Positronium hydrides and the Ps_2 molecule: Bound-state properties, positron annihilation rates, and hyperfine structure

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The bound-state spectra of the positronium hydrides $^{\infty}$HPs, TPs, DPs, ^{1}HPs, and MuPs are considered. The properties of the bound ground S states ($L=0$) in these systems and the Ps_2 molecule have been determined by extensive variational calculations. The hyperfine structure of these states is also investigated. The positron annihilation rates have been evaluated for the positronium hydrides, the Ps_2 molecule, and the Ps^- ion and compared. The positron annihilation rates $\Gamma_{n\gamma}$ (where $n \geqslant 2$) in the positronium hydrides are significantly closer to those in the Ps^- ion (the three-body system) than in the Ps_2 molecule. [S1050-2947(97)00304-1]

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I. INTRODUCTION

In the present study we consider the bound states in the so-called positronium hydrides $^{\infty}$HPs, TPs, DPs, ^{1}HPs, and MuPs, each of which has only one bound ground S state ($L=0$). The boundedness of the ground S state in each of the positronium hydrides $^{\infty}$HPs, TPs, DPs, and ^{1}HPs is well known since the paper by Ore [1]. It could be expected that the ground S state in the system MuPs (i.e., $\mu^+e^+e^-e^-$) is bounded as well. The general formula for these systems takes the form $A^+e^+e^-e^-$, where A denotes the heavy positive particle with charge $+1$ and mass m_A, e^+ designates the positron, and e^- stands for electrons. In general, all such systems can be described as positronium hydrides. The positronium molecule Ps_2 can be considered to be a specific positronium hydride, in which $m_A=1$ [2]. Our present goal is to study the bound ground S states and the positron annihilation in positronium hydrides since this process is of interest for a number of applications.

The production of the positronium hydrides in the laboratory should not be a much more complicated problem than that for the Ps^- ion [3,4]. Recently, ^{1}HPs has been created (and observed) in the collisions between positrons and methane [5]. The positronium hydrides can be produced (and then annihilated) inside and outside of hydrogen stars; therefore, the positronium hydrides play a definite role in some astrophysical models (see, e.g., [6–8] and references therein). In practice, they can be found inside the hydrogen fuel when the positron beam is used together with very intense electron beams to produce low-temperature thermonuclear ignition in a dense hydrogen plasma.

The positronium hydride $^{\infty}$HPs has been investigated previously [9–12] (all references on HPs before 1981 can be found in [12]). In all of these papers it was assumed that the properties for the $A^+e^+e^-e^-$ system with the very large (but finite) heavy particle mass m_A are almost the same as for $^{\infty}$HPs. However, the appropriate corrections for the real systems were not evaluated even approximately. In terms of this, the first goal of our present study is to compute the energies and a number of properties for all positronium hydrides $^{\infty}$HPs, TPs, DPs, ^{1}HPs, and MuPs and for the Ps_2 molecule. Another problem, which is even more important, is to consider the positron annihilation in such systems and, in particular, evaluate the zero-, one-, two-, and three-photon annihilation rates.

The present work has the following structure. The bound-state spectra of the positronium hydrides are discussed in the next section, together with some of their properties. The hyperfine structure of the positronium hydrides is considered in Sec. III. Positron annihilation in the positronium hydrides is studied in Sec. IV. Following our previous method [13], we found the annihilation probabilities for the Ps_2 molecule with the present wave function in Sec. V. It is very interesting to compare the appropriate annihilation rates for the Ps_2 molecule and those for the positronium hydrides. The final discussion can be found in Sec. VI. Some computational details are given in the Appendix. Atomic units ($\hbar=1$, $m_e=1$, and $e^+=-e^-=1$) are used throughout this work.

II. THE BOUND-STATE SPECTRA IN THE POSITRONIUM HYDRIDES

Let us consider the bound-state spectra in the positronium hydrides such as $A^+e^+e^-e^-$. In general, a state in the positronium hydrides $A^+e^+e^-e^-$ is bound if it is stable against dissociation into two neutral fragments, i.e., $A^+e^+e^-e^- \rightarrow A^+e^- + e^+e^-$. The appropriate threshold energy equals

$$E_{\rm tr}(m_A) = -\frac{0.5}{1+m_A^{-1}} - 0.25 = -\frac{(3+m_A^{-1})}{4(1+m_A^{-1})} \geqslant -\frac{3}{4} = -0.75 \ \text{a.u.} \quad (1)$$

The bound-state spectra in such systems has a quite simple structure since they contain only one bound (ground) S state ($L=0$). Moreover, the structure of these states is also simple: the total angular momentum L equals 0 and both electrons form a singlet pair, i.e., their total spin equals 0. Likewise, in the first and very good approximation (see below) we can assume that A is a spinless particle. This means that the bound state in the system $A^+e^+e^-e^-$ can be designated as a $^2S_{1/2}$ state or even as an S state. Thus, in the present study we consider the S ground bound state in each

TABLE I. Numerical values of the particle mass m_A, spin S_A, magnetic moment μ_A, and factor g used in the present calculations.

Particle	m_A [a]	S_A	μ_A [a]	g
T^+	5496.921 58	$\frac{1}{2}$	$1.622\,392\times10^{-3}$	$3.244\,784\times10^{-3}$
D^+	3670.483 014	1	$0.466\,975\,447\,9\times10^{-3}$	$0.466\,975\,447\,9\cdot10^{-3}$
$^1H^+$	1 836.152 701	$\frac{1}{2}$	$1.521\,032\,202\times10^{-3}$	$3.042\,064\,404\times10^{-3}$
μ^+	206.768 262	$\frac{1}{2}$	$4.841\,970\,97\times10^{-3}$	$9.683\,941\,94\times10^{-3}$
e^+	1.0	$\frac{1}{2}$	1.001 159 656 74	2.002 319 304 386

[a]In atomic units.
[b]In Bohr magneton μ_B, where $\mu_B=0.5$ a.u.$=9.274\,015\,43\times10^{-24}$ J$\times$T^{-1}.

of the positronium hydrides $^\infty$HPs, TPs, DPs, ^{1}HPs, and MuPs. The masses of the particles and a number of other properties used in the calculations are given in Table I.

The Hamiltonian for the positronium hydrides may be written in the form (in atomic units)

$$H=-\frac{1}{2m_A}\Delta_1-\frac{1}{2}\Delta_2-\frac{1}{2}\Delta_3-\frac{1}{2}\Delta_4+\frac{1}{r_{12}}-\frac{1}{r_{13}}-\frac{1}{r_{14}}-\frac{1}{r_{23}}-\frac{1}{r_{24}}+\frac{1}{r_{34}}, \quad (2)$$

where the notation 1 (also A or p) designates the heaviest particle A^+, the notation 2 (or $+$) means the positron, while 3 (or $-$) and 4 (or $-$) stand for electrons. The appropriate energies and a number of other properties (expectation values; see the Appendix) can be found in Tables II and III. It should be noted that the present variational energies (Table II) for all of these systems are the lowest known to date. This was unexpected since, e.g., for the $^\infty$HPs system there is an effective and accurate special procedure (see e.g., [10] or [11]), which is based on the so-called James-Coolidge variational expansion in the relative coordinates [14] and can be successfully applied for all Coulomb four-body systems in which one of the particles is significantly heavier than the three others (e.g., highly accurate results for the Li atom can be found in [15], and for the Be^+ ion in [16]).

It follows from Eq. (2) that the energy of a positronium hydride depends only upon the heavy particle mass m_A since the electron and positron masses are the same in all cases. Thus we write for the total energy of the $A^+e^+e^-e^-$ system (in the case where m_A is a very large number, i.e. $m_A\gg1$) the expansion

$$E(A^+e^+e^-e^-)=E(^\infty H^+e^+e^-e^-)+\sum_{k=1} a_k s^k, \quad (3)$$

where $s=m_A^{-1}\approx0$ is the inverse mass value and $E(^\infty H^+e^+e^-e^-)$ is the total energy for the $^\infty H^+e^+e^-e^-$ hydride. By fitting the data for the first five systems [17] from Table II we have found the first two coefficients in this formula to be

$$a_1=0.598\,937\,844\,9, \quad a_2=-0.729\,461\,502\,6. \quad (4)$$

It should be noted that the coefficient a_1 coincides (with very good accuracy) with the $\langle-\frac{1}{2}\nabla_1^2\rangle$ expectation value for $s=0$ (in $^\infty H^+e^+e^-e^-$) in Table III, i.e., 0.599 057 5 a.u. This follows directly from the Hellman-Feynman theorem [18,19]. Note also that analogous formulas can be produced for the other expectation values in such systems, e.g., for the Dirac δ functions or interparticle distances (see Table III).

