

LETTER TO THE EDITOR

Analytical approach to the helium-atom ground state using correlated wavefunctions

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Abstract. A realistic three-parameter correlated wavefunction is used to construct an exact analytical expression for the expectation value of the helium-atom Hamiltonian expressed in the interparticle coordinates. The parameters determined variationally are found to satisfy the orbital and correlation cusp conditions to a fair degree of accuracy and yield a value for the ground-state energy which is in good agreement with the exact result.

Most of our understanding of atomic theory rests on the independent-electron model which assumes each electron as moving in the combined field of the nucleus and of the average distribution of the other electrons. In this model the effect of interelectronic repulsion, globally referred to as correlation (Fano 1983), is disregarded. Such a view-point, however, leads to inaccurate results for the ground-state energy of the helium atom and its isoelectronic sequence. Thus studies of the effects of two-electron correlation have been a subject of interest from the early days of quantum mechanics (Hartree 1957).

The ground-state energies of helium and helium-like atoms are calculated by using wavefunctions constructed from the conventional orbital product, times a correlation function depending on the interelectronic distance r_{12} . These wavefunctions involve, in general, a number of adjustable parameters which are constrained to satisfy some kind of variational principle to give an improved value for the ground-state energy (Mizushima 1970). It is found that integration of the functions of r_{12} is quite difficult, so that the topic of electron correlation is often studied by using numerical routines only.

In the present letter we shall make a judicious choice for the correlated wavefunction and derive a simple analytical model in respect of this. The inevitable numerical routine will be invoked only at the last stage of the game. We shall see in the course of our study that the model presented is not only physically transparent but also numerically accurate.

In atomic units, the Schrödinger equation for the helium atom is given by

$$\left[-\frac{1}{2}\nabla_{r_1}^2 - \frac{1}{2}\nabla_{r_2}^2 - 2\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{r_{12}} - \epsilon \right] \Psi(r_1, r_2) = 0 \quad (1)$$

where r_j is the position of the j th electron relative to the nucleus. Hylleraas (1929) realized that a complete description of the S-states requires only three independent coordinates, namely, the lengths r_1 , r_2 and r_{12} of the sides of the triangle formed by the three particles. The Euler angles specifying the spatial orientation of the triangle disappear from the

dynamical equation because of symmetry considerations. This observation forms the basis for a realistic choice of the S-state wavefunction to calculate the value of ϵ in (1).

In terms of interelectronic coordinates, equation (1) for the case of S-states can be written in the form (Roothaan and Weiss 1960)

$$(H - \epsilon)\psi(r_1, r_2, r_{12}) = 0 \quad (2)$$

where

$$H = H_1 + H_2 + H_{12} + H'_{12} \quad (3)$$

with

$$H_j = -\frac{1}{2} \left(\frac{\partial^2}{\partial r_j^2} + \frac{2}{r_j} \frac{\partial}{\partial r_j} \right) - \frac{2}{r_j} \quad (4a)$$

$$H_{12} = - \left(\frac{\partial^2}{\partial r_{12}^2} + \frac{2}{r_{12}} \frac{\partial}{\partial r_{12}} \right) + \frac{1}{r_{12}} \quad (4b)$$

and

$$H'_{12} = - \left(\frac{r_1^2 - r_2^2 + r_{12}^2}{2r_1 r_{12}} \frac{\partial}{\partial r_1} + \frac{r_2^2 - r_1^2 + r_{12}^2}{2r_1 r_{12}} \frac{\partial}{\partial r_2} \right) \frac{\partial}{\partial r_{12}}. \quad (4c)$$

The vector operator del implied in (4) is given by (Hylleraas 1964)

$$\nabla_j = \hat{r}_j \frac{\partial}{\partial r_j} + \hat{r}_{12} \frac{\partial}{\partial r_{12}}. \quad (5)$$

The ground-state energy for (1) is given by

$$\epsilon = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}. \quad (6)$$

The expectation value of the Hamiltonian can be written in the explicit form

$$\begin{aligned} \langle \psi | H | \psi \rangle = & -\frac{1}{2} \iint (|\nabla_1 \psi|^2 + |\nabla_2 \psi|^2) \, d\mathbf{r}_1 \, d\mathbf{r}_2 - 2 \iint \psi^* \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \psi \, d\mathbf{r}_1 \, d\mathbf{r}_2 \\ & + \iint \psi^* \frac{1}{r_{12}} \psi \, d\mathbf{r}_1 \, d\mathbf{r}_2. \end{aligned} \quad (7)$$

For calculating the ground-state energy of helium by means of (6) and (7), we have chosen to work with the trial wavefunction (Hartree and Ingman 1933)

$$\psi(r_1, r_2, r_{12}) = e^{-\alpha(r_1+r_2)} \chi(r_{12}) \quad (8)$$

where the correlation function

$$\chi(r_{12}) = 1 - \lambda e^{-\mu r_{12}}. \quad (9)$$

The adjustable parameters of our trial wavefunction are α , λ and μ . As $r_{12} \rightarrow \infty$, $\chi(r_{12}) \rightarrow 1$. This expresses the separability of the wavefunction when the two electrons are far apart. As demanded by Hartree and Ingman (1933), we can allow $\chi(r_{12})$ to assume a small finite value for $r_{12} = 0$. Thus our choice for the wavefunction (8) is based on physically founded assumptions. In the mid 1980s, Abbott and Maslen (1986) envisaged a study similar to ours in terms of a correlated wavefunction of the form $\psi(r_1, r_2, r_{12}) = e^{-\xi(r_1+r_2)} e^{\gamma r_{12}}$. This choice was originally made by Hylleraas (1929) and rejected subsequently by Hartree and Ingman (1933) as unphysical. When the cusp conditions (Roothaan and Weiss 1960)

