

# Variational calculation of the positronium molecule in the basis of exponential functions of interparticle separations

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A multiparameter variational calculation of a four-particle nonadiabatic Coulomb system, the positronium molecule  $e^+e^-e^+e^-$ , is realized for the first time in the basis of functions exponentially depending on all interparticle separations. The eight-fold permutation symmetry of the wave function of  $e^+e^-e^+e^-$  is taken into account. Using a 90-term basis of symmetrized exponential functions, we find the variational values of the total binding energy of the positronium molecule,  $E = -0.515920$  a.u., and the energy of the molecule's dissociation into two positronium atoms,  $D = 0.015920$  a.u. = 0.433 eV. We calculate the lifetime of the positronium molecule against electron–positron annihilation,  $\tau_{e^+e^-e^+e^-} = 2.25 \times 10^{-10}$ s. These results have appreciably higher accuracy than those of previous calculations of the positronium molecule done with other sets of basis functions, and suggest that there is great potential in the use of exponential functions of interparticle separations in calculations of various four-particle nonadiabatic Coulomb systems. © 1996 American Institute of Physics. [S1063-7761(96)00507-0]

## 1. INTRODUCTION

The positronium molecule  $e^+e^-e^+e^-$  occupies a special place among four-particle Coulomb systems because the masses of the constituent particles are equal. It concludes the class of systems consisting of two pairs of identically charged particles, a class that begins with the isotopic modifications of the hydrogen molecule,  $T_2$ ,  $D_2$ , and  $H_2$ , and extends, through various mesomolecules (as the values of masses of the pairs of heavy and light particles become closer), to the case where the masses of the particles are exactly equal, or the  $e^+e^-e^+e^-$  system. Molecules of biexcitons in a solid with various values of the effective masses of electrons and holes also belong to this class of Coulomb systems. For this reason the positronium molecule serves as a standard in analyzing the binding energies of mesomolecules and biexcitons,<sup>1–3</sup> with the result that quantum mechanical calculations of this system are of great interest to the theory of four-particle Coulomb systems.

The ground state of  $e^+e^-e^+e^-$ , which is also the only state in that is stable against decay into two positronium atoms  $e^+e^-$ , is a singlet state in both the electron spins and the positron spins.

The energy operator of the positronium molecule remains unchanged not only under the exchange of identical particles (electrons or positrons) but also under permutations of particles and antiparticles (simultaneous permutation of both electrons and both positrons). If we employ the Pauli principle and the exchange antisymmetry of singlet spin functions, we see that the coordinate wave function of the ground state of the positronium molecule possesses the following eight-fold permutation symmetry:

$$\begin{aligned} \Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) &= \Psi(\mathbf{r}_3, \mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_4) = \Psi(\mathbf{r}_1, \mathbf{r}_4, \mathbf{r}_3, \mathbf{r}_2) \\ &= \Psi(\mathbf{r}_3, \mathbf{r}_4, \mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_4, \mathbf{r}_3) \\ &= \Psi(\mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \mathbf{r}_1) = \Psi(\mathbf{r}_4, \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \\ &= \Psi(\mathbf{r}_4, \mathbf{r}_3, \mathbf{r}_2, \mathbf{r}_1). \end{aligned} \quad (1)$$

Odd numbers correspond to positrons and even numbers to electrons.

A distinctive feature of the positronium molecule is that it is entirely nonadiabatic: because all the particles in it have equal masses, it is impossible to separate the motions into “fast” and “slow,” with the result that one must allow for their simultaneous mutually correlated motion. This makes calculating the positronium molecule much more complicated than calculating such adiabatic systems as the hydrogen molecule.

To date the most accurate variational calculation of the positronium molecule has been the one done by Ho,<sup>4</sup> who used a 400-term wave function. He provided the value  $E = -0.5151$  a.u. for the total binding energy of the  $e^+e^-e^+e^-$  system against decay into four separate particles, which corresponds to an energy  $D$  of dissociation of such a system into two positronium atoms equal to 0.0151 a.u. = 0.411 eV. The basis used in this calculation consisted of exponential–power functions of the interparticle separations  $r_{jk} = |\mathbf{r}_j - \mathbf{r}_k|$ , but proper exchange symmetry of the wave function was not maintained.

