Rare decays of the positronium ion and molecule, \( \text{Ps}^- \rightarrow e^-\gamma \) and \( \text{Ps}_2 \rightarrow e^+e^-\gamma, \gamma\gamma, e^+e^- \)

M. Jamil Aslam\(^{(a,b)}\), Wen Chen\(^{(a)}\), Andrzej Czarnecki\(^{(a)}\), Samiur Rahman Mir\(^{(a)}\), and Muhammad Mubasher\(^{(a)}\)

\(^{(a)}\)Department of Physics, University of Alberta, Edmonton, Alberta, Canada T6G 2E1
\(^{(b)}\)Department of Physics, Quaid-i-Azam University, Islamabad, Pakistan

Abstract

Decay rates of the positronium molecule \( \text{Ps}_2 \) into two photons and into an electron-positron pair are determined. Previous studies find that these rates are very different,

\[
\frac{\Gamma (\text{Ps}_2 \rightarrow e^+e^-)}{\Gamma (\text{Ps}_2 \rightarrow \gamma\gamma)} \simeq 250 \quad \text{(previous studies)}.
\]

This is puzzling since both processes have two body final states and are of the same order in the fine structure constant. We propose a simple calculational method and test it with the well-established decay of the positronium ion into an electron and a photon. We then employ it to correct predictions for both these \( \text{Ps}_2 \) decays. We find that previous studies overestimated the \( e^+e^- \) and underestimated the \( \gamma\gamma \) channel by factors of about 5.44 and 3.93 respectively. Our results give \( \frac{\Gamma (\text{Ps}_2 \rightarrow e^+e^-)}{\Gamma (\text{Ps}_2 \rightarrow \gamma\gamma)} \simeq 11.7 \).

1 Introduction

The lightest bound state involving an electron and a positron is positronium, \( \text{Ps} \). Its ground state is the spin-singlet para-positronium. The spin triplet is called ortho-positronium. In quantum electrodynamics (QED), due to the charge conjugation invariance, para- and ortho-positronium can decay only into an even and odd numbers of photons, respectively. At least two photons must be produced because of momentum conservation.

Positronium with an additional electron or positron forms a positronium ion \( \text{Ps}^\pm \), first observed in 1981 \[1\]. Very efficient methods of the ion production have recently been developed \[2, 3\]. The extra constituent makes one-photon annihilation, \( \text{Ps}^\pm \rightarrow e^\pm\gamma \), possible \[4\]. First theoretical studies of this decay in \( \text{Ps}^- \) \[5, 6\] and in \( \text{Ps}^+ \) \[7\] were incomplete and were corrected by Kryuchkov \[8\] who included all contributing Feynman diagrams. As a warmup for our main calculation, we confirm and simplify Kryuchkov’s analysis.

Two positronium atoms can form a molecule, \( \text{Ps}_2 \), first considered by Wheeler in his seminal study of compounds of electrons and positrons which he called polyelectrons \[9\]. Its binding energy was first computed by Hylleraas and Ore \[10\]. 70 years after that theoretical demonstration \( \text{Ps}_2 \) was discovered by Cassidy and Mills \[11\]. Various properties of \( \text{Ps}_2 \) including the precise binding energy
of its ground and excited states as well as rates of major and some minor decay modes have been established in a number of papers, including [12, 13, 14, 15, 16, 17].

In the ground state of Ps₂ electrons and positrons both form spin singlets, a feature important for this paper. This is energetically favorable because the antisymmetry, necessary for identical fermions, originates in the spin configuration. The spatial wave function is symmetric under the exchange of electron coordinates (similarly for the positrons), and therefore less curved, minimizing the kinetic energy.

Electrons’ spins are uncorrelated with those of the positrons. A random encounter of an electron with a positron can therefore result in an annihilation into an even or an odd number of photons. Typically, only one $e^+e^-$ pair annihilates and the remaining $e^+e^-$ constituents are liberated. Such processes usually produce only two photons but higher numbers are also possible, just like in atomic positronium decays [17, 18].

In addition, more than two constituents can interact in the decay process. Such reactions are rare because Ps₂ is weakly bound and inter-particle distances are large, on the order of the Bohr radius $a_B = 1/\alpha m$, where $\alpha \simeq 1/137$ is the fine structure constant and $m$ is the electron mass. Annihilation involves virtual particles whose typical propagation range is the electron Compton wavelength, suppressed by an additional factor $\alpha$. When an electron and a positron meet, the probability that there are $n$ additional constituents within a Compton distance scales approximately like $\alpha^3 n$.

Despite this huge suppression, we find these rare decays theoretically interesting. Ps₂ is the simplest known four-body bound state and serves as a model for more complicated systems such as tetraquarks [19, 20, 21, 22]. In principle, all properties of this molecule can be calculated with arbitrary precision within QED. However, this few-body system is sufficiently intricate that even some of its tree-level decays have not yet been correctly evaluated.

