

Three-body problem of two-electron atoms

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The ground-state wave function of a heliumlike atom is assumed to be $\psi = \phi(r_3)\exp(-\alpha r_> - \beta r_<)$, where $r_<, r_> = \min, \max(r_1, r_2)$, r_1 and r_2 being the distances of the electrons from the nucleus. An equation which determines the electron-electron correlation function $\phi(r_3)$ is derived and numerically solved. The parameters α and β are determined by minimizing the energy of the system. This is an extension of the Feshbach-Rubinow-type approximation which has recently been applied to the same problem. The positronium negative ion (eee^-) is also examined by the same method. It is found for the binding energies that the improvement over the Feshbach-Rubinow approximation is substantial for the eee^- system, but less significant for heliumlike atoms. It is claimed that the proposed method is particularly useful in calculating quantities which are sensitive to the short-range correlation between the electrons.

I. INTRODUCTION

As the simplest atomic systems that defy analytical solutions, the helium and heliumlike atoms have been a subject of intensive study for many years. The most extensive and accurate calculation so far done is the one due to Perkeris^{1,2} who used a variational wave function which consisted of over 1000 terms. The ground-state energy that he obtained is believed to be accurate to one part in 10^9 . However, the problem is still receiving considerable attention with a view to finding simpler methods and wave functions. Recently the Feshbach-Rubinow (FR) approximation and its improved version have been applied to the problem, with some encouraging results.^{3,4} The purpose of this paper is to report on a further attempt in the same line, with an improvement with respect to the electron-electron correlation.

Before presenting our idea, let us summarize the FR method applied to the atomic three-body problem. In this method one assumes that the wave function Ψ is a function of a single variable R ,

$$\Psi = \Phi(R), \quad R = \frac{1}{2}(r_1 + r_2 + \eta r_3), \quad (1.1)$$

where r_1 is the interparticle distance between particles 2 and 3, and likewise for r_2 and r_3 .³ Particle 3 is the nucleus and η is a variational parameter. The Schrödinger equation for the three-body system can then be reduced to a Schrödinger-like equation for Φ with an effective potential. When the original interactions are Coulomb, the effective potential for Φ turns out to be a Coulomb potential. The function Φ and energy are obtained analytically, and η is determined by minimizing the energy. Srivastava *et al.*⁴ proposed to replac-

ing R of Eq. (1.1) by

$$R = \frac{1}{2}(\alpha r_> + r_< + \eta r_3), \quad (1.2)$$

where $r_> = r_1$, $r_< = r_2$ if $r_1 > r_2$, and vice versa, and α and η are variational parameters. With R of Eq. (1.2) the screening effect is better taken care of. We will refer to the above two versions of the FR approach as FR1 and FR2.

The FR wave function is found to be of the form of

$$\Phi(R) = \exp(-\lambda R), \quad (1.3)$$

where λ is a constant and R is that of Eq. (1.1) or Eq. (1.2). Therefore, the FR method applied to this problem is in fact equivalent to a variational calculation with a trial function (1.3). It is indeed possible to show from a dimensional analysis alone that the effective potential for Φ is a Coulomb potential and that Φ takes the exponential form of Eq. (1.3).

A feature of the FR wave function which is not very satisfying is that 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 if it is also the case for r_3 . It would be interesting to see what the electron-electron correlation is like when it is treated in a more flexible manner. Motivated by the above observation we now propose the wave function

$$\psi(r_1, r_2, r_3) = \phi(r_3) \exp[-(\alpha r_> + \beta r_<)], \quad (1.4)$$

where α and β are variational parameters, while ϕ is an arbitrary function. This is an obvious generalization of the FR wave function (1.3). The Schrödinger equation for the system can again be

reduced to a Schrödinger-like equation for ϕ . Unfortunately this equation cannot be solved analytically, but it is straightforward to solve it numerically. The optimum values of α and β are found by minimizing the energy. In addition to the heliumlike atoms we will consider the bound state of the positronium negative ion (eee^+).

