

**$(e^-, e^+)$ -pair annihilation in the positronium molecule  $\text{Ps}_2$** Alexei M. Frolov,\* Sergei I. Kryuchkov,<sup>†</sup> and Vedene H. Smith, Jr.*Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6*

(Received 19 May 1994; revised manuscript received 28 November 1994)

The  $(e^-, e^+)$ -pair annihilation in the bound  $^1S_0$  state of the  $\text{Ps}_2$  molecule ( $e^-e^+e^-e^+$ ) is studied. It is shown that the expectation values of the two-, three-, and four-body Dirac  $\delta$  functions  $\langle \delta_{+-} \rangle$ ,  $\langle \delta_{++-} \rangle$  ( $\equiv \langle \delta_{+--} \rangle$ ), and  $\langle \delta_{+++} \rangle$  determine the photonless, one- and many-photon annihilation rates, i.e., the values of  $\Gamma_{0\gamma}$ ,  $\Gamma_{1\gamma}$ , and  $\Gamma_{n\gamma}$ , where  $n \geq 2$ . The appropriate analytical expressions are presented together with numerical estimates. As expected, the two-photon annihilation process dominates.

PACS number(s): 36.10.Dr, 78.70.Bj

In the present study we consider  $(e^-, e^+)$ -pair annihilation in the ground  $^1S_0$  state ( $L=0$ ) [1,2] of the Coulomb four-body system  $\text{Ps}_2$  ( $e^-e^+e^-e^+$ ) or positronium molecule [3]. The existence of this single bound state has been well known for many years [3,4]. In addition, the Coulomb three-body  $\text{Ps}^-$  ion has only one bound  $^2S_{1/2}$  state ( $L=0$ ) [5]. In contrast with these, the discrete spectrum in the two-body system  $\text{Ps}$  (or  $e^-e^+$ ) contains an infinite number of bound states. The positronium molecule is of interest in some applications [6] and has been the subject of intensive theoretical study [7–13]. We report here analytical and numerical results for the electron-positron annihilation rate in the positronium molecule.

As is well known the  $(e^-, e^+)$ -pair annihilation in the  $\text{Ps}(e^-e^+)$  system proceeds into two- and three-photons (see, e.g., [2]). Moreover, such annihilation can be observed, in principle, as an  $n$ -photon process ( $n \geq 2$ ), with the probability for annihilation into  $(n+1)$  photons of order  $\alpha$  times smaller than for  $n$  photons [2]. In the similar three-body  $\text{Ps}^-$  ion ( $e^-e^+e^-$ ) electron-positron pair annihilation can be observed also as a one-photon process [14–17]. The  $(e^-, e^+)$ -pair annihilation in the four-body positronium molecule  $\text{Ps}_2$  ( $e^-e^+e^-e^+$ ) can proceed with the emission of an arbitrary number of photons and even without  $\gamma$  radiation. If  $\Gamma_{n\gamma}$  is the  $n$ -photon annihilation rate from the ground  $^1S_0$  state of the positronium molecule, the total annihilation rate  $\Gamma$  takes the form

$$\Gamma = \Gamma_{0\gamma} + \Gamma_{1\gamma} + \Gamma_{2\gamma} + \Gamma_{3\gamma} + \dots \quad (1)$$

In terms of this notation our present goal is to evaluate numerically the appropriate rates  $\Gamma_{n\gamma}$  ( $n=0, 1, 2, 3, \dots$ ) and the sum  $\Gamma$ .

First, consider the two-photon annihilation rate  $\Gamma_{2\gamma}$ ,

which is the largest of all  $\Gamma_{2n\gamma}$  for  $n \geq 1$ . The appropriate analytical expression can be found from work by Lee [18] (see also [19]). In atomic units ( $m_e=1$ ,  $\hbar=1$ , and  $e=1$ ) for a system of  $n$  electrons and  $m$  positrons, where  $\max(n, m) > 1$ , the expression for  $\Gamma_{2\gamma}$  is [20]

$$\Gamma_{2\gamma} = \pi n m \alpha^4 c a_0^{-1} \langle \delta_{+-} \rangle, \quad (2)$$