In this paper, we focus on two decays that involve all four constituents: $\text{Ps}_2 \to e^+e^-$ and $\text{Ps}_2 \to \gamma\gamma$. The rate of the radiationless decay $\text{Ps}_2 \to e^+e^-$ was first studied in Ref. [12], subsequently re-derived and confirmed in [23] and further refined in [17],

$$\Gamma (\text{Ps}_2 \to e^+e^-; \text{Ref. [17]}) = 2.3 \cdot 10^{-9} \text{ s}^{-1}. \quad (1)$$

The rate of the so-called total annihilation, $\text{Ps}_2 \to \gamma\gamma$, was calculated more recently [24],

$$\Gamma (\text{Ps}_2 \to \gamma\gamma; \text{Ref. [24]}) = 9.0 \cdot 10^{-12} \text{ s}^{-1}. \quad (2)$$

The very different magnitudes of these rates contradict intuitive arguments presented above. Both are two-body decays involving all four constituents of Ps₂ and occurring in the same order in $\alpha$. Why do their rates differ by a large factor? Using published formulas [17, 24] one finds

$$\frac{\Gamma (\text{Ps}_2 \to e^+e^-; \text{Ref. [17]})}{\Gamma (\text{Ps}_2 \to \gamma\gamma; \text{Ref. [24]})} = \frac{512}{521} \cdot 147\sqrt{3} \simeq 250. \quad (3)$$

This is the puzzle we set out to clarify. In Sec. 2 we propose a simple approach to calculating decay amplitudes of polyelectrons such as $\text{Ps}^-$ and $\text{Ps}_2$. We test it with the example of the positronium ion decay $\text{Ps}^- \to e^-\gamma$ and find agreement with Ref. [8]. We also confirm the rate of an analogous process in the molecule, $\text{Ps}_2 \to e^+e^-\gamma$, previously published in [17]. In Sec. 3 we apply this technique to determine $\Gamma (\text{Ps}_2 \to \gamma\gamma)$, and in Sec. 4 we present our result for $\Gamma (\text{Ps}_2 \to e^+e^-)$. We find the ratio of these rates to be

$$\frac{\Gamma (\text{Ps}_2 \to e^+e^-)}{\Gamma (\text{Ps}_2 \to \gamma\gamma)} = \frac{27\sqrt{3}}{4} = 11.7. \quad (4)$$
We conclude in Sec. 5 with comments on the magnitude of our result and with an attempt to clarify what went wrong in the previous studies [23, 24, 17, 12]. Appendices present spinor configurations and symmetry factors for the Ps$^{-}$ and Ps$_2$ decay amplitudes.

2 Three-constituent annihilation process $e^+e^-e^\pm \rightarrow e^\pm\gamma$

In this section we determine the rate of an $e^+e^-$ pair annihilation in the presence of a third particle that carries away momentum and enables production of only one photon. That particle can be an electron or a positron. This process occurs in a positronium ion (Sec. 2.1) and in the molecule Ps$_2$ (Sec. 2.2). We confirm previously published results for both systems. This section demonstrates our approach to computing annihilation amplitudes and tests it in a three- and four-constituent systems. It prepares the ground for the calculation of processes in which four particles in the initial state interact, presented in Sec. 3 and 4.

2.1 Single photon decay of the positronium ion Ps$^-$ $\rightarrow$ $e^-\gamma$

The positronium ion consists of two electrons and a positron. In the vast majority of its decays, the positronium encounters an electron with which it forms a spin singlet and annihilates into two photons. (In the ground state of Ps$^-$ the electrons are in the spin-singlet state, \[^{1\downarrow+1\downarrow}\sqrt{2}\]. The positron can form a spin singlet or triplet with one of the electrons. In the latter case, the annihilation produces at least three photons and is much slower.) However, there is also a rare decay channel into a single photon, Ps$^-$ $\rightarrow$ $e^-\gamma$. It can happen either when the two-photon annihilation is followed by the absorption of one photon by the spectator electron, as shown in Fig. 1(a,b); or by a single-photon annihilation of a spin-triplet pair, with the photon scattering off the spectator electron, as in Fig. 1(c,d).

![Figure 1: Examples of contributions to the single-photon decay of the positronium ion, Ps$^- \rightarrow e^-\gamma$. Arrows indicate the spin projections on the z axis: plain arrows denote spins 1/2 and a double arrow denotes spin 1 of the photon. Four more diagrams are obtained by switching the roles of the two electrons $e^-$. In all Figures, time flows horizontally from left to right.](image)

At leading order in QED, this decay proceeds through a total of eight Feynman diagrams. In addition to the four diagrams shown in Fig. 1 there are four in which the roles of the two electrons are interchanged.

