PHYSICAL REVIEW A VOLUME 14, NUMBER 6 DECEMBER 1976

Three-body problem of two-electron atoms*

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(Received 2 August 1976)

The Feshbach-Rubinow approximation, with a modification to take better account of screening, is first applied to an illustrative one-dimensional problem. The same method is then used in realistic two-electron atoms to obtain analytic expressions for the ground-state energy and wave function. Numerical results are presented to show the improvement from earlier unmodified Feshbach-Rubinow calculations.

I. INTRODUCTION

We have recently applied[1] the Feshbach-Rubinow (FR) approximation[2] to the three-body problem of two-electron atomic systems, obtaining encouraging results. In this approximation, it is assumed at the outset that the three-body bound-state wave function depends only on a single appropriately chosen coordinate containing a few variational parameters. The problem then reduces to the solving of a single second-order differential equation, whose solutions are analytically known. In this paper we show that within the framework of this method, an improved choice of the coordinate can be made to take better account of screening, yielding a better estimate of the ground-state energy than in Ref. 1. It is again possible to obtain analytic expressions for the energy and the wave function of the system.

Before doing the calculations for the realistic case, we illustrate the method in a simple one-dimensional model[3] of a "helium-like atom," where the three particles interact via zero-range interparticle potentials. This model cannot be solved exactly,[4] and several authors[3,5,6] have recently applied different approximation techniques to estimate its ground-state energy. In the FR approximation, the solutions turn out to be simple, and the ground-state energy is lower than in other calculations. Moreover, the choice of the FR coordinate can be easily modified to yield a better estimate of the energy, suggesting a similar improvement in the realistic three-dimensional problem. Section II will be devoted to this illustrative model, while in Sec. III we shall present the improved version of the FR approximation for the realistic case of two-electron atoms.

II. ONE-DIMENSIONAL MODEL

In the model one-dimensional "helium-like atom," the Hamiltonian is given by

$$H=-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial x_2^2}\right)-Ze^2[\delta(x_1)+\delta(x_2)] +e^2\delta(x_1-x_2)\,. \tag{1}$$

Here x_1 and x_2 are the distances of the two "electrons" from the stationary "nucleus" of infinite mass at the origin, m and $-e$ are the mass and charge of an electron, and Ze is the charge of the nucleus. Quite generally, the Schrödinger equation may be exactly obtained by applying the variation $\delta\langle\Psi|H|\Psi\rangle=0$, with the restriction that $\langle\Psi|\Psi\rangle$ is finite. With Hamiltonian (1), this gives

$$\delta\int dx_1dx_2\left\{\frac{\hbar^2}{2m}\left[\left(\frac{\partial\Psi}{\partial x_1}\right)^2+\left(\frac{\partial\Psi}{\partial x_2}\right)^2\right]-Ze^2[\delta(x_1)+\delta(x_2)]\,\Psi^2+e^2\delta(x_1-x_2)\Psi^2-E\Psi^2\right\}=0\,. \tag{2}$$

Here the ranges of integration of the variables x_1 and x_2 are from $-\infty$ to ∞. In our notation, particles 1 and 2 are electrons with coordinates x_1 and x_2, and particle 3 is the nucleus with $x_3=0$. In the FR approximation it is assumed that the wave function Ψ is a function of the single non-negative variable R,

$$\Psi=\Phi(R),\quad R=\tfrac{1}{2}(r_1+r_2+\eta r_3)\,. \tag{3}$$

Here r_1 is the interparticle distance between particles 2 and 3, i.e., $r_1=|x_2|$, likewise $r_2=|x_1|$, and $r_3=|x_1-x_2|$, while η is a variational parameter.

