Positronium: Theory Versus Experiment

Richard Ley and Günter Werth

Institut für Physik, Johannes Gutenberg - Universität, D-55099 Mainz, Germany

Abstract. We have collected all known theoretical contributions to the energy levels of positronium and present a complete listing for the states $n = 1,\ 2$ and 3. We give the explicit dependence of the energy levels on the quantum numbers $n,\ L,\ S$ and J up to the order $R_\infty\alpha^3$. In the next higher order $R_\infty\alpha^4$ only the contributions to S- and P-states are completely known. The annihilation rates of para- and ortho-positronium are completely listed up to the orders $R_\infty\alpha^5$ and $R_\infty\alpha^6$, respectively. We compare calculated values of energy levels and annihilation rates with experimentally observed quantities.

1 Introduction

Positronium (Ps, e^+e^-) is the bound state of an electron and its antiparticle the positron. Both constituents are structureless and pointlike leptons. The absence of structure avoids the difficulties encountered in hydrogen due to the composite nature of the proton. The advantage, compared with muonium (μ^+e^-) is the absence of an additional free parameter like the muon mass. Ps is completely described by only two fundamental constants [1,2], the Rydberg constant

$$cR_\infty = \frac{mc^2\alpha^2}{2h} = 3\ 289\ 841\ 960.368\ (25)\ \text{MHz} \tag{1}$$

and the fine structure constant

$$\alpha = \frac{\mu_0 ce^2}{2h} = 1/137.035\ 999\ 76\ (50)\ . \tag{2}$$

The weak interaction and quantum chromo-dynamics (QCD) play no role at the present level of accuracy.

Moreover Ps is an exotic atom being an eigenstate of the charge conjugation operator. As a consequence real and virtual annihilations lead to additional Feynman diagrams which are absent in hydrogen and muonium, but can easily be tested in Ps. The disadvantage connected with annihilation is the broadening of certain energy levels.

For all these reasons Ps is an ideal candidate for precision tests of bound state quantum electrodynamics (QED).

2 Theoretical expressions for the energy levels

The S- and P-energy levels of Ps have been completely calculated [3,4] up to the order $R_\infty\alpha^4$. In the next higher order $R_\infty\alpha^5$ only the leading logarithmic contribution to S-states is known (citation in [3]). The parameters R_∞ and α are so accurate that the theoretical uncertainty results almost only from uncalculated higher order terms and is estimated to be 700 kHz for the ground state $n = 1$ and 10 kHz for excited $2P$-states. The gross structure of the energy levels scales as $1/n^2$. The contributions to fine and hyperfine structure and their uncertainties scale roughly as $1/n^3$. The explicit dependence of the energy levels on the main quantum number n, on the orbital quantum number L, on the total spin quantum number S and on the total angular momentum $J = |\vec{L} + \vec{S}|$ has been given in [5] up to the order $R_\infty\alpha^2$. In the next higher order $R_\infty\alpha^3$ the explicit dependence on the quantum numbers is not yet published to our knowledge. It can be obtained, e.g, from [6] by using their formulas (3.2) and (3.3) with the matrix elements

$$\langle L,S,J|LS|L,S,J\rangle = \frac{1}{2}[J(J+1) - L(L+1) - S(S+1)]\ , \tag{3}$$

$$\langle L=J,S=0,J|S_{12}|L=J,S=0,J\rangle = 0\ , \tag{4}$$

$$\langle L=J-1,S=1,J|S_{12}|L=J-1,S=1,J\rangle = \frac{6(J+1)}{2J+1} - 4\ , \tag{5}$$

$$\langle L=J,S=1,J|S_{12}|L=J,S=1,J\rangle = 6-4=2\ , \tag{6}$$

$$\langle L=J+1,S=1,J|S_{12}|L=J+1,S=1,J\rangle = \frac{6J}{2J+1} - 4\ , \tag{7}$$

$$\langle L=J-1,S=1,J|S_{12}|L=J+1,S=1,J\rangle = \frac{6\sqrt{J(J+1)}}{2J+1} \tag{8}$$

and

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{(2a_0)^3\, n^3\, L(L+1)(L+1/2)} \qquad \text{for } \ L \neq 0\ . \tag{9}$$

Where $a_0 = \hbar/m\alpha c \simeq 0.529\times10^{-10}$ m is the Bohr radius and

$$S_{12} = \frac{3(\vec{\sigma_1}\,\vec{r}\,)(\vec{\sigma_2}\,\vec{r}\,)}{r^2} - \vec{\sigma_1}\vec{\sigma_2} \tag{10}$$

is the tensor operator whose matrix elements are given in e.g. [7]. The tensor operator has a potential which is not central symmetric. As a consequence (10) has off-diagonal matrix elements between L and $L \pm 2$ given in (8) which mix different L-states of the same parity. This is a familiar effect in nuclei, e.g. in the deuteron whose angular momentum of 1 is a mixture of a ${}^3S_1$-state and a ${}^3D_1$-state. For Ps a similar mixture between the 3^3S_1-state and the 3^3D_1-state does not occur, because the radial part of matrix element $\left\langle 3^3S_1 \left| S_{12}/r^3 \right| 3^3D_1 \right\rangle$ is zero when calculated with hydrogenic wave functions.