In terms of the properties presented in Tables II and III we can expect that the positronium hydrides have the following structure. This is a cluster that consists of the two neutral systems: the hydrogen atom (e.g., $^\infty H^+e^-$) and the positronium atom (e^+e^-). The distances between the two electrons and between positron and nucleus are significantly larger than those between each of the positive particles and the appropriate (nearest) electron. However, the distance be-

TABLE II. Total variational energies ε, the dissociation thresholds E_{th}, the inverse mass $s=m_A^{-1}$, and the binding energies ϵ for a number of the positronium hydrides $A^+e^+e^-e^-$.

System	ε [a]	E_{tr} [a]	s	ϵ [b]
$^\infty H^+e^+e^-e^-$	−0.789 1794	−0.750 000 0	0.0	−1.066 126
$T^+e^+e^-e^-$	−0.789 0705	−0.749 909 056 542 1	$0.181\,920\,004\,760\,2\times10^{-3}$	−1.065 638
$D^+e^+e^-e^-$	−0.789 0163	−0.749 863 815 249 0	$0.272\,443\,707\,322\,9\times10^{-3}$	−1.065 394
$^1H^+e^+e^-e^-$	−0.788 8534	−0.749 727 839 716 5	$0.544\,617\,013\,310\,2\times10^{-3}$	−1.064 661
$\mu^+e^+e^-e^-$	−0.786 2998	−0.747 593 472 673 9	$0.483\,633\,218\,332\,1\times10^{-2}$	−1.053 253
$e^+e^+e^-e^-$ [c]	−0.516 0024	−0.500 000	1.0	−0.435 445

[a]In atomic units.
[b]In electron volts (1 a.u.$=$ 27.211 396 1 eV).
[c]The positronium molecule Ps_2.

TABLE III. Expectation values in atomic units ($m_e=1, \hbar=1$, and $e=1$) of some properties for the ground bound S states ($L=0$) of the positronium hydrides $A^+e^+e^-e^-$.

System / Particles	$^{\infty}H^+e^+e^-e^-$ 1 2 3 4	$T^+e^+e^-e^-$ 1 2 3 4	$D^+e^+e^-e^-$ 1 2 3 4	$^1H^+e^+e^-e^-$ 1 2 3 4	$\mu^+e^+e^-e^-$ 1 2 3 4	$e^+e^+e^-e^-$ 1 2 3 4
$\langle r_{12}\rangle$	3.660 270	3.660 855	3.661 145	3.662 019	3.675 763	6.032 613
$\langle r_{13}\rangle$	2.310 813	2.311 345	2.311 609	2.312 405	2.324 918	4.486 844
$\langle r_{23}\rangle$	3.479 405	3.479 689	3.479 831	3.480 256	3.486 942	4.486 844
$\langle r_{34}\rangle$	3.573 280	3.574 010	3.574 373	3.575 465	3.592 620	6.032 613
$\langle r_{12}^2\rangle$	16.2324	16.2378	16.2405	16.2486	16.3758	46.356 07
$\langle r_{13}^2\rangle$	7.802 02	7.805 78	7.807 65	7.813 27	7.901 84	29.102 98
$\langle r_{23}^2\rangle$	15.5698	15.5727	15.5741	15.5785	15.6464	29.102 98
$\langle r_{34}^2\rangle$	15.8516	15.8582	15.8615	15.8714	16.0275	46.356 07
$\langle r_{12}^3\rangle$	84.776	84.820	84.842	84.907	85.943	443.272
$\langle r_{13}^3\rangle$	35.059	35.085	35.098	35.137	35.751	252.748
$\langle r_{23}^3\rangle$	84.162	84.187	84.200	84.238	84.827	252.748
$\langle r_{34}^3\rangle$	84.211	84.265	84.292	84.373	85.645	443.272
$\langle r_{12}^4\rangle$	511.4	511.7	511.9	512.5	521.1	5182.5
$\langle r_{13}^4\rangle$	196.7	196.9	197.0	197.3	201.9	2797.3
$\langle r_{23}^4\rangle$	529.9	530.1	530.2	530.6	536.0	2797.3
$\langle r_{34}^4\rangle$	523.0	523.5	523.7	524.4	535.1	5182.5
$\langle r_{12}^{-1}\rangle$	0.347 507	0.347 456	0.347 431	0.347 354	0.346 161	0.220 797
$\langle r_{13}^{-1}\rangle$	0.729 728	0.729 579	0.729 505	0.729 282	0.725 789	0.368 401
$\langle r_{23}^{-1}\rangle$	0.418 519	0.418 497	0.418 487	0.418 455	0.417 954	0.368 401
$\langle r_{34}^{-1}\rangle$	0.370 607	0.370 533	0.370 496	0.370 386	0.368 662	0.220 797
$\langle r_{12}^{-2}\rangle$	0.172 206	0.172 158	0.172 134	0.172 062	0.170 943	$0.734\,489\times10^{-1}$
$\langle r_{13}^{-2}\rangle$	1.206 803	1.206 333	1.206 099	1.205 397	1.194 411	0.303 099
$\langle r_{23}^{-2}\rangle$	0.349 086	0.349 064	0.349 052	0.349 019	0.348 495	0.303 099
$\langle r_{34}^{-2}\rangle$	0.213 984	0.213 897	0.213 854	0.213 725	0.211 704	0.734489×10^{-1}
π_{12}	0.459 992	0.460 009	0.460 017	0.460 043	0.460 445	0.523 243
π_{13}	0.679 038	0.679 060	0.679 072	0.679 105	0.679 621	0.667 551
π_{23}	0.534 880	0.534 906	0.534 919	0.534 958	0.535 579	0.667 551
π_{34}	0.491 404	0.491 416	0.491 422	0.491 439	0.491 707	0.523 243
$\langle -\frac{1}{2}\nabla_1^2\rangle$	0.599 0575	0.598 7823	0.598 6455	0.598 234 3	0.591 815 7	0.129 001 5
$\langle -\frac{1}{2}\nabla_2^2\rangle$	0.136 8549	0.1368 497	0.136 8471	0.136 839 3	0.136 718 4	0.129 001 5
$\langle -\frac{1}{2}\nabla_3^2\rangle$	0.326 172 6	0.326 067	0.326 014 5	0.325 856 8	0.323 390 5	0.129 001 5
$\langle \delta_{12}\rangle$	$0.168\,514\times10^{-2}$	$0.168\,456\times10^{-2}$	$0.168\,427\times10^{-2}$	$0.168\,341\times10^{-2}$	0.166988×10^{-2}	0.635208×10^{-3}
$\langle \delta_{13}\rangle$	0.174 650	0.174 551	0.174 503	0.174 356	0.172 060	$0.220\,203\times10^{-1}$
$\langle \delta_{23}\rangle$	$0.241\,340\times10^{-1}$	$0.241\,328\times10^{-1}$	$0.241\,322\times10^{-1}$	$0.241\,303\times10^{-1}$	$0.241\,018\times10^{-1}$	$0.220\,203\times10^{-1}$
$\langle \delta_{34}\rangle$	$0.449\,670\times10^{-2}$	$0.449\,356\times10^{-2}$	$0.449\,201\times10^{-2}$	$0.448\,732\times10^{-2}$	$0.441\,451\times10^{-2}$	$0.635\,208\times10^{-3}$
$\langle \delta_{123}\rangle$	$0.910\,32\times10^{-3}$	$0.909\,62\times10^{-3}$	$0.909\,27\times10^{-3}$	$0.908\,22\times10^{-3}$	$0.891\,96\times10^{-3}$	$0.925\,80\times10^{-4}$
$\langle \delta_{134}\rangle$	0.70841×10^{-2}	$0.707\,47\times10^{-2}$	$0.707\,01\times10^{-2}$	$0.705\,60\times10^{-2}$	0.68394×10^{-2}	$0.925\,80\times10^{-4}$
$\langle \delta_{234}\rangle$	$0.378\,91\times10^{-3}$	$0.378\,70\times10^{-3}$	$0.378\,60\times10^{-3}$	$0.378\,30\times10^{-3}$	$0.373\,59\times10^{-3}$	$0.925\,80\times10^{-4}$
$\langle \delta_{1234}\rangle$	$0.179\,63\times10^{-3}$	$0.179\,41\times10^{-3}$	$0.179\,30\times10^{-3}$	$0.178\,98\times10^{-3}$	$0.173\,95\times10^{-3}$	$0.439\,08\times10^{-5}$
$\langle T\rangle$	0.789 200 1	0.789 0927	0.789 039 3	0.788 878 7	0.786 361 7	0.516 006 0
$\langle \frac{1}{2}V\rangle$	−0.789 189 8	−0.789 081 6	−0.789 027 8	−0.788 866 0	−0.786 330 7	−0.516 004 1
χ	0.131×10^{-4}	0.141×10^{-4}	0.146×10^{-4}	0.160×10^{-4}	0.394×10^{-4}	0.356×10^{-5}

tween the proton and the second (remote) electron is approximately the same as in the $^{\infty}H^-$ ion, while the distance between the first electron and the positron is approximately the same as the distance between the positron and the remote electron in the Ps^- ion. Since the total electron spin equals 0 for the positronium hydrides as well as for the H^- and Ps^- ions, the $^{\infty}H^+e^+e^-e^-$ system can be represented as the ''physical sum'' of the Ps^- and $^{\infty}H^-$ ions, i.e., in terms of