which becomes

$$\begin{aligned} \Gamma_{2\gamma} &= 4\pi \alpha^4 c a_0^{-1} \langle \delta_{+-} \rangle \\ &\approx 201.234\,961\,8 \times 10^9 \langle \delta_{+-} \rangle \text{ sec}^{-1} \end{aligned} \quad (3)$$

for  $\text{Ps}_2$  for which  $n=2$ ,  $m=2$ , and  $nm (=4)$  is the total number of electron-positron pairs. The expectation value of the Dirac delta function  $\langle \delta_{+-} \rangle$ , i.e.,

$$\langle \delta_{+-} \rangle = \frac{\langle \Psi | \delta(\mathbf{r}_- - \mathbf{r}_+) | \Psi \rangle}{\langle \Psi | \Psi \rangle}, \quad (4)$$

is used here in atomic units. In all  $\delta$  functions the subscript  $-$  denotes the electron, while  $+$  designates the positron. The velocity of light  $c$ , the Bohr radius  $a_0$ , and the fine structure constant  $\alpha$  are, respectively,

$$c = 0.299\,792\,458 \times 10^9 \text{ m sec}^{-1},$$

$$a_0 = 0.529\,177\,249 \times 10^{-10} \text{ m},$$

$$\alpha = 1/137.035\,989\,5 = 0.729\,735\,308 \times 10^{-2}$$

(Ref. [22].)

Following Jauch and Rohrlich [2] and using Eq. (3) for  $\Gamma_{2\gamma}$ , we can evaluate approximately the other  $\Gamma_{2n\gamma}$  values, i.e., the annihilation rates with the emission of even numbers of photons. Indeed, we have in atomic units

$$\begin{aligned} \Gamma_{2n\gamma} &= \alpha^{2(n-1)} \Gamma_{2\gamma} \\ &= 4\pi \alpha^{2n+2} c a_0^{-1} \langle \delta_{+-} \rangle \text{ sec}^{-1}, \end{aligned} \quad (5)$$

where  $n \geq 1$ .

To find the analytical formulas for odd numbers of photons, i.e.,  $\Gamma_{3\gamma}$  as well as  $\Gamma_{(2n+1)\gamma}$  ( $n \geq 2$ ) and  $\Gamma_{1\gamma}$ , we shall follow the approach proposed by Ferrante [23]. This method is based on consideration of the  $(e^-, e^+)$  an-

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nihilation from the bound ground state of the two-body system Ps, of the three-body ion  $\text{Ps}^-$ , and of the four-body molecule  $\text{Ps}_2$ . Note first that the energy of the ground states in all of these systems is negligible in comparison to the  $m_e c^2$  energy. Therefore, we can consider the annihilation to be the result of the electron-positron collision with energy that is very close to zero. Such a collision produces two photons (or an even number of photons) when the  $(e^-, e^+)$  pair is in the singlet state and three photons (or an odd number of photons) when this pair is in the triplet state. We recall that the indistinguishable particles in the bound states of the  $\text{Ps}^-$  ion and in the  $\text{Ps}_2$  molecule are always in singlet states [24]. Since the total number of  $(e^-, e^+)$  pairs in the  $\text{Ps}^-$  ion is two times smaller than that in the  $\text{Ps}_2$  molecule, we write the following approximate relation (the so-called Ferrante [23] relation):

$$\frac{\Gamma_{3\gamma}}{\Gamma_{2\gamma}} = \frac{2\Gamma_{3\gamma}(\text{Ps}; {}^3S_1)}{2\Gamma_{2\gamma}(\text{Ps}; {}^1S_0)} = \frac{\Gamma_{3\gamma}(\text{Ps}; {}^3S_1)}{\Gamma_{2\gamma}(\text{Ps}; {}^1S_0)} = \frac{\Gamma_{3\gamma}(\text{Ps}^-)}{\Gamma_{2\gamma}(\text{Ps}^-)}, \quad (6)$$

where  $\Gamma_{3\gamma}(\text{Ps}; {}^3S_1)$  is the three-photon annihilation rate from the  ${}^3S_1$  state of the two-body system Ps (or  ${}^3S_1$  state of the electron-positron pair), while  $\Gamma_{2\gamma}(\text{Ps}; {}^1S_0)$  is the two-photon annihilation rate from its  ${}^1S_0$  state. These values can be found, e.g., in [2]. From Eq. (6) we find the expression for  $\Gamma_{3\gamma}$

$$\begin{aligned} \Gamma_{3\gamma} &= \frac{4(\pi^2 - 9)\alpha}{9\pi} \Gamma_{2\gamma} \\ &= \frac{16(\pi^2 - 9)}{9} \alpha^5 c a_0^{-1} \langle \delta_{+-} \rangle \text{sec}^{-1}. \end{aligned} \quad (7)$$

