I. INTRODUCTION

Prior to annihilation, an electron–positron pair may form a complex resembling atomic hydrogen called positronium. Since the positron and electron have equal mass the reduced mass of the system is approximately half that of hydrogen and the “atomic” energy levels (neglecting fine and hyperfine structure effects, i.e., spin–orbit and spin–spin coupling, respectively) are likewise approximately half those of hydrogen. Hyperfine structure effects however, are far greater and similar in magnitude to fine structure due to the positron’s mass of the system is approximately half that of hydrogen. Since the positron and electron have equal mass the reduced mass of the system is approximately half that of hydrogen and the “atomic” energy levels (neglecting fine and hyperfine structure effects, i.e., spin–orbit and spin–spin coupling, respectively) are likewise approximately half those of hydrogen. Hyperfine structure effects however, are far greater and similar in magnitude to fine structure due to the positron’s greater magnetic dipole moment compared with that of the proton. Positronium decays electromagnetically into the diagnostically useful two gamma rays and occasionally into nonuseful three or more gamma rays depending on the positronium’s quantum mechanical state just prior to decay. When viewed in the rest frame of positronium conservation of momentum requires that the two photons travel in opposite directions with energy equal to the energy equivalent of the electron mass (≈0.51 MeV) less the positron–electron binding energy (6.8 eV).

The decay of positronium resembles the more familiar weak electron capture decay of certain nuclides in that it occurs from an orbital which have maximum probability density at the origin (nucleus or positron) increasing the likelihood of capture. These orbitals have zero orbital angular momentum \( l = 0 \); the total angular momentum \( J \) in this case derives from the alignment or nonalignment of the two spin one-half particles, i.e., \( J = 1 \) or \( 0 \) which are referred to as orthopositronium (o-Ps) and parapositronium (p-Ps) states, respectively. Constrained by various conservation laws, orthopositronium in a vacuum must decay into an odd number of photons, three being most probable and parapositronium into an even number of photons, two being most probable.

Although not common-place in the radiological community, positronium is one of the most highly studied atomic species in all of physics. This is because it is purely leptonic without the complication of baryons in its “nucleus.” This allows energy levels and decay rates to be calculated to very high levels of accuracy using quantum electrodynamics alone.

In the present review we pursue the less ambitious objective of describing the relevant symmetry and conservation laws of the decay, namely, parity and charge conjugation parity and how these affect the vacuum decay modes and lifetimes of these two positronium states. We also discuss in general terms the computational techniques used to calculate these bound state decay rates. In the final section we discuss positron annihilation in tissue and how it differs from that in a vacuum. We also discuss its relevance to positron emission tomography.

A. Parity

The positronium state can be considered nonrelativistically (the speed of the electron in positronium is \( \sim c/137 \)) as the product of an orbital wave function and a spin vector:

\[
\psi_{n,l,m}(\mathbf{r})|S, S_z\rangle.
\]

The orbital wave function is the hydrogen atom wave function with the electron mass replaced by the reduced mass of the electron positron pair and where \( n, l, \) and \( m \) are the usual principle \( n \) integer \( \geq 0 \), orbital \( 0 \leq l < n - 1 \) and magnetic \( |m| \leq l \) quantum numbers, respectively. The spin vectors are linear combinations of products of those of the individual particles, of which there are four possible:

\[
|S = 1, S_z = 1\rangle = |\uparrow\rangle|\uparrow\rangle,

|S = 1, S_z = 0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle|\downarrow\rangle + |\downarrow\rangle|\uparrow\rangle),

|S = 1, S_z = -1\rangle = |\downarrow\rangle|\downarrow\rangle,

|S = 0, S_z = 0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle),
\]

where, e.g., \(|\uparrow\rangle|\downarrow\rangle\rangle\rangle\)) is the product of a positron spin state with \( S_z = +1/2 \) and an electron spin state with \( S_z = -1/2 \) which produces an eigenstate of total spin \( S = 1 \) and \( z \) component
ortho and para positronium decay from a parity. Thus the parity of the spin vector is except that particles and anti-particles have opposite intrinsic.