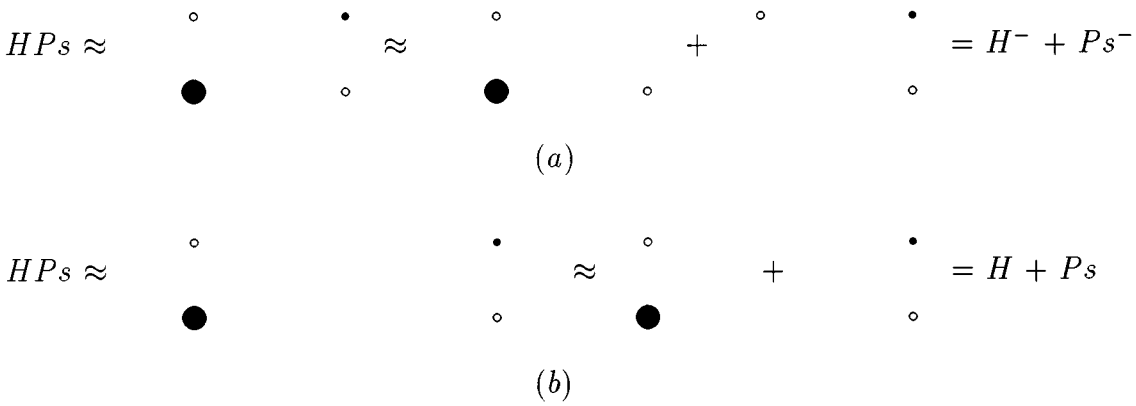

FIG. 1. Schematic structure of the HPs system in terms of (a) two three-body clusters and (b) two two-body clusters. The computational results show that the picture (a) represents significantly better the actual structure of the HPs system. In both of these pictures the small circle designates the electron, while small and large filled (circles) stand for the positron and proton (A^+), respectively.

these two three-body clusters. The main idea of such a representation is illustrated in Fig. 1. This picture shows also the principal difference between the appropriate two- and three-body cluster representations for the positronium hydrides. In terms of the three-body cluster model, the energy of the $^{\infty}\mathrm{H}^+e^+e^-e^-$ system can be approximately evaluated as the sum of the energies for the Ps^- and $^{\infty}\mathrm{H}^-$ ions, i.e.,

$$\begin{aligned} E(^{\infty}\mathrm{H}^+e^+e^-e^-) &= E(^{\infty}\mathrm{H}^-) + E(\mathrm{Ps}^-) \\ &\approx -0.527\,751\,016\,523 \\ &\quad -0.262\,005\,070\,232\,6 \\ &\approx -0.789\,756\,086\,7 \ \text{a.u.}, \end{aligned} \tag{5}$$

where the energies for the $^{\infty}\mathrm{H}^-$ and Ps^- ions are chosen from [20] (see also [21,22]). Such a simple estimation has surprising accuracy since it gives at least three correct decimal figures for the total energy of the $^{\infty}\mathrm{H}^+e^+e^-e^-$ system [23].

In the general case, when $m_A \to 1$ in the $A^+e^+e^-e^-$ system, this formula [Eq. (5)] loses accuracy very rapidly since the positron e^+ obviously influences the motion of the positive particle A^+. Actually, the total energy estimate that can be found from formula (5) lies below the real energy value for the $A^+e^+e^-e^-$ system. The largest deviation can be observed in the Ps_2 molecule, where the error is approximately 1.5% of the total energy.

III. HYPERFINE STRUCTURE OF BOUND STATES IN POSITRONIUM HYDRIDES

In the preceding section the particle A^+ has been assumed to be a spinless positive particle with charge $+1$ and mass m_A for all positronium hydrides. This means that we studied the Coulomb structure of the bound state spectra in the $A^+e^+e^-e^-$ systems. Now, let us consider the fine and hyperfine structures of the positronium hydrides. In particular, we wish to show that the respective corrections are relatively small in comparison to the Coulomb energies.

The hyperfine structure (i.e., the appropriate level shift and its splitting) is determined by the spin-spin interaction between particles. In contrast with this, the so-called fine structure arises as the result of the spin-orbit interactions for the lightest particles, i.e., for the electrons and positrons in the positronium hydrides. The general expression for the fine interaction operator of the lowest order in the positron hydrides takes the form

$$H_F = b_+ \vec{\ell}_+ \cdot \vec{s}_+ + b_- \vec{L}_- \cdot \vec{S}_- , \tag{6}$$

where $\vec{L}_-$ is the total angular momentum for the electrons, $\vec{S}_-$ is their total spin, $\vec{\ell}_+$ is the positron angular momentum and $\vec{s}_+$ is the positron spin. b_+ and b_- are two numerical constants. Since in the positronium hydrides $\vec{S}_- = 0$ (both electrons are always in the singlet state) and $\vec{\ell}_+ = 0$ (the partial positron wave function has the angular momentum $\ell = 0$, i.e., s state), we have $H_F = 0$ for all ground bound S states ($L = 0$) in such systems. Actually, this means that there is no fine structure in the positronium hydrides (in this approximation) and the possible level shift can be related only with the spin-spin interparticle interaction (or hyperfine interaction, in terms of the atomic terminology).

The appropriate general formula for the hyperfine interaction can be easily written for the positronium hydrides

$$H_{\mathrm{HF}} = -\sum_{(ij)} a_{ij} \vec{s}_i \cdot \vec{s}_j , \tag{7}$$

where the sum is calculated for all six pairs of particles. However, this expression can be simplified significantly since the nonrelativistic ground-state wave function for an arbitrary positronium hydride can be written as a product of coordinate-space and spin-space parts. The appropriate operator of the lowest order for the hyperfine interaction in the $A^+e^+e^-e^-$ system takes the form [24]

$$H_{\mathrm{HF}} = -a\vec{I}_A \cdot \vec{s}_+ - b\vec{s}_+ \cdot \vec{S}_- - c\vec{I}_A \cdot \vec{S}_- , \tag{8}$$

where $\vec{S}_-$ is the total electron spin, $\vec{s}_+$ is the positron spin, and $\vec{I}_A$ is the spin of the A particle (see Table I). Since both

TABLE IV. Hyperfine corrections in atomic units ($m_e=1$, $\hbar=1$, and $e=1$) of the lowest order for the ground bound S states ($L=0$) in the positronium hydrides $A^+e^+e^-e^-$.

Hyperfine correction	$T^+e^+e^-e^-$	$D^+e^+e^-e^-$	$^1H^+e^+e^-e^-$	$\mu^+e^+e^-e^-$
a	$1.220\,660\,8\times10^{-9}$	$1.756\,420\,2\times10^{-10}$	$1.143\,618\,0\times10^{-9}$	$3.611\,271\,2\times10^{-9}$
$\epsilon(J=0)$	$0.915\,496\times10^{-9}$		$0.857\,714\times10^{-9}$	$2.708\,453\times10^{-9}$
$\epsilon(J=\frac{1}{2})$		$1.756\,420\times10^{-10}$		
$\epsilon(J=1)$	$-0.305\,165\times10^{-9}$		$-0.285\,905\times10^{-9}$	$-0.902\,818\times10^{-9}$
$\epsilon(J=\frac{3}{2})$		$-0.878\,21\times10^{-10}$		

electrons are in the singlet state, we have $\vec{S}_-=0$ and $H_{\rm HF}=-a\vec{I}_A\cdot\vec{s}_+$, where a is a numerical factor. The explicit expression for the factor a is

$$a=\frac{8\pi\alpha^2}{3}\mu_B^2 g_A g_+\langle\delta_{A+}\rangle=\frac{2\pi\alpha^2}{3}g_A g_+\langle\delta_{A+}\rangle$$
$$\approx 2.233\,174\,540\,4\times10^{-4}g_A\langle\delta_{A+}\rangle \qquad (9)$$

where $\alpha=0.729\,735\,308\times10^{-2}$ is the fine structure constant. The Bohr magneton $\mu_B=e\hbar/2m_e$ equals $\frac{1}{2}$ in the atomic units ($e=1$, $\hbar=1$, and $m_e=1$), while its value in SI units is $9.274\,015\,43\times10^{-24}$ J T^{-1}. The masses, spin values, magnetic moments μ_A, and factors g_A are given in Table I. The value $\langle\delta_{A+}\rangle$ is the expectation value for the proton-positron Dirac δ function in atomic units, i.e.,

$$\langle\delta_{A+}\rangle=\frac{\langle\Psi|\delta(\vec{r}_A-\vec{r}_+)|\Psi\rangle}{\langle\Psi|\Psi\rangle}. \qquad (10)$$

