Positronium hydride decay into proton, electron, and one or zero photons

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Decay rates of the positronium hydride PsH, a bound state of a proton, a positron, and two electrons, are determined for two rare channels, PsH → p⁺e⁻\text{γ} and PsH → p⁺e⁻. Previous studies overestimated these rates by factors of about 2 and 700, respectively. We explain the physics underlying these wrong predictions. We confirm a range of static PsH properties, including the non-relativistic ground state energy, expectation values of inter-particle distances and their powers, and the three and four particle coalescence probabilities, using a variational method in the Gaussian basis.

I. INTRODUCTION

Positronium hydride (PsH) consists of a proton p⁺, positron e⁺, and two electrons e⁻. Stable with respect to autoionization, it decays due to electron-positron annihilation. Similarly to the case of the positronium-ion (Ps⁻), its two electrons form a spin singlet. When the positron and one of the electrons meet, they can form a spin singlet or a triplet. Their annihilation can lead to final states with any number of photons, even or odd. Here we calculate the rate of decays that result in one or no photons, as well as unbound electron and proton. This is the first calculation of these decay rates. Previously they were only estimated and we explain why those estimates were incorrect. The key issue is the role of the proton in influencing the e⁺e⁻ annihilation.

In addition, we re-evaluate the wave function of PsH using the variational method with a Gaussian basis. In order to test it, we calculate the non-relativistic ground state energy, mean inter-particle distances, and, most importantly for our purposes, probabilities of coalescence of e⁺e⁻e⁻ and of p⁺e⁺e⁻e⁻. We confirm the values of these quantities found in Ref. [1].

The paper is organized as follows: In Section II we put our study in the context of previous work on PsH. In Section III we discuss its Hamiltonian and wave function. Section IV focuses on the decay PsH → p⁺e⁻\text{γ} and Section V on PsH → p⁺e⁻. We conclude by comparing our results with previous literature in Section VI.

We use such units that \( \hbar = c = \epsilon_0 = 1 \), except for the expectation values of operators computed with the variational wave function of PsH, given in atomic units, as explained in Section III. We denote the electron mass by \( m \) and the proton mass by \( M \). Unless indicated otherwise, we neglect the binding energy of PsH in comparison with \( m \) and treat its constituents as stationary particles, neglecting their relative motion. Corrections to this approximation are suppressed by the fine structure constant \( \alpha \simeq 1/137 \).

II. BRIEF HISTORY OF PsH

In their pioneering works, Wheeler [2] and Hylleraas and Ore [3] studied small exotic molecules where one or more nuclei are replaced by positrons. Ore [4] established the stability of the PsH ground state. Since then, much theoretical work has been done on the energy of ground, metastable, and resonant states and on other properties of this system (see for example [5–12] where further references can be found).

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Experimental efforts to produce and detect this system have also been made. Pareja et al. \[13\] first reported the existence of such a bound state in a condensed phase. Further evidence was provided by Schrader et al. \[14\] in positron-methane collisions,

\[ e^+ + \text{CH}_4 \rightarrow \text{CH}_3^+ + \text{PsH}, \tag{1} \]

with an estimated binding energy, \( E_b = -1.1 \pm 0.2 \text{ eV} \), in line with most theoretical predictions.

PsH is a special case of a Coulombic system, positioned between the hydrogen molecule \( \text{H}_2 \) and dipositronium \( \text{Ps}_2 \), in which both nuclei are replaced with positrons. Since positron’s motion cannot be considered as slow, PsH is an essentially four body system.

On the theoretical side, exotic systems containing antimatter serve to test various quantum mechanical methods. Over the years, the accuracy of theoretical calculations in PsH has improved thanks to advances in computational techniques and increased hardware power. Using variational methods to obtain accurate wave functions, most of the studies performed for the ground state energy of such system are non-relativistic; relativistic effects have been calculated by Yan and Ho \[15\] and by Bubin and Varga \[1\].