This is called intrinsic parity and is conventional for leptons but for baryons, for which there is no flavor change, the parity of the system is determined by the individual particle’s parities.

i.e., the orbital wave function is an eigenstate of parity with eigenvalue \((-1)^l\). The parity of the spin vector is the product of the parities of the individual particle’s spin vector. This is called intrinsic parity and is conventional for leptons except that particles and anti-particles have opposite intrinsic parity. Thus the parity of the spin vector is \(-1\) since the positron and electron have opposite parity. The overall parity of a given positronium state is thus \(-(-1)^l\). Since both ortho and para positronium decay from a \(l=0\) state both have odd (i.e., \(-1\)) parity at decay. Parity is conserved in electromagnetic interactions, thus the photon states following the annihilation must also have odd parity.

A two photon wave function with odd parity and exhibiting the required Bose symmetry (i.e., invariance under the interchange of photon labels) is described in the Appendix. Although neither photon is found to be in a state of well defined polarization the measured or expectation value of annihilation photon polarizations are orthogonal to each other.

### B. Charge conjugation parity

Positronium is also an eigenstate of charge conjugation, i.e., the exchange of particles and antiparticles. Again the symmetry and conserved quantities go by the same name. In this case, the operation is equivalent to the application of charge conjugation at decay and the parity of the resulting photon state must be the same.

For the positronium state of Eq. (1), the parity is the product of that of the wave function and that of the spin vector. Applying the parity operator to the orbital wave function one finds

\[
P\Psi_{n,l,m}(r) = \Psi_{n,l,m}(-r) = (-1)^l \Psi_{n,l,m}(r),
\]

i.e., the orbital wave function is an eigenstate of parity with eigenvalue \((-1)^l\). The parity of the spin vector is the product of that of the wave function and that of the spin vector.

The equations of electrodynamics are invariant under an inversion of the coordinate system, i.e., reversing the sign of all vector quantities, e.g., the position vector \(\mathbf{r} \rightarrow -\mathbf{r}\). The conserved quantity in this case is also called parity and has eigenvalues of \(\pm 1\) depending on how the spin vector of the system behaves under the parity operation. Since positronium decays electromagnetically the parity of positronium prior to decay and the parity of the resulting photon state must be the same.

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\[
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A two photon wave function with odd parity and exhibiting the required Bose symmetry (i.e., invariance under the interchange of photon labels) is described in the Appendix. Although neither photon is found to be in a state of well defined polarization the measured or expectation value of annihilation photon polarizations are orthogonal to each other.

The charge conjugation parity of a photon is \(-1\). A system of \(n\) photons will have a charge conjugation parity of \((-1)^n\).

Since the laws of electrodynamics are invariant under the interchange of particle and antiparticle, charge conjugation is conserved in electromagnetic interactions and thus ortho positronium must decay into an odd number of photons. Decay into a single photon cannot conserve momentum, thus a three photon decay is the most probable. A five photon decay is reduced by 4 orders of magnitude. Parapositronium must decay into an even number of photons, two being the most probable.

### C. Decay rates

The decay rate for p-Ps in a vacuum was first calculated to lowest order of perturbation by Wheeler. This involved the determination of the unpolarized total cross section for 2 photon annihilation for electron–positron collisions at low energies:

\[
\sigma = \frac{\pi \alpha^2}{c \nu_{\text{rel}}^2 \left(\frac{\alpha m}{\hbar}\right)^2},
\]

where \(\nu_{\text{rel}}\) is the relative velocity of the 2 particles and \(\alpha=1/137.04\) is the fine structure constant. This cross section can be easily obtained by applying the Feynman rules to the lowest order Feynman diagrams for electron–positron annihilation given in Fig. 1. (Historical note: Feynman diagrams and the Feynman rules were not introduced into quantum electrodynamics until three years after Wheeler’s paper.) The decay rate was found by multiplying this cross section by the flux of colliding particles taken as the relative velocity multiplied by the particle density at the point of annihilation, i.e., the origin, taken as the square of the orbital wave function of p-Ps at the origin:

\[
\text{flux} = \nu_{\text{rel}} |\psi_{0,0}(0)|^2 = \frac{1}{\pi} \left(\frac{m c^2 \alpha}{2 \hbar}\right)^3.
\]