With the matrix elements (3) to (9) the explicit dependence of the energy levels on the quantum numbers n, L, S and J can be given up to the order $R_\infty\alpha^3$:

$$
\begin{aligned}
\frac{E(nLSJ)}{cR_\infty} = & -\frac{1}{2n^2} + \qquad (11)\\
& + \frac{\alpha^2}{n^3}\left[\frac{11}{32\,n} - \frac{1}{2L+1} + \frac{7}{6}\delta_{1S}\delta_{0L} + \right.\\
& + \frac{\delta_{1S}(1-\delta_{0L})}{2L(L+1)(2L+1)} \times \left\{ \begin{array}{ll} \dfrac{L(3L+4)}{2L+3}\,, & \text{for } J=L+1 \\ -\,1\,, & \text{for } J=L \\ -\,\dfrac{(L+1)(3L-1)}{2L-1}\,, & \text{for } J=L-1 \end{array} \right]\\
& + \frac{\alpha^3}{n^3\pi}\left[-\left(\frac{3}{2}\ln\alpha\right)\delta_{0L} - \frac{4}{3}\ln k_0(n,L) + \right.\\
& + \left\{\frac{203}{180} + \frac{7}{12\,n} + \frac{7}{3}\ln 2 + \frac{7}{6}\left(\sum_{k=1}^{n}\frac{1}{k} - \frac{1}{n} - \ln n\right)\right\}\delta_{0L} - \\
& - \frac{7}{12} \times \frac{1-\delta_{0L}}{L(L+1)(2L+1)} - \left(\frac{16}{9} + \ln 2\right)\delta_{1S}\delta_{0L} + \\
& + \frac{\delta_{1S}(1-\delta_{0L})}{4L(L+1)(2L+1)} \times \left\{ \begin{array}{ll} \dfrac{L(4L+5)}{2L+3}\,, & \text{for } J=L+1 \\ -\,1\,, & \text{for } J=L \\ -\,\dfrac{(L+1)(4L-1)}{2L-1}\,, & \text{for } J=L-1 \end{array} \right]\,.
\end{aligned}
$$

The Bethe logarithms $\ln k_0(n,L)$ in (11) are given with very high accuracy in [8] :

$$
\begin{array}{llll}
\ln k_0(1,0) = 2.984\,128\,555\,765\,498\,; & \ln k_0(2,1) = -\,0.030\,016\,708\,630\,213\,; \\
\ln k_0(2,0) = 2.811\,769\,893\,120\,563\,; & \ln k_0(3,1) = -\,0.038\,190\,229\,385\,312\,; \\
\ln k_0(3,0) = 2.767\,663\,612\,491\,822\,; & \ln k_0(3,2) = -\,0.005\,232\,148\,140\,883\,.
\end{array}
$$

The contributions in the order $R_\infty\alpha^4$ to the individual energy levels are listed in table[1] 1. We note that there is a degeneracy between the levels 3^3P_2 and 3^3D_2 up to the order $R_\infty\alpha^2$. In the next order the degeneracy is removed by 0.746 MHz (cf. Appendix).

[1] The Riemann zeta-function is here: $\zeta(3) = 1.202\,056\,903\,159\,594\,285\,4\ldots$

Table 1. Contributions to the positronium energy levels in units of cR_∞. In order to keep the size of the table as small as possible the following contributions which must be added to all energy levels have been omitted: the lowest order contribution $-\frac{1}{2n^2}$ and the contribution with the Bethe logarithm $-\frac{4}{3}\frac{\alpha^3}{n^3\pi}\ln k_0(n,L)$