Since the positronium ion is very weakly bound, we consider the annihilating particles to be at rest, similarly to the standard analysis of the positronium atom annihilation [25]. We define the z-axis along the spin of the positron.
Since the ion \( \text{Ps}^- \) is a spin 1/2 system, its decay amplitude is fully characterized by two complex parameters. For example, we can choose the probability amplitudes of the photon emission along the spin as one parameter, and in the opposite direction as the other. In fact, it is sufficient to calculate one of them: if the photon is emitted along the initial spin direction, it must be right-handed, because of the angular momentum conservation: in this case, the electron emitted in the opposite direction is also right handed so the total projection of the spin on the \( z \) axis is 1/2 as in the initial state. When the photon is emitted in the opposite direction, it must be left handed by the same argument. The two amplitudes do not interfere because they describe distinct states (right versus left handed particles). Because of parity conservation in QED, probabilities of observing photons of each handedness must be equal. Thus if we are interested only in the decay rate, it is sufficient to calculate one of the amplitudes and multiply the resulting rate by 2.

We shall assume that a right handed photon and a right handed electron are produced. Their momenta are along the positive and negative \( z \) axis, respectively.

In Fig. 1, in panels (a,b) the annihilating \( e^+e^- \) pair is a spin singlet, and in (c,d) it is a spin triplet. Since we choose the \( z \) axis along the positron spin, that spin is always up. It is immediately clear that amplitudes (a) and (d) vanish. In (a), the annihilating electron forms a spin singlet with the positron, so that electron’s spin points down. But such an electron cannot emit a photon whose spin points up. In (d), the annihilation occurs in a spin triplet, so the spectator electron’s spin is initially down; again, it cannot emit the needed photon. Thus in our approach only two amplitudes require an evaluation. (Similar considerations will simplify our calculation of the decay \( \text{Ps}_2 \rightarrow \gamma\gamma \) described in Sec. 3.)

Since we neglect the motion of initial state particles, their spinors take a simple form. We write products of spinors on each of the two fermion lines as a combination of Dirac gamma matrices (cf. Appendix A). Multiplying these spinor combinations by QED expressions for vertices and propagators, the total amplitude for all eight diagrams becomes

\[
\mathcal{M}(e^+e^-e^- \rightarrow e^-\gamma)_{\text{free}} = \frac{1}{\sqrt{2}} \left( \mathcal{M}_{e^+e^-e^-} - \mathcal{M}_{e^+e^+e^-} \right) = \left[ \frac{2}{\sqrt{3}} - \frac{2}{\sqrt{3}} \right] \frac{e^3}{4m^3} = \frac{(4\pi\alpha)^{3/2}}{\sqrt{3}m^3}, \tag{5}
\]

where \( \alpha = \frac{e^2}{4\pi} \) (we use such units that \( \epsilon_0, \hbar, \) and \( c \) are 1).

The free-particle amplitude in Eq. (5) is related to the case of bound particles by (25, page 149)

\[
\mathcal{M}(e^+e^-e^- \rightarrow \gamma + e^-)_{\text{bound}} = \Psi(0,0,0)\mathcal{M}(e^+e^-e^- \rightarrow e^-\gamma)_{\text{free}}, \tag{6}
\]

where \( \Psi(0,0,0) \) is the probability amplitude of all constituents of the ion being at the origin. Its absolute value squared is the expectation value of a product of two-particle delta functions (27),

\[
|\Psi(0,0,0)|^2 = \langle \delta^3(\mathbf{r}_{e^+e^-}) \delta^3(\mathbf{r}_{e^-e^-}) \rangle \equiv \langle \delta_{+-} \rangle a_B^{-6} \simeq 3.589 \cdot 10^{-5} \alpha^6 m^6, \tag{7}
\]

where \( a_B = 1/(\alpha m) \) is the Bohr radius. In the computation of the decay rate this expectation value must be divided by 2! for the two identical electrons in the initial state [see Eq. (57)]. Another factor arises from the integration over the direction of the photon emission: the probability of positron’s spin projection on an axis with the polar angle \( \theta \) is \( \cos^2(\theta/2) \) whose average is 1/2. Remembering factor 2 accounting for both photon polarizations we find the decay rate,

\[
\Gamma \left( \text{Ps}^- \rightarrow e^-\gamma \right) = \frac{\langle \delta_{+-} \rangle}{2!} \cdot \frac{1}{2} \cdot \frac{1}{2} \cdot \frac{1}{9\pi} \cdot \left[ \frac{(4\pi\alpha)^{3/2}}{\sqrt{3}m^3} \right]^2 \alpha^6 m^6 \cdot 2m \tag{8}
\]

\[
= \frac{64}{27} \langle \delta_{+-} \rangle \pi^2 \alpha^9 m = 0.0382 \text{ s}^{-1}. \tag{9}
\]
Factor $1/9\pi$ results from the two-body phase space with momentum $4m/3$ in the center-of-mass frame. The last factor in (8), $2m$, comes from the electron spinor in the final state. Our result agrees with Ref. [8] which has 0.0392 using an older value of $\langle\delta_{++}\rangle$ [1].