The annihilation rates  $\Gamma_{(2n+1)\gamma}$  with an odd number of photons ( $n \geq 2$ ) can be evaluated from the  $\Gamma_{3\gamma}$  value in the same manner as  $\Gamma_{2n\gamma}$  from  $\Gamma_{2\gamma}$  [see Eq. (5)], i.e.,

$$\begin{aligned} \Gamma_{(2n+1)\gamma} &= \alpha^{2(n-1)} \Gamma_{3\gamma} \\ &= \frac{16(\pi^2 - 9)}{9} \alpha^{2n+3} c a_0^{-1} \langle \delta_{+-} \rangle \text{sec}^{-1}. \end{aligned} \quad (8)$$

The one-photon annihilation rate  $\Gamma_{1\gamma}$  can be also determined from the analogous relation. However, in the two-body system Ps this process is forbidden and hence the right-hand side of this formula must involve only the respective values for the three-body  $\text{Ps}^-$  ion. Likewise, the one-photon annihilation proceeds as a triple collision process, i.e., either as an  $(e^-, e^-, e^+)$  collision in the  $\text{Ps}^-$  ion and in the  $\text{Ps}_2$  molecule or as an  $(e^-, e^+, e^+)$  collision in the  $\text{Ps}_2$  molecule [25]. Obviously, the fast electron is emitted in the first case and the fast positron in the second. For the  $\text{Ps}_2$  molecule both triple collisions can take place, while for the  $\text{Ps}^-$  ion only the first one. As a result the appropriate Ferrante relation for  $\Gamma_{1\gamma}$  takes the form

$$\frac{\Gamma_{1\gamma}}{\Gamma_{2\gamma}} = 2 \frac{\Gamma_{1\gamma}(\text{Ps}^-)}{\Gamma_{2\gamma}(\text{Ps}^-)}. \quad (9)$$

After a few simple transformations Eq. (9) can be transformed with the help of the result for  $\Gamma_{1\gamma}(\text{Ps}^-)$  [14–17] to the form (in atomic units)

$$\Gamma_{1\gamma} = \frac{64\pi^2}{3} \xi \alpha^8 c a_0^{-1} \frac{\langle \delta_{+-} \rangle}{\langle \delta_{+-}, \text{Ps}^- \rangle} \langle \delta_{+--}, \text{Ps}^- \rangle \text{sec}^{-1}. \quad (10)$$

The value of the proportionality constant  $\xi$  was given as 1 by Chu and Pönish [14], 2 by Misawa and Mills [15], and  $\frac{4}{9}$  by Kryuchkov [1]. We shall use the value  $\frac{4}{9}$  [17]. The best values to date for  $\langle \delta_{+-}, \text{Ps}^- \rangle$  is  $2.073\,319\,88 \times 10^{-2}$  and for  $\langle \delta_{+--}, \text{Ps}^- \rangle$  is  $0.358\,996 \times 10^{-4}$  [16]. By using these values formula (10) reduces to the form

$$\begin{aligned} \Gamma_{1\gamma} &= \frac{16\pi}{3} \xi \alpha^4 \frac{\langle \delta_{+--}, \text{Ps}^- \rangle}{\langle \delta_{+-}, \text{Ps}^- \rangle} \Gamma_{2\gamma} \\ &= W_{\gamma, 2\gamma}^F \Gamma_{2\gamma} \\ &= 0.365\,637\,575 \times 10^{-10} \Gamma_{2\gamma}, \end{aligned} \quad (11)$$

where  $W_{\gamma, 2\gamma}^F$  is the one-photon internal conversion coefficient for the  $\gamma$  radiation determined from Ferrante's relation.