level	$\frac{\alpha^2}{n^3}$	$\frac{\alpha^3}{n^3\pi}\times$				$\frac{\alpha^4}{n^3}\times$							$\frac{\alpha^5\ln^2\alpha}{n^3\pi}$
$n^{2S+1}L_J$		$\ln\alpha$	$\ln 3$	$\ln 2$	1	$\ln\alpha$	$\ln 3$	$\ln 2$	$\frac{\ln 2}{\pi^2}$	$\frac{1}{\pi^2}$	$\frac{\zeta(3)}{\pi^2}$	1	
1^1S_0	$-\frac{21}{32}$	$-\frac{3}{2}$	0	$+\frac{7}{3}$	$+\frac{77}{45}$	$+\frac{1}{4}$	0	$-\frac{7}{8}$	-5	$+\frac{1}{8}$	$+\frac{75}{16}$	$+\frac{8881}{6912}$	$-\frac{23}{30}$
1^3S_1	$+\frac{49}{96}$	$-\frac{3}{2}$	0	$+\frac{4}{3}$	$-\frac{1}{15}$	$-\frac{1}{6}$	0	$+\frac{79}{36}$	-4	$+\frac{2815}{648}$	$+\frac{11}{8}$	$-\frac{441}{256}$	$-\frac{151}{60}$
2^1S_0	$-\frac{53}{64}$	$-\frac{3}{2}$	0	$+\frac{7}{6}$	$+\frac{931}{360}$	$+\frac{1}{4}$	0	$-\frac{9}{8}$	-5	$+\frac{1}{8}$	$+\frac{75}{16}$	$+\frac{77177}{55296}$	$-\frac{23}{30}$
2^3S_1	$+\frac{65}{192}$	$-\frac{3}{2}$	0	$+\frac{1}{6}$	$+\frac{97}{120}$	$-\frac{1}{6}$	0	$+\frac{85}{36}$	-4	$+\frac{2815}{648}$	$+\frac{11}{8}$	$-\frac{8143}{6144}$	$-\frac{151}{60}$
2^1P_1	$-\frac{31}{192}$	0	0	0	$-\frac{7}{72}$	0	0	0	0	0	0	$+\frac{3001}{55296}$	0
2^3P_0	$-\frac{95}{192}$	0	0	0	$-\frac{25}{72}$	0	0	$+\frac{1}{4}$	0	$-\frac{203}{288}$	$-\frac{3}{8}$	$-\frac{30215}{55296}$	0
2^3P_1	$-\frac{47}{192}$	0	0	0	$-\frac{5}{36}$	0	0	$+\frac{1}{24}$	0	$-\frac{179}{1728}$	$-\frac{1}{16}$	$+\frac{745}{55296}$	0
2^3P_2	$-\frac{43}{960}$	0	0	0	$-\frac{1}{45}$	0	0	$-\frac{3}{40}$	0	$+\frac{13}{64}$	$+\frac{9}{80}$	$+\frac{587909}{6912000}$	0
3^1S_0	$-\frac{85}{96}$	$-\frac{3}{2}$	$-\frac{7}{6}$	$+\frac{7}{3}$	$+\frac{553}{180}$	$+\frac{1}{4}$	$-\frac{1}{4}$	$-\frac{7}{8}$	-5	$+\frac{1}{8}$	$+\frac{75}{16}$	$+\frac{1211}{768}$	$-\frac{23}{30}$
3^3S_1	$+\frac{9}{32}$	$-\frac{3}{2}$	$-\frac{7}{6}$	$+\frac{4}{3}$	$+\frac{233}{180}$	$-\frac{1}{6}$	$+\frac{1}{6}$	$+\frac{79}{36}$	-4	$+\frac{2815}{648}$	$+\frac{11}{8}$	$-\frac{9089}{6912}$	$-\frac{151}{60}$
3^1P_1	$-\frac{7}{32}$	0	0	0	$-\frac{7}{72}$	0	0	0	0	0	0	$+\frac{121}{2304}$	0
3^3P_0	$-\frac{53}{96}$	0	0	0	$-\frac{25}{72}$	0	0	$+\frac{1}{4}$	0	$-\frac{203}{288}$	$-\frac{3}{8}$	$-\frac{3797}{6912}$	0
3^3P_1	$-\frac{29}{96}$	0	0	0	$-\frac{5}{36}$	0	0	$+\frac{1}{24}$	0	$-\frac{179}{1728}$	$-\frac{1}{16}$	$+\frac{95}{6912}$	0
3^3P_2	$-\frac{49}{480}$	0	0	0	$-\frac{1}{45}$	0	0	$-\frac{3}{40}$	0	$+\frac{13}{64}$	$+\frac{9}{80}$	$+\frac{76163}{864000}$	0
3^1D_2	$-\frac{41}{480}$	0	0	0	$-\frac{7}{360}$								0
3^3D_1	$-\frac{27}{160}$	0	0	0	$-\frac{7}{90}$								0
3^3D_2	$-\frac{49}{480}$	0	0	0	$-\frac{1}{36}$								0
3^3D_3	$-\frac{127}{3360}$	0	0	0	$+\frac{29}{2520}$								0

To demonstrate the use of table 1 we give an explicit example:

$$\frac{E(3^3S_1)}{cR_\infty} = -\left\{\frac{1}{18}\right\} + \frac{\alpha^2}{27}\left\{+\frac{9}{32}\right\} + \tag{12}$$
$$+\frac{\alpha^3}{27\,\pi}\left\{-\frac{4}{3}\ln k_0(3,0) - \frac{3}{2}\ln\alpha - \frac{7}{6}\ln 3 + \frac{4}{3}\ln 2 + \frac{233}{180}\right\} +$$
$$+\frac{\alpha^4}{27}\left\{-\frac{1}{6}\ln\alpha + \frac{1}{6}\ln 3 + \frac{79}{36}\ln 2 - 4\frac{\ln 2}{\pi^2} + \frac{2815}{648\,\pi^2} + \frac{11}{8}\frac{\zeta(3)}{\pi^2} - \frac{9089}{6912}\right\}$$
$$+\frac{\alpha^5\ln^2\alpha}{27\,\pi}\left\{-\frac{151}{60}\right\}.$$

The contributions in table 1 and, e.g. in equation (12) containing the factor $\ln 3$ result in full generality from factors $\ln n$ which for $n = 2$ are contracted with the contributions containing $\ln 2$. The apparent divergence of $\ln n$ for large n is prohibited since it always occurs in the combination [cf. equation(11)]:

$$\left(\sum_{k=1}^{n}\frac{1}{k} - \frac{1}{n} - \ln n\right) \rightarrow \gamma_E = 0.577\ldots \text{ (Euler's constant)} \quad \text{for} \quad n \rightarrow \infty\,.$$

For comparison with theoretical publications we note that

$$\left(\sum_{k=1}^{n}\frac{1}{k} - \frac{1}{n}\right) = \Psi(n) + \gamma_E\,,$$

where $\Psi(n)$ is called the *logarithmic derivative of the Γ-function*. The numerical values of the energy levels for the different orders in α are given in the appendix.