II. REDUCTION OF THE SCHRÖDINGER EQUATION

For an S-state of a three-body system, the Schrödinger equation reads

$$\sum_{\text{cyc1}} \left\{ -\frac{\hbar^2}{2} \left[\left(\frac{1}{m_2} + \frac{1}{m_3} \right) \left(\frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1} \frac{\partial}{\partial r_1} \right) + \frac{1}{m_1} \frac{r_2^2 + r_3^2 - r_1^2}{r_2 r_3} \frac{\partial^2}{\partial r_2 \partial r_3} \right] + V_1(r_1) \right\} \Psi = E\Psi. \quad (2.1)$$

This can be identified with the Euler-Lagrange equation for $\delta I=0$, where

$$I = \int_0^\infty dr_1 \int_0^\infty dr_2 \int_{|r_1-r_2|}^{r_1+r_2} dr_3 r_1 r_2 r_3 F(r_1, r_2, r_3) \quad (2.2)$$

with

$$F(r_1, r_2, r_3) = \sum_{\text{cyc1}} \left\{ \frac{\hbar^2}{2} \left[\left(\frac{1}{m_2} + \frac{1}{m_3} \right) \left(\frac{\partial \Psi}{\partial r_1} \right)^2 + \frac{1}{m_1} \frac{r_2^2 + r_3^2 - r_1^2}{r_2 r_3} \frac{\partial \Psi}{\partial r_2} \frac{\partial \Psi}{\partial r_3} \right] + V_1(r_1) \Psi^2 \right\} - E\Psi^2. \quad (2.3)$$

For a heliumlike atom, we put $m_1 = m_2 = m$ (electron mass), $m_3 \rightarrow \infty$, $V_1(r) = V_2(r) = -Ze^2/r$, and $V_3(r) = e^2/r$.

If we use Eq. (1.4) for Ψ , the r_1 and r_2 integrations in I can be done, and we obtain

$$I = \frac{\hbar^2}{m} \int_0^\infty dz [A(z)(\phi'^2 + \kappa^2 \phi^2) + 2B(z)\phi\phi' + C\phi^2], \quad (2.4)$$

where $z = r_3$, $\phi' = d\phi/dz$, $\kappa^2 = -Em/\hbar^2$. The functions A , B , and C are defined by

$$A(z) = 2z \iint dx dy xy e^{-2(\alpha x + \beta y)}, \quad (2.5)$$

$$2B(z) = - \iint dx dy [\alpha y (z^2 + x^2 - y^2) + \beta x (y^2 + z^2 - x^2)] e^{-2(\alpha x + \beta y)}, \quad (2.6)$$

$$C(z) = -2 \iint dx dy \left(\frac{me^2}{\hbar^2} [Zz(x+y) - xy] - \frac{\alpha^2 + \beta^2}{2} xyz \right) e^{-2(\alpha x + \beta y)}. \quad (2.7)$$

Here the integrations are done for $\{0 < x - y < z, x + y > z\}$. Explicit expressions for A , B , and C are given in the Appendix. Note that $A(z)$ is positive definite. The variation $\delta I=0$ yields

$$A\phi'' + A'\phi' + (B' - C - \kappa^2 A)\phi = 0, \quad (2.8)$$

which can be rewritten

$$\frac{d^2 f}{dz^2} - [\kappa^2 + v(z)]f = 0, \quad (2.9)$$

where

$$f(z) = A^{1/2}(z)\phi(z), \quad (2.10)$$

$$v(z) = \frac{A''}{2A} - \left(\frac{A'}{2A} \right)^2 - \frac{B' - C}{A}. \quad (2.11)$$

Thus the three-body problem has been reduced to that of two electrons with an effective potential $v(z)$.

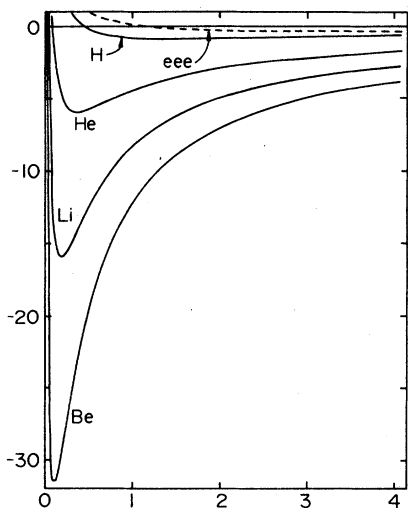
If we assume that $\alpha = \beta$, which corresponds to FR1, $v(z)$ is given by

$$v(z) = \alpha^2 - \alpha^2 \left(\frac{u(1+u)}{3+3u+u^2} \right)^2 + \frac{2me^2\alpha}{\hbar^2} \frac{3-3(2Z-1)u-(6Z-1)u^2}{u(3+3u+u^2)}, \quad (2.12)$$

where $u = 2\alpha z$. This effective potential v is like an attractive Coulomb potential for very large z , and a repulsive Coulomb potential for very small z . For $\alpha \neq \beta$, which corresponds to FR2, the expression for $v(z)$ becomes quite complicated but its qualitative behavior remains the same as that of Eq. (2.12). Figure 1 shows $v(z)$ for $\alpha \neq \beta$ (for optimal values of α and β). This $v(z)$ resembles the internuclear potentials in a diatomic molecule. This resemblance is not accidental. For example, if the two electrons in H^- are replaced by protons and the H^- nucleus by an electron, the H^- ion becomes a H_2^+ molecule. Hence the mechanism for the effective interaction between the two electrons in H^- is similar to that for the two protons in the H_2^+ molecule.⁵

