \partial\Psi_l \rangle \\ & + \langle \partial\Psi_l | H | \partial\Psi_l \rangle. \end{aligned} \quad (18)$$

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

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

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 pre-assigned 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-

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