PHYSICAL REVIEW A VOLUME 26, NUMBER 3 SEPTEMBER 1982

Variational method for a three-body problem of two-electron atoms

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(Received 31 December 1981)

The ground-state wave function of a heliumlike atom is assumed to be $\Psi = N(1+\mu\lambda r_{12}) \times \exp[-\mu(\beta r_> + r_<)]$, where $r_<, r_> = \min, \max(r_1, r_2)$, r_1 and r_2 are the distances of the electrons from the nucleus, and r_{12} is the distance between the electrons. The parameters μ, β, and λ are determined by minimizing the energy of the system and it can be reduced to a two-parameter problem. Numerical results are presented to show the improvement for the ground-state energy from the two- or three-parameter calculations.

The helium and heliumlike atoms have been a subject of intensive study for many years. Pekeris[1] used a variational wave function containing 1078 terms. Although we can get an extremely accurate wave function and energy if we use a function with a hundred or so terms, we lose the simple physical interpretation. "The more accurate the calculations become the more the concepts tend to vanish into thin air."[2] So helium and heliumlike atoms are still receiving considerable attention with a view to finding simpler wave functions.

The trial wave function for the ground state in the usual one-parameter example given in textbooks[3] is

$$\Psi = (\alpha^3/\pi a_0^3)\exp[-\alpha(r_1+r_2)/a_0] \ , \tag{1}$$

where a_0 is the radius of the first Bohr orbit in hydrogen and α is interpreted as an effective nuclear charge as seen by the electrons. In Eq. (1) the coordinates of the two electrons enter the wave function with equal weight. Srivastava and Bhaduri[4] proposed a modified trial wave function

$$\Psi = N\exp[-\alpha(sr_> + r_<)/a_0], \quad r_1 \neq r_2 \tag{2}$$

where $r_<, r_> = \min, \max(r_1, r_2)$ and $s \leq 1$. The reasoning is that 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. But Eq. (2) does not take the interaction between electrons into account and therefore cannot account for much of the correlation energy.

Srivastava *et al.*[5] use the Feshbach-Rubinow approximation to obtain analytic expressions for the ground-state energy and wave function. They assume that the wave function is a function of a single variable R,

$$\Psi = \Phi(R), \quad R = \tfrac{1}{2}(sr_> + r_< + \eta r_{12}) \ , \tag{3}$$

and the wave function is found to be of the form of

$$\Phi(R) = \exp(-\lambda R) \ , \tag{4}$$

where λ is a constant and R is that of Eq. (3). Therefore, their method is in fact equivalent to a three-parameter variational calculation with a trial function (4). They show the improvement from unmodified Feshbach-Rubinow calculations.[6] But Eq. (4) is not very satisfying because there is little flexibility with respect to the electron-electron correlation, i.e., it is restricted to the exponential form. The exponential form for r_1 and r_2 is probably a good approximation but it is not clear whether this is also the case for r_{12}. Lie *et al.*[7] proposed the wave function

$$\Psi(r_1, r_2, r_{12}) = \phi(r_{12})\exp[-(\alpha r_> + \beta r_<)] \ , \tag{5}$$

where α and β are variational parameters, while ϕ is an arbitrary function. The improvement is better but not very significant for heliumlike atoms. We can get a similar effect by using a simple three-parameter trial wave function

$$\Psi = N(1+\mu\lambda r_{12})\exp[-\mu(\beta r_> + r_<)] \ , \tag{6}$$

where μ, β, λ are the variational parameters. The variational calculations are easy because of the exponential nature of the wave function and the results are better than those obtained by Eqs. (1), (2), and (4). It is convenient to rewrite Eq. (6) in the form

$$\Psi = N(1+\mu\lambda r_{12})\exp\{-\mu[(\beta+1)(r_1+r_2)/2 + (\beta-1)|r_1-r_2|/2]\} \ . \tag{7}$$