It should be mentioned here that Ferrante's method can be applied directly, in principle, only to two-body contact processes. This suggests that the probability of such a process is proportional to the expectation value of the two-body Dirac  $\delta$  function, i.e., in our case  $\approx \langle \delta_{\pm} \rangle$  [26]. Actually, the one-photon annihilation is the triple contact process, i.e., its probability approximately equals  $\langle \delta_{+--} \rangle$  (or  $\langle \delta_{++-} \rangle$ ). Therefore, we expect that in this case Ferrante's relation has a different form [compare Eqs. (6) and (9)]. Moreover, the value of  $\Gamma_{1\gamma}$  can be found directly from the numerical value of  $\langle \delta_{+--} \rangle$  for the  $\text{Ps}_2$  molecule. Indeed, by following [14–17] we write the appropriate expression for  $\Gamma_{1\gamma}$

$$\Gamma_{1\gamma} = \frac{16\pi^2}{3} \xi \alpha^8 c a_0^{-1} (\langle \delta_{++-} \rangle + \langle \delta_{+--} \rangle) \text{sec}^{-1} \quad (12)$$

or, since in the case considered  $\langle \delta_{++-} \rangle \equiv \langle \delta_{+--} \rangle$ , we have [27]

$$\Gamma_{1\gamma} = \frac{32\pi^2}{3} \xi \alpha^8 c a_0^{-1} \langle \delta_{++-} \rangle \text{sec}^{-1}. \quad (13)$$

It is easy to show from these two different expressions, Eqs. (10) and (13), for  $\Gamma_{1\gamma}$  that in the  $\text{Ps}_2$  molecule the following relation between the expectation values for the Dirac  $\delta$  functions  $\langle \delta_{+-} \rangle$  and  $\langle \delta_{+--} \rangle (\equiv \langle \delta_{++-} \rangle)$ :

$$\begin{aligned} \langle \delta_{++-} \rangle &= 2 \frac{\langle \delta_{+-} \rangle}{\langle \delta_{+-}, \text{Ps}^- \rangle} \langle \delta_{+--}, \text{Ps}^- \rangle \\ &= 0.346\,300\,6 \times 10^{-2} \langle \delta_{+-} \rangle \end{aligned} \quad (14)$$

should hold. This equality does hold approximately and obviously the possible deviation between these expectation values for the triple  $\delta$  function determined from the variational calculations and from Eq. (14) can serve to indicate the accuracy of Ferrante's approximate relation for the one-photon annihilation rate.

The zero-photon (or photonless) annihilation rate  $\Gamma_{0\gamma}$  cannot be evaluated from Ferrante's relations even ap-

proximately since this process is forbidden in the relevant two- and three-body systems. We determine it by the following direct calculation. To start with, 36 Feynman diagrams correspond to this process in the lowest order. Six of them are presented in Fig. 1. The others can be obtained by interchanging the initial electrons, initial positrons, and two intermediate photons. The results of calculations show that all of them contribute strongly to the result. The momenta of both electrons and positrons are negligible in comparison to  $m_e c$ , which gives the scale of the transition amplitude change and that of the final momenta. Also, the energy of the bound ground state in the  $\text{Ps}_2$  molecule is negligible in comparison with  $m_e c^2$ . So the first nonvanishing term in the amplitude expansion in the  $\mathbf{p}_i/m_e c$  parameters can be obtained by substitution of the  $(m_e c^2, 0, 0, 0)$  four-vector instead of all initial momenta [here the four-momentum  $p$  has components  $(E, \mathbf{p})$ ]. Thus the transition amplitude does not depend on the initial three-dimensional momentum  $\mathbf{p}$  in this approximation. Bearing this in mind it is possible to correlate the annihilation rate and the value of the four-particle density of the  $\text{Ps}_2$  molecule with all of the particles at the same point. The photonless annihilation rate  $\Gamma_{0\gamma}$  in the posi-

tronium molecule can be obtained in a way similar to the one used in [17,28]. The answer is (in units with  $\hbar=1, c=1$ )

$$\Gamma_{0\gamma} = \frac{|\Psi(0)|^2}{4} \int \frac{2\pi |A|^2}{\Pi_{\text{in}}(2E)\Pi_{\text{out}}(2E)} \frac{1}{(2\pi)^3} \times \frac{E_1 E_2}{E_1 + E_2} |\mathbf{p}_1| d\Omega, \quad (15)$$

