PHYSICAL REVIEW A VOLUME 58, NUMBER 1 JULY 1998

Boundary-condition-determined wave function for the ground state of positronium ion $\bar{e}ee$

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(Received 9 December 1997)

We have developed a one-parameter, model wave function for the positronium ion $\bar{e}ee$, which incorporates the correct cusp and coalescence properties when two particles are close to each other, and the asymptotic property when one of the electrons is far away. The predicted values for the energy and other properties are close to the exact values and generally superior to the values from a 13-parameter wave function. [S1050-2947(98)03307-1]

PACS number(s): 31.10.+z

I. INTRODUCTION

Ever since the discovery of positronium, the negative positronium ion $\bar{e}ee$ has attracted a great deal of attention. It was originally shown by Wheeler [1], and by Hylleraas [2], that the electron is bound to the positronium with a binding energy of at least 0.19 eV. Since then many elaborate calculations have been carried out to obtain accurate values for the binding energy and for other properties of the system such as the average value of the distance between the two electrons. These calculations are generally based on the variational approach with a large number of variational parameters. Some of these follow: by Kolos *et al.* [3] with 50 terms, by Schroeder [4] with six parameters, by Frost *et al.* [5] with 50 terms, by Cavaliere *et al.* [6] with six and ten parameters, by Bhatia and Drachman [7] with 203 terms, by Ho [8] with 125 terms, and Frolov and Yeremin [9] with 700 terms. These calculations yield for the binding energy of the last electron a value of 0.012 005 a.u. It may be mentioned that Frolov and Yeremin [9] have obtained the energy to an accuracy of 13 significant digits. However, the variational wave functions do not emphasize the structural properties of the system. It is of considerable interest to develop wave functions which illustrate some of the important properties such as the behavior of the wave function when two particles are close to each other or when they are far away from each other. Wave functions which provide a clear illustration of these properties provide a deeper understanding of the structure of the system.

Recently [10], we have developed parameter-free wave functions for the ground state of two-electron atoms and ions, based on some general local properties of the exact wave functions. These wave functions, in addition to being very simple, provide accurate values for the binding energies and expectation values of r^{2n}. The predictions are particularly striking for H^- where they are far better than the predictions of two-parameter wave functions, and quite close to the essentially exact, variational values of the energy. Here we extend the analysis to the case of the positronium ion, $\bar{e}ee$. Since the mass of $\bar{e}$ is equal to the mass of the electron, unlike the situation in H^-, the details are modified in a significant way. In particular, the center of mass not being at the positive charge brings in essential changes in the asymptotic behavior. Based on the local properties, we develop a one-parameter wave function which clearly exhibits the structural properties of the positronium ion in different regions. It gives a value of $-0.261\,03$ a.u. for the total energy and also reliable values for other properties such as $\langle r_{ij}\rangle$.

II. SOME LOCAL PROPERTIES OF THE WAVE FUNCTIONS

Here we briefly discuss some general, local properties of the wave functions. We use atomic units.

A. The Hamiltonian

The Hamiltonian for a three-particle system is given by

$$H=\sum_{i=1}^{3}\frac{1}{2m_i}p_i^2+\sum_{i<j}^{3}\frac{q_iq_j}{r_{ij}}, \tag{1}$$

where $\vec{r}_{ij}=\vec{r}_i-\vec{r}_j$. After separating out the center of mass term, the kinetic energy can be written as

$$T=\frac{1}{2m_{ij}}p_{ij}^2+\frac{1}{2m_{ij,k}}p_{ij,k}^2, \tag{2}$$

where

$$m_{ij}=\frac{m_im_j}{m_i+m_j}, \tag{3}$$

$$m_{ij,k}=\frac{(m_i+m_j)m_k}{m_i+m_j+m_k}. \tag{4}$$

Here, p_{ij} is the relative momentum of the particles i and j, and $p_{ij,k}$ is the relative momentum of particle k and the center of mass of particles i and j. The kinetic energy can also be written as

$$T=\frac{1}{2m_{ij}}p_{ij}^2+\frac{1}{2m_{kj}}p_{kj}^2+\frac{1}{m_j}\vec{p}_{ij}\cdot\vec{p}_{kj}. \tag{5}$$

The form in Eq. (2) is convenient for analyzing the asymptotic behavior of the wave function, and the form in Eq. (5) is convenient for the calculation of the expectation values of the energy.