An interesting problem is the study of electron-positron annihilation in PsH producing zero, one, two, and in general \( n \) photons. What makes it more interesting is that the electron and proton can either be free or form a bound hydrogen state. Refs. \[16–18\] considered both bound and unbound final states. In case of unbound electron and \( p^\pm \) final states, estimates were given for the two photon annihilation rate \( \Gamma_{2\gamma} = \Gamma(\text{PsH} \rightarrow p^+ e^- \gamma\gamma) \), the dominant process. The rate of annihilation into three or more photons (\( \Gamma_{n\gamma}, n \geq 3 \)) can be found using \( \Gamma_{2\gamma} \) and the rate of the \( n\gamma \) decay in a positronium atom. This is the subject of Ferrante relations \[19\], justified in \[20\].

Decays with one or no photons have been estimated using analogous \( \text{Ps}^- \) and \( \text{Ps}_2 \) results \[21,22\] in the absence of a dedicated QED calculation for PsH. Filling this gap is the main motivation of this paper.

III. **PsH Wave Function and Hamiltonian**

We label coordinates of the proton with 1, positron with 2, and electrons with 3 and 4. The PsH wave function is a product of spatial and spin parts, antisymmetrized with respect to permuting the electrons,

\[ \psi = \chi_2^\uparrow \left( \chi_3^\downarrow \chi_4^\downarrow - \chi_3^\uparrow \chi_4^\uparrow \right) (1 + P_{34}) \phi_S \tag{2} \]

where \( \chi_\text{s} \) denote spin states; \( P_{34} \) is the permutation operator of the electrons; and \( \phi_S \) is the S-wave spatial wave function. In the Gaussian basis \[23\], that spatial part is written as

\[ \phi_S = \sum_{i=1}^{N} c_i^S \exp \left[ -\sum_{a<b} w_{ab}^S r_{ab}^2 \right] \tag{3} \]

where \( w_{ab} \) are real coefficients and \( N \) is the number of trial functions (basis size). Factors of \( 1/\sqrt{2} \) from the permutation operator and \( 1/\sqrt{4\pi} \) from the S-state wave function are absorbed in the normalization of linear coefficients \( c_i^S \).

The proton, much heavier than the remaining constituents, is sometimes treated as a static source of the electric field \[24\]. In our approach, we follow the analogy with dipositronium \[23\] and include the motion of all four bodies. However, we neglect the magnetic moment of the proton throughout this paper so that the spin of the positron is the total angular momentum of PsH, a constant. The Coulomb Hamiltonian is

\[ \hat{H} = \sum_{i=1}^{4} \frac{\hat{p}_i^2}{2m_i} + \sum_{i<j} V(r_{ij}) \]

\[ = \frac{\hat{p}_1^2}{2m_1} + \frac{\hat{p}_2^2}{2m_2} + \frac{\hat{p}_3^2}{2m_3} + \frac{\hat{p}_4^2}{2m_4} + \alpha \sum_{i<j} \frac{z_i z_j}{r_{ij}}, \tag{4} \]
where \( z_i \) equals \(-1\) for \( e^-\) and \(+1\) for \( e^+\) and \( p^+\). Electron and positron masses are denoted by \( m_2 = m_3 = m_4 = m \). In atomic units (a.u.) we take \( m = 1 \) and \( m_1 = M \approx 1836 \).

Let \( \vec{A}_i \) denote the absolute coordinates and \( \vec{r}_{ij} \) the relative coordinates. The inter-particle distances are \( r_{ij} = \sqrt{(\vec{A}_i - \vec{A}_j)^2} \). In terms of these coordinates, the Hamiltonian (4) becomes

\[
\hat{H} = -\frac{1}{2\mu_{12}} \left[ \nabla^2_{\vec{r}_{12}} + \nabla^2_{\vec{r}_{13}} + \nabla^2_{\vec{r}_{14}} \right] - \frac{1}{m_1} \left[ \nabla_{\vec{r}_{12}} \cdot \nabla_{\vec{r}_{13}} + \nabla_{\vec{r}_{12}} \cdot \nabla_{\vec{r}_{14}} + \nabla_{\vec{r}_{13}} \cdot \nabla_{\vec{r}_{14}} \right] + \alpha \left[ \frac{21.52}{r_{12}} + \frac{21.54}{r_{13}} + \frac{21.54}{r_{14}} + \frac{22.53}{r_{23}} + \frac{22.54}{r_{24}} \right].
\]