### 2.2 Single photon decay of the molecule $Ps_2 \to e^+e^-\gamma$

Any three of the four constituents of $Ps_2$ can give rise to the process analogous to Fig. 1, possibly with the non-annihilating electron replaced by a positron. This doubles the rate (not the amplitude: the non-annihilating particle participating in the hard process becomes fast so the two processes are distinguishable and do not interfere [17]). There is however an additional symmetry factor $1/2!$ due to identical positrons, as discussed in Appendix B.

The ground state wave function of $Ps_2$ is symmetric in space (to minimize the kinetic energy). Since it must be anti-symmetric in both electron and positron pairs, both electron and positron pairs form spin singlets. The spin wave function is

$$\chi_s = \frac{e_{\uparrow}e_{\downarrow} - e_{\downarrow}e_{\uparrow}}{\sqrt{2}} \cdot \frac{e_{\uparrow}e_{\uparrow} - e_{\uparrow}e_{\uparrow}}{\sqrt{2}}. \quad (10)$$

An extra factor 2 in the amplitude from the two ways of assigning the positron role (annihilating or not) is partially cancelled by $1/\sqrt{2}$ in the positron spin wave function. In total, the numerical coefficient is twice that in the $Ps^-$ decay rate,

$$\Gamma (Ps_2 \to e^+e^-\gamma) = 2 \cdot \frac{\langle\delta_{++}\rangle_{Ps_2}}{(2!)^2} \cdot \frac{1}{2} \cdot \frac{1}{9\pi} \cdot \left[ \frac{\sqrt{2} \cdot (4\pi\alpha)^{3/2}}{\sqrt{3}m^3} \right]^2 \alpha^6m^6 \cdot 2m \quad (11)$$

$$= \frac{128}{27} \langle\delta_{++}\rangle_{Ps_2} \pi^2\alpha^9m, \quad (12)$$

in agreement with [17].

### 3 Two-photon annihilation of $Ps_2$

The two-photon annihilation of the molecule, $Ps_2 \to \gamma\gamma$, is a rare process in which both $e^+e^-$ pairs annihilate. Examples of contributing diagrams are shown in Fig. 2.

In this section we recalculate the rate of $Ps_2 \to \gamma\gamma$ using explicit electron and positron spinors, as explained in Sec. 2. Since our result differs from that of Ref. [24], we describe our calculation and selected intermediate results in some detail.

We choose the $z$ axis along the momentum of final state photons. We assume the photons are right handed (they must have equal helicity because the initial state has zero angular momentum), and at the end multiply the decay rate by 2 to account for left handed photons.

Fig. 2 shows three types of diagrams, A, B, and C. In A-type diagrams, both annihilating pairs contribute a photon to the final state. There are $2^4 = 16$ diagrams of this type: the order of photon vertices can be reversed of each fermion line (factor $2^2$), the electrons can be assigned to either annihilating pair (factor 2), and the final-state photons can be interchanged (factor 2).

In B-type diagrams, both photons in the final state are emitted from the annihilation of single $e^+e^-$ pair. The virtual photon resulting from the other $e^+e^-$ is absorbed by the electron or the
Figure 2: Three types of contributions to the two-photon decay $\text{Ps}_2 \rightarrow \gamma\gamma$. Diagrams of type C turn out not to contribute to $\text{Ps}_2$ decays. One example of external particles’ spins is shown: a spin-up fermion cannot emit a spin-down photon.

The situation for the C-type diagrams is similar to that of the B-type except, in this case, the photon emitted from the triplet $e^+e^-e^-$ pair is absorbed by the virtual electron. Interchanging electrons, positrons, and real photons gives 8 C-type diagrams. Due to the spin configuration of $\text{Ps}_2$, Eq. (10), C-type diagrams do not contribute. In case of aligned spins of the $e^+e^-$ pair annihilating into a single photon, the remaining $e^+$ and $e^-$ must also have aligned spins and cannot emit two photons with opposite spins, as shown in the last panel of Fig. 2. If the spins of the $e^+e^-$ pair are opposite, C-type diagrams vanish identically but we do not have an intuitive interpretation.

Following the strategy of the calculation of $\text{Ps}_- \rightarrow e^-\gamma$, and using the expressions of spinors in terms of gamma matrices given in Appendix A, we find the matrix element for free particles annihilating at rest,

$$
A = -\frac{1}{2} \cdot \frac{ie^4}{m^4}, \quad B = \frac{1}{4} \cdot \frac{ie^4}{m^4}, \quad C = 0,
$$

$$
M_{\gamma\gamma} = A + B + C = -\frac{ie^4}{4m^4}.
$$

Accounting for the spin wave function in Eq. (10) we find the amplitude for the free-particle case,

$$
M(e^+e^-e^+e^- \rightarrow \gamma_R\gamma_R)_{\text{free}} = \frac{1}{2} \left( M_{\gamma_R^+\gamma_R^+\gamma_R^-\gamma_R^-} + M_{\gamma_R^+\gamma_R^-\gamma_R^+\gamma_R^-} - M_{\gamma_R^+\gamma_R^-\gamma_R^-\gamma_R^+} - M_{\gamma_R^-\gamma_R^+\gamma_R^+\gamma_R^-} \right) = \frac{(4\pi\alpha)^2}{2m^4}.
$$

