

Second Bound State of the Positronium Molecule and Biexcitons

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A new, hitherto unknown bound state of the positronium molecule, with orbital angular momentum $L = 1$ and negative parity, is reported. This state is stable against autodissociation even if the masses of the positive and negative charges are not equal. The existence of a similar state in two dimensions has also been investigated. The fact that the biexcitons have a second bound state may aid in the better understanding of their binding mechanism. [S0031-9007(98)05416-7]

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Although the hydrogen and positronium molecule are both quantum-mechanical fermionic four-body systems of two positively and two negatively charged identical particles on the two opposite ends of the $(M+, M+, m-, m-)$ -type Coulombic systems, their properties are extremely different. Their experimental and theoretical “history” reflects these dissimilarities. The spectrum of the hydrogen molecule has already been known in the last century long before the birth of quantum mechanics, and the first theoretical calculation of Heitler and London is 70 years old [1]. The existence of the positronium molecule (Ps_2) was first theoretically predicted by Ore [2] half a century ago. The positronium molecule, however, has not been experimentally found yet, and therefore the theoretical calculations are especially important.

Between the H_2 and Ps_2 molecule one can continuously change the mass ratio $\sigma = m/M$ and the particles form a bound molecule. In solid state physics these “biexcitons” (system of two holes and two electrons) play a particularly important role. The typical mass ratio in the biexcitonic molecules is $m/M = 0.67$, therefore the properties of these species are rather similar to that of Ps_2 . A few years ago the biexcitons were experimentally observed in GaAs/AlGaAs quantum wells [3].

While in the case of the H_2 molecule many bound excited states have been observed and later theoretically studied, in the case of the Ps_2 molecule only the ground state has been predicted. Unlike the H_2 molecule, the Ps_2 is a complicated nonadiabatic four-body system where only the $L = 0$ state has been investigated so far. The aim of this paper is to explore the spectra of the Ps_2 and the biexciton molecules and to look for their possible bound excited states.

To calculate the binding energies of these molecules, the stochastic variational method (SVM) [4] has been used [5]. Our trial function is assumed in the form

$$\Phi_{kLS} = \mathcal{A} \left\{ \chi_{SM_S} \mathcal{Y}_{KLM_L}(\mathbf{v}) \exp \left[-\frac{1}{2} \sum_{i,j=1}^3 A_{kij} \mathbf{x}_i \cdot \mathbf{x}_j \right] \right\}, \quad (1)$$

with

$$\mathbf{v} = \sum_{i=1}^3 u_{ki} \mathbf{x}_i, \quad (2)$$

where \mathbf{x}_1 and \mathbf{x}_2 are the distance vectors between the positive and negative charges in the first and second atom, \mathbf{x}_3 is the distance vector between the center-of-masses of the two atoms, χ_{SM_S} is a spin function, $\mathcal{Y}_{KLM}(\mathbf{x}) = x^{2K+L} Y_{LM}(\hat{\mathbf{x}})$, “ k ” is the index of the basis states and \mathcal{A} is an antisymmetrizer. The above trial function, the “correlated Gaussian basis” is known to provide a high quality wave function and very precise energy [6–8]. The correlation between the particles plays a very important role in the systems considered and it is efficiently represented by the nondiagonal elements of A_k . The most adequate values of the nonlinear parameters u_{ki} and A_{kij} are selected by a random optimization [5]. The dimension of the basis is increased one by one until the required convergence is reached. This procedure has proved to be efficient, leading to nearly optimal parameters at a relatively low computational cost.

The spectrum of systems made up of positrons and electrons is shown in Fig. 1. Both the Ps^- ion and the Ps_2 molecule are known to have one bound state, and these states have been studied by quite a few different methods including variational [9–13] and quantum Monte Carlo (QMC) methods [14]. As a test, we compare our result to those of these calculations. The convergence of the energy as a function of basis size N is shown in Table I. Our results for the Ps_2 molecule improve the best previous variational results and it is in a good agreement with the recent QMC calculation of Bressanini *et al.* [14].

The main aim of this paper is to seek other bound excited states of the Ps_2 molecule and biexcitons. To this end we applied our method for all possible combinations of states with $L = 0, 1, 2, 3$ orbital angular momenta and $S = 0, 1, 2$ spins. No bound excited states have been found for $\sigma = 1$ except for one case. In the case of $L = 1$ (with negative parity) and $S = 0$ our calculation predicts the existence of a second bound state of the Ps_2

FIGURES

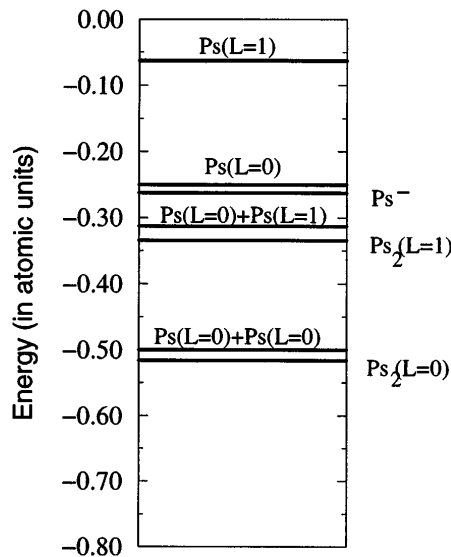


FIG. 1. Bound states of the electron-positron systems.