(5)

where \( \mu_{ij} = \frac{m_im_j}{m_i+m_j} \) is the reduced mass and in our case \( \mu_{12} = \mu_{13} = \mu_{14} \). Translating from absolute to relative coordinates, we have ignored the kinetic energy of the centre-of-mass motion of the PsH system.

| \( \langle r_{p^+e^-} \rangle \) | \( \langle r_{e^-e^-} \rangle \) | \( \langle r_{p^+e^-} \rangle \) | \( \langle r_{e^-e^-} \rangle \) | \( \langle r_{p^+e^-} \rangle \) |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Bubin           | 3.663 50        | 3.481 18        | 2.313 16        | 3.577 0         | 16.272          |
| Ours            | 3.663 47        | 3.481 16        | 2.313 15        | 3.577 0         | 16.272          |
| Ref. [1]        | 15.593 54       | 7.824 79        | 15.895 94       | 0.172 0         | 0.349           |
| Ours            | 15.593 22       | 7.824 54        | 15.895 43       | 0.172 0         | 0.349           |
| \( \langle r_{e^-e^-} \rangle \) | \( \langle 1/r^2_{p^+e^-} \rangle \) | \( \langle 1/r_{p^+e^-} \rangle \) | \( \langle 1/r_{e^-e^-} \rangle \) | \( \langle 1/r^2_{p^+e^-} \rangle \) |
| Ref. [1]        | 0.213 65        | 0.213 65        | 0.343 30        | 0.418 43        | 0.729           |
| Ours            | 0.213 62        | 0.213 65        | 0.343 30        | 0.418 43        | 0.729           |
| \( \langle 1/r_{e^-e^-} \rangle \) | \( \langle T \rangle \) | \( \langle V \rangle \) | \( \langle \hat{H} \rangle \) | \( \langle \delta^+_{e^-e^-} \delta^+_{e^-e^-} \rangle \) |
| Ref. [1]        | 0.370 33        | --              | --              | --              | -0.788 87       |
| Ours            | 0.370 33        | 0.788 87        | -1.577 74       | -0.788 87       | 3.7147 \times 10^{-4} |
| \( \langle \delta^+_{p^+e^-} \delta^+_{p^+e^-} \rangle \) | \( \langle \delta^+_{e^-e^-} \delta^+_{e^-e^-} \rangle \) | \( \langle \delta^+_{p^+e^-} \delta^+_{p^+e^-} \rangle \) | \( \langle \delta^+_{e^-e^-} \delta^+_{e^-e^-} \rangle \) | \( \langle \delta^+_{p^+e^-} \delta^+_{p^+e^-} \rangle \) |
| Ref. [1]        | 8.6 \times 10^{-4} | 3.16 \times 10^{-5} | 6.32 \times 10^{-3} | 7.533 \times 10^{-3} | 1.9038 \times 10^{-4} |
| Ours            | 8.8 \times 10^{-4} | 3.12 \times 10^{-5} | 6.09 \times 10^{-3} | 7.3087 \times 10^{-3} | 1.8018 \times 10^{-4} |

Table I. Values of physical parameters for the PsH calculated using Gaussian wave functions, compared with results of Ref. [1]. All values are given in atomic units where the unit of length is the Bohr radius \( h/(\alpha mc) \). Basis size is always 1000.

The expectation value of the Hamiltonian with the wave function in Eq. (3) approximates the ground state energy in terms of six exponents \( w_{ab}^{6S} \). These six parameters are determined, for each of the \( N \) elements of the basis, following the optimization method described in [22]. The results for a range of parameters of the PsH system are given in Table II along with the corresponding values calculated in Ref. [1]. We find good agreement, especially for the non-relativistic ground state energy \( \langle \hat{H} \rangle \). The binding energy (dissociation energy) is (in atomic units, taking \( \alpha^2mc^2 \) as the unit energy)

\[
E_b = -\langle \hat{H} \rangle + E^H + E^{Ps}
= -\langle \hat{H} \rangle - \frac{3}{4} \text{a.u.},
\]

(6)
where $\langle \hat{H} \rangle$ is given in Table I and the ground state energies of hydrogen and positronium are $-\frac{1}{2}$ a.u. and $-\frac{1}{4}$ a.u., respectively. The results we will use in Sections IV and V are

$$\langle \delta e^+ e^- \delta e^+ e^- \rangle = 3.73 (2) \cdot 10^{-4},$$  \hspace{1cm} (7)

$$\langle \delta p^+ e^+ \delta p^+ e^+ \delta e^+ e^- \rangle = 1.85 (1) \cdot 10^{-4}. \hspace{1cm} (8)$$

The central values are arithmetic means of the results in Ref. [1] and ours. Their differences are used as error estimates.