$$\left(\frac{1}{\psi} \frac{\partial \psi}{\partial r_1} \right)_{r_1=0} = \left(\frac{1}{\psi} \frac{\partial \psi}{\partial r_2} \right)_{r_2=0} = -Z \quad (10a)$$

and

$$\left(\frac{1}{\psi} \frac{\partial \psi}{\partial r_{12}} \right)_{r_{12}=0} = \frac{1}{2} \quad (10b)$$

are satisfied, the wavefunctions gave a found-state energy -2.8555 au in contrast to the exact value -2.9037 au. Interestingly, if the conditions in (10) are relaxed by allowing $Z \rightarrow Z - 0.14$ and $\gamma = 0.26$, an improved result of -2.8896 au could be obtained. As opposed to the wavefunctions used by Abbott and Maslen (1986), the continuum distorted wavefunction (CDW) of Pluvinae (1950) is based on a perfectly legitimate physical assumption that the correlation energy arises from a repulsive Coulomb potential which can support continuous spectrum only. But the use of CDW does not permit an analytical approach to the problem and also it gives a poor ground-state energy of -2.8780 au.

To construct an expression for $\langle \psi | H | \psi \rangle$ by using the wavefunction in (8), one would, ideally, like to calculate the integrals involved by the use of well known Hylleraas coordinates $u = r_{12}$, $s = r_1 + r_2$ and $t = r_1 - r_2$. Unfortunately, this approach does not lead to an analytical expression for the energy expectation value (Morse and Feshbach 1953). We thus take recourse to the use of the Fourier transforms (Deb 1994)

$$\frac{e^{-\lambda r}}{r} = \frac{1}{2\pi^2} \int \frac{e^{i\mathbf{p}\cdot\mathbf{r}}}{(\lambda^2 + p^2)} d\mathbf{p} \quad (11)$$

and

$$\frac{1}{r_{12}} = \frac{1}{2\pi^2} \int \frac{e^{i\mathbf{R}\cdot(\mathbf{r}_1 - \mathbf{r}_2)}}{R^2} d\mathbf{R}. \quad (12)$$

For $\langle \psi | \psi \rangle$ and $\langle \psi | H | \psi \rangle$ we have found that

$$\langle \psi | \psi \rangle = \frac{\pi^2}{\alpha^3} \left[\frac{1}{\alpha^3} - \frac{2\lambda}{(\mu + 2\alpha)^5} (\mu^2 + 10\mu\alpha + 32\alpha^2) + \frac{\lambda^2}{8(\mu + \alpha)^5} (\mu^2 + 5\mu\alpha + 8\alpha^2) \right] \quad (13)$$

and

$$\langle \psi | H | \psi \rangle = A - B + C \quad (14)$$

with

$$A = \frac{\pi^2}{\alpha^3} \left[\frac{1}{\alpha} - \frac{2\lambda\alpha^2}{(\mu + 2\alpha)^5} (3\mu^2 + 30\mu\alpha + 32\alpha^2) + \frac{\lambda^2}{8(\mu + \alpha)^5} (\mu^4 + 5\mu^3\alpha + 11\mu^2\alpha^2 + 15\mu\alpha^3 + 8\alpha^4) \right] \quad (15a)$$

$$B = \frac{\pi^2}{\alpha^3} \left[\frac{4}{\alpha^2} - \frac{16\lambda\alpha}{(\mu + 2\alpha)^4} (\mu + 8\alpha) + \frac{\lambda^2\alpha}{(\mu + \alpha)^4} (\mu + 4\alpha) \right] \quad (15b)$$

and

$$C = \frac{\pi^2}{\alpha^3} \left[\frac{5}{8\alpha^2} - \frac{\lambda}{(\mu + 2\alpha)^4} (\mu^2 + 8\mu\alpha + 20\alpha^2) + \frac{\lambda^2}{8(\mu + \alpha)^4} (\mu^2 + 4\mu\alpha + 5\alpha^2) \right]. \quad (15c)$$

Minimizing the energy with respect to variations in the parameters of $\psi(r_1, r_2, r_{12})$ we get $\alpha = 1.8395$, $\lambda = 0.586$ and $\mu = 0.379$. For these parameters the correlation cusp condition (10b) comes out to be 0.5365 which is not far from the exact value and, more significantly, the ground-state energy is found to be -2.8894 au. Very recently, Tripathy *et al* (1995) derived an interesting approach to compute the ground-state energies of the helium isoelectronic sequence. Their method consists of introducing variational parameters

in the Hamiltonian rather than in the trial wavefunction. Physically, the parameters used, on the one hand, screen the nuclear charge and, on the other hand, produce a change in the centrifugal potential term that appears in the radial part of the one-electron Schrödinger equation. The interelectronic interaction is repulsive. Therefore, mechanistically, one may think of this repulsion resulting in some kind of positional displacement for the electronic wavefunction such that the correlated atomic state might not be associated only with pure s orbitals. This justifies the claim that correlation can also be accounted for by introducing variational parameters in the Hamiltonian. However, the two-parameter wavefunction used by Tripathy *et al* (1995) yields a number for the ground-state energy of helium which is little inferior to what we have obtained.

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