The diagonalization of the $H_{\rm HF}$ operator yields the energies $\epsilon(J=0)=\frac{3}{4}a$ and $\epsilon(J=1)=-\frac{1}{4}a$ for all positronium hydrides, except only for the DPs system. Here J denotes the total spin value for the nucleus-positron pair. In particular, $J=0$ means the singlet state, while $J=1$ designates the appropriate triplet state. For the DPs system there are the doublet state with $J=\frac{1}{2}$ and quadruplet state with $J=\frac{3}{2}$. The respective energies are $\epsilon(J=\frac{1}{2})=a$ and $\epsilon(J=\frac{3}{2})=-\frac{1}{2}a$. The numerical results for these hyperfine corrections can be found in Table IV. Actually, it follows from Table IV that these corrections are very small in comparison to the appropriate Coulomb energies. For instance, they do not change the Coulomb energies in Table II in any significant decimal figure. This is a very important result for our present purposes.

IV. POSITRON ANNIHILATION IN POSITRONIUM HYDRIDES

Positron annihilation in the positronium hydrides $A^+e^+e^-e^-$ can be written in terms of the general equation

$$A^+e^+e^-e^-=[A^++e^-]+n\gamma \quad , \qquad (11)$$

where n means the total number of the emitted γ quanta or photons. The expression $[A^++e^-]$ designates that the final state in the two-body system A^+e^- is either a bound state or a state from its continuous spectrum (i.e., an unbound state). In most cases the final state is not of interest for the consideration of positron annihilation, in contrast with the so-called annihilation rates (or probabilities) $\Gamma_{n\gamma}$. These values depend upon n and the expectation value for the appropriate Dirac δ functions.

Positron annihilation in positronium hydrides was initially considered long ago [25]. Later, the positron annihilation in $^\infty H^+e^+e^-e^-$ was studied in a few papers [9–11]. Actually, only results for the $^\infty H^+e^+e^-e^-$ system can be found in the modern literature. Moreover, in all previous papers only the two-photon annihilation rate $\Gamma_{2\gamma}$ was estimated. Obviously, the two-photon annihilation is the dominant process, but it is very interesting to evaluate even approximately the probabilities for positron annihilation when the total number of the emitted photons differs from two.

The two-photon annihilation rate $\Gamma_{2\gamma}$ for positronium hydrides can be found from the general formula for a system that contains n electrons and one positron (i.e. n electron-positron pairs)

$$\Gamma_{2\gamma}=\pi n\alpha^4 c a_0^{-1}\langle\delta_{+-}\rangle$$
$$\approx 50.308\,740\,45\times10^9 n\langle\delta_{+-}\rangle \quad \sec^{-1}, \qquad (12)$$

where $n=2$ for all positronium hydrides. In this formula the velocity of light c is $0.299\,792\,458\times10^9$ m $\sec^{-1}$, the fine structure constant $\alpha=0.729\,735\,308\times10^{-2}$, and the Bohr radius is $0.529\,177\,249\times10^{-10}$ m [26,27]. In Eq. (12) the expectation value of the electron-positron Dirac δ function $\langle\delta_{+-}\rangle$

$$\langle\delta_{+-}\rangle=\frac{\langle\Psi|\delta(\vec{r}_--\vec{r}_+)|\Psi\rangle}{\langle\Psi|\Psi\rangle} \qquad (13)$$

is used in atomic units. The approximate values for the highest annihilation rates $\Gamma_{n\gamma}$ with an even number of photons (i.e., $n=2k>2$) can be easily found from $\Gamma_{2\gamma}$. Indeed, $\Gamma_{n\gamma}=\alpha^{2(k-1)}\Gamma_{2\gamma}$, where $n=2k\geq2$. The results for the many-photon annihilation rates $\Gamma_{n\gamma}$ in the positronium hydrides and Ps_2 molecule can be found in Table V.

To find the three-photon annihilation rate $\Gamma_{3\gamma}$ we shall apply the so-called Ferrante relations [28]. However, the method used in our previous work [13] cannot be generalized directly to the positronium hydrides for the following reasons. In [13] we considered the consequence of the appropriate two-, three- and four-body polyelectron systems such as Ps, Ps^-, and Ps_2. The principal point was that the bound state spectra of the Ps^- ion and the Ps_2 molecule are completely similar [29]. Therefore, the Ferrante relation can be used for the Ps_2 molecule if it works for the Ps^- ion. Un-

TABLE V. Approximate many-photon annihilation rates $\Gamma_{n\gamma}$ (in $\sec^{-1}$), where $n=0,1,2,\ldots,10$, for the positronium hydrides, Ps_2 molecule, and Ps^- ion.

Rate	$^{\infty}H^+e^+e^-e^-$	$T^+e^+e^-e^-$	$D^+e^+e^-e^-$	$^1H^+e^+e^-e^-$	$\mu^+e^+e^-e^-$	$e^+e^+e^-e^-$	$e^+e^-e^-$
$\Gamma_{0\gamma}$	9.160×10^{-8}	9.149×10^{-8}	9.143×10^{-8}	9.127×10^{-8}	8.870×10^{-8}	2.239×10^{-9}	
$\Gamma_{1\gamma}$	8.077×10^{-1}	8.072×10^{-1}	8.070×10^{-1}	8.0635×10^{-1}	7.963×10^{-1}	1.973×10^{-1}	$3.826\,03\times10^{-2}$
$\Gamma_{2\gamma}$	2.4361×10^{9}	2.4360×10^{9}	2.4359×10^{9}	2.4357×10^{9}	2.4328×10^{9}	4.4451×10^{9}	$2.092\,80\times10^{9}$
$\Gamma_{3\gamma}$	2.1870×10^{6}	2.1869×10^{6}	2.1868×10^{6}	2.1866×10^{6}	2.1841×10^{6}	3.9909×10^{6}	$1.878\,81\times10^{6}$
$\Gamma_{4\gamma}$	1.2972×10^{5}	1.2972×10^{5}	1.2971×10^{5}	1.2970×10^{5}	1.2955×10^{5}	2.3673×10^{5}	$1.1144\,4\times10^{5}$
$\Gamma_{5\gamma}$	1.1646×10^{2}	1.1645×10^{2}	1.1645×10^{2}	1.1644×10^{2}	1.1630×10^{2}	2.1252×10^{2}	1.00049×10^{2}
$\Gamma_{6\gamma}$	6.9080	6.9077	6.9075	6.9069	6.8988	12.606	5.934 56
$\Gamma_{7\gamma}$	6.2016×10^{-3}	6.2013×10^{-3}	6.2012×10^{-3}	6.2007×10^{-3}	6.1934×10^{-3}	1.1317×10^{-2}	$5.327\,74\times10^{-3}$
$\Gamma_{8\gamma}$	3.6786×10^{-4}	3.6784×10^{-4}	3.6783×10^{-4}	$3.678\,0\times10^{-4}$	3.6737×10^{-4}	6.7128×10^{-4}	$3.160\,23\times10^{-4}$
$\Gamma_{9\gamma}$	$3.302\,5\times10^{-7}$	$3.302\,3\times10^{-7}$	3.3022×10^{-7}	3.3020×10^{-7}	3.2981×10^{-7}	6.0265×10^{-7}	$2.837\,10\times10^{-7}$
$\Gamma_{10\gamma}$	1.9589×10^{-8}	1.9588×10^{-8}	1.9588×10^{-8}	1.9586×10^{-8}	1.9563×10^{-8}	3.5747×10^{-8}	$1.682\,87\times10^{-8}$

fortunately, for the positronium hydrides the appropriate two-body systems are unknown and the three-body systems (e.g., $H^+e^+e^-$) have no bound state (details can be found in [30]). Actually, the bound states can be found only in the four-body systems, i.e., in the positronium hydrides themselves.

