1
Introduction

1.1 Historical remarks

The prediction, and subsequent discovery, of the existence of the positron, e^+, constitutes one of the great successes of the theory of relativistic quantum mechanics and of twentieth century physics. When Dirac (1930) developed his theory of the electron, he realized that the negative energy solutions of the relativistically invariant wave equation, in which the total energy E of a particle with rest mass m is related to its linear momentum p by

$$E^2 = m^2c^4 + p^2c^2, \tag{1.1}$$

had real physical significance. He therefore postulated that the 'sea' of electron states with negative energies between $-mc^2$ and $-\infty$ was normally fully occupied in accordance with the Pauli exclusion principle, and would be unobservable. A vacancy in this ensemble, however, would manifest itself as a positively charged particle with a positive rest mass which, on the basis of uncalculated Coulomb energy corrections and the particles then known, Dirac assumed to be the proton. It was soon realized that this was not the case and that the theory actually predicted the existence of a new particle with the rest mass of the electron and an equal but opposite charge – the positron.

The positron was subsequently discovered by Anderson (1933) in a cloud chamber study of cosmic radiation, and this was soon confirmed by Blackett and Occhialini (1933), who also observed the phenomenon of pair production. There followed some activity devoted to understanding the various annihilation modes available to a positron in the presence of electrons; radiationless, single-gamma-ray and the dominant two-gamma-ray processes were considered (see section 1.2). The theory of pair production was also developed at this time (see e.g. Heitler, 1954).

In 1934 Mohorovičić proposed the existence of a bound state of a positron and an electron which, he (incorrectly) suggested, might be responsible for unexplained features in the spectra emitted by some stars. However, as summarized by Kragh (1990), Mohorovičić's ideas on the properties of this new atom were somewhat unconventional, and the name 'electrum' which he gave to it did not become widespread but was later replaced by the present appellation, positronium (Ruark, 1945), with the chemical symbol Ps.

Other significant developments took place in the 1940s. In 1949 DeBenedetti and coworkers discovered that the two gamma-rays emitted following positron annihilation in various solids deviated from precise collinearity, i.e. the angle between them was not exactly 180°, as would be expected from the annihilation of an electron–positron pair at rest. Although this deviation amounted to only a few milliradians, it was correctly interpreted as being due mainly to the effect of the motion of the bound electrons in the material, the positron having essentially thermalized. Somewhat earlier, DuMond, Lind and Watson (1949) had made an accurate measurement of the energy and width of the annihilation gamma-ray line using a crystal spectrometer. They found the width to be greater than that associated with the instrumental resolution, and they attributed this to Doppler broadening arising predominantly from electronic motion. These investigations laid the foundations for later advances in positron solid state physics, which were themselves to underpin the development of low energy positron beams.

In 1946 Wheeler undertook a theoretical study of the stability of various systems of positrons and electrons, which he termed polyelectrons. He found, as expected, that positronium was bound, but that so too was its negative ion ($e^-e^+e^-$). This entity, Ps^-, was not observed until much later (Mills, 1981), after the development of positron beams.

Positronium itself was eventually discovered in 1951 by Deutsch and its properties were investigated in an elegant series of experiments based around positron annihilation in gases. Many of the techniques developed then are still in use today. This advance stimulated further experimental and theoretical studies of the basic properties of the ground state of positronium (particularly the triplet 1^3S_1 state, ortho-positronium), including the hyperfine structure, the annihilation lifetime, elucidation of the selection rules governing annihilation and the calculation of the spectrum of photon energies emitted in the three-gamma-ray annihilation mode. Some of these topics are described in detail elsewhere in this book.

The recent production of relativistic antihydrogen (Baur *et al.*, 1996; Blanford *et al.*, 1998), and the prospect of its formation at very low energies (see Chapter 8), when detailed spectroscopic and other studies of this system should become possible, makes it appropriate to mention the antiproton. This particle, whose existence had been predicted by analogy with the positron, was discovered in 1955 by Chamberlain, Segrè, Weigand and Ypsilantis using the 6.2 GeV Bevatron accelerator at the Lawrence Berkeley Laboratory, California, USA.

For positron collision physics, a revolutionary advance came with the discovery and development of low energy positron beams. In a study of secondary electron emission by positrons, Cherry (1958) found that 'positrons in the energy interval 0–5 eV, very numerous in comparison to those in equal intervals at somewhat higher energies, were emitted from a chromium-on-mica surface when it was irradiated by a ^{64}Cu positron beta spectrum'. However, the efficiency of conversion from fast to slow positrons was only approximately 10^{-8}. This work was, in fact, predated by that of Madansky and Rasetti (1950), who unsuccessfully searched for low energy positron emission from a variety of samples. These experiments were largely ignored until the late 1960s and the work of Groce *et al.* (1968).