The photon momentum is $2m$ so the phase space gives $\frac{1}{8\pi} \cdot \frac{1}{2}$ where we have accounted for identical bosons in the final state. Since the initial state has zero angular momentum, the distribution of photons is isotropic. Remembering again about both photon helicities we find the decay rate of
the bound state,

\[
\Gamma (\text{Ps}_2 \to \gamma \gamma) = 2 \cdot \frac{1}{16 \pi} \left[ \frac{(4\pi \alpha)^2 \gamma^2}{2m^2} \right]^2 \langle \delta_{++--} \rangle \alpha^9 m^9 \frac{1}{(2!)^2}
\]

\[
= 2\pi^3 \alpha^{13} \langle \delta_{++--} \rangle m.
\]

(17)

Using \( \langle \delta_{++--} \rangle = 4.5614 \cdot 10^{-6} \) from [17], confirmed in Ref. [24],

\[
\Gamma (\text{Ps}_2 \to \gamma \gamma) = 3.65 \cdot 10^{-11} \text{ s}^{-1}.
\)

(18)

Instead of our coefficient 2 in Eq. (17), Ref. [24] has 521/1024. As a result, they underestimate the rate of \( \text{Ps}_2 \to \gamma \gamma \) by the factor

\[
\frac{2048}{521} = 3.93.
\]

(19)

4 Annihilation of Ps\(_2\) into \(e^+e^-\)

Fig. 3 shows examples of four types of diagrams contributing to the annihilation \(\text{Ps}_2 \to e^+e^-\). More diagrams are generated by changing the order of photon vertices wherever more than one photon couples to an electron-positron line. In group C there are also diagrams where the lower positron line absorbs the photon resulting from the annihilation.

![Diagram of annihilation of Ps\(_2\) into \(e^+e^-\)]

Figure 3: Four groups of contributions to the annihilation \(\text{Ps}_2 \to e^+e^-\). In group I, a single virtual photon produces the final state; such diagrams do not contribute to the decay of the molecule \(\text{Ps}_2\), which has angular momentum 0.

To evaluate their contributions to the decay of \(\text{Ps}_2\), we work in the rest frame of the molecule. We choose the \(z\) axis along the outgoing electron’s momentum and assume that it has spin up with
Bizarrely, the large ratio (see our Eq. (3)) of averaging over all possible initial spins and summing of the final-state spins (Eq. (2) in Ref. [24]).

Regarding $P_s^2$ element there is a net factor 2 just like in Eq. (15). Together these factors give $\sqrt{3}$. The decay rate is found similarly to Eq. (17). Phase space is determined by electron’s momentum, $\sqrt{3}m$, and gives a factor $\sqrt{3}/4\pi$. There are two factors $2m$ for the final state fermions. In the matrix element there is a net factor 2 just like in Eq. (15). Together these factors give

$$\Gamma (P_s^2 \rightarrow e^+e^-) = 2 \cdot \frac{\sqrt{3}}{16\pi} \left[ \frac{2 \cdot 3 \sqrt{3} (4\pi \alpha)^2}{\sqrt{2} \cdot 16m^5} \right]^2 \frac{\langle \delta_{++} \rangle \alpha^9 m^9}{(2!)^2} (2m)^2$$

$$= \frac{27\sqrt{3} \alpha^3}{2} \frac{\langle \delta_{++} \rangle m}{2} \approx 4.27 \cdot 10^{-10} \text{ s}^{-1}. \quad (22)$$

The value previously published is $\Gamma (P_s^2 \rightarrow e^+e^-)$; Ref. [17] = $2.32 \cdot 10^{-9} \text{ s}^{-1}$. That reference has 147 instead of our 27 in Eq. (23) and overestimates the rate by the factor

$$147/27 = 5.44. \quad (24)$$

## 5 Conclusion

The goal of this study has been to explain the large ratio of about 250 of previously published predictions for $\Gamma (P_s^2 \rightarrow e^+e^-)$ and $\Gamma (P_s^2 \rightarrow \gamma\gamma)$. We have demonstrated in Eqs. (19) and (24) that previous studies overestimated the first rate by 5.44 and underestimated the second one by 3.93. Correcting for these factors we find the ratio of 250/(5.44·3.93) = 11.7.