where  $A$  is the transition amplitude, calculated according to the Feynman rules [17,29].  $|\Psi(0)|^2$  indicates the value of the four-particle density of  $\text{Ps}_2$  at the quadruple-collision point or, in other words, it is the expectation value for the  $\delta_{++--}$  function in the ground state of the positronium molecule, i.e.,  $|\Psi(0)|^2 = |\Psi(0,0,0,0,0,0)|^2 = \langle \delta_{++--} \rangle$ . The meaning of the other symbols in this equation can be also found in [17,29]. It is easy to show that antisymmetry of this amplitude  $A$  with respect to the permutation of the initially indistinguishable particles (for the singlet states both the electron-electron and the positron-positron pairs) leads to  $|A|^2 = \sum_{s_5 s_6} 4 |M_{s_5 s_6 \uparrow \downarrow \uparrow \downarrow}|$ . Here  $s_5$  and  $s_6$  are the spins of the final electron and positron and the arrows show the spin states of the initial electrons and positrons. In this expression summation is over all possible final states of the particles. The square of the wave function of the relative motion  $|\Psi|^2$  is divided by 4 because of the presence of two pairs of indistinguishable particles in the initial state and the fact that this wave function is normalized to unity with integration over the entire six-dimensional space.

The standard way to calculate  $|A|^2$  using the corresponding technique of traces [28,29] is not efficient here because of the large number of terms to be calculated ( $36 \times 36 = 1296$ ). Due to the simplicity of the initial and final states in this case it was more convenient to first calculate the amplitude  $A$  itself, using Dirac spinors of the corresponding states. Calculation with the use of the MATHEMATICA computer program [30] yields the expression

$$\Gamma_{0\gamma} = \frac{147\sqrt{3}\pi^3}{2} \alpha^4 \Lambda^9 \left[ \frac{c}{\Lambda} \right] \langle \delta_{++--} \rangle \text{sec}^{-1}, \quad (16)$$

where  $\Lambda = \hbar/mc$  is the Compton wavelength of the electron. In atomic units this result takes the form [31]

$$\begin{aligned} \Gamma_{0\gamma} &= \frac{147\sqrt{3}\pi^3}{2} \alpha^{12} c a_0^{-1} \langle \delta_{++--} \rangle \\ &\approx 0.509\,919\,29 \times 10^{-3} \langle \delta_{++--} \rangle \text{sec}^{-1}, \end{aligned} \quad (17)$$

where  $\langle \delta_{++--} \rangle$  is in atomic units. It can be also written in the form

$$\begin{aligned} \Gamma_{0\gamma} &= \frac{147\sqrt{3}\pi^2}{4} \alpha^8 \frac{\langle \delta_{++--} \rangle}{\langle \delta_{+-} \rangle} \Gamma_{2\gamma} \\ &= W_{0,2\gamma} \Gamma_{2\gamma} \\ &\approx 0.505\,173\,540\,9 \times 10^{-14} \frac{\langle \delta_{++--} \rangle}{\langle \delta_{+-} \rangle} \Gamma_{2\gamma}, \end{aligned} \quad (18)$$