Nevertheless, the Ferrante relations can be applied to the positronium hydrides since their structure can be represented as the Ps^- ion in the field of the proton. Moreover, the structure of the Ps^- ion in this case is approximately the same as for the free ion (see Sec. II). Therefore, the Ferrante relation can be applied to the positronium hydrides since it works for the free Ps^- ion. In other words, we assume that the proton's presence gives proportional corrections to both $\Gamma_{2\gamma}$ and $\Gamma_{3\gamma}$, i.e.

$$\frac{\Gamma_{2\gamma}(\mathrm{HPs})}{\Gamma_{3\gamma}(\mathrm{HPs})}=\frac{\Gamma_{2\gamma}(\mathrm{Ps}^-)}{\Gamma_{3\gamma}(\mathrm{Ps}^-)}, \tag{14}$$

where $\Gamma_{2\gamma}(Ps^-)$ and $\Gamma_{3\gamma}(Ps^-)$ are the appropriate two- and three-photon annihilation rates for the Ps^- ion. Finally, after a number of simple transformations [13], we find the expression

$$\Gamma_{3\gamma}(\mathrm{HPs})=\frac{4(\pi^2-9)\alpha}{9\pi}\Gamma_{2\gamma}(\mathrm{HPs})\approx 4.516\,459\,701\times10^{7}n\langle\delta_{+-}(\mathrm{HPs})\rangle \quad \sec^{-1}, \tag{15}$$

where $n=2$. Now, by applying the found value of $\Gamma_{3\gamma}(\mathrm{HPs})$ and the approximate relation $\Gamma_{(2n+1)\gamma}(\mathrm{HPs})=\alpha^{2(n-1)}\Gamma_{3\gamma}(\mathrm{HPs})$ we can estimate approximately all annihilation rates $\Gamma_{(2n+1)\gamma}(\mathrm{HPs})$ with an odd number of photons ($n\geqslant 2$).

A. The first one-photon annihilation rate

The one-photon positron annihilation can proceed in the positronium hydrides $A^+e^+e^-e^-$ as the regular two-photon annihilation, followed by internal conversion of one of the two emitted γ quanta either by the second (remaining) electron or by the particle A^+ [31]. In the first case the fast electron is emitted and the overall equation takes the form

$$A^+e^+e^-e^-=A^++e^-(0.510\,999\,06\ \mathrm{MeV})+\gamma. \tag{16}$$

The γ quantum energy is also 0.510 999 06 MeV. The second case

$$A^+e^+e^-e^-=A^+(0.510\,999\,06\ \mathrm{MeV})+e^-+\gamma \tag{17}$$

differs from this since there is no fast electron emission and, in principle, the two-body hydrogenlike system A^+e^- can be found in one of its bound states. According to this, we can find in the positronium hydrides $A^+e^+e^-e^-$ two different one-photon annihilation rates, which are designated below as $\Gamma_\gamma(\mathrm{HPs},e^-)$ and $\Gamma_\gamma(\mathrm{HPs},A^+)$, so that $\Gamma_\gamma(\mathrm{HPs})=\Gamma_\gamma(\mathrm{HPs},e^-)+\Gamma_\gamma(\mathrm{HPs},A^+)$. In this subsection we consider the first one-photon annihilation rate, i.e., $\Gamma_\gamma(\mathrm{HPs},e^-)$.

By applying the approach from [32] we can write the following expression for $\Gamma_\gamma(HPs,e^-)$:

$$\Gamma_\gamma(\mathrm{HPs},e^-)=y\frac{16\pi^2}{3}\zeta\alpha^8ca_0^{-1}\langle\delta_{+--}(\mathrm{HPs})\rangle=y\times1.065\,757\,44\times10^{3}\langle\delta_{+--}(\mathrm{HPs})\rangle \quad \sec^{-1}, \tag{18}$$

where the value of the proportionality constant $\zeta=\frac{4}{9}$ is used (this value was found in [32]; for more details see the discussion and references in [13,20]). The unknown factor y can be found from accurate quantum-electrodynamics calculations. We shall assume below that $y=1$. This means that in terms of such an approximation there is no difference between one-photon positron annihilation in the Ps^- ion and that in the $A^+e^+e^-e^-$ hydrides. For our present purposes this is a very good approximation. However, it should be noted that the conversion of a γ quantum in the Ps^- ion can be only complete, while in the $A^+e^+e^-e^-$ hydrides one finds also the so-called partial conversion, i.e., the $(\gamma,e^-+\gamma')$ process, which can be described as Compton scattering of annihilation γ quanta in the Coulomb field of the A^+ particle.

The formula for $\Gamma_\gamma(\mathrm{HPs},e^-)$ can be rewritten in another form

$$\Gamma_\gamma(\mathrm{HPs},e^-)=y\frac{8\pi}{3}\zeta\alpha^4\frac{\langle\delta_{+--}(\mathrm{HPs})\rangle}{\langle\delta_{+-}(\mathrm{HPs})\rangle}\Gamma_{2\gamma}(\mathrm{HPs})$$

$$= W_{\gamma,2\gamma}(e)\Gamma_{2\gamma}(\mathrm{HPs})$$
$$= y\times 1.055\,838\,579\times 10^{-8}\frac{\langle\delta_{+--}(\mathrm{HPs})\rangle}{\langle\delta_{+-}(\mathrm{HPs})\rangle}$$
$$\times\Gamma_{2\gamma}(\mathrm{HPs}), \tag{19}$$

where $W_{\gamma,2\gamma}(e)$ is the one-photon internal conversion coefficient for the γ radiation. Thus the approximate value (at $y=1$) for the $W_{\gamma,2\gamma}(e)$ coefficient is $1.055\,838\,579\times 10^{-8}R$, where R is the ratio of the respective δ functions.

B. The second one-photon annihilation rate

Let us consider now the opposite case, i.e., when the emitted photon is converted by the particle A^+ (or proton) in the positronium hydride $A^+e^+e^-e^-$. The appropriate annihilation rate can be designated as $\Gamma_\gamma(\mathrm{HPs},A^+)$. It can be shown that the value of $\Gamma_\gamma(\mathrm{HPs},A^+)$ does not differ significantly from the $\Gamma_\gamma(\mathrm{HPs},e^-)$ value, i.e. $\Gamma_\gamma(\mathrm{HPs},A^+)\approx\Gamma_\gamma(\mathrm{HPs},e^-)$, and we can use the relation $\Gamma_\gamma(\mathrm{HPs},A^+)=u\Gamma_\gamma(\mathrm{HPs},e^-)$, where the factor u approximately equals 1. This means actually that (i) $\Gamma_\gamma(\mathrm{HPs})=\Gamma_\gamma(\mathrm{HPs},e^-)+\Gamma_\gamma(\mathrm{HPs},A^+)=(1+u)\Gamma_\gamma(\mathrm{HPs},e^-)\approx 2\Gamma_\gamma(\mathrm{HPs},e^-)$ and (ii) the $\Gamma_\gamma(\mathrm{HPs},A^+)$ value is very small in comparison to $\Gamma_{2\gamma},\Gamma_{3\gamma}$, etc.

However, in this case (in contrast with all other cases) the question about the final state for the hydrogenlike two-body system A^+e^- is of specific interest. Indeed, in this case the particle A^+ takes the energy $E_e\approx 0.510\,999\,06$ MeV and begins to move. Its velocity is determined by the relation

$$v_A=v(A^+)=c\frac{\sqrt{E_e^2+2m_AE_e}}{m_A+E_e}=0.299\,792\,458\times 10^9$$
$$\times\frac{\sqrt{1+2\cdot x}}{1+x}\ \mathrm{m\ sec^{-1}}=\frac{1}{\alpha}\frac{\sqrt{1+2x}}{(1+x)}\quad \text{a.u.}, \tag{20}$$

where $x=m_A(\mathrm{MeV})/0.510\,999\,06$ MeV and m_A is the particle energy at rest in MeV. It follows from this formula that after positron annihilation in the ${}^\infty\mathrm{H}^+e^+e^-e^-$, we find $v({}^\infty\mathrm{H}^+)=0$ and the remaining ${}^\infty\mathrm{H}^+e^-$ is probably in the bound state, while for the Ps_2 molecule $v(e^+)=(\sqrt{3}/2)c$ and the appropriate system e^+e^- is definitely unbound. For the real positronium hydrides such as TPs, DPs, ^{1}HPs, and MuPs the final system (i.e., T, D, ^{1}H, and μ^+e^- atoms) can be found after positron annihilation either in the bound or in the unbound state. Let us evaluate the appropriate probabilities.

First, let us compare the respective time values. The electron-positron annihilation itself takes time which can be estimated as

$$\tau_a=\frac{\Lambda_e}{c}\approx\frac{3.861\,593\,223\times 10^{-13}}{2.997\,924\,58\times 10^8}$$
$$\approx 1.288\,088\,5\times 10^{-21}\ \mathrm{sec}, \tag{21}$$

where Λ_e is the Compton wavelength of the electron. The changes in the electronic structure proceed for the characteristic time, which is approximately equal to

$$\tau_e=\frac{a_0}{v}\approx\frac{0.529\,177\,249\times 10^{-10}}{\alpha\times 2.997\,924\,58\times 10^8}$$
$$\approx 2.418\,884\,332\times 10^{-17}\ \mathrm{sec}, \tag{22}$$

where a_0 is the Bohr radius and v is the electron speed in the first Bohr orbit.