Since we impose the condition that $R\geqslant0$, it follows from the geometry of the system that $1+\eta\geqslant0$. It is now straightforward to change the independent variables x_1 and x_2 in Eq. (2) to r_2 and R, and perform the r_2 integrations directly. On doing the variation, one then gets the Schrödinger-like equation

$$-\frac{\hbar^2}{2m}\left[\frac{d^2\Phi}{dR^2}+\frac{1}{R}\,\frac{d\Phi}{dR}\right]-\frac{e^2}{R}\;\frac{Z-\frac{1}{4}\eta-\frac{1}{4}}{1+\frac{1}{2}\eta^2+\frac{1}{2}\eta}\,\Phi =\frac{(\eta+2)E}{(\eta+1)(1+\frac{1}{2}\eta^2+\frac{1}{2}\eta)}\,\Phi\,. \tag{4}$$

If we now make the transformation $\Phi(R) = R^{-1/2}u$, the equation for u reduces to the usual radial Coulomb equation with an effective centrifugal term corresponding to $l = -\frac{1}{2}$, whose solutions are analytically known. In atomic units of $me^4/\hbar^2$, the ground-state energy is

$$E_0 = -\frac{1+\eta}{1+\frac{1}{2}\eta}\,\frac{(Z-\frac{1}{4}\eta-\frac{1}{4})^2}{1+\frac{1}{2}\eta+\frac{1}{2}\eta^2}\,, \tag{5}$$

and the ground-state unnormalized[7] wave function is

$$\Phi_0(R) = \exp\left[-2\frac{R}{a}\,\frac{Z-\frac{1}{4}\eta-\frac{1}{4}}{1+\frac{1}{2}\eta+\frac{1}{2}\eta^2}\right], \quad a = \frac{\hbar^2}{me^2}\,. \tag{6}$$

For a given Z, E_0 of Eq. (5) should be minimized by varying η. For $Z = 2$, we find that the optimum η is -0.1585, yielding $E_0 = -3.136$ in a.u. This is lower than the HF result[5] of -3.083, and is slightly better than the estimate of Kiang and Niégawa,[6] which was -3.105. Note that if we put $\eta = 0$ in Eq. (5), we obtain $E_0 = -(Z-\frac{1}{4})^2$, which is just the one-parameter variational result.[3] A nonzero value of η takes account of interelectronic correlations in the wave function, yielding better results.

We shall now improve the method by modifying the choice of the variable R on which the wave function depends. Note from Eq. (3) that the coordinates of the two electrons entered with equal weight in the wave function. However, 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 due to shielding. This would suggest that the FR method may be modified by defining a new variable R by

$$R = \tfrac{1}{2}(\alpha r_> + r_< + \eta r_3)\,, \quad r_1 \neq r_2 \tag{7}$$

where $r_> = r_1$, $r_< = r_2$ if $r_1 > r_2$, and vice versa. Now there are two variational parameters α and η in the calculation, and the conditions $\alpha + \eta > 0$ and $1 + \eta > 0$ must be obeyed for $R \geqslant 0$. Note that

$$\alpha r_> + r_< = \tfrac{1}{2}(\alpha+1)(r_1+r_2) + \tfrac{1}{2}(\alpha-1)|r_1-r_2|\,,$$

and for the special case when $r_1 = r_2$, we keep the variable R continuous by defining it as

$$R = \tfrac{1}{2}\left[\tfrac{1}{2}(\alpha+1)(r_1+r_2) + \eta r_3\right], \quad r_1 = r_2\,. \tag{8}$$

As before, starting from Eq. (2), and assuming that the three-body wave function is only a function of the continuous variable R, a Schrödinger-like equation may be derived in an analogous manner. This equation is

$$-\frac{\hbar^2}{2m}\left(\frac{d^2\Phi}{dR^2} + \frac{1}{R}\,\frac{d\Phi}{dR}\right) - \frac{e^2}{R}\,\frac{[Z-(\alpha+\eta)/2(1+\alpha)](1+\alpha)(2\eta+1+\alpha)}{(1+\alpha)(1+\alpha^2)+\eta(1+2\alpha+3\alpha^2)+4\alpha\eta^2+2\eta^3}\,\Phi$$
$$= \frac{4E(1+\alpha+\eta)}{(1+\alpha)(1+\alpha^2)+\eta(1+2\alpha+3\alpha^2)+4\alpha\eta^2+2\eta^3}\,\Phi\,. \tag{9}$$