The decay rate was thus found,

\[
\Gamma_{\text{Ps} \rightarrow 2\gamma} = 4 \cdot \text{flux} \cdot \sigma = \frac{1}{2} \left(\frac{m c^2 \alpha^5}{\hbar}\right) = 8.032 \times 10^9 \text{ s}^{-1}.
\]

The factor of 4 is introduced above since \(\sigma\) is the unpolarized cross section whereas only 1 of 4 possible spin orientations of the electron–positron pair are consistent with p-Ps as is seen from Eq. (2). In a substantially more involved calculation the decay rate of o-Ps was determined to lowest order by Ore and Powell as

\[
\Gamma_{\text{Ps} \rightarrow 2\gamma} = 4 \cdot \text{flux} \cdot \sigma = \frac{1}{2} \left(\frac{m c^2 \alpha^5}{\hbar}\right) = 8.032 \times 10^9 \text{ s}^{-1}.
\]
\[ \Gamma (\text{o-Ps}\rightarrow 3 \gamma) = \frac{2(\pi^2 - 9)}{9\pi} \frac{mc^2}{\hbar} \alpha^6 = 7.211 \times 10^6 \text{ s}^{-1}. \] (7)

The additional power of the fine structure constant \( \alpha \) follows directly from the Feynman rules given the additional photon in o-Ps decay.

The first part of Wheeler’s treatment of the decay of p-Ps, i.e., the determination of \( \sigma \) illustrates the usual type of problem considered in quantum electrodynamics which is the calculation of scattering or interaction cross sections where free particles are input and free particles are output. These accelerator problems are conveniently treated using perturbation theory where each term in the perturbation expansion is graphically represented by a Feynman diagram. The annihilation of a free electron-positron pair with momenta \( p \) and \( -p \) into two free photons is expressed in lowest order of perturbation by the diagrams in Fig. 1, from which the annihilation amplitude \( M(p) \) can be calculated by a straightforward application of the Feynman rules.\(^5\) In positronium the electron and positron are not free particles but form a bound state which frustrates this approach in any calculation of decay rates greater than lowest order of perturbation, as in Wheeler’s calculation. In modern higher order calculations the annihilation process and bound state aspects are separated or factored. An annihilation amplitude \( M(p) \) for free particles is calculated to the desired order of perturbation in the usual way then the bound state or orbital wave function, Eq. (1), is incorporated into the calculation by using its Fourier transform \( \psi(p) \) as a weighting factor to average \( M(p) \) over \( p \). The decay rate is found by squaring this average amplitude and integrating over photon directions.\(^6\) In lowest order the Fourier weighting procedure leads to the \( |\psi_{1,0,0}(0)|^2 \) term in Eq. (5).

Another difference between the scattering and bound state calculation is in the treatment of the electron and positron spins. Scattering problems always consider input and output particles in states of well defined spin or polarization (at least at the beginning of the calculation). If unpolarized beams are used and final polarizations are not observed, the appropriate averages and sums over spin and polarization indices are performed after squaring the amplitude. In positronium the individual electron and positron are not in states of well defined spin although the system as a whole is in a state of well defined total angular momentum as described (nonrelativistically) by Eq. (2). In lowest order these spin considerations can be dispensed with by simply including the factor 4 in Eq. (6). This is because the effect of o-Ps, i.e., the other 3 possible spin orientations, is higher order [note the \( \alpha^8 \) term in Eq. (7)]. When calculating p-Ps decay in higher orders this trick cannot be used. Modern higher order calculations require performing an appropriate spin sums before squaring the Feynman amplitude. As with the scattering case there are elegant and powerful projection operator techniques for carrying out these sums and averages.