Since $\tau_a\ll\tau_e$, the so-called sudden approximation should be very good for consideration of annihilation in the polyelectron systems, including positronium hydrides. In this approximation the amplitude to find the final system in the final state $\phi_{fi}(\vec{r}_{k_1},\vec{r}_{k_2},\ldots,\vec{r}_{k_n})$ is represented as the overlap integral [33]

$$A_{\mathrm{in;fi}}=\int d\vec{r}_{k_1}d\vec{r}_{k_1}\cdots d\vec{r}_{k_n}\phi_{\mathrm{in}}(\vec{r}_{k_1},\vec{r}_{k_2},\ldots,\vec{r}_{k_n})$$
$$\times\phi_{\mathrm{fi}}(\vec{r}_{k_1},\vec{r}_{k_2},\ldots,\vec{r}_{k_n})$$
$$=\int d\vec{r}_{k_1}d\vec{r}_{k_2}\cdots d\vec{r}_{k_n}[\hat{S}\hat{P}\Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)]$$
$$\times\phi_{\mathrm{fi}}(\vec{r}_{k_1},\vec{r}_{k_2},\ldots,\vec{r}_{k_n}), \tag{23}$$

where $\Psi(\vec{r}_1,\ldots,\vec{r}_N)$ is the initial wave function for the many-body system (i.e., its wave function before annihilation in the present study) and $\phi_{\mathrm{fi}}(\vec{r}_{k_1},\ldots,\vec{r}_{k_n})$ is the known wave function for the final state. We assume that both of these functions Ψ and ϕ_{fi} are given in the symmetrical form on all identical particles and they are normalized to unity in the whole space.

It should be noted that the total number of variables can be changed after the physical process (e.g., after positron annihilation) or they can correspond to different particles, which are produced in the result of such a process. The operator $\hat{P}=\hat{P}(\vec{r}_{k_1},\vec{r}_{k_2},\ldots,\vec{r}_{k_n};\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_n)$ is the projection operator, which corresponds to the real physical process (i.e. $\hat{P}^2=\hat{P}$ and $\hat{P}^+=\hat{P}$). The operator $\hat{S}=\hat{S}(\vec{r}_{i_1},\vec{r}_{i_2},\ldots,\vec{r}_{i_n};\vec{r}_{k_1},\vec{r}_{k_2},\ldots,\vec{r}_{k_n})$ is the symmetrization operator. This operator permutes indistinguishable particles, which either take part in the process or can be found in the final state. The probability of finding the system A^+e^- in the final state, after annihilation equals $\omega_{\mathrm{fi}}=|A_{\mathrm{in,fi}}|^2$.

In the case of the positronium hydrides $A^+e^+e^-e^-$ we have

$$\phi_{\mathrm{in}}=\hat{S}\hat{P}\Psi=[\Psi(0,r_{A3},0,0,0,0)+\Psi(0,0,0,r_{A4},0,0)]\frac{1}{\sqrt{4\pi}}, \tag{24}$$

where the subscripts 3 and 4 stand for the electrons and A designates the particle A^+. The wave function Ψ is determined variationally by solving the initial four-body problem for the $A^+e^+e^-e^-$ system.

When the final hydrogenlike system A^+e^- is at rest after the positron annihilation the final-state wave function $\phi_{fi}(\vec{r}_{k_1},\ldots,\vec{r}_{k_n})$ takes the form

$$\phi_{\rm fi}=\varphi_{n\ell}(r)Y_{\ell m}\left(\frac{\vec{r}}{r}\right)=\varphi_{n\ell}(r)Y_{\ell m}(\hat{r}), \tag{25}$$

where $\hat{r}=\vec{r}/r$ and $\varphi_{n\ell}(r)$ are the radial eigenfunctions of the discrete spectrum for the hydrogenlike A^+e^- system [24]. $Y_{\ell m}(\hat{r})$ are the usual spherical harmonics [34]. In this case the overlap integrals Eq. (23) take the form

$$A_{\rm in;fi}=A_{{\rm in};n\ell}=\int_0^{+\infty}[\Psi(0,0,0,r,0,0)+\Psi(0,r,0,0,0,0)]\varphi_{n\ell}(r)r^2dr. \tag{26}$$

This case corresponds to the n-photon annihilation process in the positronium hydrides, where $n\geqslant 2$ and after positron annihilation the particle A^+ is immovable. Note also that when the γ quantum is converted by the remaining electron the final state for the A^+e^- system is definitely unbound (see the previous and following subsections).

Now, to complete our consideration we need to study only the case when the emitting γ quantum is converted by the heavy particle A^+, which begins to move. In this case the final state $\phi_{\rm fi}$ is represented in the form

$$\phi_{\rm fi}=\varphi_{n\ell}(r)Y_{\ell m}\left(\frac{\vec{r}}{r}\right)\exp(\imath\vec{q}_{Ae}\cdot\vec{R}_{Ae}), \tag{27}$$

where $\varphi_{n\ell}(r)$ and $Y_{\ell m}(\vec{r}/r)$ are the same as determined above. The function $\exp(\imath\vec{q}_{Ae}\cdot\vec{R}_{Ae})$ corresponds to the free motion (in outside space) of the final hydrogenlike A^+e^- system. Here $\vec{R}_{Ae}$ are the coordinates for the center of mass of the system A^+e^-, i.e.,

$$\vec{R}_{Ae}=\frac{m_e\vec{r}_e+M_A\vec{R}_A}{m_e+M_A}=\frac{m_e\vec{r}_{Ae}}{m_e+M_A}+\vec{R}_A, \tag{28}$$

where $\vec{r}_{Ae}=\vec{r}_e-\vec{R}_A$ are the electron coordinates with respect to the nucleus $\vec{R}_A$ [i.e., $\vec{r}=\vec{r}_{Ae}$, where $\vec{r}$ is used in Eq. (27)]. The variable $\vec{R}_A$ can be left out since for our present purposes only internal variables (i.e., $\vec{r}_{Ae}=\vec{r}$) are important.

Finally, we find for $\phi_{\rm fi}$

$$\phi_{\rm fi}=\varphi_{n\ell}(r)Y_{\ell m}\left(\frac{\vec{r}}{r}\right)\exp\left(\imath\frac{\vec{q}_{Ae}}{1+M_A}\vec{r}\right) \tag{29}$$

in atomic units. By applying the well-known plane-wave expansion we can compute the amplitude and then find the appropriate total probability to find the quasiatom A^+e^- in the $|n\ell\rangle$ bound state

$$\omega_{n\ell}=(2\ell+1)\left|\int_0^{+\infty}[\Psi(0,0,0,r,0,0)+\Psi(0,r,0,0,0,0)]\times j_\ell(q_e r)\varphi_{n\ell}(r)r^2dr\right|^2, \tag{30}$$

where the parameter q_e takes the form (in atomic units):

$$q_e=\frac{q_{Ae}}{1+M_A}=v_{Ae}=v_A\sqrt{\frac{M_A}{1+M_A}}, \tag{31}$$

where the value of v_A after annihilation has been determined above [Eq. (20)].

Now, from Eq. (30) we can calculate the probability of finding the moving A^+e^- system to be bound after positron annihilation: $\omega_B=\Sigma_{n,\ell}\omega_{n,\ell}$, while for an unbound state we have $\omega_U=1-\omega_B$. In particular, the total probability for the system to be in the rotationally excited bound states (with $\ell\geqslant 1$) equals $\omega_{\ell\geqslant 1}=\Sigma_{n,\ell\geqslant 1}\omega_{n,\ell}$, where $n=s+\ell+1$, $s=0,1,2,\ldots$ [35].

C. Zero-photon annihilation rate

Since each of the positronium hydrides is a four-body system, positron annihilation can proceed also as a process without emitting γ radiation. The first emitted γ quantum is converted by the remaining electron, while the second emitted γ quantum is converted by the particle A^+. Actually, it is almost impossible to find the two-body system A^+e^- in the bound state after zero-photon annihilation in the $A^+e^+e^-e^-$ hydride. It is easy to understand that such a process has a relatively small probability, which is represented in the form

$$\Gamma_{0\gamma}({\rm HPs})=\xi\frac{147\sqrt{3}\pi^3}{2}\alpha^{12}ca_0^{-1}\langle\delta_{A+--}\rangle\quad {\rm sec}^{-1}, \tag{32}$$

where $\langle\delta_{A+--}\rangle$ is the so-called four-particle δ function and all other values are the same as determined above. The unknown, dimensionless factor ξ is approximately equal to 1. For the Ps_2 molecule its value is exactly 1 [13].