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B. Asymptotic behavior

The ground-state eigenfunction of the Hamiltonian H in Eq. (1) can be expanded in terms of the one-particle energy eigenfunctions:

$$H\psi = E\psi, \tag{6}$$

$$\psi = \sum_n u_n(\vec{r}_{ij,k})\phi_n(\vec{r}_{ij}), \tag{7}$$

$$\left(-\frac{1}{2m_{ij}}\nabla_{ij}^2 + \frac{q_iq_j}{r_{ij}}\right)\phi_n = E_n^{(1)}\phi_n. \tag{8}$$

Substituting the expression for ψ into Eq. (6), and projecting out the state ϕ_n, we get for $r_{ij,k}\rightarrow\infty$

$$\left(\frac{1}{2m_{ij,k}}p_{ij,k}^2 + q_k(q_i+q_j)\frac{1}{r_{ij,k}}\right)u_n = -\epsilon_n u_n \quad \text{for} \quad r_{ij,k}\rightarrow\infty, \tag{9}$$

$$\epsilon_n = E_n^{(1)} - E. \tag{10}$$

The asymptotic form of u_n is given by

$$u_n \rightarrow r_{ij,k}^{[-q_k(q_i+q_j)(m_{ij,k}/2\epsilon_n)^{1/2}-1]}e^{-(2m_{ij,k}\epsilon_n)^{1/2}r_{ij,k}}. \tag{11}$$

Clearly, the leading behavior is from the smallest value of ϵ_n, i.e., corresponding to $n=0$. Therefore we have

$$\psi \rightarrow r_{ij,k}^b e^{-ar_{ij,k}}\phi_0(r_{ij}), \quad r_{ij,k}\rightarrow\infty \tag{12}$$

$$a = (2m_{ij,k}\epsilon_0)^{1/2}, \tag{13}$$

$$b = -\frac{q_k(q_i+q_j)m_{ij,k}}{a} - 1. \tag{14}$$

$$\vec{r}_{ij,k} = \vec{r}_{kj} - \frac{m_i}{m_i+m_j}\vec{r}_{ij}, \tag{15}$$

with ϵ_0 being the binding energy of particle k. Expanding $r_{ij,k}$ in inverse powers of r_{kj}, we get

$$\psi \rightarrow r_{kj}^b e^{-ar_{kj}+a[m_i/(m_i+m_j)][(\vec{r}_{kj}\cdot\vec{r}_{ij})/r_{kj}]}\phi_0(r_{ij}), \quad r_{kj}\rightarrow\infty. \tag{16}$$

For the case of the positronium ion $\bar{e}ee$, we use the indices 1,2 to characterize the two electrons and 3 to characterize the positron. Then when electron 1 is far away, we get

$$\psi \rightarrow \frac{1}{r_{13}}e^{-ar_{13}+(1/2)a(\vec{r}_{13}\cdot\vec{r}_{23})/r_{13}}e^{-(1/2)r_{23}}, \quad r_{13}\rightarrow\infty \tag{17}$$

$$a = (4\epsilon_0/3)^{1/2}, \tag{18}$$

where ϵ_0 is the binding energy of the last electron. The second term in the exponent would be negligibly small if the $\bar{e}$ is replaced by a proton. This is the major modification introduced by the positron mass being comparable to the mass of the electron. To understand clearly the implications of this term, we note that $\epsilon_0 \approx 0.012$, and $\frac{1}{2}a \approx 0.06$, so that expanding the second exponential, one obtains

$$\psi \rightarrow \frac{1}{r_{13}}e^{-ar_{13}-(1/2)r_{23}}\left(1+\frac{1}{2}a\frac{\vec{r}_{13}\cdot\vec{r}_{23}}{r_{13}}\right) \quad \text{for} \quad r_{13}\rightarrow\infty. \tag{19}$$

The presence of the second term in the large parentheses is just a consequence of the fact that when $\vec{r}_{13}$ is parallel to $\vec{r}_{23}$, electron 2 is closer to the center of mass of particles 1 and 3 than when $\vec{r}_{13}$ is antiparallel to $\vec{r}_{23}$.