3 Theoretical expressions for the annihilation rates

The contributions from Feynman diagrams with virtual annihilation have complex values. Their real parts lead to energy shifts (which are absent in hydrogen and muonium), their imaginary parts lead to annihilation rates. Since Ps is an eigenstate to the charge conjugation operator with the eigenvalue $(-1)^{L+S}$ and since a n-photon state is an eigenstate to the charge conjugation operator with the eigenvalue $(-1)^n$ it is strictly specified that $^1S_0$-states (para-Ps) decay into an even number of photons and that $^3S_1$-states (ortho-Ps) decay into an odd number of photons. The annihilation rates scale roughly as $1/n^3$. For non S-states the annihilation is completely negligible compared to radiative transitions.

For the 1^1S_0 ground state of para-Ps a complete calculation of the two photon decay up to the order $R_\infty\alpha^5$ has recently been given in [9] . The most precise theoretical value for the branching ratio of the four photon decay is given in [10].

We summarize:

$$\begin{aligned}
\lambda(\text{para}) &= \lambda_2 \ + \ \lambda_4 \ + \ \lambda_6 \ + \ \cdots \ = \ 7\,989.510\,(23) \times 10^6 \ \mathrm{s}^{-1} \ , \\
\lambda_2 &= \lambda_2^{(0)} \left\{ 1 - \frac{\alpha}{\pi}\left(5 - \frac{\pi^2}{4}\right) - \right. \\
&\qquad \left. - \, 2\alpha^2 \ln\alpha + \left(\frac{\alpha}{\pi}\right)^2 [\, 1.75\,(30)\,] - \frac{3\alpha^3}{2\pi} \ln^2\alpha + \cdots \right\} \\
&= 7\,989.498\,(23) \times 10^6 \ \mathrm{s}^{-1} \ , \qquad (13) \\
\frac{\lambda_4}{\lambda_2} &= 1.479\,3\,(18) \ \times 10^{-6} \ = \ \left(\frac{\alpha}{\pi}\right)^2 [\, 0.274\,17\,(34)\,] \ , \\
\lambda_4 &= 0.011\,85\,(3) \ \times 10^6 \ \mathrm{s}^{-1} \ , \\
\lambda_2^{(0)} &= \frac{mc^2\alpha^5}{2\hbar} \ = \ 2\pi c R_\infty \alpha^3 \ = \ 8\,032.502\,808\,(90) \times 10^6 \ \mathrm{s}^{-1} \ .
\end{aligned}$$

For the 1^3S_1 ground state of ortho-Ps a complete calculation of the three photon decay up to the order $R_\infty\alpha^6$ has recently been given in [11]. The most precise theoretical value for the branching ratio of the five photon decay is given in [12]:

$$\begin{aligned}
\lambda(\text{ortho}) &= \lambda_3 \ + \ \lambda_5 \ + \ \lambda_7 \ + \ \cdots \ = \ 7.039\,941\,(20) \times 10^6 \ \mathrm{s}^{-1} \ , \\
\lambda_3 &= \lambda_3^{(0)} \left\{ 1 + \frac{\alpha}{\pi} [-10.286\,606\,(10)\,] \ + \right. \\
&\qquad \left. + \, \frac{\alpha^2}{3} \ln\alpha + \left(\frac{\alpha}{\pi}\right)^2 [\, 44.52\,(26)\,] - \frac{3\alpha^3}{2\pi} \ln^2\alpha + \cdots \right\} \\
&= 7.039\,934\,(20) \times 10^6 \ \mathrm{s}^{-1} \ , \qquad (14) \\
\frac{\lambda_5}{\lambda_3} &= 0.959\,1\,(8) \ \times 10^{-6} \ = \ \left(\frac{\alpha}{\pi}\right)^2 [\, 0.177\,76\,(15)\,] \ , \\
\lambda_5 &= 6.8\,(1) \ \mathrm{s}^{-1} \ , \\
\lambda_3^{(0)} &= \frac{mc^2\alpha^6}{\hbar} \times \frac{2\,(\pi^2 - 9)}{9\pi} \ = \ 4\pi c R_\infty \alpha^4 \times \frac{2\,(\pi^2 - 9)}{9\pi} \\
&= 7.211\,166\,97\,(11) \times 10^6 \ \mathrm{s}^{-1} \ .
\end{aligned}$$

The theoretical uncertainties of λ_2 and λ_3 result to almost equal parts from the uncertainty of the $(\alpha/\pi)^2$- coefficient and from an estimate of the uncalculated higher order contributions which are taken to be 50 % of the highest leading logarithmic term.

4 Comparison between theory and experiment

The theoretical predictions for transition frequencies and decay rates in Ps have presently reached a level of precision which is a challenge to experimentalists!

4.1 Spectroscopy

For the spectroscopic results it can be seen from table 2 that in general there is reasonable agreement between theory and experiment within one or two standard deviations.