Equation (2.9) has a "bound-state" solution which decays like $f(z) \sim e^{-\kappa z}$ as $z \rightarrow \infty$. This does not necessarily mean that $\phi = A^{-1/2}f$ decays as $z \rightarrow \infty$. In fact, $A(z)$ decays like $e^{-2\alpha z}$ (in both cases of $\alpha = \beta$ and $\alpha \neq \beta$), hence ϕ decays if and only if $\kappa > \alpha$. Let us add that even if ϕ does not decay, Ψ itself is normalizable. At $z=0$, f starts with $f(0)=0$. But, since $A(z) \propto z$ for $z \approx 0$, $\phi(0)$ is not zero.

So far we have considered heliumlike atoms.

FIG. 1. "Effective potential" $v(z)$ in atomic units.

For the eee^+ system, we put $m_1 = m_2 = m_3 = m$ and $z = 1$. The only change is that the function C gets an additional term which originates from the terms containing $1/m_3$ in Eq. (2.3). Because of this the effective potential gets an additional term which is repulsive. The details are relegated to the Appendix.

III. RESULTS AND DISCUSSIONS

We have done the calculations in two approximations I and II. In I we put $\alpha = \beta$. This is an extension of FR1. In approximation II we take $\alpha \neq \beta$, an extension of FR2. The energies for heliumlike atoms and eee^+ are shown in Table I and compared with previous results. The FR2 result for eee^+ is not available. All numerical results in this paper are given in atomic units, i.e., energy in 2 Ry and distance in Bohr radius. The accuracy improves in the order of FR1, I, FR2, II. The im-

TABLE I. Ground-state energies. ^a

System	FR1	I	FR2	II	Best estimates
H ⁻	0.5079	0.5094	0.5206	0.5215	0.5278
He	2.8896	2.8913	2.8983	2.8996	2.9037
Li ⁺	7.2668	7.2685	7.2748	7.2761	7.2799
Be ⁺⁺	13.6429	13.6446	13.6506	13.6519	13.6556
eee^+	0.2391	0.2441		0.2562	0.262

^a The negative of the energies in a.u. The columns I and II show the results of the present calculations, with $\alpha = \beta$ for I and $\alpha \neq \beta$ for II. The results of FR1 and FR2 are taken from Refs. 3 and 4, respectively. The best estimates are from Ref. 2, for heliumlike atoms and from Ref. 6 for eee^+ .

TABLE II. Comparison of variational parameters in FR2 and II. ^a

System	FR2		II	
	α'	β'	α	β
H ⁻	0.6504	0.9434	0.6495	0.9352
He	1.724	1.931	1.719	1.921
Li ⁺	2.736	2.930	2.730	2.920
Be ⁺⁺	3.802	3.929	3.740	3.915
eee^+			0.2379	0.4454

^a The values are given in atomic units, i.e., energy in 2 Ry and distance in Bohr radius.

provement of II over FR2, and that of I over FR1 are not very significant for heliumlike atoms, but the improvement of I over FR1 is quite substantial for eee^+ . This is probably because the electron-electron correlation is more important in eee^+ than in the other systems.

Next, let us compare the values of the variational parameters in FR2 and II. Recall that the unnormalized FR2 wave function is given by Eq. (1.3), i.e.,

$$\Phi = e^{-\lambda R} = \exp[-\frac{1}{2} \lambda \eta r_3 - (\alpha' r_2 + \beta' r_1)], \quad (3.1)$$

where

$$\alpha' = \frac{1}{2} \alpha \lambda, \quad \beta' = \frac{1}{2} \lambda. \quad (3.2)$$

This α' (not α) and β' of FR2 correspond to α and β of II, respectively. All these constants in Eqs. (3.1) and (3.2) are given in Ref. 4. Table II compares α' and β' of FR2 with α and β of II; α' and β' are slightly larger than α and β .

For the asymptotic behavior of $\phi(z)$ for $z \rightarrow \infty$, we pointed out in Sec. II that the criterion for convergence is $\kappa > \alpha$. In the atomic units that we are using, $\kappa = |E|^{1/2}$. We show $\kappa - \alpha$ in the approximations I and II in Table III. It is clear that $\phi(z)$ for large values of z is more suppressed in approximation II than in I. Note that ϕ converges for eee^+ and for H⁻ in approximation II, while it diverges in other cases.