For $\alpha = 1$, this reduces to the earlier Eq. (4). Just as before, the solution is obtained analytically, and the ground-state energy is given by

$$E_0 = -\frac{(1+\alpha)^2(1+\alpha+2\eta)^2[Z-(\alpha+\eta)/2(1+\alpha)]^2}{2(1+\alpha+\eta)[(1+\alpha)(1+\alpha^2)+\eta(1+2\alpha+3\alpha^2)+4\alpha\eta^2+2\eta^3]}\,. \tag{10}$$

For a given Z, this expression is minimized by varying the parameters α and η. In case of $Z = 2$, we find the optimum values to be $\alpha = 0.8666$, $\eta = -0.1079$, and the corresponding $E_0 = -3.1481$ in a.u. The modification of the FR method proposed here has thus further lowered the ground-state energy by 0.012 a.u. We now proceed to incorporate this modification in realistic two-electron atomic systems.

III. TWO-ELECTRON ATOMIC PROBLEM

For simplicity, we assume the nucleus to be of infinite mass and stationary at the origin. Designating the electron coordinates by $\vec{x}_1$ and $\vec{x}_2$, the Hamiltonian in this case is

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - Ze^2\left(\frac{1}{x_1} + \frac{1}{x_2}\right) + \frac{e^2}{|\vec{x}_1 - \vec{x}_2|}\,. \tag{11}$$

In order to derive the FR equations, one proceeds exactly as in Sec. II, and defines the scalar variables $r_1 = |\vec{x}_2|$, $r_2 = |\vec{x}_1|$, and $r_3 = |\vec{x}_1 - \vec{x}_2|$. The variational equation analogous to (2) in terms of r_1, r_2, and r_3 is now given by

$$\delta\int_0^\infty dr_1\int_0^\infty dr_2\int_{|r_1-r_2|}^{r_1+r_2} dr_3\, r_1r_2r_3\left\{\frac{\hbar^2}{2m}\left[\left(\frac{\partial\Psi}{\partial r_1}\right)^2 + \left(\frac{\partial\Psi}{\partial r_2}\right)^2 + 2\left(\frac{\partial\Psi}{\partial r_3}\right)^2 + \frac{r_2^2+r_3^2-r_1^2}{r_2r_3}\left(\frac{\partial\Psi}{\partial r_2}\right)\left(\frac{\partial\psi}{\partial r_3}\right)\right.\right.$$
$$\left.\left. + \frac{r_1^2+r_3^2-r_2^2}{r_1r_3}\left(\frac{\partial\Psi}{\partial r_1}\right)\left(\frac{\partial\Psi}{\partial r_3}\right)\right] + \left[\frac{e^2}{r_3} - Ze^2\left(\frac{1}{r_1} + \frac{1}{r_2}\right) - E\right]\Psi^2\right\} = 0\,. \tag{12}$$

TABLE I. Ground-state energy[a] of He-like atoms.

Two-electron system	Previous calculation[b] $-E_0$	Present calculation[c] α	η	$-E_0$	Best estimate[d] of $-E_0$
H^-	0.5079	0.6894	−0.1735	0.5206	0.5278
He	2.8896	0.8931	−0.1102	2.8983	2.9037
Li^+	7.2668	0.9340	−0.0767	7.2748	7.2799
Be^{++}	13.6429	0.9522	−0.0587	13.6505	13.6556

[a] The energy is given in a.u.

[b] Reference 1.

[c] The optimum values of α and η which minimize E_0 of Eq. (14) are shown.

[d] Reference 8.