In Ref. 5 a variational calculation of the positronium molecule used Gaussian functions exponentially depending on the squares of all the interparticle separations and accurately accounted for the eight-fold permutation symmetry (1) of the coordinate part of the wave function. Calculations with a 750-term wave function yielded the following

values of the total binding energy and the dissociation energy of the positronium molecule:  $E = -0.51580$  a.u. and  $D = 0.01580$  a.u.  $= 0.430$  eV. These results are appreciably more accurate than those of Ref. 4. At the same time, the fact that Gaussian functions do not have the required “sharpness” at the points of pair collisions of particles and fall off too rapidly at large interparticle separations slows down the convergence of the variational procedure and may have a strong effect on the calculated expectation values of the physical quantities that depend on interparticle separations, such as the electron–positron collision probability, which determines the rate of electron–positron annihilation.

In view of what has been said, it seems appropriate to calculate the positronium molecule in a basis of functions that exponentially depend on the first powers of all the interparticle separations  $r_{jk} = |\mathbf{r}_j - \mathbf{r}_k|$ . The high quality of such basis functions is corroborated by numerous calculations of three-particle systems.<sup>6–9</sup> The main difficulty here is the need to calculate ten-dimensional integrals with nonseparable integration variables (such integrals determine the matrix elements of the energy operator of a four-particle system). The problem is much more complicated than calculating the matrix elements of the energy operator of three-particle Coulomb systems, which can easily be calculated using parametric coordinates.

A special method for calculating integrals for four-particle systems in the basis of exponential functions of the interparticle separations was developed by Fromm and Hill.<sup>10</sup> The first application of this method to model problems, to the bosonic analog of the lithium atom, and to a four-particle system bound by gravitational forces with calculations of the diagonal matrix element of the energy operator in the basis of a single exponential function, produced promising results.<sup>11,12</sup>

In Ref. 13 it was shown that calculating all the matrix elements (diagonal and off-diagonal) of the energy operator of a four-particle Coulomb system in an exponential basis reduces to calculating only two types of integrals: normalization integrals and the Coulomb-interaction integrals. With the results of Ref. 10 this opened a real possibility for variational calculations of four-particle Coulomb systems in a broad class of bases of exponential functions.

The aim of the present work is to realize this possibility in calculations of the energy and the physical properties of

the positronium molecule. We also develop a unique method of practical calculation of four-particle Coulomb systems in the basis of functions that exponentially depend on all the interparticle separations.

## 2. THE VARIATIONAL CALCULATION METHOD

Let us take a system of four particles with masses  $m_j$  and charges  $q_j$  ( $j = 1, 2, 3, 4$ ). The energy operator of this system is

$$H = -\frac{1}{2} \sum_{j=1}^4 \frac{\Delta_j}{m_j} + \sum_{j<k}^4 \frac{q_j q_k}{r_{jk}}. \quad (2)$$

Here we use the atomic system of physical units. We introduce a system of basis functions that depend exponentially on all six separations of the four particles:

$$\Phi_b = \exp\left(-\sum_{j<k}^4 b_{jk} r_{jk}\right), \quad \Phi_c = \exp\left(-\sum_{j<k}^4 c_{jk} r_{jk}\right). \quad (3)$$

Each function contains six variable parameters  $b_{jk} = b_{kj}$  (or  $c_{jk} = c_{kj}$ ), whose set is symbolized by the label  $b$  (or  $c$ ) on the function  $\Phi$ .

The exponential basis function  $\Phi_b$  of Eq. (3) can be graphically represented by a square whose vertices correspond to separate particles and whose sides and diagonals represent the interparticle separations (Fig. 1). Such functions must be square-integrable. This means that only such sets of exponential parameters  $b_{jk}$  are permissible for which  $\Phi_b$  tends to zero for all imaginable ways of dividing the square into two parts. There are seven ways to do this: four correspond to detaching one of the vertices and involve increasing three interparticle separations without limit, and three correspond to the three ways in which the square can be cut into two parts with two particles in each and involve increasing four interparticle separations without limit. For the function  $\Phi_b$  to tend to zero in each of these seven cases, the sum of the exponential parameters for those interparticle separations that increase without limit must be positive. Hence the admissible sets of exponential parameters  $b_{jk}$  obey the following system of seven inequalities:

TABLE I. The parameters  $b_{jk}$  of the first ten exponential basis functions and the values of the binding energy  $E$  (a.u.) of the ground state of the positronium molecule obtained by successive introduction of these functions into the variational calculations.

