

Helium atom revisited

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Abstract : The ground state energy of He atom is reexamined in a new formalism. With the introduction of an effective hamiltonian, a regular perturbation method is developed systematically which derives simply a very good result.

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The ground state (GS) of the helium atom, the simplest two electron system, has been well investigated using mainly the Ritz variational method with appropriate variational parameters to reflect the effect of the correlation and screening. Thus the one parameter variational wave function of Kellner [1] takes reasonably good account of the screening while the more extensive variational wavefunction (Hyllerass type [2]) of Pekeris (2078 terms) gives the very accurate estimate of the GS energy [3]. Chandrasekhar and Herzberg [4] with only 18 parameters obtained the GS energy remarkably close to the most accurate value. Subsequently, many authors [5–9] with varying degree of sophistication have reported reasonably good estimate of the GS energy (Table 1). Similarly, there have been some other calculations [10–14] (e.g. the recent one [14] by de Saavedra and Buendia) which may briefly be called improvised variational approach giving very accurate GS energy. Despite these moderate to superior calculation, the interest in the two electron systems remains unabated perhaps because of the challenging quest for even simpler and more transparent methods. It is in this spirit that we present in this communication our simple method which is a combination of an effective soluble hamiltonian and the Rayleigh-Schrödinger Perturbation Theory (RSPT). The essence of the method, which leads to a good estimate of the GS energy, lies in a suitable partitioning of the exact hamiltonian into a soluble one (including a parameter) with a complete basis set and a perturbation. Thus the exact hamiltonian in atomic units ($e = \hbar = m = 1$)

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

is recast identically to

$$H = H_0 + H_{\text{int}} \quad (2)$$

$$\text{where } H_0 = \left[-\nabla_1^2 / 2 + V_{\text{eff}}(r_1) \right] + \left[-\nabla_2^2 / 2 + V_{\text{eff}}(r_2) \right], \quad (3)$$

$$H_{\text{int}} = \left[-2(1/r_1 + 1/r_2) - V_{\text{eff}}(r_1) - V_{\text{eff}}(r_2) + 1/r_{12} \right], \quad (4)$$

and $v_{\text{eff}}(r)$ the effective potential which for the purpose of this work is chosen to be $v_{\text{eff}}(r) = -Z/r$, where Z is an unknown parameter to be determined presently. H_0 in this form is exactly solvable with a basis

$$\psi_{ij}(r_1, r_2) = \varphi_i(r_1) \varphi_j(r_2), \quad (5)$$

φ 's being Coulomb functions φ_d , φ_c , in the discrete and the continuum respectively, given by

$$\begin{aligned} \varphi_d = \psi_{nlm} &= - \left[\frac{(2v_n)^3 (n-l-1)!}{2n[(n+l)!]^3} \right]^{1/2} (2v_n)^l r^l L_{n+l}^{2l+1}(2v_n r) Y_{lm} \\ &= \frac{1}{2\pi i} \left[\frac{(2v_n)^3 (n-l-1)!}{2n[(n+l)!]^3} \right]^{1/2} (2v_n)^l r^l Y_{lm} e^{-v_n r} \\ &\quad \times \oint \frac{e^{-v_n \left(\frac{r}{1-t} \right)}}{t^{n-l} (1-t)^{2l+1}} dt, \end{aligned} \quad (6)$$

with $v_n = Zn$

$$\begin{aligned} \text{and } \varphi_c &= \frac{1}{(2\pi)^{3/2}} e^{\pi Z/2k} \Gamma(1 - iZ/k) e^{ikr} F(iZ/k, 1, ikr - ik.r) \\ &= \frac{1}{2\pi i} \frac{1}{(2\pi)^{3/2}} e^{\pi Z/2k} \Gamma(1 - iZ/k) e^{ikr} \int (t-1)^\alpha t^{-1+\alpha} e^{i(kr-k.r)t} dt, \end{aligned} \quad (7)$$

where the integral transformation in (6) and (7) has been used, as in refs [15,16], for simplifying the matrix elements of the second order RSPT, which we will presently describe.

In this basis, the unperturbed energy E_0 is given by

$$E_0 = \langle \psi_{Rk} | H_0 | \psi_{Rk} \rangle = -Z^2,$$

where $\psi_{Rk} = \varphi_R(r_1) \varphi_R(r_2)$, $\varphi_R(r) = (Z^3/\pi)^{1/2} e^{-Zr}$ with Z still unknown.

We now fix Z by requiring that the first order correction $E^{(1)} = \langle \psi_{Rk} | H_{\text{int}} | \psi_{Rk} \rangle = 2Z(Z - 27/16)$ be zero. This prescription recovers the familiar one parameter variational result $Z = 27/16$! Thus the first order RSPT result is identical with the one parameter variational result.

The next order correction $E^{(2)}$ is explicitly negative and consist of three terms

$$E^{(2)} = - \sum_{ij \neq RR} \frac{|\langle \psi_{RR} | H_{int} | \psi_{ij} \rangle|^2}{E_{ij} - E_{RR}} = E_{gg}^{(2) dd} + E_{gg}^{(2) cd} + E_{gg}^{(2) cc}, \quad (8)$$

where the notations in the last line evidently refer to three possibilities of the final states namely, both one particle states are discrete (dd), one discrete and one continuum (cd or dc) and both continuum (cc). In the evaluation of the three terms of (8), the $1/r_{12}$ term of H_{int} needs special attention. The integral representations of (6) and (7), together with the Fourier transform of $1/r_{12}$, have been gainfully employed (details to be presented elsewhere) to simplify the calculation of the three terms of (8). It turns out that the matrix elements in $E_{RR}^{(2) dd}$ are obtained in closed analytic form while those in $E_{RR}^{(2) cd}$ and $E_{RR}^{(2) cc}$ are reduced to one dimensional integrals which are evaluated numerically.

The result of these calculations is

$$E^{(2)} = E_{RR}^{(2) dd} + E_{RR}^{(2) cd} + E_{RR}^{(2) cc} = -0.02177 - 0.01567 - 0.01436 \\ = -0.0518 \quad (9)$$

Therefore, our calculated energy upto second order in RSPT is given by

$$E = E^0 + E^{(1)} + E^{(2)} = -2.8994.$$

Interestingly, this second order RSPT result is also identical, upto the quoted figures with one of the variational results, namely that of Wu [8] who has obtained his result from a three parameter variational wave function. In Table 1 we have presented our result together with some selective set of results of variational calculations.

Table 1. Results for the GS energy of He atom obtained by different authors.

Pekeris [3]	-2.903724
Chandrasekhar [4]	-2.903716
Srivastava and Bhaduri [5]	-2.873
Patil [6]	-2.895
Abott and Maslen [7]	-2.890
Tripathy <i>et al</i> [9]	-2.88403
Wu [8]	-2.8994
Ours	-2.8994

In sum, we have presented a simple method of effective hamiltonian and RSPT to deal with the exact He Hamiltonian to second order in RSPT. The first order not only fixes the effective hamiltonian but reproduces the simplest one parameter variational result. The second order reproduces another three parameter variational result ! Correlation in this model is systematically brought in each order of RSPT. Details will be presented elsewhere together with the results of other isoelectronic systems.

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