Table 2. Comparison between experiment and theory for some transition frequencies and energy level differences. Where two values are given for the experimental error the first one is statistical and the second one is systematic. For the differences between the $2P$-states all experimental uncertainties have been added in quadrature. The theoretical uncertainties are estimates of the yet uncalculated higher order contributions

	Experiment [MHz]		Theory [MHz] [3] [4]
$1^3S_1 \to 2^3S_1$	$1\,233\,607\,216.40 \pm 3.20$	[13]	$1\,233\,607\,222.166 \pm 0.600$
$1^3S_1 \to 1^1S_0$	$203\,389.10 \pm 0.74$	[14]	$203\,392.010 \pm 0.500$
	$203\,387.50 \pm 1.60$	[15]	
$2^3S_1 \to 2^1S_0$	not yet measured		$25\,424.672 \pm 0.060$
$2^3S_1 \to 2^3P_0$	$18\,499.65 \pm 1.20 \pm 4.00$	[16]	$18\,498.246 \pm 0.090$
	$18\,504.10 \pm 10.0 \pm 1.70$	[17]	
$2^3S_1 \to 2^3P_1$	$13\,012.42 \pm 0.67 \pm 1.54$	[16]	$13\,012.407 \pm 0.090$
	$13\,001.30 \pm 3.90 \pm 0.90$	[17]	
$2^3S_1 \to 2^3P_2$	$8\,624.38 \pm 0.54 \pm 1.40$	[16]	$8\,626.709 \pm 0.090$
	$8\,619.60 \pm 2.70 \pm 0.90$	[17]	
	$*$ $8\,628.40 \pm 2.80$	[18]	
$2^3S_1 \to 2^1P_1$	$11\,180.00 \pm 5.00 \pm 4.00$	[16]	$11\,185.372 \pm 0.090$
	$11\,181.00 \pm 13.00$	[19]	
$2^3P_0 - 2^3P_1$	$5\,487.23 \pm 4.50$	[16]	$5\,485.839 \pm 0.010$
	$5\,502.80 \pm 10.9$	[17]	
$2^3P_2 - 2^3P_1$	$4\,388.04 \pm 2.25$	[16]	$4\,385.698 \pm 0.010$
	$4\,381.70 \pm 4.91$	[17]	
$2^1P_1 - 2^3P_1$	$1\,832.40 \pm 6.60$	[16]	$1\,827.035 \pm 0.010$
	$1\,820.30 \pm 13.60$	[19]	

$*$ measured in a magnetic field of 54 Gauss with a kinetic energy of some eV.

However there is one exception: the most precise experimental value for the ground state hyperfine splitting [14] is 3.2 standard deviations below the theory if we add the experimental and the theoretical uncertainties in quadrature. This experiment has been performed in a 0.8 Tesla magnetic field where a Breit-Rabi transition at 2.5 GHz having a line width of 10 MHz is used to determine the hyperfine splitting of 203 GHz. Considering the problems with the line shape and the pressure shift a discrepancy of 3 MHz should probably be taken not to serious. In any case, as a control, the hyperfine splitting at 25.4 GHz in the excited state $n = 2$ should be directly measured in zero magnetic field. This can be done with the technique used in [16] by observing the disappearance of the electric dipole transition $2^3S_1 \rightarrow 2^3P_0$ at 18.5 GHz when the metastable state 2^3S_1 is depopulated by the magnetic dipole transition $2^3S_1 \rightarrow 2^1S_0$.

In future improvements the uncertainties of the fine structure transitions $2^3S_1 \rightarrow 2P$ can be reduced to less than 0.5 MHz by using higher positron intensities and by eliminating known systematic errors.

The Doppler-free two photon transition $1^3S_1 \rightarrow 2^3S_1$ at 1.23×10^{15} Hz[2] [13] can be improved to an accuracy limited only by the natural line width of 1 MHz if recent techniques for the frequency counting in the optical region are used [20,21,22].

For the intensities of the allowed dipole transitions $2^3S_1 \rightarrow 2^3P_{J=0,1,2}$ at 18.5, 13.0 and 8.6 GHz theory predicts intensity ratios of 1:2:3 which result from Clebsch-Gordan coefficients determining the relative size of the electric dipole matrix elements. These intensity ratios have been confirmed in [16].

The one photon transition $2^3S_1 \rightarrow 2^1P_1$ is strictly forbidden in zero magnetic field by charge conjugation invariance (in contrast to corresponding transitions in hydrogen). However in a magnetic field singlet- and triplet-states are mixed and the transition becomes observable. The intensity and the frequency shift in weak magnetic fields B are proportional to B^2. The frequency given in table 2 is obtained by extrapolation to zero field. From the data in [16] and [19] an upper limit for a possible C-violating matrix element was deduced which corresponds to a suppression factor of more than 1000 for this transition compared to allowed electric dipole transitions.

4.2 Annihilation rates

From table 3 it can be seen that the only serious discrepancy between theory and experiment occurs for the decay rate of ortho-Ps as given in [25] and [26] by the Ann Arbor group. Whereas recent studies of the thermalization of Ps in gases [32] and of the temperature dependence of Ps decay rates [33] seem to be able to bring the decay rate in gases [$7.0514\,(14) \times 10^6$ s^{-1}] down to the vacuum decay rate [$7.0482\,(16) \times 10^6$ s^{-1}] a discrepancy of more than five standard deviations to the theory remains [34]. This well established and long lasting discrepancy has triggered an intense search for exotic and forbidden decay modes of ortho-Ps which resulted in an exclusion limit much below 10^{-3} for such decays. It is now experimentally proven that exotic decays cannot explain the discrepancy. On the other hand a group in Tokyo has reported a decay rate measurement in perfect agreement with theory [27]. To overcome the controversial situation completely

[2] The two photons have the wave length $\lambda = 486$ nm.

new experiments are necessary which differ from the old measurements by possible systematic errors. There are some proposals which all need high positron intensities as produced, e.g., by a LINAC [35] :

- Look at the decay of a large ensemble of Ps atoms confined simultaneously in a vacuum apparatus.
- Use a Lyman-α photon from the excited state $n = 2$ as a start pulse for Ps formation in the ground state.
- Use a fast beam of Ps atoms produced by ionization of an accelerated beam of negative positronium ions Ps$^-$ ($e^+e^-e^-$).
- Look at the spatial distribution of the decay γ -quanta from polarized Ps.

