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Variational method for two-electron atoms*

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A simple two-parameter trial wave function for the helium atom and helium-like ions is proposed on physical grounds. A variational calculation for the ground-state energy yields a much better result than the usual one-parameter example given in textbooks.

I. INTRODUCTION

Most courses in quantum mechanics in senior undergraduate and first year graduate classes include the variational method for obtaining an upper limit to the ground-state energy of a quantum-mechanical system. The application of the method to the helium atom with only one parameter in the trial wave function serves as a simple and useful illustration in most texts.[1] More elaborate variational calculations,[2,3] involving many variational parameters, yield very accurate estimates of the ground-state energy. In this paper we show that on physical grounds a simple two-parameter trial wave-function for the helium problem can be constructed which yields a much better estimate of the energy than the one-parameter calculation.

In the textbook example of the problem, the trial wave function for the ground state is taken as a product of two normalized hydrogenic 1s wave functions,

$$\psi(\mathbf{r}_1,\mathbf{r}_2) = (\alpha^3/\pi a_0{}^3) \exp[-\alpha(r_1 + r_2)/a_0], \quad (1)$$

with α as the variational parameter. Here $\mathbf{r}_1$ and $\mathbf{r}_2$ are the position vectors of the two electrons with respect to the nucleus as the origin, and $a_0 = \hbar^2/me^2$ is the radius of the first Bohr orbit in hydrogen. The singlet spin part of the wave function need not be considered since the Hamiltonian is taken to be spin independent. The parameter α is interpreted as an effective nuclear charge as seen by the electrons. Its optimum value, obtained by minimizing the expectation value of the Hamiltonian, is found to be $27/16$ (<2) for the helium atom, which is reasonable since each electron is partially screened from seeing the full charge of the nucleus due to the presence of the other electron. Note that in Eq. (1) the coordinates of the two electrons enter the wave function with equal weight. We now propose a modified trial wave function based on the following reasoning. For those electronic configurations of the system in which the two electrons are at unequal distances from the nucleus, the outer electron should experience a smaller effective charge than the inner one. This would suggest introducing an additional parameter s (≤ 1) in a trial wave function of the following form:

$$\psi(\mathbf{r}_1,\mathbf{r}_2) = N \exp[-\alpha(sr_> + r_<)/a_0], \quad r_1 \ne r_2, \quad (2)$$

where $r_> = r_1$, $r_< = r_2$ if $r_1 > r_2$, and vice versa. Note that

$$sr_> + r_< = [(s + 1)/2] (r_1 + r_2)$$
$$+ [(s - 1)/2]|r_1 - r_2|, \quad (3)$$

so for the special case when $r_1 = r_2$,

$$\psi(\mathbf{r}_1,\mathbf{r}_2) = N \exp[-\alpha(s + 1)(r_1 + r_2)/2a_0]. \quad (4)$$

Although the trial wave function (2) contains two varia-

tional parameters α and s, the calculation of the normalizing constant N and the expectation value of the Hamiltonian is simple because of the exponential nature of the wave function. Note also that the present choice of the wave function preserves the symmetry between the coordinates r_1 and r_2 of the two electrons.

In Sec. II, a variational calculation for two-electron atomic systems will be done with the trial wave function (2). The calculation is simple enough for classroom presentation and reduces to the standard one-parameter form with $s = 1$. The improvement in the results for helium and helium-like ions is discussed in Sec. III.

II. VARIATIONAL CALCULATION

The Hamiltonian of the helium atom, ignoring nuclear motion, spin–orbit coupling, and relativistic effects is

$$H = - \frac{\hbar^2}{2m} (\nabla_1{}^2 + \nabla_2{}^2) - Ze^2 \left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{r_{12}}, \quad (5)$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ is the distance between the two electrons, and Ze is the nuclear charge. For helium $Z = 2$, but it takes other integral values for helium-like ions.

In calculating the expectation value of H with the trial wave function (2), one should split up the integral range in the following way:

$$\int_0^\infty dr_1 \int_0^\infty dr_2 = \int_0^\infty dr_1 \int_0^{r_1} dr_2$$
$$+ \int_0^\infty dr_1 \int_{r_1}^\infty dr_2.$$

It is then quite straightforward to evaluate the different terms, and we shall only quote the final results. The normalizing constant N is determined from the equation

$$N^{-2} = \int \int |\psi(\mathbf{r}_1,\mathbf{r}_2)|^2 \, d\mathbf{r}_1 \, d\mathbf{r}_2$$
$$= \frac{\pi^2 a_0{}^6 [2(10s^2 + 5s + 1)]}{\alpha^6 s^3 (s + 1)^5}. \quad (6)$$

The expectation value of the Hamiltonian is

$$\langle H \rangle = \langle T_1 \rangle + \langle T_2 \rangle + \langle V_1 \rangle + \langle V_2 \rangle + \langle V_{12} \rangle, \quad (7)$$

where

$$\langle T_1 \rangle = -(\hbar^2/2m) \int \int \psi^*(\mathbf{r}_1,\mathbf{r}_2)\nabla_1{}^2\psi(\mathbf{r}_1,\mathbf{r}_2) \, d\mathbf{r}_1 \, d\mathbf{r}_2$$
$$= (\hbar^2/2m) \int \int |\nabla_1\psi(\mathbf{r}_1,\mathbf{r}_2)|^2 \, d\mathbf{r}_1 \, d\mathbf{r}_2$$
$$= [(s^2 + 1)/4]\alpha^2(e^2/a_0), \quad (8)$$

$$\langle V_1 \rangle = -Ze^2 \int \int \psi^*(\mathbf{r}_1, \mathbf{r}_2)(1/r_1)\psi(\mathbf{r}_1, \mathbf{r}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2$$
$$= -Z[(s+1)/2]\alpha(e^2/a_0), \quad (9)$$

and

$$\langle V_{12} \rangle = e^2 \int \int \psi^*(\mathbf{r}_1, \mathbf{r}_2)(1/r_{12})\psi(\mathbf{r}_1, \mathbf{r}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2$$
$$= [s(s+1)(4s+1)/(10s^2+5s+1)]\alpha(e^2/a_0). \quad (10)$$