TABLE III. Convergence of ϕ . ^a

System	Approximation	
	I	II
H ⁻	-0.129	0.073
He	-0.148	-0.016
Li ⁺	-0.154	-0.036
Be ⁺⁺	-0.158	-0.045
eee^+	0.134	0.265

^a $\phi \sim \exp[-(\kappa - \alpha)z]$. The values of $\kappa - \alpha$ in a.u. are shown.

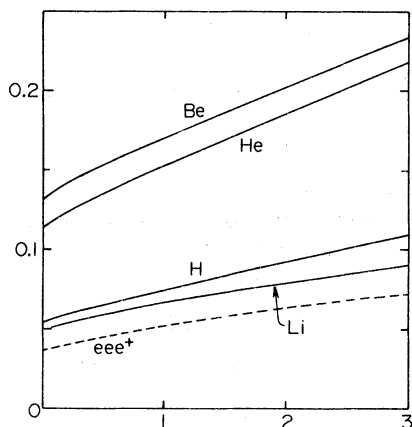


FIG. 2. "Correlation function" $\phi(z)$ in atomic units. For H^- , He, Li^+ , Be^{++} , the figure shows $\phi/10$, $\phi/10^2$, $\phi/10^3$, $\phi/10^3$, respectively. $\phi(0)$ for the five cases are H^- (0.543), He (11.41), Li^+ (49.31), Be^{++} (131.3), and eee^+ (0.036).

The function $\phi(z)$ for $z=0 \sim 3$ a.u. is shown in Fig. 2. The normalization of ϕ is such that⁷

$$\int_0^\infty f^2(z) dz = \int_0^\infty A(z) \phi^2(z) dz = 1. \quad (3.4)$$

Note that the curvature (second derivative) of ϕ at short distances is negative. This is because of the repulsion in $v(z)$ at short distances. On the other hand, ϕ in the FR method is exponential and hence its curvature is always positive. For eee^+ , ϕ reaches its maximum at $z \sim 7$ a.u., and the difference from the FR cases is quite appreciable. This is the reason why the improvement in the energy is quite significant for the eee^+ system. Even for other systems (H^- , He, ...), if one is going to evaluate some quantity which is sensitive to the electron-electron correlation, our wave function could give appreciably better results than the FR wave functions. In order to substantiate this claim let us examine the expectation value $\langle \delta(\vec{r}_1 - \vec{r}_2) \rangle$. Its accuracy is a sensitive test of

TABLE IV. Expectation value $\langle \delta(\vec{r}_1 - \vec{r}_2) \rangle$.

System	MCFC ^a	FR2	II	Best estimates ^b
H^-	0.004 34	0.004 34	0.002 95	0.002 74
He	0.135 7	0.124 2	0.107 4	0.106 3
Li^+		0.585 8	0.536 3	
Be^{++}		1.627	1.529	
eee^+			0.000 162	

^a Multiconfiguration frozen-core approximation with (1s, 2s', 2p, 2p') (Ref. 8).

^b See Refs. 8 and 9.

the electron-electron correlation at short distances. With the wave function of Eq. (1.4) and the normalization condition (3.3), we obtain

$$\langle \delta(\vec{r}_1 - \vec{r}_2) \rangle = \phi^2(0)/8\pi(\alpha + \beta)^3. \quad (3.4)$$

In the FR approximation it is given by the same formula with the substitutions

$$\begin{aligned} \alpha &\rightarrow \alpha', \quad \beta \rightarrow \beta', \\ \phi^2(0) &\rightarrow 2^5 \lambda^6 / (5! p), \end{aligned} \quad (3.5)$$

where p is a constant defined by Eq. (A2) of Ref. 4. Table IV summarizes the results and compares with those of other calculations. In view of its simplicity, the accuracy of our results is quite remarkable.

Note added in proof. Contrary to what we said in note 5, $v(z)$ in approximation II does not go to zero as $z \rightarrow \infty$. The correct limit of $v(\infty)$ is given by

$$v(\infty) = -(\beta^2 - \alpha^2) \begin{cases} \left(\frac{me^2 Z}{\hbar^2 \beta} - \frac{1}{2} \right) & \text{for } H^-, \text{He}, \dots \\ \left(\frac{me^2}{\hbar^2 \beta} - 1 \right) & \text{for } eee^+. \end{cases}$$

Because of this change the discussions on the asymptotic behavior of $f(z)$ and $\phi(z)$ are not valid, and Table III becomes irrelevant. All other results are not affected.

