On the Ground State of H^-

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A simple and effective method is described to calculate the ground state energy of H^- starting with the Hartree Fock wavefunction. The expectation values of the operators $\langle \boldsymbol{r}_1 \cdot \boldsymbol{r}_2\rangle$, $\langle r_1{}^n + r_2{}^n\rangle$ and $\langle \boldsymbol{p}_1 \cdot \boldsymbol{p}_2\rangle$ can be estimated easily with the present procedure. Oscillator strength sums $S(k)$ for $k = -1, 0, 1$ are also evaluated.

1. Introduction

The effectiveness of an atomic theory is often judged by its capability to produce correct results for the negative species of a given isoelectronic sequence. The correlated wavefunction of Hyllerass [1], though reproducing satisfactorily all results, is mostly designed for two electronic atoms. The many body theory of Brueckner and Goldstone, later developed by many workers [2], is another powerful approach. The second electron of the H^- ion is loosely bound to the H-atom. The Hartree Fock theory fails to reproduce the bound state of the H^- ion because the correlation between the electrons is very significance in this case. The many body perturbation theory (MBPT) was first applied for H^- by Das et al. [3] with considerable success.

Recently two of the present authors have demonstrated [4, 5, 6] that it is possible to evaluate the effect of the electron correlation in a variation perturbation scheme starting with the zeroth-order Hartree Fock wavefunction. This procedure shall here be applied to H^-. The purpose is twofold, firstly to assess the correctness of the theory and secondly to compare it with the many body perturbation theory. The results are extremely encouraging.

2. Theory

Non relativistic Hamiltonian (in a.u.) for a two particle system is of the form

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

where

$$\frac{1}{r_{12}} = \sum_l \sum_m \frac{4\pi}{2l+1} \frac{r_<^l}{r_>^{l+1}} Y_l^m(1)\, Y_l^{m*}(2), \tag{2}$$

Ψ_0 and E_0 are the unperturbed ground state Hartree Fock wave function and energy, respectively. Ψ_0 may be written as [6]

$$\Psi_0 = \frac{1}{\sqrt{2!}} \sum_{i,J} A_{ij}\, r_1^{n_i} r_2^{n_J} e^{-\xi_i r_1 - \xi_J r_2} Y_0^0(1)\, Y_0^0(2) \cdot [\alpha(1)\beta(2) - \alpha(2)\beta(1)]. \tag{3}$$

The wavefunction corrected for the electron correlation due to the interelectronic repulsion term $1/r_{12}$ may be written as

$$\Phi = N[\Psi_0 + \partial\Psi], \tag{4}$$

where the normalization constant N upto second order terms is given by

$$N = 1 - \tfrac{1}{2}\langle \partial\Psi / \partial\Psi\rangle \tag{5}$$

and the correction $\partial\Psi$ may be written as

$$\partial\Psi = \sum_{l=0}^{l=\alpha} \partial\Psi_l, \tag{6}$$

where $\partial\Psi_l$ is the correction for a specific value of l in (2). In the present case, due to the angular symmetry the orthogonality condition reduces to

$$\langle \Psi_0 / \partial\Psi_0\rangle = 0. \tag{7}$$

The contribution of the correlation to the energy upto second order terms is

$$\begin{aligned} \Delta E &= \sum_{l=0}^{l=\alpha} \Delta E_l \\ &= \sum_{l=0}^{l=\alpha} \Bigg[-\left(E_0 + \sum_{I=0}^{I=l} \Delta E_I - \Delta E_l\right) \langle \partial\Psi_l | \partial\Psi_l\rangle \\ &\quad + 2\left\langle \partial\Psi_l \middle| H \middle| \Psi_0 + \sum_{I=0}^{I=l} \partial\Psi_I - \partial\Psi_l \right\rangle \\ &\quad + \langle \partial\Psi_l | H | \partial\Psi_l\rangle \Bigg], \end{aligned} \tag{8}$$

where ΔE_l is the contribution for a given value of l. In a systematic procedure the value of l is increased until ΔE reaches an asymptotic value. At each step a new configuration is added.

By taking proper care of the orthogonality condition (7), ΔE_l is optimized variationally. The $\partial\Psi_l$'s

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