Vacuum decay rates have been calculated to order \( \alpha^7 \) for para positronium and order \( \alpha^8 \) for ortho positronium with results\(^1\)

\[ \lambda (\text{p-Ps}) = 7.98951 \times 10^9 \text{ s}^{-1}, \]

\[ \lambda (\text{o-Ps}) = 7.03994 \times 10^9 \text{ s}^{-1}. \]

The inverse of the decay rates give the mean lifetimes of the states i.e., 125 ps for p-Ps and 142 ns for o-Ps. It should be stated that for some years the theoretical decay rate of ortho-positronium was in slight disagreement with observation.\(^9,10\) This was referred to as the orthopositronium paradox. More recent precise measurements\(^11\) however, are in very good agreement with theory.

**II. DISCUSSION: POSITRONS IN TISSUE**

Although little has been published regarding the specifics of positron or positronium chemistry in tissue much has been published regarding this chemistry in organic and inorganic liquids and thus a reasonable picture for positron dynamics in tissue can be surmised.

After a positron is ejected from a nucleus it rapidly thermalizes by means a series of collisions with bound electrons of the medium. This process is similar to the thermalization of electrons from beta emitters, the primary difference being that electrons are attracted to the positive nuclei of the medium where the electron density (and likelihood of a collision) is greatest, whereas positrons are repelled.\(^12\) Thus the thermalization of positrons is a slower process than that of electrons. The probability of “in flight” annihilation prior to thermalization in tissue is low. Estimations based on Heitler\(^13\) are on the order of 2%.\(^14\) After a positron has thermalized it may combine directly with an electron of opposed spin resulting in a 2 photon annihilation or it may form positronium. The fraction of positrons forming Ps is the Ps yield. Using the technique of Positron Age-Momentum-Correlation (AMOC) Castellaz et al.\(^15\) have measured the Ps yields in a variety of liquids for an external 4 MeV positron beam. The Ps yield in water was found to be 38% and in other liquids (organic solvents) as high as 70% in spite of positron recoil effects at the liquid surface. It seems reasonable to expect the yield from lower energy sources embedded in tissue, as in PET, to be higher than the 38% for water\(^15\) due to the lack of surface effects and the lower instance of in-flight annihilation.

It is believed that the primary mechanisms of Ps formation in liquid are the spur process\(^16\) where the positron unites with an electron liberated during thermalization and the Ore Gap mechanism\(^17,18\) where the energy released by Ps formation (the binding energy 6.8 eV) combines with residual kinetic energy of the positron to dissociate a bound electron. Assuming that all spin states for electrons and positrons are equally probable we should expect o-Ps and p-Ps to be produced in the ratio 3:1 and this is in fact observed in liquids.\(^15\)

Once formed p-Ps is observed to decay in liquids with its vacuum lifetime \( \sim 125 \) ps. The observed lifetime of o-Ps in liquids is considerably shorter than its vacuum value due to pick-off annihilation where a second electron with opposed spin reacts with the positron in th o-Ps atom resulting in a two photon annihilation. This pick-off process is described by the bubble model of Ferrell.\(^19\) In this the o-Ps is self
confined to a bubble. The system is described quantum mechanically as a particle in a rigid spherical box. The ground state energy implies a pressure at the surface of the bubble which is balanced by surface tension. This determines the size of the bubble as well as the likelihood of o-Ps interacting with the electrons of atoms near the surface of the bubble. The model predicts a pick-off rate proportional to the square root of the surface tension of the liquid. This is observed experimentally. The pick-off rate is also influenced by dissolved gases, decreasing in the presence of oxygen.\textsuperscript{20} The observed lifetime of o-Ps in water is 1800 ps compared to the much longer vacuum lifetime of 140 ns, thus we may conclude that most annihilation in tissue result in a useful two-photon decay.