No.	$E$	$b_{12}$	$b_{13}$	$b_{14}$	$b_{23}$	$b_{24}$	$b_{34}$
1	-0.507668	0.08888	-0.05076	0.40739	0.59532	-0.07417	0.23941
2	-0.509973	0.29006	0.30257	0.26620	0.52320	-0.21604	0.32261
3	-0.512567	0.17069	-0.06124	0.30705	0.60531	0.03662	0.25555
4	-0.513333	0.25009	0.35926	0.22436	0.19923	0.49186	0.29205
5	-0.514304	0.59370	-0.39897	0.53941	0.33149	-0.20958	0.35407
6	-0.514596	0.05849	0.37970	0.34465	0.86553	0.65427	-0.26394
7	-0.514889	0.17652	0.36861	0.31756	0.47620	-0.34005	0.49400
8	-0.515147	-0.01894	0.12177	0.79120	0.28426	0.02878	0.07761
9	-0.515317	0.32994	-0.00788	1.00996	0.12186	0.20072	0.33450
10	-0.515360	-0.10449	0.24121	0.57587	0.30012	0.36569	-0.00953

$$\begin{aligned}
b_{12}+b_{13}+b_{14}>0, & \quad b_{12}+b_{23}+b_{24}>0, \\
b_{13}+b_{23}+b_{34}>0, & \quad b_{14}+b_{24}+b_{34}>0, \\
b_{12}+b_{13}+b_{24}+b_{34}>0, & \quad b_{14}+b_{13}+b_{24}+b_{23}>0, \\
b_{12}+b_{23}+b_{34}+b_{14}>0. & 
\end{aligned} \tag{4}$$

Allowing for the eight-fold symmetry (1) of the coordinate wave function of positronium, we constructed symmetrized eight-term combinations  $\Psi_b$  of the basis functions  $\Phi_b$  specified in (3):

$$\Psi_b = (1 + P_{12}P_{34})(1 + P_{13} + P_{24} + P_{13}P_{24})\Phi_b, \tag{5}$$

where  $P_{jk}$  is the exchange operator for particles  $j$  and  $k$ .

The variational test function was built as a linear combination of  $N$  functions of the type  $\Psi_b$  whose parameters  $b_{jk}$  obey the conditions (4). The matrix elements of the energy operator (2) of a four-particle system in the basis of the exponential functions  $\Phi_b$  were calculated by employing a special algorithm that we developed using the results of Refs. 10 and 11. The parameters of the first ten functions  $\Phi_b$  used in building the functions  $\Psi_b$  specified in (5) were carefully optimized. They are listed in Table I together with the calculated values of the total binding energy of the positronium molecule that were obtained after inclusion of the basis function with the given number  $N$  into the ever-growing basis of one, two, three, etc. functions  $\Psi_b$  (up to ten functions). The parameters of the basis functions with  $N > 10$  were chosen at random from fixed intervals by analogy with calculations of three-particle systems.<sup>9</sup> Here the parameters  $b_{12}$ ,  $b_{13}$ ,  $b_{24}$ , and  $b_{34}$ , which in Fig. 1 correspond to the horizontal sizes of the square and the diagonals, were taken from the interval  $-0.5$  to  $0.5$ , and the parameters  $b_{14}$  and  $b_{23}$ , corresponding to the vertical sides, were taken from the interval  $0$  to  $1$ .

The dependence of the variational value of the total binding energy  $E$  (a.u.) of the ground state of the positronium molecule on the number  $N$  of basis functions is illustrated by Table II.

For the maximum number  $N$  of basis functions used in our calculations (90) we arrived at the following variational values of the total binding energy of the positronium molecule and the energy of dissociation into two positronium atoms:

TABLE II. The variational value of the total binding energy  $E$  (a.u.) of the ground state of the positronium molecule as a function of the number  $N$  of exponential basis functions.