Acknowledgements

We are grateful for encouraging and stimulating discussions with Savely Karshenboim, Alexander Yelkhovsky and Ralph Conti.

Appendix

Here we give the numerical results for the energy levels in table 1 for the different orders in α. At the end of each equation we have rounded the numerical results. As uncertainties for the S-levels we took 50% of the leading logarithmic contribution in the order $R_\infty\alpha^5$, for the P-levels we took 10% of the known order $R_\infty\alpha^4$, for the uncertainty of the $3D$-levels (where the order $R_\infty\alpha^4$ is yet

Table 3. Comparison between experiment and theory for the annihilation rates and branching ratios in para-Ps (1^1S_0) and ortho-Ps (1^3S_1). For completeness some decay rates of the Ps negative ion (Ps$^-$, $e^+e^-e^-$) are included

	Experiment		Theory	
λ(para)	$7.990\,9\ (17)\ \times 10^9\ s^{-1}$	[23]	$7.989\,510\ (23)\ \times 10^9\ s^{-1}$	[9]
$\lambda_4\ /\ \lambda_2$	$1.50\ (7)(9)\ \times 10^{-6}$	[24]	$1.479\,3\ (18)\ \times 10^{-6}$	[10]
	$1.48\ (13)(12)\ \times 10^{-6}$	[10]		
λ(ortho)	$7.051\,4\ (14)\ \times 10^6\ s^{-1}$	[25]	$7.039\,941\ (20)\ \times 10^6\ s^{-1}$	[11]
	$7.048\,2\ (16)\ \times 10^6\ s^{-1}$	[26]		
	$7.039\,8\ (25)(15)\ \times 10^6\ s^{-1}$	[27]		
$\lambda_5\ /\ \lambda_3$	$2.2\ \left(^{+2.6}_{-1.6}\right) \pm 0.5\ \times 10^{-6}$	[12]	$0.959\,1\ (8)\ \times 10^{-6}$	[12]
$Ps^- \to 1\gamma + e^-$	not yet measured		$3.9\ \times 10^{-2}\ s^{-1}$	[28]
$Ps^- \to 2\gamma + e^-$	$2.09\ (9)\ \times 10^9\ s^{-1}$	[29]	$2.086\,122\,2\ (5)\ \times 10^9\ s^{-1}$	[30]
$Ps^- \to 3\gamma + e^-$	not yet measured		$1.845\ \times 10^6\ s^{-1}$	[31]

unknown) we took the full contribution of the corresponding $3P$-levels

$$\frac{E(1^1S_0)}{cR_\infty} = (-\,1\,644\,920\,980.183\,75 \;-\; 114\,967.478\,60 \;+\; 2\,738.640\,61 \;- \\ -\; 2.978\,54 \;-\; 0.402\,19\,)\ \mathrm{MHz} \;=\; -\,1\,645\,033\,212.402\,47\ \mathrm{MHz} \\ \to\; -\,(\,1\,645\,033\,212.40 \,\pm\, 0.30)\ \mathrm{MHz}\ ;$$

$$\frac{E(1^3S_1)}{cR_\infty} = (-\,1\,644\,920\,980.183\,75 \;+\; 89\,419.150\,02 \;+\; 1\,733.143\,80 \;+ \\ +\; 8.817\,38 \;-\; 1.320\,23\,)\ \mathrm{MHz} \;=\; -\,1\,644\,829\,820.392\,78\ \mathrm{MHz} \\ \to\; -\,(\,1\,644\,829\,820.39 \,\pm\, 0.70)\ \mathrm{MHz}\ ;$$

$$\frac{E(2^1S_0)}{cR_\infty} = (-\,411\,230\,245.045\,94 \;-\; 18\,134.751\,09 \;+\; 357.393\,65 \;- \\ -\; 0.445\,14 \;-\; 0.050\,27\,)\ \mathrm{MHz} \;=\; -\,411\,248\,022.898\,79\ \mathrm{MHz} \\ \to\; -\,(\,411\,248\,022.899 \,\pm\, 0.030)\ \mathrm{MHz}\ ;$$

$$\frac{E(2^3S_1)}{cR_\infty} = (-\,411\,230\,245.045\,94 \;+\; 7\,413.577\,49 \;+\; 231.706\,55 \;+ \\ +\; 1.700\,19 \;-\; 0.165\,03\,)\ \mathrm{MHz} \;=\; -\,411\,222\,598.226\,74\ \mathrm{MHz} \\ \to\; -\,(\,411\,222\,598.227 \,\pm\, 0.090)\ \mathrm{MHz}\ ;$$

$$\frac{E(2^1P_1)}{cR_\infty} = (-\,411\,230\,245.045\,94 \;-\; 3\,535.706\,19 \;-\; 2.909\,56 \;+ \\ +\; 0.063\,29\,)\ \mathrm{MHz} \;=\; -\,411\,233\,783.598\,40\ \mathrm{MHz} \\ \to\; -\,(\,411\,233\,783.598 \,\pm\, 0.010)\ \mathrm{MHz}\ ;$$