C. Cusp and coalescence conditions

When two particles i,j with masses m_i, m_j and charges q_i, q_j approach each other, $r_{ij}\rightarrow 0$, two terms in the Hamiltonian dominate. These are the Coulomb interaction between these particles, and the kinetic energy of the two particles. In the center of mass frame of these two particles, one has

$$\left(-\frac{1}{2m_{ij}}\nabla_{ij}^2 + \frac{q_iq_j}{r_{ij}}\right)\psi = O(1) \quad \text{for} \quad r_{ij}\rightarrow 0, \tag{20}$$

where m_{ij} is the reduced mass of the particles i and j. Expanding the wave function in terms of spherical harmonics,

$$\psi = \sum_{l,m} g_{lm}(r_{ij})Y_l^m(\theta_{ij},\phi_{ij}), \tag{21}$$

and projecting out an lm state, we get

$$\frac{d^2}{dr_{ij}^2}[r_{ij}g_{lm}(r_{ij})] - \frac{l(l+1)}{r_{ij}}g_{lm}(r_{ij}) - 2m_{ij}q_iq_jg_{lm}(r_{ij}) = O(r_{ij}^{l+1}) \quad \text{for} \quad r_{ij}\rightarrow 0. \tag{22}$$

Substituting

$$g_{lm}(r_{ij}) = r_{ij}^l(a_0 + a_1r_{ij} + \cdots) \tag{23}$$

into Eq. (22), one obtains

$$a_1 = \frac{m_{ij}q_iq_j}{(l+1)}a_0. \tag{24}$$

This is essentially a realization of the Kato condition [11].

For the case of two electrons in the singlet state, the leading term is the $l=0$ term so that

$$a_1 = \frac{1}{2}a_0, \quad ee \text{ in singlet state}, \tag{25}$$

and the corresponding g_{00} has the behavior

$$g_{00} \rightarrow a_0(1+\tfrac{1}{2}r_{ij}) \quad \text{for} \quad r_{ij}\rightarrow 0, \text{ singlet state}. \tag{26}$$

For $\bar{e}$ getting close to an electron, one has

$$a_1 = -\frac{1}{2}a_0, \quad g_{00} \rightarrow a_0(1-\tfrac{1}{2}r_{ij}) \quad \text{for} \quad r_{ij}\rightarrow 0. \tag{27}$$

We now consider a model wave function for the ground state of the $\bar{e}ee$ system incorporating the asymptotic condition in Eq. (19) and the cusp and coalescence conditions in Eqs. (26) and (27).

III. MODEL WAVE FUNCTION AND ITS IMPLICATIONS

For the description of the wave function of the negative positronium ion $\bar{e}ee$, we treat $\bar{e}$ as the point of reference and use the notation $\vec{r}_1$ and $\vec{r}_2$ to describe the positions $\vec{r}_{13}$ and $\vec{r}_{23}$ of the two electrons with respect to the positron. Then the Hamiltonian corresponding to Eq. (5) is given by

$$H=-\nabla_1^2-\nabla_2^2-\vec{\nabla}_1\cdot\vec{\nabla}_2-\left(\frac{1}{r_1}+\frac{1}{r_2}-\frac{1}{|\vec{r}_1-\vec{r}_2|}\right). \tag{28}$$

A. Model wave function

Based on the asymptotic condition in Eq. (19) and the cusp and coalescence conditions in Eqs. (26) and (27), we propose for the ground-state wave function,

$$H\psi=E\psi, \tag{29}$$

$$\psi=C\left(e^{-(1/2)r_1}e^{-ar_2}\frac{1}{1+br_2}+e^{-(1/2)r_2}e^{-ar_1}\frac{1}{1+br_1}\right)\times\left(1+\frac{1}{2}a\frac{\vec{r}_1\cdot\vec{r}_2}{(r_1^2+r_2^2)^{1/2}}\right)f(r_{12}), \tag{30}$$

where

$$a=\left[\frac{4}{3}\left(-\frac{1}{4}-E\right)\right]^{1/2}, \tag{31}$$

$$b=\frac{1}{2}-a, \tag{32}$$

and $f(r_{12})$ is a correlation function. The choice of a in Eq. (31), with positronium ground-state energy of $-1/4$, ensures that the correct asymptotic behavior given in Eq. (19) is incorporated. The choice of b in Eq. (32) ensures that the coalescence condition in Eq. (27) is satisfied for r_1 or $r_2 \to 0$. The function $f(r_{12})$ is the correlation function which is introduced to incorporate the cusp condition in Eq. (26).