In Ref. 1, the usual FR approximation was made by assuming that the wave function is dependent only on a single non-negative variable R, as defined by Eq. (3). In this section, we first give the new differential equation that is obtained by the modified choice of the coordinate R as defined by Eqs. (7) and (8). The main steps of the derivation are given in the Appendix. By writing $u = R^{5/2}\Phi(R)$, the Schrödinger-like equation that we get is

$$\frac{\hbar^2}{2m}\left(\frac{1+\alpha^2+2\eta^2}{4}p+\frac{n}{4}q\right)\left(-\frac{d^2u}{dR^2}+\frac{15}{4R^2}u\right) - \frac{e^2}{R}(Zs-t)u = pEu\,, \qquad (13)$$

where p, q, s, and t are R-independent parameters, given completely in terms of the variational parameters α and η, and are defined in the Appendix. As in Ref. 1, this is again the wave equation of a particle in a Coulomb potential with effective orbital momentum $l = \frac{3}{2}$, and the solutions are known analytically. For the special case with $\alpha = 1$, a little algebra will show that Eq. (13) reduces to Eq. (10) of Ref. 1. The ground-state energy is now given by

$$E_0 = -\frac{2}{(\frac{5}{2})^2 p}\,\frac{(Zs-t)^2}{(1+\alpha^2+2\eta^2)p+\eta q}\,, \qquad (14)$$

and the unnormalized ground-state wave function is

$$\Phi_0 = R^{-5/2}u_0(R) = \exp\left(-\frac{8(Zs-t)/5}{(1+\alpha^2+2\eta^2)p+\eta q}\,\frac{R}{a}\right). \qquad (15)$$

For a given Z, E_0 is minimized with respect to the parameters α and η, and the corresponding results for He-like atomic systems are displayed in Table I. For comparison, we also show in the table the results obtained in Ref. 1 where $\alpha = 1$, and the best available results[8] from extensive variational calculations. It should be mentioned that our formalism can be easily modified to take account of the motion of the nucleus, but in Table I all values of E_0, including those in the last column, are with the assumption that the nuclear mass is infinite. From Table I we note that in every case except H^-, the best variational estimate for E_0 is lower than our result by about 0.005 a.u., while for H^- this difference is 0.007 a.u. The modified FR method that we have formulated here has the merit of yielding simple analytic expressions for the energy and the wave function of two-electron atomic systems, but cannot compete in accuracy with elaborate variational calculations. The numerical results obtained here could have been obtained more directly, of course, by choosing a trial wave function of an exponential form in the variable $R = \frac{1}{2}(\alpha r_> + r_< - r_3)$. Our paper shows that for the variable chosen, the exponential is the optimum functional form for Coulomb potentials.

ACKNOWLEDGMENTS

The authors would like to thank Yuki Nogami for many useful discussions. One of us (M.K.S.) would like to thank the Physics Department of McMaster University for financial support, enabling him to spend the summer of 1976 there.

APPENDIX

We summarize here the steps to obtain Eq. (13). Let $R, R_2 = r_2$, and $R_3 = r_3$ be the new variables. Then, since Φ is a function of R only, the integrations in Eq. (12) over the other variables (R_2, R_3) may be performed. The region $r_1 > r_2$ need only be considered as Φ and the various terms in Eq. (12) are symmetric in r_1 and r_2. Denoting half of the total volume element by $\int(dr)$, we have

$$\int (dr) = \int_0^\infty dr_1 \int_0^{r_1} dr_2 \int_{r_1-r_2}^{r_1+r_2} dr_3 r_1 r_2 r_3$$

$$= \frac{2}{\alpha^2} \int_0^\infty dR \left[\int_0^{2R/(1+\alpha)} dR_2 \int_{[2R-(1+\alpha)R_2]/(\alpha+\eta)}^{[2R-(1-\alpha)R_2]/(\alpha+\eta)} dR_3 + \int_{2R/(1+\alpha)}^{2R/(1+\alpha+2\eta)} dR_2 \int_{[2R-(1+\alpha)R_2]/\eta}^{[2R-(1-\alpha)R_2]/(\alpha+\eta)} dR_3 \right]$$

$$\times R_2 R_3 (2R - R_2 - \eta R_3)$$

$$= p \int R^5 dR , \qquad \text{(A1)}$$

where

$$p = \frac{64}{15} \; \frac{2(1+\alpha+\eta)^2[2-(1+\alpha+\eta)(1-5\alpha-4\eta)] + \eta(1+\alpha)(1+\alpha+2\eta) - 3(\alpha+\eta)(1+\alpha)^2 - (1+\alpha)^2}{(1+\alpha)^3(\alpha+\eta)^3(1+\alpha+2\eta)^4} . \qquad \text{(A2)}$$