molecule. In that system, the spins of the positronium atoms are coupled to zero. In this spin state, the Ps_2 molecule can dissociate into two Ps atoms (bosons) only if the relative orbital angular momentum is even. Consequently, the Ps_2 molecule with $L = 1$ and negative parity cannot decay into the ground states of two Ps atoms [$\text{Ps}(L = 0) + \text{Ps}(L = 0)$]. The energy of this $\text{Ps}_2(L = 1)$ state ($E = -0.334408$ a.u.; see Table I) is lower than the energy of the relevant threshold (-0.3125 a.u.; see Fig. 1), and this state is therefore stable against autodissociation into $\text{Ps}(L = 0) + \text{Ps}(L = 1)$. The binding energy of this state is 0.5961 eV, which is about 40% more than that of the ground state of Ps_2 (0.4355 eV).

The binding mechanism of this second bound state is very special. The constituents are fermions, but in the decaying channel they form bosons (Ps atoms or excitons). The Pauli principle, however, forbids the odd partial waves between bosons so the biexcitons with $L = 1$ and negative parity cannot decay into two excitons. A somewhat similar situation, that is a second bound state which cannot decay due to parity conservation, exists in the H^- ion as well. By changing the mass ratio in that

($M+, m-, m-$) system, however, this state disappears, so the Ps^- ion has only one bound state.

Before discussing the spatial distribution of this molecule, let's recall that the average distance $\langle r_{e^+e^-} \rangle$ between the electron and the positron is 3 a.u. in the ground state of the Ps atom, while it is 10 a.u. in the first excited state. The root mean square radius (rms) of the ground state of the Ps_2 molecule is found to be 3.614 a.u. The rms radius of the second bound state is 5.661 a.u., 1.5 times larger than that of the ground state. This is not surprising if one assumes that the second bound state is essentially a system of a Ps atom in its ground and a Ps atom in its first (spatially extended) excited state. To check the validity of this assumption we have restricted the model space to include only this type of configuration. [This can be achieved by a special choice of the u_{ki} parameters in Eq. (2)]. The energy converged to -0.323 a.u., that is, the $\text{Ps}(L = 0) + \text{Ps}(L = 1)$ system with zero relative orbital angular momentum, forms a bound state with energy close to that of $L = 1$ state of the Ps_2 molecule, therefore this configuration is likely to be the dominant configuration in this molecule. There is a second configuration, the $\text{Ps}^- - e^+$ (or $\text{Ps}^+ - e^-$) with $L = 1$ relative orbital motion, which intuitively may look important because two oppositely charged particles attract each other, but it is merely bound ($E = -0.315$ a.u.). On the other hand, by increasing the mass M of the positively charged particles toward infinity, one arrives at the energy of the $C^1 \prod_u 2p\pi$ state of the H_2 molecule. This state is formed by the excited and the ground states of the H atom. Consequently, the second bound state of the biexciton molecule is dominantly formed by an interacting pair of a ground state exciton and an $L = 1$ excited state exciton.

The average distances, the average square distances, the scale factor $\eta = -V/(2T)$, and the probability of finding two particles in the same space point are listed in Table II for both the $L = 0$ and $L = 1$ states of the Ps_2 molecule. The closeness of the scale factor to unity proves the convergence of the results. The average distances show that in the $L = 1$ state the two atoms are well separated. One cannot give a direct geometrical picture of the ground or excited state because the variance $\Delta r_{ij} = \sqrt{\langle r_{ij}^2 \rangle - \langle r_{ij} \rangle^2}$ is large.

TABLE I. Total energies of the Ps_2 molecule in atomic units.

Method	$\text{Ps}_2(L = 0)$	$\text{Ps}_2(L = 1)$
SVM ($N = 100$)	-0.515 981 750	-0.334 399 869
SVM ($N = 200$)	-0.516 002 271	-0.334 405 027
SVM ($N = 400$)	-0.516 003 769	-0.334 407 971
SVM ($N = 800$)	-0.516 003 778	-0.334 408 112
Ref. [9]	-0.516 002	
QMC [13]	-0.51601 \pm 0.00001	

TABLE II. Ground and excited state expectation values (in a.u.).