**IV. ONE-PHOTON DECAY $\text{PsH} \rightarrow p^+ e^- \gamma$**

Four types of diagrams can contribute to the decay $\text{PsH} \rightarrow p^+ e^- \gamma$, as shown in Fig. 1. In all of them, an $e^+ e^-$ pair annihilates into one or two photons. One of the produced photons is absorbed by the spectator electron or by the proton.

![Diagrams contributing to the decay $\text{PsH} \rightarrow p^+ e^- \gamma$.](image)

Figure 1. Diagrams contributing to the decay $\text{PsH} \rightarrow p^+ e^- \gamma$. Electrons and positrons are represented by solid straight lines and the proton by a double line. Blobs indicate two possible orderings of photon couplings.
We want to argue that the dominant (by far) contribution is provided by diagrams in Fig. 1A and B, where a photon is absorbed by the spectator electron. Diagrams C and D are strongly suppressed and can be neglected. Since PsH is weakly bound, its constituents’ velocities are small and can be neglected. In that limit, the proton can be treated as a static source of Coulomb photons. In group C, the two-photon annihilation occurs only for a spin-singlet $e^+e^-$ pair. The spin-singlet projector contains $\gamma_5$ and, for the amplitude not to vanish, Dirac matrices $\gamma^{1,2,3}$ must be supplied by vertices and by electron’s propagator. Interaction with a Coulomb photon, coupled via $\gamma^0$, does not contribute. Similarly, in group D, the matrix $\gamma^0$ has a zero matrix element between spinors of a positron and an electron at rest.

For this reason, it is sufficient to consider groups A and B, up to corrections suppressed by powers of $\alpha$ which are small and beyond the scope of this work. These two groups are the same as the diagrams responsible for the positronium ion decay $\text{Ps}^- \rightarrow e^-\gamma$, first evaluated in [26] and recently confirmed in [27]. The only difference is in the coalescence probability of $e^-e^-e^+$ which is much larger in PsH than in the ion, thanks to the attraction of electrons to the proton.

When the ion $\text{Ps}^-$ is isolated, we know that it is approximately a Ps atom accompanied by an electron far away [28]. In the presence of a proton, this configuration becomes more compact. If PsH resembles a hydrogen molecule, one may expect the two electrons to be predominantly between the proton and the positron, binding the system. It is reasonable to expect that the probability of $e^-e^-e^+$ coalescence to scale like the inverse volume of the system, which we can estimate as proportional to $1/r_e^3$, where $r_e$ is the mean distance between the electrons. Using numbers in Table I and those for the ion from Ref. [26], we get the volume ratio $[r\ (\text{Ps}^-)/r\ (\text{PsH})]^3$ equal about 13.6. This is consistent with the ratio of coalescence probabilities: for PsH, Eq. (7) gives $\langle \delta_{e^-e^-} \delta_{e^-e^-} \rangle = 3.73 \cdot 10^{-4}$, which is about 10 times larger than 0.35875(2) $\cdot 10^{-4}$ in the ion $\text{Ps}^-$ [29]. This consistency among various estimates obtained with the variational approach is reassuring.

Finally, we obtain the one-photon decay rate by substituting the PsH value of $\langle \delta_{e^-e^-} \delta_{e^-e^-} \rangle$ into Kryuchkov’s [26] result for the $\text{Ps}^-$,

$$\Gamma (\text{PsH} \rightarrow p^+e^-) = \frac{64\pi^2}{27} \alpha^2 \frac{m}{\langle \delta_{e^-e^-} \delta_{e^-e^-} \rangle} = 0.398 (8) \text{ s}^{-1}. \quad (9)$$

We have quadrupled the error arising from the numerical evaluation of the coalescence probability to account for corrections of higher order in $\alpha$.