The Hamiltonian for a two-electron atom with a stationary nucleus can be written as

$$H = -\tfrac{1}{2}(\nabla_1^2 + \nabla_2^2) - Z\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{r_{12}} \ , \tag{8}$$

where Z is the atomic number of the two-electron ion being considered, ∇_1^2 and ∇_2^2 are the Laplacian operators with respect to the coordinates of the two electrons, and lengths and energies are expressed in atomic units ($e = m = \hbar = 1$). The volume element is

$$dv = 8\pi^2 r_{12} r_1 r_2 dr_{12} dr_1 dr_2 = \pi^2 u (s^2 - t^2)\, du\, ds\, dt \ , \tag{9}$$

where $u = r_{12}$, $s = r_1 + r_2$, $t = r_1 - r_2$ are the Hylleraas coordinates[8] and $-u \leqslant t \leqslant u$, $0 \leqslant u \leqslant s < \infty$. Since Ψ [Eq. (7)] is symmetric with t, the contribution in the integral from $-t$ is identical with that from $+t$. We therefore restrict ourselves to positive values of t in the integrals and multiply the volume element by a factor of 2. If we set $\sigma = \mu\beta$, $\tau = \mu t$, and $\eta = \mu u$, the resulting volume element is then found to be

$$dv = \frac{2\pi^2}{\mu^6} \eta (\sigma^2 - \tau^2)\, d\tau\, d\eta\, d\sigma \ . \tag{10}$$

The normalizing constant N is determined by

$$N^{-2} = \frac{2\pi^2}{\mu^6} \int_0^\infty e^{-(\beta+1)\sigma} d\sigma \int_0^\sigma \eta (1 + 2\lambda\eta + \lambda^2 \eta^2) d\eta \int_0^\eta (\sigma^2 - \tau^2) e^{-(\beta-1)\tau} d\tau = \frac{\pi^2}{\mu^6} N(\beta, \lambda) \tag{11}$$

and

$$N(\beta, \lambda) = \frac{2(10\beta^2 + 5\beta + 1)}{\beta^3(\beta+1)^5} + \frac{2\lambda(72\beta^3 + 47\beta^2 + 18\beta + 3)}{\beta^4(\beta+1)^6} + \frac{6\lambda^2(56\beta^4 + 42\beta^3 + 22\beta^2 + 7\beta + 1)}{\beta^5(\beta+1)^7} \ . \tag{12}$$

The expectation value of the Hamiltonian is

$$\langle H \rangle = \langle T \rangle + \langle V \rangle + \langle V_{12} \rangle = \frac{T(\beta, \lambda)}{N(\beta, \lambda)} \mu^2 - \frac{V(\beta, \lambda)}{N(\beta, \lambda)} \mu + \frac{V_{12}(\beta, \lambda)}{N(\beta, \lambda)} \mu = E(\mu, \beta, \lambda) \ , \tag{13}$$

where

$$\begin{aligned} T(\beta, \lambda) = {} & \tfrac{1}{2}(\beta^2 + 1) N(\beta, \lambda) + \frac{2\lambda^2(10\beta^2 + 5\beta + 1)}{\beta^3(\beta+1)^5} - \frac{\lambda(13\beta^2 + 6\beta + 1)}{\beta^3(\beta+1)^4} - \frac{\lambda(\beta-1)(3\beta+1)}{\beta^3(\beta+1)^4} \\ & - \frac{3\lambda^2(35\beta^3 + 21\beta^2 + 7\beta + 1)}{2\beta^4(\beta+1)^5} - \frac{3\lambda^2(\beta-1)(5\beta^2 + 4\beta + 1)}{2\beta^4(\beta+1)^5} \ , \end{aligned} \tag{14}$$

$$V(\beta, \lambda) = \frac{2Z(10\beta^2 + 5\beta + 1)}{\beta^3(\beta+1)^4} + \frac{2\lambda Z(59\beta^3 + 41\beta^2 + 17\beta + 3)}{\beta^4(\beta+1)^5} + \frac{3\lambda^2 Z(77\beta^4 + 63\beta^3 + 37\beta^2 + 13\beta + 2)}{\beta^5(\beta+1)^6} \ , \tag{15}$$

$$V_{12}(\beta, \lambda) = \frac{2(4\beta+1)}{\beta^2(\beta+1)^4} + \frac{4\lambda(10\beta^2 + 5\beta + 1)}{\beta^3(\beta+1)^5} + \frac{\lambda^2(72\beta^3 + 47\beta^2 + 18\beta + 3)}{\beta^4(\beta+1)^6} \ . \tag{16}$$