Following our earlier work [13], we rewrite the expression for the $\Gamma_{0\gamma}$(HPs) in a different form

$$\Gamma_{0\gamma}({\rm HPs})=\xi\frac{147\sqrt{3}\pi^2}{4}\alpha^8\frac{\langle\delta_{A+--}(HPs)\rangle}{\langle\delta_{+-}(HPs)\rangle}\Gamma_{2\gamma}({\rm HPs})=W_{0,2\gamma}\Gamma_{2\gamma}({\rm HPs})=\xi\times 0.505\,173\,540\,9\times 10^{-14}\frac{\langle\delta_{A+--}({\rm HPs})\rangle}{\langle\delta_{+-}({\rm HPs})\rangle}\Gamma_{2\gamma}({\rm HPs}), \tag{33}$$

where $W_{0,2\gamma}$ is the two-photon internal conversion coefficient for the Ps_2 molecule. Unfortunately, the expression for the factor ξ is unknown. However, to evaluate the order of magnitude for $\Gamma_{0\gamma}$(HPs) we can assume that $\xi=1$ (as for the Ps_2 molecule). Such an evaluation is given in Table V.

V. POSITRON ANNIHILATION IN THE POSITRONIUM MOLECULE

Positron annihilation in the positronium molecule Ps_2 was studied in detail in our previous work [13]. However, in [13] we used in the calculations a wave function that was not as accurate as the present one. Now, we apply a significantly better wave function for the positronium molecule. The variational expression for this wave function contains 200 basis functions with better optimized exponents. Its yields the lowest energy for the Ps_2 molecule, $-0.516\,002\,4$ a.u., while the best value known previously is $-0.515\,980$ a.u. [36].

The improved results for a number of properties of the

Ps_2 molecule can be found from Table III together with those for the positronium hydrides. We note that the ''bond length'' between a positron and A^+, namely, $\langle r_{12}\rangle$, increases with decreasing mass of A^+ and the ''stiffness'' of the bond measured by the Pearson coefficient $\pi_{12}=\sqrt{\langle r_{12}^2\rangle/\langle r_{12}\rangle^2-1}$ does the same. The same statement holds for the electron-electron bond descriptors $\langle r_{34}\rangle$ and π_{34}. In general, the positronium hydrides are all about the same geometrical ''size'' and much more compact than Ps_2.

Following in detail [13], we have calculated a number of the different annihilation rates for the Ps_2 molecule (as well as for the Ps^- ion). They are given in Table V, and their comparison with the appropriate values for the positronium hydrides is very interesting. In particular, all $\Gamma_{n\gamma}$ (n is an arbitrary integer) for the positron hydrides $A^+e^+e^-e^-$ decrease monotonically when the mass m_A diminishes. It can be explained easily, since in this case the appropriate δ-function expectation values change respectively. On the comparison with the Ps_2 molecule and Ps^- ion we note the following. According to [37–40], the two-photon annihilation rate for the polyelectron system that contains n electrons and m positrons is determined by the general relation

$$\Gamma_{2\gamma}=C_n^1C_m^1\langle\delta_{+-}\rangle B=nm\langle\delta_{+-}\rangle B, \tag{34}$$

where the C_n^k are the binominal coefficients, $\langle\delta_{+-}\rangle$ is the expectation value for the electron-positron δ function and $B=50.308\,740\,45\times10^9$ sec^{-1}.

The physical meaning of the factor B is quite simple. It is the annihilation rate for the (e^-,e^+) pair, which is in an indefinite spin state. If such a pair is in the $^1S_0$ state (or para-state) then $\Gamma_{2\gamma}=4\pi\alpha^4ca_0^{-1}\langle\delta_{+-}\rangle$ sec^{-1}, while for the $^3S_1$ state (or orthostate) $\Gamma_{2\gamma}=0$. Since the $^1S_0$ state is nondegenerate and the $^3S_1$ state has the multiplicity 3, for an arbitrary (e^-,e^+) pair in the S state with the indefinite total spin we find

$$\Gamma_{2\gamma}=\frac{1}{1+3}[\Gamma_{2\gamma}(^1S_0)+3\Gamma_{2\gamma}(^3S_1)]=\pi\alpha^4ca_0^{-1}\langle\delta_{+-}\rangle$$
$$=B\langle\delta_{+-}\rangle, \tag{35}$$

where $B=50.308\,740\,45\times10^9$ sec^{-1}.

It follows from Eq. (34) that the more electron-positron pairs (nm) in the system the larger the value found for $\Gamma_{2\gamma}$ (and, moreover, for all $\Gamma_{n\gamma}$, where $n\geq2$). The larger $\Gamma_{2\gamma}$ value means the shorter lifetime $\tau_{2\gamma}$ for such a polyelectron system against two-photon annihilation ($\tau_{2\gamma}\simeq1/\Gamma_{2\gamma}$).

It should be mentioned in conclusion that the $\langle\delta_{+-}\rangle$ expectation values are quite close to each other for all positronium hydrides ($\approx2.40\times10^{-2}$ a.u.), the Ps_2 molecule ($\approx2.20\times10^{-2}$ a.u.), and the Ps^- ion ($\approx2.07\times10^{-2}$ a.u.) [41]. Therefore, the deviations in the $\Gamma_{2\gamma}$ values (as well as in all $\Gamma_{n\gamma}$ values, where $n\geq2$) are related mainly with the total number of the electron-positron pairs in the system. In contrast with this, the expectation values of the $\langle\delta_{+--}\rangle$ are comparable only for the Ps_2 molecule and Ps^- ion. For the positronium hydrides the values of $\langle\delta_{+--}\rangle$ and $\langle\delta_{++--}\rangle$ are significantly larger than those for the Ps_2 molecule. This means that the difference in the $\Gamma_{1\gamma}$ and $\Gamma_{0\gamma}$ can be explained mainly in terms of the deviations in the $\langle\delta_{+--}\rangle$ and $\langle\delta_{A+--}\rangle$ expectation values. Likewise, in the present study the $\Gamma_{1\gamma}$ and $\Gamma_{0\gamma}$ values for the positronium hydrides contain the three parameters (y,u and ξ) that must be determined in further quantum-electrodynamics calculations.

VI. CONCLUSION

Thus the bound-state spectra have been considered in the present study for the positronium hydrides, such as $^\infty$HPs, TPs, DPs, ^{1}HPs, and MuPs. A number of basic properties for such systems have been calculated numerically by applying the very extensive variational expansion on the so-called six-dimensional (or four-body) gaussioids [42]. In particular, a quite accurate interpolation formula is presented for the dependence $E(m_A^{-1})$. Also, we considered the fine and hyperfine structures for the bound states in such systems. The analysis of the (e^-,e^+) pair or positron annihilation is the main content of the present work. The appropriate values of $\Gamma_{n\gamma}$ ($n=0,1,2,\ldots,10$) are calculated numerically or evaluated approximately for all five positronium hydrides as well as for the positronium molecule (Ps_2) and for the positronium ion Ps^-. It is shown that the many-photon annihilation rates $\Gamma_{n\gamma}$ (where $n\geq2$) for the positronium hydrides are significantly closer to the appropriate values for the Ps^- ion than those for the Ps_2 molecule. For these values we can write

$$\Gamma_{n\gamma}(Ps^-)<\Gamma_{n\gamma}(HPs)<\Gamma_{n\gamma}(Ps_2) \tag{36}$$

and, moreover, $\Gamma_{n\gamma}(HPs)\approx\Gamma_{n\gamma}(Ps^-)$. It should be mentioned that the presented formulas for the $\Gamma_\gamma(HPs,e^-)$, $\Gamma_\gamma(HPs,H^+)$, and $\Gamma_{0\gamma}(HPs)$ contain the three unknown factors y,u, and ξ, which are close to unity. The exact values of these factors should be found in the following quantum-electrodynamics considerations. Also, we discussed the final-state problem for the remaining (after annihilation) quasiatomic A^+e^- system.

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APPENDIX

To compute the bound state in the considered Coulomb four-body systems we used the variational expansion in the basis of the many-dimensional gaussoids proposed in [42]. The appropriate six-dimensional (or four-body) variational anzatz is

$$\Psi_{L=0}=\mathcal{A}_{1234}\sum_{k=1}^{N}C_k\exp(-\alpha_{12}^kr_{12}^2-\alpha_{13}^kr_{13}^2-\alpha_{23}^kr_{23}^2-\alpha_{14}^kr_{14}^2$$
$$-\alpha_{24}^kr_{24}^2-\alpha_{34}^kr_{34}^2) \tag{A1}$$

where C_k are the linear variational parameters and α_{ij}^k are the non-linear parameters. The operator $\mathcal{A}_{1234}$ designates the appropriate symmetrizer (or antisymmetrizer), i.e., a projection operator that produces the final wave function with the correct permutation symmetry. Actually, in the present study

there are a maximum of two different pairs of identical particles and the operator $\mathcal{A}_{1234}$ can be easily constructed.