V. ZERO-PHOTON DECAY $\text{PsH} \rightarrow p^+e^-$

PsH can also decay with only an electron and a proton in the final state, $\text{PsH} \rightarrow p^+e^-$, when photons produced in the $e^+e^-$ annihilation are absorbed by surviving components of PsH (internal conversion). This channel is very suppressed because it requires all four constituent to coalesce, and also it is of a higher order in $\alpha$. Its signature is a relativistic electron with energy of about $3m$. Since our result for this decay differs from previous studies by orders of magnitude, we describe our calculation in detail.

Diagrams contributing to the decay $\text{PsH} \rightarrow p^+e^-$ are shown in Fig. 2. They are divided into three groups A, B, C, differing by the topology of the photon exchange. Working in the leading order in the velocities of the constituent particles, one can neglect groups B and C, by the same reasoning as at the beginning of Section IV.

We therefore evaluate only diagrams in group A, shown in Fig. 3. We frame the calculation as a decay of $\text{Ps}^-$ in an external Coulomb field. Choosing the $z$ axis along the polarization of the positron, we compute the amplitude of the electron emission along that axis. The electron emitted in that direction must be right-handed since it carries the spin of the initial state. The amplitude of emission at a non-zero polar angle $\theta$ will be multiplied by $\cos(\theta/2)$, resulting in a factor $\langle \cos^2(\theta/2) \rangle = 1/2$ in the decay rate. That factor is canceled when the rate of decay into a left-handed electron is included. (If daughter electrons’ polarization is not observed, their angular distribution is isotropic because of $\cos^2(\theta/2) + \sin^2(\theta/2) = 1.$)
Figure 2. Diagrams contributing to the decay \( \text{PsH} \rightarrow p^+e^- \) with no photons in the final state. As in Fig. 1, blobs denote two orderings of photon couplings.

Figure 3. Diagrams of group A for the decay \( \text{PsH} \rightarrow p^+e^- \) in the limit of an infinitely massive proton. Dashed line denotes interaction with the Coulomb field of the proton.

The daughter electron carries the rest energy of the initial state, \( E_f = 3m \). For it to be on the mass shell, the Coulomb photon exchanged with the nucleus (dashed line in Fig. 3) must carry momentum \( p_f = 2\sqrt{2}m \) in the \( z \) direction. Its propagator supplies factor of \( e/ (8m^2) \) to the amplitude. The remaining factors for the amplitudes pictured in Fig. 3 are (amplitudes 3 and 4 contain a minus sign relative to 1, 2, due to permutation of fermion operators)

\[
\mathcal{M}_1 = \mathcal{M}_2 = -\frac{e^3}{8\sqrt{2}m^3}, \quad \mathcal{M}_3 = -\frac{e^3}{16\sqrt{2}m^3}, \quad \mathcal{M}_4 = \frac{3e^3}{16\sqrt{2}m^3},
\]

\[
\mathcal{M} = \sqrt{2}(\mathcal{M}_1 + \mathcal{M}_2 + \mathcal{M}_3 + \mathcal{M}_4) = -\frac{e^3}{8m^3},
\]

where the factor of \( \sqrt{2} \) arises from the electron spin singlet wave function, \( (\uparrow \downarrow - \downarrow \uparrow)/\sqrt{2} \); there are two equal contributions divided by \( \sqrt{2} \). These results are obtained assuming free particles annihilating at rest, using the daughter electron’s spinor \( u_f^\dagger = \begin{pmatrix} 1 & 0 \end{pmatrix} / \sqrt{2} \). In order to account for the binding,
the amplitude is multiplied $^{27}$ by the PsH wave function at zero separation among the positron and electrons. The square of the amplitude is summed over the final states. The rate is a product of four factors: final-state normalization, amplitude squared, phase space, and the coalescence probability that includes $1/2!$ accounting for identical electrons,

$$\Gamma (\text{PsH} \rightarrow p^+ e^-) = \frac{1}{u^f u_f} \cdot \left( \frac{e^4}{64 m^3} \right)^2 \frac{4 \pi p_f E_f}{(2\pi)^2} \frac{(c\alpha m)^9 \langle \delta_{p+ -} \rangle}{2!}$$

$$= \frac{\sqrt{2}}{8} \pi^3 \alpha^{13} \langle \delta_{p+ -} \rangle m,$$

where $\langle \delta_{p+ -} \rangle$ denotes $\langle \delta_{p+ e^+} \delta_{p+ e^-} \delta_{e^- e^-} \rangle = 1.85 (1) \cdot 10^{-4}$ given in Eq. (8). Using this value we get the rate

$$\Gamma (\text{PsH} \rightarrow p^+ e^-) = 1.31 (7) \cdot 10^{-10} \text{ s}^{-1}.$$  