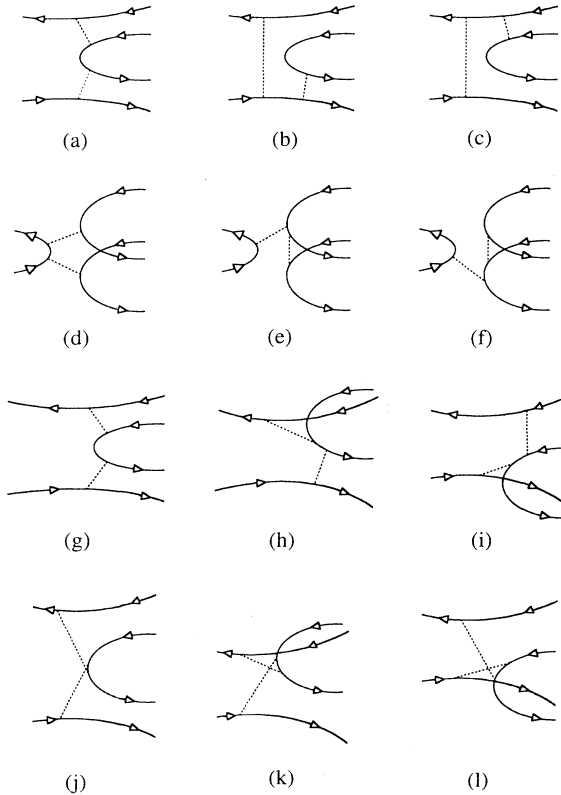


FIG. 1. Six basic Feynman diagrams for the lowest order (a)–(f). The six exchange diagrams (g)–(l) with the initial electrons interchanged are shown only for the first basic diagram since the other cases are analogous.

where  $W_{0,2\gamma}$  is the two-photon internal conversion coefficient for the  $\text{Ps}_2$  molecule.

The formulas presented above determine the various partial annihilation rates and the total probability of the electron-positron pair annihilation in the ground  $^1S_0$  state ( $L=0$ ) of the four-body system  $\text{Ps}_2$  (positronium molecule). Note that the annihilation rates  $\Gamma_{2\gamma}$  and  $\Gamma_{3\gamma}$  for the ground state of the positronium molecule were evaluated previously [32] with the use of a simplified Hylleraas-type [3] wave function. In fact, the positronium molecule was approximated as a weakly bound cluster system consisting of two neutral (two-body) Ps systems which are far away from each other. As expected, the obtained numerical result was  $\langle \delta_{+-} \rangle \approx \langle \delta_{+-}; \text{Ps} \rangle$ . In reality this approximate relation has the form

$$\langle \delta_{+-} \rangle \approx \langle \delta_{+-}; \text{Ps}^- \rangle \approx \frac{1}{2} \langle \delta_{+-}; \text{Ps} \rangle.$$

This shows that the real structure of the  $\text{Ps}_2$  molecule

$$\begin{aligned} \langle \alpha | &= \exp(-\alpha_{12}r_{12}^2 - \alpha_{13}r_{13}^2 - \alpha_{23}r_{23}^2 - \alpha_{14}r_{14}^2 - \alpha_{24}r_{24}^2 - \alpha_{34}r_{34}^2), \\ | \beta \rangle &= \exp(-\beta_{12}r_{12}^2 - \beta_{13}r_{13}^2 - \beta_{23}r_{23}^2 - \beta_{14}r_{14}^2 - \beta_{24}r_{24}^2 - \beta_{34}r_{34}^2) \end{aligned} \quad (19)$$

take the form

$$\langle \alpha | \delta_{41} | \beta \rangle = \left[ \frac{\pi}{\sqrt{D}} \right]^3, \quad (20)$$

where  $D = (a_{12} + a_{24} + a_{23})(a_{13} + a_{34} + a_{23}) - a_{23}^2$  for the two-body 41- $\delta$  function. Here the subscripts 1 and 2 designate electrons, while 3 and 4 stand for the positrons and  $a_{ij} = \alpha_{ij} + \beta_{ij}$ . The formulas for the other two-particle 21-, 31-, 32-, 42-, and 43- $\delta$  functions can be obtained from this expression by simple permutations. The analytical formula for the three-particle 321- $\delta$  function is

$$\langle \alpha | \delta_{321} | \beta \rangle = \left[ \frac{\pi}{a_{14} + a_{24} + a_{34}} \right]^{3/2}. \quad (21)$$

Analogous expressions can be found for the other expectation values of the three-particle 431-, 432-, and 421- $\delta$  functions. For the four-particle  $\delta$  function we find

TABLE I. The lower and upper estimates (low and up) for the expectation values in atomic units of two-, three-, and four-body electron-positron  $\delta$  functions for the ground bound state of the  $\text{Ps}_2$  molecule. The subscript  $-$  denotes an electron, while  $+$  designates a positron.