ACKNOWLEDGMENT

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APPENDIX

Let us show some details of the integrals in Eqs. (2.5)–(2.7). It is convenient to introduce

$$s = x + y, \quad t = x - y, \quad \gamma = \alpha + \beta, \quad \epsilon = \alpha - \beta, \quad (A1)$$

and

$$G_{mn}(z) = \int_0^z dt \int_z^\infty ds s^m t^n e^{-(\gamma s + \epsilon t)}. \quad (A2)$$

Then A , B , and C are given by

$$A(z) = \frac{1}{4} z (G_{20} - G_{02}), \quad (A3)$$

$$B(z) = -\frac{1}{8} (\gamma z^2 G_{10} - \epsilon z^2 G_{01} + \epsilon G_{21} - \gamma G_{12}), \quad (A4)$$

$$C(z) = \frac{m}{\hbar^2} \left(-Z e^2 z G_{10} + \frac{e^2 A(z)}{z} \right) + \frac{\gamma^2 + \epsilon^2}{4} A(z). \quad (A5)$$

The functions G_{mn} are a product of a Γ function and an incomplete Γ function and are given by

$$G_{10} = (1 + \gamma z) e^{-\gamma z} (1 - e^{-\epsilon z}) / \gamma^2 \epsilon, \quad (\text{A6})$$

$$G_{01} = e^{-\gamma z} [1 - (1 + \epsilon z) e^{-\epsilon z}] / \gamma \epsilon^2, \quad (\text{A7})$$

$$G_{20} = (2 + 2\gamma z + \gamma^2 z^2) e^{-\gamma z} (1 - e^{-\epsilon z}) / \gamma^3 \epsilon, \quad (\text{A8})$$

$$G_{02} = e^{-\gamma z} [2 - (2 + 2\epsilon z + \epsilon^2 z^2) e^{-\epsilon z}] / \gamma \epsilon^3, \quad (\text{A9})$$

$$G_{21} = G_{20} [1 - (1 + \epsilon z) e^{-\epsilon z}] / \epsilon (1 - e^{-\epsilon z}), \quad (\text{A10})$$

$$G_{12} = G_{02} (1 + \gamma z) / \gamma. \quad (\text{A11})$$

In the limit of $\epsilon \rightarrow 0$, we find

$$A(z) = (1/2\gamma^5) u^2 (1 + u + \frac{1}{3} u^2) e^{-u}, \quad (\text{A12})$$

$$B(z) = (-1/12\gamma^4) u^3 (1 + u) e^{-u}, \quad (\text{A13})$$

$$C(z) = \frac{m e^2}{2\hbar^2 \gamma^4} u [1 - (2Z - 1)u - (2Z - \frac{1}{3})u^2] e^{-u} + \frac{1}{4} \gamma^2 A(z), \quad (\text{A14})$$

where $u = \gamma z = 2\alpha z$.

The formulas given above are for heliumlike atoms. For the eee^* system, A and B remain the same while C is given by

$$C(z) = [C(z) \text{ of (A5) with } Z = 1] + \frac{1}{4} (\gamma^2 + \epsilon^2) A(z) + \frac{1}{16} (\gamma^2 - \epsilon^2) z (G_{20} + G_{02} - 2z^2 G_{00}). \quad (\text{A15})$$

¹We confine ourselves throughout our paper to the ground state of the nonrelativistic system with Coulomb forces only. The mass of the nucleus is taken to be infinite.

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⁴M. K. Srivastava, R. K. Bhaduri, and A. K. Dutta, Phys. Rev. A 14, 1961 (1976).

⁵However, there is a subtle difference. In our case the nucleus is fixed in space but electrons are not. The internuclear potential for H_2^+ approaches the ground-

state energy of a H atom as the separation becomes infinite. This has a clear physical interpretation. Our $v(z)$ goes to zero for $z \rightarrow \infty$, and we have no clear physical picture to explain this asymptotic behavior of $v(z)$.

⁶A. A. Frost, M. Inokuti, and J. P. Lowe, J. Chem. Phys. 41, 482 (1964).

⁷ Ψ is normalized by $\int \int \int \Psi^2 xyz \, dx dy dz = 1$, where the integration range is the same as that for Eq. (2.2), i.e., $\{|x - y| < z, x + y > z\}$. This means that $\int \int \Psi^2 d\vec{r}_1 d\vec{r}_2 = 8\pi^2$.

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⁹C. L. Perkeris, Phys. Rev. 126, 1470 (1962).