Expectation value	$\text{Ps}_2(L = 0)$	$\text{Ps}_2(L = 1)$
$\langle r_{e^-e^-}^2 \rangle$	46.371	96.047
$\langle r_{e^+e^-}^2 \rangle$	29.111	80.152
$\langle r_{e^-e^-} \rangle$	6.033	8.856
$\langle r_{e^+e^-} \rangle$	4.487	7.568
$\langle \delta(r_{e^-e^-}) \rangle$	0.00063	0.00015
$\langle \delta(r_{e^+e^-}) \rangle$	0.022	0.011
$-\langle V \rangle / (2\langle T \rangle)$	0.999 999 970	0.999 998 4

In the positronium limit ($\sigma = 1$) we deal with antiparticles and the electron-positron pair can annihilate. The most dominant annihilation is accompanied by the emission of two photons with energy about 0.5 MeV each. To have an estimate for the decay due to the annihilation we have substituted the probability density of an electron at the position of a positron into the formula (64) of Ref. [9]. Roughly speaking, the lifetime is inversely proportional to the probability of finding an electron and a positron in the same position [$\langle \delta(r_{e^+e^-}) \rangle$; see Table II]. The lifetime due to the annihilation is estimated to be 1.8 ns. This is about 2 times that of the ground state.

The dependence of the biexciton binding energy on the mass ratio m/M is shown in Fig. 2. The change of the binding energy in the ground and the excited states is similar. Both the ground and excited states become less bound by changing the mass ratio from H_2 to Ps_2 , though the binding of the excited state decreases somewhat to a lesser extent. The energy of the transition from the excited $L = 1$ to the ground $L = 0$ state is also shown in this figure. This transition may take place in an external field, for example.

The continued advance in microfabrication has allowed the creation of semiconductor systems (quantum dots) where the electrons (or excitons, biexcitons, etc.) are laterally confined. This technical possibility has intensified the interest in two-dimensional (2D) systems for the last few years. It is intriguing, therefore, to investigate the existence of the second bound state of the biexcitons in two dimension. To this end we set the azimuthal angles of all the vectors \mathbf{x}_i and \mathbf{v} to $\pi/2$ and choose $L = M$. With this particular choice the angular dependence of the wave

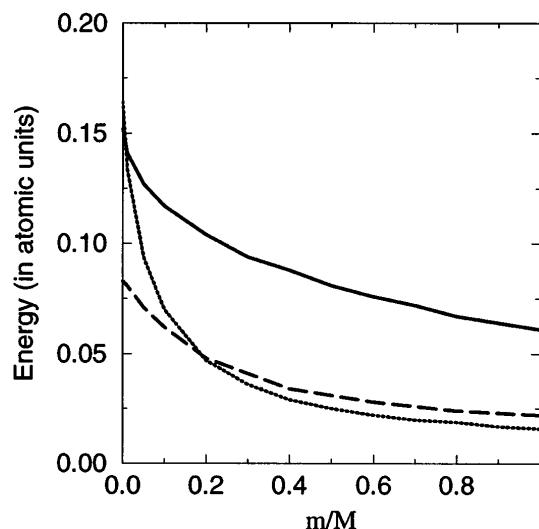


FIG. 2. Energies of the biexcitons as a function of mass ratio. The dotted line is the binding energy of the ground state, and the dashed line is that of the first excited state. The continuous line shows the energy difference of the first excited and the ground states. Note that the energy difference is divided by 3 so as to fit the figure.

function is given by $(v_x + iv_y)^M$ (where v_x and v_y are the x and y component of \mathbf{v}).

After repeating the calculation for the two-dimensional Ps_2 molecule we found that its energy is $-2.192\,858$ a.u. This is in good agreement with the QMC result -2.1928 ± 0.0001 [15]. Note that the energy of the Ps atom in two dimension is $E_L = -1/(2L + 1)^2$. The size of this system is very small: Its rms radius is 1.125 a.u., which is smaller than one third of the radius in 3D. The interesting property of these systems in 2D is that their binding energy considerably increases (more than 10 times of that of the 3D case) and their spatial extension is much smaller, accordingly.

The energy of the Ps_2 molecule with $L = 1$ (negative parity) is -1.2788 a.u. and the rms radius is 2.55 a.u. By comparing this energy to the energy of the relevant threshold (-1.1111 a.u.) we can conclude that the second bound state of the Ps_2 molecule exists in 2D as well. The binding energy of the second bound state in 2D is about 8 times that of the 3D case.

A second bound state of the biexcitons which exists in both 2D and 3D is reported for the first time. The existence of this state is due purely to the Pauli principle. This bound state is in the continuum but its autodissociation is forbidden. It is shown that not only the ground but the $C^1 \prod_u 2p\pi$ excited state of the H_2 -like molecule also survive the change of mass ratio σ of the heavier and lighter particles in the whole $[0, 1]$ interval of σ .

Recent experiments have shown the existence of the biexciton molecules but the theoretical and experimental binding energies of biexcitons disagree [3,16,17]. There are different suggestions to resolve this discrepancy, e.g., in terms of fractional dimensions, localization, etc. All of these models are based on the fact that the biexcitons under practical conditions are not pure Coulombic four-body systems in the "vacuum." Some models assume that in the biexcitons the Coulomb interaction is slightly modified, like, e.g., $[1 - \exp(-\gamma r)]/r$. Our calculation confirms that the second bound state survives this distortion of the potential as well. Experimental confirmation of the existence of the second bound state would be very useful because it would help to pinpoint the most realistic model of the biexcitons in quantum wells. The fact that the binding energy is relatively large gives a hope that experimental measurements for the second bound state are not much more difficult than those of the ground state.

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