The spatial resolution of PET imaging is ultimately limited by the positron range prior to annihilation which depends on the initial kinetic energy of the positron and a lack of collinearity of the annihilation radiation due to residual momentum of the positron or positronium at the time of decay. The range of a positron in tissue varies with its initial kinetic energy and is almost 4 mm for 1 MeV. As is generally known, the decay energy of a given positron emitting isotope is shared between the positron and its neutrino in a random manor with the positron receiving on average one-third the total energy. For example, the decay energy (i.e., maximum beta kinetic energy) of fluorine-18 is 0.64 MeV and the average beta energy is approximately one-third this value. The distribution of energies results in a range distribution which for fluorine-18 has a FWHM of approximately 1.0 mm.

In the center of mass frame of a 2 photon decay the momentum of each photon is simply $mc$ with $m$ the mass of the electron or positron. The residual momentum of Ps is related to its residual kinetic energy (KE) by

$$\sqrt{2 \cdot KE \cdot (2m)} = 2\sqrt{KE \cdot m}, \quad (8)$$

which, in the worst case, shown in Fig. 2 is perpendicular to the direction of the annihilation radiation and shared equally between the 2 photons. The deviation from collinearity of the two photons in the lab frame when $KE \ll mc^2$ is

$$2\theta = 2 \cdot \frac{\sqrt{KE \cdot m}}{mc} = 2 \cdot \sqrt{\frac{KE}{mc^2}}. \quad (9)$$

Using the AMOC technique Castellaz et al.\textsuperscript{15} have observed that in solutions “early” Ps decays, i.e., those of p-Ps, have significantly more Doppler broadening of the annihilation spectrum than late decays, i.e., o-Ps decays. This indicates considerably more residual momentum in p-Ps at the time of decay and that the noncollinearity of annihilation radiation in PET imaging is the result of p-Ps and not o-Ps. The full width at half maximum of noncollinear events in $^{18}$F annihilation radiation in an aqueous solution has been measured as 0.47 degrees.\textsuperscript{16} This angular deviation is consistent with a KE of 8.6 eV. For the typical geometry of a PET scanner this level of deviation from collinearity results in a degradation of spatial resolution (FWHM) of 1.2 mm. Thus, although positron range and annihilation collinearity place a limit on the ultimate PET resolution, in practice aperture size plays a major role in determining resolution in PET imaging of fluorine-18. In the case of positron emitters that have a maximum beta particle emitted kinetic energy of 3 MeV or more, the positron range plays an increasing or major role in determining PET resolution.

The decay of positronium illustrates several fundamental symmetries and conservation laws. The energy of the annihilation radiation is essentially that of the rest energy of an electron for two photon decay. The conservation of momentum is responsible for the noncollinearity of the annihilation radiation and fixes a limit to the ultimate resolution of PET imaging. The conservation of angular momentum and parity are related and constrain the measured polarizations of the annihilation radiation. Charge conjugation parity determines that the vacuum decay of p-Ps results in an even number of photons and that of o-Ps an odd number photons.

**APPENDIX: ODD PARITY TWO PHOTON WAVE FUNCTION**

The wave function of a photon with momentum $k$ and transverse polarization $\hat{\epsilon}_1$ can be taken as

$$e^{i(k \cdot r - \omega t)} |\hat{\epsilon}_1\rangle. \quad (A1)$$

The symmetrized wave function for a two photon state with momenta $k$ and $-k$ and polarizations $\hat{\epsilon}_1$ and $\hat{\epsilon}_2$, respectively, can be written as

$$\Psi(r_1 - r_2) = e^{i(k \cdot (r_1 - r_2) - 2\omega t)} |\hat{\epsilon}_1\rangle |\hat{\epsilon}_2\rangle + e^{i(-k \cdot (r_1 - r_2) - 2\omega t)} |\hat{\epsilon}_2\rangle |\hat{\epsilon}_1\rangle, \quad (A2)$$