Why do our results differ from previous studies? We believe that in those works the spin wave function of $P_s^2$ was not properly taken into account. In the case of $P_s^2 \rightarrow e^+e^-$, Ref. [12] says that the squared decay amplitude is $\sum_{s_5s_6} 4 |M_{s_5s_6\uparrow\downarrow}|$ (we think there a trivial typo there: the square is missing) where $s_5s_6$ are the spins of the daughter electron and positron, and arrows indicate spins of the positrons and electrons in the initial state. We also fix the initial spin configuration as $\uparrow\downarrow\uparrow\downarrow$ (while computing amplitudes; we do eventually account for the full spin wave function of $P_s^2$), but instead of summing over all possible $s_5s_6$, we take only $s_5 = -s_6$ and sum over the two values of $s_5$. The reason for this is that the total spin projection of the final state must be zero, since the initial state is a scalar. As a result, we find that the group of diagrams I in Fig. 3 does not contribute, whereas Ref. [12] states all of them contribute strongly to the result. As a result, Ref. [12] (and its subsequent refinements) overestimates the rate by a factor of about 5.44. We also note that by summing over all $s_5s_6$, Ref. [12] includes some contributions from triplet configurations of initial electrons (and positrons): the initial-state electron spin configuration $\uparrow\downarrow$ is a mixture of the singlet ($\uparrow\downarrow - \downarrow\uparrow)/\sqrt{2}$ and the triplet ($\uparrow\uparrow + \downarrow\downarrow)/\sqrt{2}$, whereas $P_s^2$ contains only the singlet.

Regarding $P_s^2 \rightarrow \gamma\gamma$, Ref. [24] seems to disregard the spin wave function of the initial state, averaging over all possible initial spins and summing of the final-state spins (Eq. (2) in Ref. [24]). Bizarrely, the large ratio (see our Eq. (3)) of $e^+e^-$ and $\gamma\gamma$ rates is attributed to different numbers
of photon-electron vertices in both processes. It is clear from Figs. 2 and 3 that the number of vertices is four in both processes.

Indeed, both processes are of the same order in $\alpha$ and both involve $n = 2$ extra participants in comparison to the leading decay $\text{Ps}_2 \rightarrow e^+e^-\gamma\gamma$. The remaining factor 11.7 between the two rates can be attributed to the difference in momentum carried by the final state particles. Electrons, being massive, carry a smaller momentum. Note that the two-body phase space, although proportional to the daughter particle momentum, is actually larger by $\sqrt{3}$ for the $e^+e^-$ channel than for the $\gamma\gamma$ channel because in the latter case there is a factor 1/2 for identical bosons. The smaller momentum of the electrons results in smaller values of some $t$-channel propagators (they are less negative than in the $\gamma\gamma$ case).

In summary, we believe that our calculational approach clarifies and simplifies studies of polyelectron decays. For example, in the case of the decay $\text{Ps}^- \rightarrow e^-\gamma$, in Ref. [8] eight amplitudes were first formally summed and their sum was squared, resulting in 64 terms. Their evaluation was characterized as rather involved and demanding a computer algebra system. In our approach not only can the calculation be done by hand, but also the mechanism of the decay is transparent.

**Acknowledgements**

We thank Arkady Vainshtein for helpful discussions. M.J.A. and A.C. gratefully acknowledge the hospitality of the Banff International Research Station (BIRS) where parts of this work were done. This work was supported by the Natural Sciences and Engineering Research Council of Canada.

**A Spinors used in matrix elements**

Assuming that initial state particles are at rest, $p_i = (m, 0, 0, 0)$, electron and positron spinors are

$$
\begin{align*}
\upsilon^\uparrow &= \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, & \upsilon^\downarrow &= \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}, & \upsilon^\uparrow &= \begin{pmatrix} 0 \\ 0 \\ 0 \\ -1 \end{pmatrix}, & \upsilon^\downarrow &= \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}.
\end{align*}
$$

(25)

Their products yield four by four matrices that we express in terms of combinations of Dirac matrices,

$$
\begin{align*}
\upsilon^\uparrow\upsilon^\downarrow &= \frac{1}{2} \left( 1 + \gamma^0 \gamma^1 + i\gamma^2 \right), & \upsilon^\uparrow\upsilon^\uparrow &= \frac{1}{2} \left( 1 + \gamma^0 \gamma^5 + \gamma^3 \right), \\
\upsilon^\downarrow\upsilon^\downarrow &= \frac{1}{2} \left( 1 + \gamma^0 \gamma^1 - i\gamma^2 \right), & \upsilon^\downarrow\upsilon^\uparrow &= \frac{1}{2} \left( 1 + \gamma^0 \gamma^5 - \gamma^3 \right).
\end{align*}
$$

(26)

Four-momenta of the final state photon ($k_1$) and electron ($k_2$) are

$$
\begin{align*}
k_1 &= \left( \frac{4}{3}m, 0, 0, \frac{4}{3}m \right), & k_2 &= \left( \frac{5}{3}m, 0, 0, -\frac{4}{3}m \right).
\end{align*}
$$

(27)

The spinor of the final state electron in $\text{Ps}^- \rightarrow e^-\gamma$ is

$$
\upsilon^\uparrow(k_2) = \sqrt{\frac{4}{3}} \begin{pmatrix} 1 & 0 & -\frac{1}{2} & 0 \end{pmatrix}.
$$