We can minimize the energy for μ, i.e., $\partial \langle H \rangle / \partial \mu = 0$, it yields

$$\mu = \frac{1}{2} \left[\frac{V(\beta, \lambda)}{T(\beta, \lambda)} - \frac{V_{12}(\beta, \lambda)}{T(\beta, \lambda)} \right] \ . \tag{17}$$

Substituting the optimum μ from Eq. (17) in Eq. (13), the energy of the system may now be expressed in terms of β and λ,

$$E(\beta, \lambda) = -\frac{1}{4} \left[\frac{V(\beta, \lambda)}{T(\beta, \lambda)} - \frac{V_{12}(\beta, \lambda)}{T(\beta, \lambda)} \right] \left[\frac{V(\beta, \lambda)}{N(\beta, \lambda)} - \frac{V_{12}(\beta, \lambda)}{N(\beta, \lambda)} \right] \ . \tag{18}$$

TABLE I. Expectation values of various operators for the ground state of He-like atoms. Values of $-\langle T \rangle / (\langle V \rangle + \langle V_{12} \rangle)$ are included to indicate the degree of agreement with the virial theorem.

Two-electron system	$\langle T \rangle$	$\langle V \rangle$	$\langle V_{12} \rangle$	$-\langle T \rangle / (\langle V \rangle + \langle V_{12} \rangle)$
H^-	0.521 294	−1.376 439	0.333 850	0.500 000
He	2.899 420	−6.753 986	0.955 147	0.500 000
Li^+	7.275 719	−16.127 523	1.576 085	0.500 000
Be^{2+}	13.651 332	−29.501 752	2.199 089	0.500 000

TABLE II. Ground-state energy of He-like atoms. The energy is given in atomic units.

Two-electron system	Two-parameter calculation[a]	Three-parameter calculation[b]	Present calculation[c]				Ref. 1
	$-E_0$	$-E_0$	μ	β	λ	$-E_0$	$-E_0$
H^-	0.506	0.5206	0.92999	0.6897	0.3457	0.5213	0.5278
He	2.873	2.8983	1.92476	0.8951	0.1528	2.8994	2.9037
Li^+	7.246	7.2748	2.92620	0.9355	0.0953	7.2757	7.2799
Be^{2+}	13.621	13.6506	3.92702	0.9532	0.0690	13.6513	13.6556

[a] From Ref. 4.

[b] From Ref. 5.

[c] The optimum values of μ, β, and λ that minimize $E(\mu, \beta, \lambda)$ of Eq. (13) are shown.

It is now reduced to a two-parameter problem. Equation (18) is minimum for some optimun values β and λ, yielding the ground-state upper bound E_0 for the energy.

The numerical procedure for obtaining the optimum values of β and λ is simple. First a value for β ($\beta \leq 1$) is picked and has been kept constant while the value of λ has been modified, in succession, until those values of β and λ are found which make $E(\beta, \lambda)$ a minimum. Then λ has been kept constant and the value of β has been modified, in succession; this further lowers the magnitude of $E(\beta, \lambda)$. This cycling has been repeated until the minimum of $E(\beta, \lambda)$ has been found.

In Table I the wave function is checked for agreement with the virial theorem, which predicts $-\langle T\rangle/(\langle V\rangle + \langle V_{12}\rangle) = 0.5$.

In Table II 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 two-[4] and three-parameter[5] variational calculations, and also the results from Ref. 1. In view of the simplicity, the accuracy of our results is quite remarkable.

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