$$\frac{E(2^3P_0)}{cR_\infty} = (-\,411\,230\,245.045\,94 \;-\; 10\,835.228\,64 \;-\; 15.626\,16 \;- \\ -\; 0.571\,67\,)\ \mathrm{MHz} \;=\; -\,411\,241\,096.472\,41\ \mathrm{MHz} \\ \to\; -\,(\,411\,241\,096.472 \,\pm\, 0.010)\ \mathrm{MHz}\ ;$$

$$\frac{E(2^3P_1)}{cR_\infty} = (-\,411\,230\,245.045\,94 \;-\; 5\,360.586\,80 \;-\; 5.028\,99 \;+ \\ +\; 0.028\,27\,)\ \mathrm{MHz} \;=\; -\,411\,235\,610.633\,46\ \mathrm{MHz} \\ \to\; -\,(\,411\,235\,610.633 \,\pm\, 0.010)\ \mathrm{MHz}\ ;$$

$$\frac{E(2^3P_2)}{cR_\infty} = (-\,411\,230\,245.045\,94 \;-\; 980.873\,33 \;+\; 0.905\,43 \;+ \\ +\; 0.078\,54\,)\ \mathrm{MHz} \;=\; -\,411\,231\,224.935\,30\ \mathrm{MHz} \\ \to\; -\,(\,411\,231\,224.935 \,\pm\, 0.010)\ \mathrm{MHz}\ ;$$

$$\frac{E(3^1S_0)}{cR_\infty} = (-\,182\,768\,997.798\,19 \;-\; 5\,744.994\,52 \;+\; 106.977\,71 \;- \\ -\; 0.104\,34 \;-\; 0.014\,90\,)\ \mathrm{MHz} \;=\; -\,182\,774\,635.934\,24\ \mathrm{MHz} \\ \to\; -\,(\,182\,774\,635.934 \,\pm\, 0.009)\ \mathrm{MHz}\ ;$$

$$\frac{E(3^3S_1)}{cR_\infty} = (-\,182\,768\,997.798\,19 \;+\; 1\,824.880\,61 \;+\; 69.737\,09 \;+$$

$$
\begin{aligned}
& + 0.530\,70 \;-\; 0.048\,90\;)\ \mathrm{MHz} \\
&= \;-\;182\,767\,102.698\,69\ \mathrm{MHz} \\
&\to \;-\;(-\;182\,767\,102.699\;\pm\;0.030)\ \mathrm{MHz}\ ; \\
\frac{E(3^1P_1)}{cR_\infty} &= (-\;182\,768\,997.798\,19 \;-\; 1\,419.351\,59 \;-\; 0.697\,84 \;+ \\
& + 0.018\,15\;)\ \mathrm{MHz} \;=\; -\;182\,770\,417.829\,47\ \mathrm{MHz} \\
&\to \;-\;(\;182\,770\,417.829\,5\;\pm\;0.004\,0)\ \mathrm{MHz}\ ; \\
\frac{E(3^3P_0)}{cR_\infty} &= (-\;182\,768\,997.798\,19 \;-\; 3\,582.173\,05 \;-\; 4.465\,72 \;- \\
& - 0.170\,39\;)\ \mathrm{MHz} \;=\; -\;182\,772\,584.607\,35\ \mathrm{MHz} \\
&\to \;-\;(\;182\,772\,584.607\,4\;\pm\;0.004\,0)\ \mathrm{MHz}\ ; \\
\frac{E(3^3P_1)}{cR_\infty} &= (-\;182\,768\,997.798\,19 \;-\; 1\,960.056\,95 \;-\; 1.325\,82 \;+ \\
& + 0.008\,47\;)\ \mathrm{MHz} \;=\; -\;182\,770\,959.172\,49\ \mathrm{MHz} \\
&\to \;-\;(\;182\,770\,959.172\,5\;\pm\;0.004\,0)\ \mathrm{MHz}\ ; \\
\frac{E(3^3P_2)}{cR_\infty} &= (-\;182\,768\,997.798\,19 \;-\; 662.364\,07 \;+\; 0.432\,52 \;+ \\
& + 0.024\,34\;)\ \mathrm{MHz} \;=\; -\;182\,769\,659.705\,40\ \mathrm{MHz} \\
&\to \;-\;(\;182\,769\,659.705\,4\;\pm\;0.004\,0)\ \mathrm{MHz}\ ; \\
\frac{E(3^1D_2)}{cR_\infty} &= (-\;182\,768\,997.798\,19 \;-\; 554.223\,00 \;-\; 0.187\,92\;)\ \mathrm{MHz} \\
&= \;-\;182\,769\,552.209\,11\ \mathrm{MHz} \\
&\to \;-\;(\;182\,769\,552.209\;\pm\;0.020\;)\ \mathrm{MHz};\ ; \\
\frac{E(3^3D_1)}{cR_\infty} &= (-\;182\,768\,997.798\,19 \;-\; 1\,094.928\,37 \;-\; 1.067\,09\;)\ \mathrm{MHz} \\
&= \;-\;182\,770\,093.793\,65\ \mathrm{MHz} \\
&\to \;-\;(-\;182\,770\,093.794\;\pm\;0.170\;)\ \mathrm{MHz}\ ; \\
\frac{E(3^3D_2)}{cR_\infty} &= (-\;182\,768\,997.798\,19 \;-\; 662.364\,07 \;-\; 0.313\,51\;)\ \mathrm{MHz} \\
&= \;-\;182\,769\,660.475\,77\ \mathrm{MHz} \\
&\to \;-\;(\;182\,769\,660.476\;\pm\;0.009\;)\ \mathrm{MHz}\ ; \\
\frac{E(3^3D_3)}{cR_\infty} &= (-\;182\,768\,997.798\,19 \;-\; 245.248\,51 \;+\; 0.278\,58\;)\ \mathrm{MHz} \\
&= \;-\;182\,769\,242.768\,12\ \mathrm{MHz} \\
&\to \;-\;(\;182\,769\,242.768\;\pm\;0.025\;)\ \mathrm{MHz}\ .
\end{aligned}
$$