(28)
B  Symmetry Factors for $\text{Ps}^-$ and $\text{Ps}_2$

The leading Fock state of $\text{Ps}^-$, a bound state of two electrons and a positron, is

$$|\text{Ps}^- (P)\rangle = \int \tilde{dk}_1 \tilde{dk}_2 \psi_{s_1s_2s_3} (k_1, k_2, P) a_{s_1}^\dagger (k_1) a_{s_2}^\dagger (k_2) b_{s_3} (P - k_1 - k_2) |0\rangle, \quad (29)$$

where $\tilde{dk}_i = \frac{d^3 k_i}{(2\pi)^3}$ and $a_{s}^\dagger (k) (b_{s} (k))$ creates an electron (positron) with momentum $k$ and spin projection $s$ and $P$ is the total momentum of the ion. In Eq. (29) and onwards, summation over repeated indices is understood. In the $\text{Ps}^-$ ground state, the wave function factorizes,

$$\psi_{s_1s_2s_3} (k_1, k_2, P) = \psi (k_1, k_2, P) \chi_{s_1s_2s_3}, \quad (30)$$

where $\chi_{s_1s_2s_3} = \frac{1}{\sqrt{2}} (\uparrow\downarrow - \downarrow\uparrow) \uparrow$ is the spin wave function, anti-symmetric in the electron spins $s_1$ and $s_2$, and $\psi (k_1, k_2, P)$ is symmetric in $k_1$ and $k_2$. The corresponding position space wave function is

$$\Phi (r_1, r_2, r_3) = \int \tilde{dk}_1 \tilde{dk}_2 \exp [ik_1 \cdot r_1 + ik_2 \cdot r_2 + i (P - k_1 - k_2) \cdot r_3] \psi (k_1, k_2, P), \quad (31)$$

$$= e^{iP \cdot r_3} \int \tilde{dk}_1 \tilde{dk}_2 \exp [ik_1 \cdot (r_1 - r_3) + ik_2 \cdot (r_2 - r_3)] \psi (k_1, k_2, P), \quad (32)$$

$$\equiv e^{iP \cdot r_3} \phi (\rho_1, \rho_2), \quad (33)$$

where $\rho_1 = r_1 - r_3$ and $\rho_2 = r_2 - r_3$ are positions of the two electrons relative to the positron. The Jacobian of this shift is 1 and

$$\phi (\rho_1, \rho_2) = \int \tilde{dk}_1 \tilde{dk}_2 \exp (ik_1 \cdot \rho_1 + ik_2 \cdot \rho_2) \psi (k_1, k_2, P), \quad (34)$$

The spatial wave function is normalized by the condition $\int d^3 \rho_1 d^3 \rho_2 |\phi (\rho_1, \rho_2)|^2 = 1$, giving $\int \tilde{dk}_1 \tilde{dk}_2 |\psi_{s_1s_2s_3} (k_1, k_2, P)|^2 = 1$. To find the normalization of $|\text{Ps}^- (P)\rangle$ we use anti-commutation relations,

$$\{ a_s (k), a_{s'}^\dagger (k') \} = \{ b_s (k), b_{s'}^\dagger (k') \} = (2\pi)^3 \delta^3 (k - k') \delta_{ss'}, \quad (35)$$

$$\{ a_s (k), b_{s'}^\dagger (k') \} = \{ a_{s} (k), b_{s'} (k') \} = 0,$$

and find, using the anti-symmetry $\psi^*_{s'_1s'_2s'_3} (k_2, k_1, P) = -\psi_{s_1s_2s_3}^* (k_1, k_2, P)$,

$$\langle \text{Ps}^- (P') | \text{Ps}^- (P) \rangle = \int \prod_{i=1}^{2} \tilde{dk}_i \tilde{dk}'_i \psi^*_{s_1s_2s_3} (k_1, k_2, P) \psi_{s'_1s'_2s'_3}^* (k'_1, k'_2, P') \cdot (2\pi)^9 \delta^3 (P - P') \delta_{s_1s'_1} \delta_{s_2s'_2} \delta_{s_3s'_3} \delta^3 (k'_1 - k_1) \delta_{s'_1s_1} \delta^3 (k'_2 - k_2) \delta_{s'_2s_2} \delta^3 (k'_3 - k_3) \delta_{s'_3s_3} \quad (36)$$

The factor 2 is related to the indistinguishability of the two electrons. We compensate for it while calculating the decay rate.

In the case of $\text{Ps}_2$, the spin wave function is anti-symmetric in both electrons and positrons, hence repeating the above steps we obtain a factor of $(2!)^2 = 4$ in the normalization; we divide by it when calculating the decay rates of $\text{Ps}_2 \rightarrow \gamma \gamma, e^+ e^-$. 

10
References

[1] A. P. Mills, Jr., *Observation of the Positronium Negative Ion*, Phys. Rev. Lett. **46**, 717–720 (1981).

