The effect of non-linear variational parameters on the energy convergence of Coulomb three-body systems

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Cox *et al.* [1] applied the series solution method, developed by Pekeris [2] for the Schrödinger equation for two-electron atoms and generalized by Frost *et al.*[3] to handle any three particles with a Coulomb interaction, to calculate the ^{1}S and ^{3}S states of helium and low Z helium-like systems with nucleus fixed and with nucleus in motion and showed that a non-linear variational parameter accelerated convergence of the energy. The wavefunction is expanded in a triple orthogonal set in three perimetric coordinates. The perimetric coordinates are defined as $z_i = r_j + r_k - r_i$ where the r_i are interparticle distances, and the z_i have the advantage of being independent over their range of 0 to ∞. The wavefunction takes the form

$$\psi(z_1, z_2, z_3) = e^{-\frac{1}{2}(\alpha z_1 + \beta z_2 + \gamma z_3)} L_l(\alpha z_1) L_m(\beta z_2) L_n(\gamma z_3)$$

Previous work fulfilled the condition $\alpha = \beta = \frac{1}{2}\gamma = \sqrt{-E}$ corresponding to an exponential dependence of the form $e^{-\alpha(r_1+r_2)}$ without any dependence on r_3, which is in principle an exact form as the exponential term contains the correct asymptotic behaviour of the solution of the Schrödinger equation for two electron atoms.

However, the convergence of molecular-type systems (such as H_2^+, HD^+, *etc.*) was very slow compared to that of atomic-type systems (such as H^-, He, *etc.*). Following the work of Gálvez *et al.* [4], [5], we have recently implemented a second and third non-linear parameter, whilst preserving the orthogonality of the Laguerre basis functions. Here we present the results of these studies, evaluated in terms of the rate of energy convergence and the accuracy of various expectation values. It is found that an explicit exponential dependence on r_3 is crucial for obtaining reasonable convergence of molecular-type systems.

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