To present explicit formulas for the matrix elements we use the [42] notation

$$\langle\alpha| = \langle\alpha^{(k)}| = \exp\left(-\sum_{i>j=1}^{A} \alpha_{ij}^{k} \cdot r_{ij}^{2} \right),$$

and

$$|\beta\rangle = |\beta^{(\not)}\rangle = \exp\left(-\sum_{i>j=1}^{A} \beta_{ij}^{\not} r_{ij}^{2} \right), \tag{A2}$$

where A is the total number of the particles in the system. In the present case $A=4$. In this notation the overlap matrix element $\langle\alpha|\beta\rangle$ takes the form

$$\langle\alpha|\beta\rangle = \langle\alpha^{(k)}|\beta^{(\not)}\rangle = \pi^{3A-(1/2)} D^{-3/2}, \tag{A3}$$

where D is the determinant of the $(A-1)\times(A-1)$ matrix with the matrix elements

$$b_{ii} = \sum_{j\neq i}^{A} (\alpha_{ij}^{k} + \beta_{ij}^{\not}), \quad i = 1,2,\ldots,A-1$$

$$b_{ij} = -\alpha_{ij}^{k} - \beta_{ij}^{\not}, \quad i \neq j = 1,2,\ldots,A-1 \quad . \tag{A4}$$

For an arbitrary potential that may be written as the sum of the central (partial) potentials, i.e., $W = \Sigma_{(ij)} V_{(ij)}(r_{ij})$, the formula for the appropriate matrix elements takes the form

$$\sum_{(ij)} \langle\alpha|V_{(ij)}(r_{ij})|\beta\rangle = \frac{4}{\sqrt{\pi}} \langle\alpha|\beta\rangle \times \sum_{(ij)} \int_{0}^{+\infty} V_{(ij)}\left(x\sqrt{\frac{D_{ij}}{D}} \right) \exp(-x^2) \cdot x^2 dx, \tag{A5}$$

where $D_{ij} = \partial D/\partial\alpha_{ij} = \partial D/\partial\beta_{ij}$. The explicit expressions for five (and even more) forms of the potentials often used in calculations can be found in [42] [including formulas for lower bound estimates (E_L) for an arbitrary A-particle system]. In particular, matrix elements of the Coulomb potential energy are (in quasi-atomic-units)

$$\sum_{(ij)} \langle\alpha|V_{ij}(r_{ij})|\beta\rangle = \sum_{(ij)} \left\langle \alpha \left| \frac{q_i q_j}{r_{ij}} \right| \beta \right\rangle = 2\sqrt{\frac{D}{\pi}} \langle\alpha|\beta\rangle \sum_{(ij)} \frac{q_i q_j}{\sqrt{D_{ij}}}, \tag{A6}$$

where (ij) = (21), (31), (32), (41), (42), and (43) and $\langle\alpha|\beta\rangle$ is the appropriate overlap matrix element. In Eq. (A6) the q_i $(i=1,2,\ldots,A)$ are the charges of the particles and $D_{ij} = \partial D/\partial\alpha_{ij} = \partial D/\partial\beta_{ij}$. The matrix elements for the kinetic energy take the form (in quasi-atomic-units)

$$\langle\beta|T|\alpha\rangle = \frac{3}{2D}\left[\sum_{ijk=1}^{A} \frac{\alpha_{ik}\beta_{jk}}{m_k} (D_{ik} + D_{jk} - D_{ij}) \right] \langle\beta|\alpha\rangle, \tag{A7}$$

where m_i $(i=1,2,\ldots,A)$ are the masses of the particles and $i \neq j \neq k$. The following symmetrization of the given expressions on the identical particles does not present any special difficulties.

For an arbitrary self-adjoint operator $\hat{X}$ the corresponding property (or the expectation value) is determined as

$$\langle X\rangle = \frac{\langle\psi|\hat{X}|\psi\rangle}{\langle\psi|\psi\rangle} \quad , \tag{A8}$$

where $|\psi\rangle$ is the appropriate wave function found in variational calculations. When $\hat{X} = f(r_{ij})$ we used the formula to compute the appropriate matrix elements

$$\langle\alpha|f(r_{ij})|\beta\rangle = \langle\alpha^{(k)}|f(r_{ij})|\beta^{(\not)}\rangle = \frac{4}{\sqrt{\pi}} \langle\alpha|\beta\rangle \times \int_{0}^{+\infty} f\left(x\sqrt{\frac{D_{ij}}{D}} \right) \exp(-x^2) x^2 dx. \tag{A9}$$

In particular, for $f(y) = y^{2n-1}$ $(n = 0,1,2,\ldots)$ we find

$$\langle\alpha|r_{ij}^{2n-1}|\beta\rangle = \frac{2}{\sqrt{\pi}} \langle\alpha|\beta\rangle n! \left(\frac{D_{ij}}{D} \right)^{(2n-1)/2}, \tag{A10}$$

while for $f(y) = y^{2n}$ $(n = 0,1,2,\ldots)$ we have

$$\langle\alpha|r_{ij}^{2n}|\beta\rangle = \langle\alpha|\beta\rangle \frac{(2n+1)!!}{2^n} \left(\frac{D_{ij}}{D} \right)^{n}, \tag{A11}$$

where $(2n+1)!!$ means $1\times3\times5\times\cdots\times(2n+1)$. When $f(y) = y^{-2}$ the appropriate formula takes the form

$$\langle\alpha|r_{ij}^{-2}|\beta\rangle = 2\langle\alpha|\beta\rangle \frac{D}{D_{ij}}. \tag{A12}$$

It should be noted that by applying the expectation values given in Table III we can calculate a number of other properties, e.g., the Pearson correlation coefficients π_{ij},

$$\pi_{ij} = \frac{\sqrt{\langle r_{ij}^2\rangle - \langle r_{ij}\rangle^2}}{\langle r_{ij}\rangle}, \tag{A13}$$

and $\langle \mathbf{r}_{ij} \cdot \mathbf{r}_{kl} \rangle$ values.

Let us consider the analytical formulas for the δ functions, which can be also found in [13]. First, it should be mentioned that all expectation values for the *cusp* values [43] vanish since for Eq. (A1) one finds

$$\lim_{\vec{r}_i \to \vec{r}_j} \delta(\vec{r}_i - \vec{r}_j) \frac{\partial \Psi_{L=0}}{\partial r_{ij}} = 0 \tag{A14}$$

and $\Psi_{L=0}$ is a finite function at the $\vec{r}_i = \vec{r}_j$ point. This means that direct *cusp* value calculations are impossible for the variational expression on the many-dimensional Gaussian basis functions such as Eq. (A1).

The analytical expressions for two-, three-, and four-particle δ functions can be found, e.g., in [13]. The simplest expression can be found for the four-particle delta-function

$$\langle\alpha|\delta_{4321}|\beta\rangle=1. \tag{A15}$$

The analytical formula for the three-particle (321) δ function is

$$\langle\alpha|\delta_{321}|\beta\rangle=\left(\frac{\pi}{a_{14}+a_{24}+a_{34}}\right)^{3/2}, \tag{A16}$$

where $a_{ij}=\alpha_{ij}+\beta_{ij}$. Analogous expressions for the other expectation values of the three-particle (431), (432), and (421), δ functions can be obtained from this expression by simple permutations. For the two-body (41) δ function we find

$$\langle\alpha|\delta_{41}|\beta\rangle=\left(\frac{\pi}{\sqrt{B}}\right)^{3}, \tag{A17}$$

where $B=(a_{12}+a_{24}+a_{23})(a_{13}+a_{34}+a_{23})-a_{23}^2$ Again, all formulas for the other two-particle (21), (31), (32), (42), and (43) δ functions can be obtained from this expression by simple permutations.

The so-called dimensionless virial factor χ (see Table III) is

$$\chi=\left|1+\frac{2\langle T\rangle}{\langle V\rangle}\right|\approx 0, \tag{A18}$$

where $\langle T\rangle$ is the expectation value of the kinetic energy, while $\langle V\rangle$ is the expectation value of the potential energy. The deviation of this parameter from zero indicates the quality of the wave function used. In the case $\chi=0$ the virial theorem holds exactly (see, e.g., [44]).

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nificantly even at small e^--e^+ distances. The energy of this field on the K-shell distances can be evaluated to be approximately 50–100 keV, which is not negligible in comparison with $m_e c^2 \approx 510.999\,06$ keV. As a result, one finds that the expression for Γ_γ (a) does not contain any many-particle δ functions and (b) the numerical value Γ_γ is quite comparable with the $\Gamma_{2\gamma}$ value ($\Gamma_\gamma : \Gamma_{2\gamma} \approx 0.1-0.2$) for these systems. However, this case is not of interest in our present study.

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