B. Correlation function $f(r_{12})$

The correlation function $f(r_{12})$ has been analyzed [10] for the two-electron atoms and ions, in an essentially perturbative approach. We extend this analysis to the case of the positronium ion.

Consider a wave function of the form

$$\psi=\phi_0(r_1,r_2)f(r_{12}), \tag{33}$$

$$\phi_0(r_1,r_2)=e^{-(1/2)(r_1+r_2)}. \tag{34}$$

This has the correct behavior for r_1 or $r_2 \to 0$. Substituting the function ψ in the Schrödinger equation in Eq. (29), we get

$$E\psi=-\frac{1}{2}\psi-\frac{1}{4}\left(\frac{\vec{r}_1\cdot\vec{r}_2}{r_1r_2}\right)\psi-\phi_0\nabla_{12}^2 f+\frac{1}{2}\phi_0\left(\frac{\vec{r}_1}{r_1}-\frac{\vec{r}_2}{r_2}\right)\cdot\vec{\nabla}_{12}f+\frac{1}{r_{12}}\psi. \tag{35}$$

For $r_{12}\to 0$, this leads to

$$\nabla_{12}^2 f-\frac{1}{r_{12}}f+\left(\frac{3}{4}+E\right)f=O(r_{12}). \tag{36}$$

Expanding f in powers of r_{12},

$$f=a_0+a_1r_{12}+a_2r_{12}^2+\cdots \tag{37}$$

and substituting in Eq. (36), we get

$$2a_1-a_0=0, \tag{38}$$

$$6a_2-a_1+\left(\frac{3}{4}+E\right)a_0=0, \tag{39}$$

which lead to

$$a_1=\frac{1}{2}a_0, \tag{40}$$

$$a_2=\frac{1}{6}\left(\frac{1}{2}-\frac{3}{4}-E\right)a_0. \tag{41}$$

Here, the first relation is the cusp condition in Eq. (26). Now for the positronium ion, energy $E\approx-0.2610$, so that a_2 is indeed very small and we take it to be zero:

$$a_2\approx 0. \tag{42}$$

Based on these conditions, we take for the correlation function $f(r_{12})$,

$$f(r_{12})=1-\left(\frac{1}{1+\lambda}\right)\left(1+\frac{\lambda}{2}r_{12}\right)e^{-\lambda r_{12}}, \tag{43}$$

which satisfies the conditions in Eqs. (40) and (42). The parameter λ is treated as a variational parameter.

C. Calculation of the energy

The wave function ψ in Eq. (30) is used to calculate the energy of $\bar{e}ee$ as

$$E=\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}, \tag{44}$$

with the correlation function $f(r_{12})$ in Eq. (43), and the Hamiltonian in Eq. (28). It should be noted that the parameter a in Eq. (31) depends on E and is therefore determined iteratively so as to yield a self-consistent E. The parameter λ is determined by minimizing the energy.

The calculation of the energy E in Eq. (44) is greatly simplified by the use of the identity

$$\int(\phi f)(\vec{\nabla}_i\cdot\vec{\nabla}_j)(\phi f)d\tau=\int[f^2\phi\vec{\nabla}_i\cdot\vec{\nabla}_j\phi-\phi^2(\vec{\nabla}_if)\cdot(\vec{\nabla}_jf)]d\tau, \tag{45}$$

TABLE I. The values of the variational parameter λ, normalization constant C in Eq. (30), and the predicted values of the total energy E and average values of different functions of the $\overline{ee}$ and ee separations $\vec{r}_{1p}$ and $\vec{r}_{12}$.