References

1. P. J. Mohr and B. N. Taylor: *CODATA Recommended Values of the Fundamental Physical Constants*: J. Phys. Chem. Ref. Data **28**, No. 6, p. 1809 (1999)

2. P. J. Mohr and B. N. Taylor: *this edition*, pp. 145– 156
3. A. Czarnecki, K. Melnikov and A. Yelkhovsky: Phys. Rev. A **59**, 4316 (1999)
4. K. Pachucki and S. G. Karshenboim: Phys. Rev. Lett. **80**, 2101 (1998)
5. R. N. Fell: Phys. Rev. Lett. **68**, 25 (1992)
6. S. N. Gupta, W. W. Repko and C. J. Suchyta III: Phys. Rev. D **40**, 4100 (1989)
7. A. Messiah: *Quantum Mechanics*, Vol. II, p. 554 and p. 579 (Problem XIII.11), North Holland 1962
8. G. W. F. Drake and R. A. Swainson: Phys. Rev. A **41**, 1243 (1990)
9. A. Czarnecki, K. Melnikov and A. Yelkhovsky: Phys. Rev. A **61**, 052502 (2000)
10. S. Adachi *et al.*: Phys. Rev. A **49**, 3201 (1994) and S. Adachi: Bachelor's thesis, Tokyo Metropolitan University, 1990 (in Japanese, unpublished)
11. G. S. Adkins, R. N. Fell and J. Sapirstein: Phys. Rev. Lett. **84**, 5086 (2000)
12. T. Matsumoto *et al.*: Phys. Rev. A **54**, 1947 (1996)
13. M. S. Fee *et al.*: Phys. Rev. Lett. **70**, 1397 (1993) and Phys. Rev. A **48**, 192 (1993)
14. M. W. Ritter *et al.*: Phys. Rev. A **30**, 1331 (1984)
15. A. P. Mills, Jr., and G. H. Bearman: Phys. Rev. Lett. **34**, 246 (1975) corrected in: A. P. Mills, Jr.: Phys. Rev. A **27**, 262 (1983)
16. D. Hagena *et al.*: Phys. Rev. Lett. **71**, 2887 (1993) and R. Ley *et al.*: Hyperfine Interactions **89**, 327 (1994)
17. S. Hatamian, R. S. Conti and A. Rich: Phys. Rev. Lett. **58**, 1833 (1987)
18. A. P. Mills, Jr., S. Berko and K. F. Canter: Phys. Rev. Lett. **34**, 1541 (1975)
19. R. S. Conti *et al.*: Phys. Lett. A **177**, 43 (1993)
20. R. Holzwarth *et al.*: Phys. Rev. Lett. **85**, 2264 (2000)
21. F. Biraben, T.W. Hänsch *et al.*: *this edition*, pp. 17–41
22. G. Hagel *et al.*: *this edition*, pp. 328–334
23. A. H. Al-Ramadhan and D. W. Gidley: Phys. Rev. Lett. **72**, 1632 (1994)
24. H. von Busch *et al.*: Phys. Lett. B **325**, 300 (1994)
25. C. I. Westbrook, D. W. Gidley, R. S. Conti and A. Rich: Phys. Rev. A **40**, 5489 (1989): measurement in gases
26. J. S. Nico, D. W. Gidley, A. Rich and P. W. Zitzewitz: Phys. Rev. Lett. **65**, 1344 (1990): measurement in vacuum
27. S. Asai, S. Orito and N. Shinohara: Phys. Lett. B **357**, 475 (1995): measurement in SiO_2 powder
28. S. I. Kryuchkov: J. Phys. B: At.Mol.Opt.Phys. **27**, L61 (1994)
29. A. P. Mills, Jr.: Phys. Rev. Lett. **50**, 671 (1983)
30. Y. K. Ho: Phys. Rev. A **48**, 4780 (1993)
31. A. M. Frolov and V. H. Smith, Jr.: Phys. Rev. A **49**, 3580 (1994)
32. M. Skalsey, J. J. Engbrecht, R. K. Bithell, R. S. Vallery and D. W. Gidley: Phys. Rev. Lett. **80**, 3727 (1998)
33. R. S. Vallery, A. E. Leanhardt, M. Skalsey and D. W. Gidley: J. Phys. B: At. Mol. Opt. Phys. **33**, 1047 (2000)
34. R. S. Conti *et al.*: *this edition*, pp. 103–121
35. G. Brauer (Editor): *Wissenschaftlich-Technische Berichte, Forschungszentrum Rossendorf*, FZR-295, July 2000, p. 71 (in English)