No.	$E$
10	-0.515360
20	-0.515567
30	-0.515731
40	-0.515796
50	-0.515846
60	-0.515872
70	-0.515887
80	-0.515909
90	-0.515920

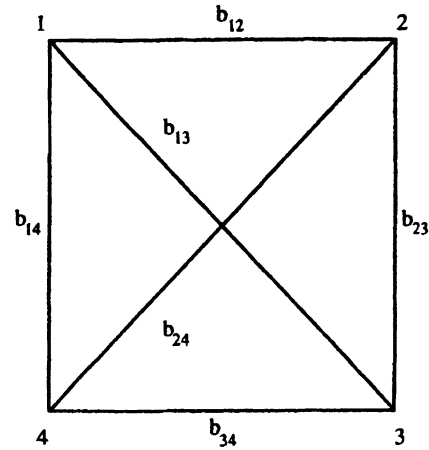


FIG. 1. The exponential basis function  $\Phi_b$  for calculating the positronium molecule  $e^+e^-e^+e^-$ . The labels 1 and 3 at the vertices of the square indicate positrons, and the labels 2 and 4 indicate electrons. The sides and diagonals of the square are labeled by the exponential parameters determining the dependence of the basis function on the separation of the respective particles.

$$E = -0.515920 \text{ a.u.}, \quad D = 0.015920 \text{ a.u.} = 0.433 \text{ eV.} \tag{6}$$

The convergence of the variational calculation is illustrated by Fig. 2. Clearly, the value of  $E$  in (6), with four significant figures, is the desired accurate value of the binding energy of the positronium molecule. Here the variational calculation in the basis of symmetrized exponential functions converges notably faster than in the exponential-power basis of Ref. 4 and the Gaussian basis of Ref. 5. In particular, by  $N = 8$ , our calculations yielded a value of  $E$  that was below  $-0.5151$  a.u., the value obtained in Ref. 4 with 400 basis functions, and at  $N = 42$  we got a value that was below  $-0.51580$ , the value obtained in Ref. 5 with a basis of 750 symmetrized Gaussian functions.

Table III lists the average values of the reciprocal interparticle separations  $1/r_{jk}$  and the delta functions  $\delta(\mathbf{r}_{jk})$  for the unlike and like charged pairs of particles in the positronium molecule, found here with the 90-term exponential basis and calculated in Ref. 5 with a 600-term function in the Gaussian basis. Clearly, refinement of the calculated values as the Gaussian basis is replaced by the exponential has an effect on the third significant figure in the average values of the reciprocal interparticle separations and on the second significant figure in  $\langle \delta(\mathbf{r}_{jk}) \rangle$ .

Our calculations with a 90-term wave function yielded the following average values for the kinetic and potential energies of the positronium molecule:  $E_{\text{kin}} = -2\langle \Delta_1 \rangle = 0.51628$  a.u., and  $E_{\text{pot}} = 2\langle 1/r_{13} - 2/r_{12} \rangle = -1.03220$  a.u.. This corresponds to a virial ratio  $-2E_{\text{kin}}/E_{\text{pot}} = 1.000349$ . Thus the error to within which the virial theorem is true amounts to 0.03%. Optimization of the overall scale of coordinates of all the particles in the test function affects only the seventh significant figure in the total binding energy  $E$  of the system but the fourth significant figures in the quantum mechanical average values of the physical quantities listed in Table II; they were calculated after optimizing the overall general scale of the wave function.

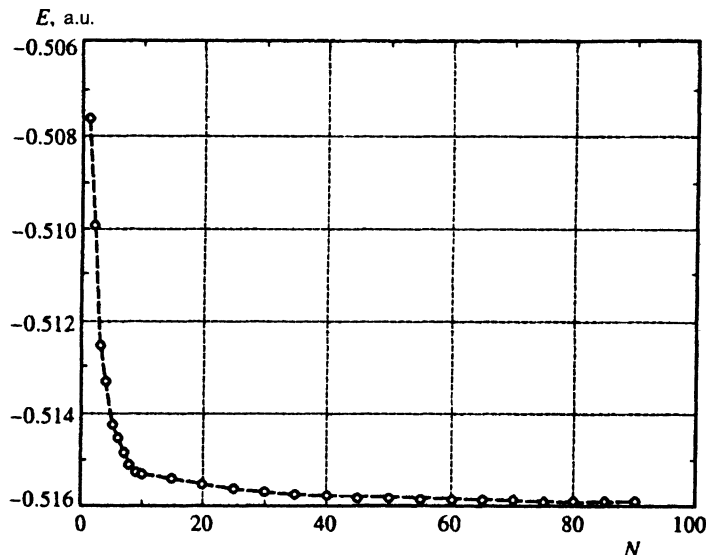


FIG. 2. The variational value of the total binding energy  $E$  of the positronium molecule as a function of the number  $N$  of exponential basis functions.