	Our results (one parameter)	13-parameter results (Ref. [8])	Exact results (Refs. [7,8])
λ	0.262		
C	0.014 921		
E	$-0.261\,03$	$-0.261\,01$	$-0.262\,00$
$\langle r_{1p}\rangle$	5.452	5.114	5.489
$\langle r_{1p}^2\rangle$	48.31	38.83	48.39
$\langle r_{1p}^{-1}\rangle$	0.3369	0.3429	0.3398
$\langle r_{12}\rangle$	8.513	7.842	8.548
$\langle r_{12}^2\rangle$	94.31	74.81	93.13
$\langle r_{12}^{-1}\rangle$	0.1591	0.1639	0.1556
$\langle \delta(\vec{r}_{1p})\rangle$	0.019 39	0.019 43	0.020 73
$\langle r_{1p}^4\rangle$	1.076×10^4		
$\langle r_{12}^4\rangle$	2.326×10^4		

which follows from integration by parts. This identity is a generalization of the identity for the special case of $i=j$, which was obtained by Siebbles *et al.* [12]. Some of the details of the calculation are given in the Appendix.

D. Results

The results of the calculation are given in Table I, along with the results from 13-parameter calculations [8], and essentially exact results [7,8] using 125 and 203 terms. Our results with a one-parameter wave function incorporating some local properties are close to the exact results and are generally superior to the results using 13 parameters. This emphasizes the importance of the local properties of the wave function, when two particles are close to each other or when they are far away from each other. In particular, we note that if the term in Eq. (30) proportional to $\vec{r}_1\cdot\vec{r}_2$ is not included, the energy changes from the present value of -0.2610 to about -0.2562 which is a poor result.

We also note that since our wave function incorporates the correct asymptotic behavior, its predictions for the average values of higher powers of separation r_{1p} between an electron and the positron and r_{12} between the two electrons, are expected to be quite reliable. However, since the asymptotic exponent a of the wave function in Eq. (30) depends on E and our binding energy is slightly smaller, the exact results for $\langle r_{1p}^4\rangle$ and $\langle r_{12}^4\rangle$ are expected to be smaller than our predictions by about 5%. In a general way, the asymptotic properties and cusp and coalescence properties are of great importance in developing simple model wave functions for the positronium ion, which not only provide physical insight into the physical structure in different regions, but also allow us to obtain accurate values for different properties of the system.

APPENDIX

Some of the terms required for the evaluation of the average energy are as follows:

$$\nabla^2 e^{-(1/2)\,r}=\left(\frac{1}{4}-\frac{1}{r}\right)e^{-(1/2)r}, \tag{A1}$$

$$\nabla^2 e^{-ar}\left(\frac{1}{1+br}\right)=\left(a^2-\frac{2a}{r}+\frac{2b^2}{(1+br)^2}-\frac{2b}{r(1+br)}+\frac{2ab}{1+br}\right)e^{-ar}\left(\frac{1}{1+br}\right), \tag{A2}$$

$$(\vec{\nabla}_1\cdot\vec{\nabla}_2)e^{-(1/2)r_1-ar_2}\left(\frac{1}{1+br_2}\right)=\frac{1}{2}\left(\frac{\vec{r}_1\cdot\vec{r}_2}{r_1r_2}\right)\left(a+\frac{b}{1+br_2}\right)e^{-(1/2)r_1-ar_2}\left(\frac{1}{1+br_2}\right), \tag{A3}$$

$$\vec{\nabla}_1\left(1+\frac{1}{2}a\frac{\vec{r}_1\cdot\vec{r}_2}{(r_1^2+r_2^2)^{1/2}}\right)f(r_{12})=\left(1+\frac{1}{2}a\frac{\vec{r}_1\cdot\vec{r}_2}{(r_1^2+r_2^2)^{1/2}}\right)\vec{\nabla}_1 f(r_{12})+\frac{a}{2}\left(\frac{\vec{r}_2}{(r_1^2+r_2^2)^{1/2}}-\frac{(\vec{r}_1\cdot\vec{r}_2)\vec{r}_1}{(r_1^2+r_2^2)^{3/2}}\right)f(r_{12}), \tag{A4}$$

$$\vec{\nabla}_1 f(r_{12})=\frac{\lambda}{2(1+\lambda)}(1+\lambda r_{12})\frac{\vec{r}_{12}}{r_{12}}e^{-\lambda r_{12}}. \tag{A5}$$

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