Estimate	$\langle \delta_{+-} \rangle$	$\langle \delta_{++-} \rangle \equiv \langle \delta_{+--} \rangle$	$\langle \delta_{++++} \rangle$
low	$2.17 \times 10^{-2}$	$8.0 \times 10^{-5}$	$3.0 \times 10^{-6}$
up	$2.20 \times 10^{-2}$	$9.5 \times 10^{-5}$	$4.5 \times 10^{-6}$

with good accuracy is not in the form of two weakly interacting two-body neutral clusters.

In the present article the needed numerical results for the expectation values of Dirac  $\delta$  functions were computed with the help of the variational procedure proposed by Kolesnikov and Tarasov (see, e.g., [33] and references therein). The analytical expressions for the respective elements of Dirac two-particle  $\delta$  functions in terms of their basis functions [33]

$$\langle \alpha | \delta_{4321} | \beta \rangle = 1. \quad (22)$$

However, the convergence for all expectation values of Dirac  $\delta$  functions was obviously insufficient, and we present in Table I lower and upper estimates for the  $\delta_{+-}$ ,  $\delta_{++-}$ , and  $\delta_{++++}$  expectation values [34]. From the results in Table I we have determined lower and upper estimates for the annihilation rates which are given in Table II. We can expect that the exact values of  $\Gamma_{n\gamma}$ , where  $n=0, 1, 2, \dots, 10$ , lie between the appropriate lower and upper estimates [34], i.e.,

$$\Gamma_{n\gamma}^{\text{low}} \leq \Gamma_{n\gamma} \leq \Gamma_{n\gamma}^{\text{up}}. \quad (23)$$

Table I shows that the accuracy achieved for the expectation value of the two-particle  $\delta$  function  $\langle \delta_{+-} \rangle$  is greater than that for the three- and four-particle  $\delta$  functions. We wish to note that at the present time the inaccuracies in the  $\delta$ -function expectation values mean that

TABLE II. The lower and upper estimates for the many-photon annihilation rates  $\Gamma_{n\gamma}$ , where  $n=0, 1, 2, 3, 4, \dots, 10$ , and for the total annihilation rate  $\Gamma$  in  $\text{sec}^{-1}$ .

Rate	$\Gamma_{0\gamma}$	$\Gamma_{1\gamma}$	$\Gamma_{2\gamma}$	$\Gamma_{3\gamma}$	$\Gamma_{4\gamma}$	$\Gamma_{5\gamma}$
Low	$0.1530 \times 10^{-8}$	0.1602	$0.4381 \times 10^{10}$	$0.3933 \times 10^7$	$0.2333 \times 10^6$	$0.2094 \times 10^3$
Up	$0.2295 \times 10^{-8}$	0.1624	$0.4441 \times 10^{10}$	$0.3987 \times 10^7$	$0.2365 \times 10^6$	$0.2123 \times 10^3$
Rate	$\Gamma_{6\gamma}$	$\Gamma_{7\gamma}$	$\Gamma_{8\gamma}$	$\Gamma_{9\gamma}$	$\Gamma_{10\gamma}$	$\Gamma$
Low	$0.1242 \times 10^2$	$0.1115 \times 10^{-1}$	$0.6615 \times 10^{-3}$	$0.5939 \times 10^{-6}$	$0.3523 \times 10^{-7}$	$0.4385 \times 10^{10}$
Up	$0.1259 \times 10^2$	$0.1131 \times 10^{-1}$	$0.6707 \times 10^{-3}$	$0.6021 \times 10^{-6}$	$0.3571 \times 10^{-7}$	$0.4446 \times 10^{10}$

the annihilation problem for the  $\text{Ps}_2$  molecule has not been solved finally. Therefore, further numerical considerations seem to be needed and in particular it would be very useful to have calculations with other basis functions which have the correct asymptotic behavior (see, e.g., [8]) or the use of the Hiller-Sucher-Feinberg relations instead of the  $\delta$  functions [35]. The data in Table II show that the two-photon process dominates; in fact,  $\Gamma_{2\gamma} \gg \Gamma_{3\gamma} > \Gamma_{4\gamma} \gg \Gamma_{5\gamma} > \Gamma_{6\gamma} \gg \Gamma_{1\gamma} > \Gamma_{7\gamma} > \Gamma_{8\gamma}$

$$> \Gamma_{9\gamma} > \Gamma_{10\gamma} > \Gamma_{0\gamma}.$$

It is a pleasure to thank Professor Richard J. Drachman (NASA, Maryland), Professor Allen P. Mills, Jr. (Bell Laboratories, New Jersey), and Professor Alex T. Stewart (Queen's University, Ontario) for helpful discussions and the Natural Sciences and Engineering Research Council of Canada for financial support.