Knowing  $\langle \delta(\mathbf{r}_{12}) \rangle$ , which is the probability density of the collision of positron number 1 and electron number 2, makes it possible to calculate the lifetime of the positronium molecule from the known rate of annihilation of the positronium atom  $e^+e^-$ . The probability of annihilation of an electron–positron pair is proportional to the expectation  $\langle \delta(\mathbf{r}_{12}) \rangle$  and depends on the mutual orientation of the spins of the colliding particles. According to Ref. 16, the lifetime of the positronium atom  $e^+e^-$  is  $\tau_S = 1.25 \times 10^{-10}$  s for singlet parapositronium in which the electron and the positron have antiparallel spins, and  $\tau_T = 1.4 \times 10^{-7}$  s for triplet orthopositronium in which the electron and the positron have parallel spins.

In the positronium molecule there is no correlation between the electron and positron spins, so that each electron–positron collision occurs with probability 3/4 for parallel particle spins and probability 1/4 for antiparallel particle spins. At the same time, in the positronium molecule there may be annihilation in each of the four electron–positron pairs, while in the positronium atom this may happen only in one pair. Hence the reciprocal lifetime of the positronium molecule is related to the reciprocal lifetimes of orthopositronium and parapositronium atoms as follows:

$$1/\tau_{e^+e^-e^+e^-} = (3/\tau_T + 1/\tau_S) \langle \delta(\mathbf{r}_{12}) \rangle_{e^+e^-e^+e^-} / \langle \delta(\mathbf{r}_{12}) \rangle_{e^+e^-}, \quad (7)$$

where  $\langle \delta(\mathbf{r}_{12}) \rangle_{e^+e^-} = 1/8\pi = 0.0397887$  a.u. is the probability density of an electron–positron collision in the positronium atom. Combining (7) and the values of  $\langle \delta(\mathbf{r}_{12}) \rangle_{e^+e^-e^+e^-}$  listed in Table III, we arrive at the follow-

TABLE III. Average values of the reciprocal interparticle separations and the probability density of pair particle collisions in the positronium molecule calculated in a 600-term Gaussian basis and a 90-term exponential basis.

Basis	$\langle r_{12}^{-1} \rangle$	$\langle r_{13}^{-1} \rangle$	$\langle \delta(\mathbf{r}_{12}) \rangle$	$\langle \delta(\mathbf{r}_{13}) \rangle$
Gaussian	0.3692	0.2226	0.02065	0.000680
Exponential	0.3683	0.2206	0.02206	0.000616

ing values of the lifetime of the positronium molecule calculated in the exponential basis:  $\tau_{e^+e^-e^+e^-} = 2.25 \times 10^{-10}$  s. (The value  $\tau_{e^+e^-e^+e^-} = 2.40 \times 10^{-10}$  s corresponds to the calculations in Ref. 5 with a Gaussian basis.)

Thus, the quadrupling of the number of possible electron–positron pairs in the positronium molecule is balanced by the decrease in the statistical weight of the singlet states of the electron–positron pairs, and the high diffusivity of the charge cloud of this molecule leads to a doubling of the molecule’s lifetime in comparison to that of the parapositronium atom.

### 3. CONCLUSION

Our results suggest that the use of exponential functions of interparticle separations in precision variational calculations of various four-particle nonadiabatic Coulomb systems is promising. The complication in the computation procedure introduced by using an exponential basis instead of a Gaussian basis is fully balanced by improvement of the approximation of the multiparticle wave function, which ensures considerable refinement of the variational calculation and acceleration of convergence. In allowing for all these merits of the exponential basis, the primary interest lies within precision calculations in this basis of various four-particle mesomolecular system, which occupy an intermediate position between the hydrogen molecule and the positronium molecule, whose energies are now known only as estimates.<sup>2</sup>

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