(14)

VI. CONCLUSIONS

We have determined rates of two rare decays of the ground state of positronium hydride and confirmed a number of basic properties for this system using the variational principle with a Gaussian basis.

In the case of one photon annihilation, $\text{PsH} \rightarrow p^+ e^- \gamma$, where one of the photons produced in the $e^+ e^-$ annihilation can be absorbed either by the electron or by the proton, we have demonstrated that the proton contribution is negligible. When the electron absorbs the photon, the decay resembles that of the already extensively studied $\text{Ps}^-$ ion. We find (see Eq. (13))

$$\Gamma (\text{PsH} \rightarrow p^+ e^-) = 0.398 (8) \text{ s}^{-1}.$$  

(15)

The assigned error includes the spread of values of the coalescence probability, higher order $\alpha$ corrections, and much smaller proton recoil effects. This result should be compared with previous estimates. Ref. $^{20}$ assumed (incorrectly) that the contribution of the photon absorption by the proton “does not differ significantly from” that by the electron and thus obtained a rate about twice larger than we did, $0.8077 \text{ s}^{-1}$ (Table V in Ref. $^{20}$). Similarly, Ref. $^{30}$ repeated the claim that absorptions by the electron and by the proton contribute approximately equally and obtained $0.787501 \text{ s}^{-1}$ using a slightly different coalescence probability. We stress, once again, that the photon absorption by the proton is suppressed by the velocity of constituents of PsH, equivalent to a suppression by $\alpha$.

The other decay channel we considered was the radiationless decay $\text{PsH} \rightarrow p^+ e^-$ for whose rate we found in Eq. (14) $1.31 (7) \cdot 10^{-10} \text{ s}^{-1}$. The previous estimate $^{20}$, $9.16 \times 10^{-8} \text{ s}^{-1}$, is larger by a factor of almost 700. That estimate was obtained by using the dipositronium $\text{Ps}_2$ result (Eq. (32) in Ref. $^{20}$). There are two problems with this reasoning. First, the $\text{Ps}_2$ formula used in Ref. $^{20}$ was incorrect even for $\text{Ps}_2$: it overestimated the zero-photon decay rate of $\text{Ps}_2$ by a factor of about 5.44 $^{27}$. What about the remaining factor of 700/5.44 $\approx 130^7$? The $\text{Ps}_2$ decay is quite different from that of PsH. The numerical coefficient in $\text{Ps}_2$ is $27 \sqrt{3}/2 \approx 23$ $^{27}$ instead of that in PsH being $\sqrt{2}/8 \approx 0.18$ (see our Eq. (13)). Their ratio is $23/0.18 \approx 130$, explaining the remaining discrepancy.

This large ratio has several sources: different symmetry factors, the proton not contributing in PsH, and, crucially, different particle virtualities. In the PsH decay, the emitted electron carries a large momentum with a magnitude of $\sqrt{8m}$. The propagator of the Coulomb photon supplying this momentum introduces a large suppression factor. Just to illustrate how this leads to large numbers, consider the diagram similar to Fig. 2A in the decay $\text{Ps}_2 \rightarrow e^+ e^-$: the denominators in the propagators of the photons and of the virtual electron are, in units of $1/m^2$, $-1/2, -1/2, 1/4$, producing $1/16$. Now consider denominators in Fig. 2A for PsH $\rightarrow p^+ e^-$: $1/4, 1/8, -1/8$, giving $-1/256$. Rates involve squares of these products, favoring the $\text{Ps}_2$ rate by the relative factor of 256. This illustrates how the ratio of 130 of the $\text{Ps}_2$ and PsH rates is quite natural.
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