or after a little algebra,

$$\Psi(r_1 - r_2) = \frac{1}{2} \left[ |\hat{\epsilon}_1\rangle |\hat{\epsilon}_2\rangle + |\hat{\epsilon}_2\rangle |\hat{\epsilon}_1\rangle \right] e^{i(k \cdot (r_1 - r_2) - 2\omega t)}$$

$$+ e^{i(-k \cdot (r_1 - r_2) - 2\omega t)} + \frac{1}{2} \left[ |\hat{\epsilon}_1\rangle |\hat{\epsilon}_2\rangle + |\hat{\epsilon}_2\rangle |\hat{\epsilon}_1\rangle \right] e^{i(-k \cdot (r_1 - r_2) - 2\omega t)} - |\hat{\epsilon}_2\rangle |\hat{\epsilon}_1\rangle e^{i(-k \cdot (r_1 - r_2) - 2\omega t)} - |\hat{\epsilon}_1\rangle |\hat{\epsilon}_2\rangle e^{i(k \cdot (r_1 - r_2) - 2\omega t)}. \quad (A3)$$

In the above equation both terms individually have the required Bose symmetry of interchange of boson indices (i.e., $1 \leftrightarrow 2$). The first term exhibits even parity and the second term odd parity. The two photon decay state of para positronium is described by the (suitably normalized) second term above,
\[ \Psi(r) = \frac{1}{\sqrt{2}} \left[ |\hat{\epsilon}_1\rangle|\hat{\epsilon}_2\rangle - |\hat{\epsilon}_2\rangle|\hat{\epsilon}_1\rangle \right] \times \left\{ e^{i(kr-2\omega t)} - e^{i(-kr-2\omega t)} \right\}, \]

(A4)

where we have replaced \( r = r_1 - r_2 \). Without loss of generality the vectors \( \hat{\epsilon}_1 \) and \( \hat{\epsilon}_2 \) can be taken as orthogonal since any common component will cancel. It should be noted that the polarization term of the two photon state in Eq. (A4) is a superposition of different polarizations of the individual photons, i.e., following a 2 photon decay of p-Ps neither photon by itself is in a state of well defined polarization. Nonetheless, the expectation value of relative polarization can be calculated. Consider a correctly symmetrized two photon state with polarizations

\[ \hat{a} = \hat{\epsilon}_1 \quad \text{and} \quad \hat{b} = \hat{\epsilon}_1 \cos(\theta) + \hat{\epsilon}_2 \sin(\theta), \]

(A5)

i.e.,

\[ \frac{1}{\sqrt{2}} \left[ |\hat{a}\rangle|\hat{b}\rangle - |\hat{b}\rangle|\hat{a}\rangle \right]. \]

(A6)

The expectation value for observing this polarization state in a two photon decay is found directly by

\[ \left| \langle \hat{b} | \langle \hat{a} | (|\hat{\epsilon}_1\rangle|\hat{\epsilon}_2\rangle - |\hat{\epsilon}_2\rangle|\hat{\epsilon}_1\rangle) \right| = \sin^2(\theta), \]

(A7)

which is maximum when \( \theta = 90^\circ \). Thus, the conservation of parity requires that the measured polarization of the 2 photon annihilation radiation be orthogonal.\(^4\) In addition to this constraint imposed on the polarization of annihilation radiation, parity conservation fixes the form of the output state when calculating Ps decay rates from transition probability with quantum electrodynamics.

\( \hat{\epsilon}_1 \) and \( \hat{\epsilon}_2 \) in Eq. (A4) can alternatively be interpreted as left and right hand circular polarizations relative to \( \mathbf{k} \). Then the polarization term in Eq. (A4) can, by comparison with the last expression in Eq. (2), be identified as a state of zero angular momentum. Thus the two photon decay is consistent with the zero angular momentum of p-Ps.

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