[2] Y. Nagashima, T. Hakodate, A. Miyamoto, and K. Michishio, *Efficient emission of positronium negative ions from Cs deposited W(100) surfaces*, New J. Phys. **10**, 123029 (2008).

[3] Y. Nagashima, *Experiments on positronium negative ions*, Physics Reports **545**, 95 – 123 (2014).

[4] E. Fermi and G. E. Uhlenbeck, *On the Recombination of Electrons and Positrons*, Phys. Rev. **44**, 510–511 (1933).

[5] S. Misawa and A. P. Mills, Jr. ATT Bell Laboratories, Technical Memorandum (unpublished) (1985).

[6] Y. K. Ho, *Positron annihilation in the positronium negative ion*, Journal of Physics B: Atomic and Molecular Physics **16**, 1503–1509 (1983).

[7] M.-C. Chu and V. Pönisch, *Calculation of the one-photon decay rate of the polyelectron P^++−*, Phys. Rev. C **33**, 2222–2223 (1986).

[8] S. I. Kryuchkov, *On the one-photon annihilation of the Ps− ion*, J. Phys. B **27**, L61 (1994).

[9] J. A. Wheeler, *Polyelectrons*, Ann. N. Y. Acad. Sci. **48**, 219–238 (1946).

[10] E. A. Hylleraas and A. Ore, *Binding Energy of the Positronium Molecule*, Phys. Rev. **71**, 493–496 (1947).

[11] D. B. Cassidy and A. P. Mills, Jr., *The production of molecular positronium*, Nature **449**, 195 (2007).

[12] A. M. Frolov, S. I. Kryuchkov, and V. H. Smith, *(e−, e+)-pair annihilation in the positronium molecule Ps2*, Phys. Rev. A **51**, 4514–4519 (1995).

[13] A. M. Frolov and V. H. Smith, *Positronium hydrides and the Ps2 molecule: Bound-state properties, positron annihilation rates, and hyperfine structure*, Phys. Rev. A **55**, 2662–2673 (1997).

[14] K. Varga, J. Usukura, and Y. Suzuki, *Second Bound State of the Positronium Molecule and Biexcitons*, Phys. Rev. Lett. **80**, 1876–1879 (1998).

[15] M. Puchalski, A. Czarnecki, and S. G. Karshenboim, *Positronium-ion decay*, Phys. Rev. Lett. **99**, 203401 (2007), 0711.0008.

[16] M. Puchalski and A. Czarnecki, *Dipole Excitation of Dipositronium*, Phys. Rev. Lett. **101**, 183001 (2008), 0810.0013.

[17] A. M. Frolov, *Annihilation of electron-positron pairs in the positronium ion Ps− and bipositronium Ps2*, Phys. Rev. A **80**, 014502 (2009).
[18] A. Czarnecki and S. G. Karshenboim, *Decays of Positronium*, in B. B. Levchenko and V. I. Savrin, editors, *Proc. XIV Intl. Workshop on High Energy Physics and Quantum Field Theory (QFTHEP’99, Moscow 1999)*, page 538, MSU-Press, Moscow (2000), hep-ph/9911410.

[19] A. Czarnecki, B. Leng, and M. B. Voloshin, *Stability of tetrons*, Phys. Lett. B 778, 233–238 (2018), 1708.04594.

[20] M. Karliner and J. L. Rosner, *Discovery of doubly-charmed Ξ_{cc} baryon implies a stable (bb̄ud) tetraquark*, Phys. Rev. Lett. 119, 202001 (2017), 1707.07666.

[21] A. Ali, C. Hambrock, and M. J. Aslam, *A Tetraquark interpretation of the BELLE data on the anomalous Υ(1S)π⁺π⁻ and Υ(2S)π⁺π⁻ production near the Υ(5S) resonance*, Phys. Rev. Lett. 104, 162001 (2010), [Erratum: Phys.Rev.Lett. 107, 049903 (2011)], 0912.5016.

[22] E. Hernández, J. Vijande, A. Valcarce, and J.-M. Richard, *Spectroscopy, lifetime and decay modes of the T_{bb}⁻ tetraquark*, Phys. Lett. B 800, 135073 (2020), 1910.13394.

[23] D. H. Bailey and A. M. Frolov, *Positron annihilation in the bipositronium Ps2*, Phys. Rev. A 72, 014501 (2005).

[24] J. Pérez-Ríos, S. T. Love, and C. H. Greene, *Two-Photon Total Annihilation of Molecular Positronium*, EPL 109, 63002 (2015), 1412.5246.

[25] M. E. Peskin and D. V. Schroeder, *An Introduction to Quantum Field Theory*, Addison–Wesley, Reading, MA (1997).

[26] R. Feynman, R. Leighton, and M. Sands, *The Feynman Lectures on Physics, Volume III: Quantum Mechanics*, Perseus Books, Philadelphia (2010).

[27] A. M. Frolov, *Highly accurate evaluation of the singular properties for the positronium and hydrogen negative ions*, J. Phys. A 40, 6175 (2007).