A straightforward though lengthy manipulation yields the following for the various terms in Eq. (12):

$$\int \left(\alpha \frac{r_1^2 + r_3^2 - r_2^2}{r_1 r_3} + \frac{r_2^2 + r_3^2 - r_1^2}{r_2 r_3} \right) (dr) = q \int R^5 dR , \qquad \text{(A3)}$$

$$\int \left(\frac{1}{r_1} + \frac{1}{r_2} \right) (dr) = s \int R^4 dR , \qquad \text{(A4)}$$

$$\int \frac{1}{r_3} (dr) = t \int R^4 dR , \qquad \text{(A5)}$$

where

$$q = \frac{256}{15} \; \frac{2(1+\alpha+\eta)^3[2(1+\alpha+\alpha^2) - \eta(1-\alpha)] - 2(1+\alpha)(1+\alpha+\eta)(1+\alpha+2\eta+\eta^2) - (1+\alpha)^3(2+3\alpha+4\eta)}{(1+\alpha)^3(\alpha+\eta)^3(1+\alpha+2\eta)^4} , \qquad \text{(A6)}$$

$$s = \frac{16}{3} \; \frac{2(1+\alpha+\eta)^2[5(\alpha+\eta)-1] - 2\eta^3 + \eta(1-\alpha)^2 + 3(1-\alpha^2)}{(1+\alpha)^2(\alpha+\eta)^3(1+\alpha+2\eta)^3} , \qquad \text{(A7)}$$

$$t = \frac{16}{3} \; \frac{4(\alpha+\eta)(1+\alpha+\eta)^2 + (1+\alpha)(1+\alpha+2\eta)}{(1+\alpha)^3(\alpha+\eta)^2(1+\alpha+2\eta)^3} . \qquad \text{(A8)}$$

Using these results and performing the variation indicated in Eq. (12) leads to the following differential equation for Φ:

$$-\frac{\hbar^2}{2m} \left(\frac{1+\alpha^2+2\eta^2}{4} p + \frac{\eta}{4} q \right) \frac{1}{R^5} \frac{d}{dR} \left(R^5 \frac{d\Phi}{dR} \right) - (Zs - t) \frac{e^2}{R} \Phi = pE\Phi . \qquad \text{(A9)}$$

This reduces to Eq. (13) of the text on making the substitution $u = R^{5/2}\Phi$.

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*Research supported by National Research Council of Canada.

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[1] R. K. Bhaduri and Y. Nogami, Phys. Rev. A 13, 1986 (1976).

[2] H. Feshbach and S. I. Rubinow, Phys. Rev. 98, 188 (1955). R. K. Bhaduri, Y. Nogami, and W. van Dijk, Nucl. Phys. B 1, 269 (1967); 2, 316(E) (1967).

[3] I. R. Lapidus, Am. J. Phys. 43, 790 (1975).

[4] For three identical bosons of the same mass, interacting with zero-range attractive potentials of identical strength, the problem is exactly solvable. See J. B. McGuire, J. Math. Phys. 5, 622 (1964).

[5] Y. Nogami, M. Vallières, and W. van Dijk, Am. J. Phys. 44, 886 (1976).

[6] D. Kiang and A. Niégawa, Phys. Rev. A 14, 911 (1976).

[7] When normalizing a wave function which depends only on R as defined by Eq. (3), note that

$$\int_{-\infty}^{+\infty} dx_1 \int_{-\infty}^{+\infty} dx_2 = \frac{8(\eta+2)}{(\eta+1)^2} \int_0^\infty R\, dR .$$

[8] C. L. Pekeris, Phys. Rev. 112, 1649 (1958).