In the above, we have expanded $1/r_{12}$ in spherical harmonics[1] and performed the integration over the polar angles to obtain (10). The expectation values $\langle T_2 \rangle$ and $\langle V_2 \rangle$ are respectively equal to $\langle T_1 \rangle$ and $\langle V_1 \rangle$ by symmetry. The expectation value of the Hamiltonian is therefore given by

$$\langle H \rangle = \frac{(s^2+1)}{2}\alpha^2\frac{e^2}{a_0} - Z(s+1)\alpha\frac{e^2}{a_0}$$
$$+ \frac{s(s+1)(4s+1)}{10s^2+5s+1}\alpha\frac{e^2}{a_0}$$
$$= \frac{s^2+1}{2}\alpha^2$$
$$- \frac{(s+1)[(10Z-4)s^2+(5Z-1)s+Z]}{10s^2+5s+1}\alpha$$
$$= E(\alpha,s), \quad (11)$$

in atomic units of e^2/a_0. For $s = 1$, this reduces to the result given in Schiff[1]:

$$E(\alpha) = \alpha^2 - (2Z - \tfrac{5}{8})\alpha. \quad (12)$$

The estimate for the ground-state energy E_0 is obtained as usual by minimizing $E(\alpha,s)$ of Eq. (11) with respect to the two parameters α and s. Some further simplification may, however, be done analytically. Note that in Eq. (11) the first term represents the kinetic and the second the potential energy of the system. Application of the variational condition

$$\left.\frac{\partial}{\partial \alpha}E(\alpha,s)\right|_{\alpha_0} = 0$$

leads to

$$\alpha_0 = (s+1)[(10Z-4)s^2+(5Z-1)s+Z]$$
$$\times [(s^2+1)(10s^2+5s+1)]^{-1}. \quad (13)$$

From Eqs. (13) and (11), it may be seen that the magnitude of the potential energy is just twice that of the kinetic energy of the system, which is the statement of the virial theorem for Coulomb force. Substituting the optimum α_0 from Eq. (13) in Eq. (11), the energy of the system may now be expressed in terms of the single parameter s:

$$E(s) = -(s+1)^2[(10Z-4)s^2+(5Z-1)s+Z]^2$$
$$\times [2(s^2+1)(10s^2+5s+1)^2]^{-1}. \quad (14)$$

This expression is minimum for some optimum $s = s_0$, yielding the ground-state upper bound E_0 for the energy. This may be obtained for a given Z by plotting the function $E(s)$ as a function of s, or by finding the real root s_0 of the fifth-order algebraic equation $dE/ds = 0$ in the computer.

III. RESULTS

In Table I we display the numerical results for the first four members of the helium isoelectronic sequence. For comparison, we also show in the table the results of the one-parameter variational calculation when $s = 1$, and also the best available results[4] from extensive variational calculations. The present choice of the trial wave function makes the most improvement in H$^-$, which was unbound in the one-parameter calculation and is now bound. As the atomic number increases, the Coulomb field of the nucleus as seen by an electron is less sensitive to the position of the other electron, and the parameter s approaches unity. While it is not surprising that a two-parameter variational calculation yields better results than a one-parameter one, it is gratifying to show that the improved calculation can be done almost as easily.

Finally, we note that the trial wave function (2), when written in the form

$$\psi(\mathbf{r}_1,\mathbf{r}_2) = N\exp\left[-\frac{s+1}{2}\alpha\frac{r_1+r_2}{a_0}\right]$$
$$\times \exp\left[-\frac{s-1}{2}\alpha\frac{|r_1-r_2|}{a_0}\right],$$

may be looked upon as a generalization of the Hylleraas-like function

$$\psi = N\exp[-\alpha'(r_1+r_2)/a_0](1+c|r_1-r_2|), \quad (15)$$

where α' and c are the two variational parameters. However, the two-parameter Hylleraas trial wave function is *not* the same as Eq. (15), since it is given by[2]

$$\psi_{\text{Hylleraas}} = N\exp[-\alpha'(r_1+r_2)/a_0]$$
$$\times (1+c|\mathbf{r}_1-\mathbf{r}_2|). \quad (16)$$

Our simple wave function (2) does not contain any angular correlations and therefore cannot account for much of the correlation energy.

ACKNOWLEDGMENTS

Table I. Ground-state energy[a] of helium-like atomic systems.

Two-electron system	One-parameter calculation[b] $-E_0$	Present calculation[c]			Best estimate[d] of $-E_0$
		α_0	s_0	$-E_0$	
H$^-$	0.473	0.9144	0.4598	0.506	0.528
He	2.848	1.8560	0.8172	2.873	2.904
Li$^+$	7.223	2.8477	0.8872	7.246	7.280
Be^{2+}	13.598	3.8443	0.9183	13.621	13.656

[a] The energy is given in atomic units, rounded off to the third decimal place.

[b] With trial wave function given by Eq. (1).

[c] The optimum values of α_0 and s_0 that minimize $E(\alpha,s)$ of Eq. (11) are shown.

[d] From Ref. 4.

support, enabling him to spend the summer of 1976 there.

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