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- [1] To designate an arbitrary bound state in the polyelectron systems  $e_n^- e_m^+$  in the nonrelativistic  $LS$  approximation we use the notation  $^{2S+1}L_J$ , where  $S$ ,  $L$ , and  $J$  are the values of the spin, orbital, and total angular momentum, respectively.
- [2] J. M. Jauch and E. Rohrlich, *The Theory of Photons and Electrons* (Springer-Verlag, New York, 1976).
- [3] E. A. Hylleraas and A. Ore, Phys. Rev. **71**, 491 (1947). From this result, i.e., from the boundedness of the  $\text{Ps}_2$  molecule in the ground  $^1S_0$  state, it is easy to show that this state is stable in an arbitrary symmetric four-body system  $Z^+ Z^+ e^- e^-$  with unit charges and that its energy lies between that of the  $\text{Ps}_2$  and  $\text{H}_2$  (with infinite proton masses) systems. This follows from the specific charge-mass symmetry of the Coulomb four-body Hamiltonian for such systems.
- [4] A. Ore, Phys. Rev. **71**, 913 (1947).
- [5] Actually this state is a doublet of two degenerate states (in the nonrelativistic  $LS$  approximation). However, for our present purposes we consider them as one state. The same situation is true in the two-body system  $\text{Ps}$  where the ground  $S$  state can be represented as the mixture of four degenerate states (one singlet and three triplet states, in the  $LS$  approximation), i.e.,  $^1S_0 + ^3S_1$  [2].
- [6] A. P. Mills, Jr., in *Positron Scattering in Gases*, edited by J. W. Humbertson and M. R. C. McDowell (Plenum, New York, 1984) p. 121, and references therein.
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- $$\Gamma_{2\gamma} = 4\pi\alpha^4 c a_0^{-1} \langle \delta_{+-} \rangle \text{ sec}^{-1},$$
- while for the  $^3S_1$  state (ortho)  $\Gamma_{2\gamma} = 0$ . Since the  $^1S_0$  state is nondegenerate and the  $^3S_1$  state has multiplicity 3, for an arbitrary electron-positron pair in the  $S$  state, with its total spin undefined (i.e., it is not conserved), we find
- $$\Gamma_{2\gamma} = \frac{1}{4} [\Gamma_{2\gamma}(^1S_0) + 3\Gamma_{2\gamma}(^3S_1)]$$
- $$= \pi\alpha^4 c a_0^{-1} \langle \delta_{+-} \rangle \text{ sec}^{-1}.$$
- For a polyelectron system of  $n$  electrons and  $m$  positrons the number of  $(e^-, e^+)$  pairs is  $nm$  and one finds Eq. (2). In the case of the three-body  $\text{Ps}^-$  ion ( $nm = 2$ ) Eq. (2) also gives the correct value for  $\Gamma_{2\gamma}$ , which agrees with the result found in experiments. Another approach has been followed in [13]. They found the lifetime for  $\text{Ps}_2$  to be twice as large as the experimentally known value for the  $\text{Ps}^-$  ion [21]. For the  $\text{Ps}^-$  ion this method gives incorrect numbers for the two-photon annihilation rate and lifetime.
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- [34] These estimates were determined from a number of calculations. Our best result (102 basis functions) for the energy was found to be  $-0.515\,963\,7$  a.u. The expectation values for  $\delta$  functions in these calculations were  $\langle \delta_{+-} \rangle \approx 0.021\,755$ ,  $\langle \delta_{++-} \rangle \approx 9.3831 \times 10^{-5}$ , and  $\langle \delta_{+--+} \rangle \approx 4.298 \times 10^{-6}$ . It should be noted that there is no bound principle for the  $\delta$ -function expectation values. Therefore, the mentioned lower and upper estimates have no rigorous lower and upper bound properties (in contrast to the energy). Presently, we can suppose only that the exact values lie inside of the given intervals.
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