The decisive breakthrough in the development of positron beams probably came with the work of Canter *et al.* (1972) who discovered the smoked MgO moderator. Although only a very small fraction, 3×10^{-5}, of the incident β^+ activity was converted into a usable low energy beam, this advance paved the way for the ensuing rapid progress. Later in the same decade, the phenomenon of positron emission and re-emission from various surfaces, carefully prepared under ultra-high vacuum conditions, was investigated, mainly by Mills and his coworkers (see e.g. Mills, 1983a), and a physical understanding was obtained of the processes involved. As this understanding grew, so too did the efficiency of moderation (as the conversion process from fast to slow positrons is known); this culminated in the solid neon moderator (Mills and Gullikson, 1986) and variants thereof, which have moderation efficiencies close to 10^{-2}, fully six orders of magnitude greater than that in the seminal observation by Cherry (1958).

The mechanisms involved in the emission and re-emission of positrons from surfaces, and the attendant formation of beams with well-defined energies, are central to the main theme of this book and are described in greater detail in section 1.4.

1.2 Basic properties of the positron and other positronic systems

1 Positrons

The positron has an intrinsic spin of one half and is thus a fermion. According to the CPT theorem, which states that the fundamental laws of physics are invariant under the combined actions of charge conjugation (C), parity (P) and time reversal (T), its mass, lifetime and gyromagnetic ratio are equal to those of the electron, and it has the same magnitude of electric charge, though of opposite sign. There are at present no known exceptions to the CPT theorem.

Experimentally it has been shown from studies involving trapped particles that the gyromagnetic ratios of the electron and the positron are equal to within 2 parts in 10^{12} (Van Dyck, Schwinberg and Dehmelt, 1987). The magnitudes of the charges of the electron and the positron have been found by Hughes and Deutch (1992) to be equal to 4 parts in 10^8 in an analysis of the measured charge-to-mass ratios and the values of the Rydberg constant derived from the energy spectra of hydrogen and positronium. A more stringent, though indirect, limit of 1 part in 10^{18} for the difference in charge magnitude was derived by Müller and Thoma (1992), in a method based on limits for the neutrality of atomic matter. They concluded that, because equal numbers of electrons and positrons contribute to the vacuum polarization of atoms, there would be an overall net charge on matter unless the charges of the two particles balanced precisely.

Current theories of particle physics predict that, in a vacuum, the positron is a stable particle, and laboratory evidence in support of this comes from experiments in which a single positron has been trapped for periods of the order of three months (Van Dyck, Schwinberg and Dehmelt, 1987). If the CPT theorem is invoked then the intrinsic positron lifetime must be $\geq 4 \times 10^{23}$ yr, the experimental limit on the stability of the electron (Aharonov *et al.*, 1995).

When a positron encounters normal matter it eventually annihilates with an electron after a lifetime which is inversely proportional to the local electron density. In condensed matter lifetimes are typically less than 500 ps, whilst in gases this figure can be considered as a lower limit, found either at very high gas densities or when the positron forms a bound state or long-lived resonance with an atom or molecule.

Annihilation of a positron with an electron may proceed by a number of mechanisms, and the Feynman diagrams for the radiationless process, which results in electron emission, and for the single-, two- and three-gamma processes are given in Figure 1.1. The positron can also annihilate with an inner shell electron in a radiationless process, the consequent energy release giving rise to nuclear excitation (see Saigusa and Shimizu, 1994, for a summary). The most probable of these annihilation processes, when the positron and electron are in a singlet spin state, is the two-gamma process, the cross section for which was derived by Dirac (1930) to be

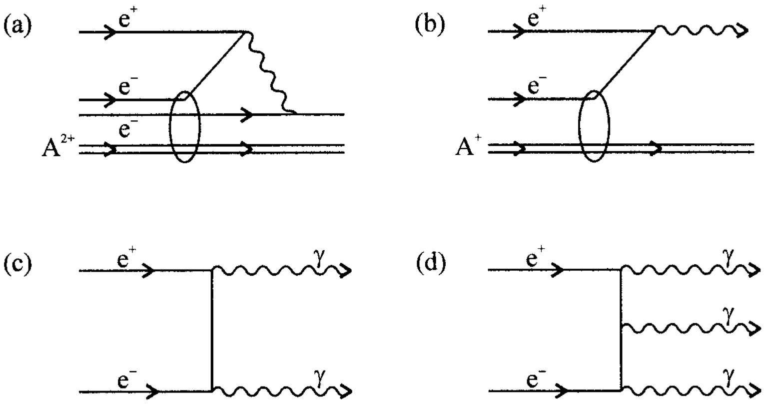

Fig. 1.1. Feynman diagrams of the lowest order contributions to (a) radiationless, (b) one-gamma, (c) two-gamma, (d) three-gamma-ray annihilation. A^{2+} and A^+ denote the charge states of the remnant atomic ion.

$$\sigma_{2\gamma} = \frac{4\pi r_0^2}{\gamma+1}\left[\frac{\gamma^2+4\gamma+1}{\gamma^2-1}\ln\left(\gamma+\sqrt{\gamma^2-1}\right)+\sqrt{\gamma^2-1}-\frac{\gamma+3}{\sqrt{\gamma^2-1}}\right], \tag{1.2}$$

where $r_0 = e^2/(4\pi\epsilon_0 mc^2)$ is the classical radius of the electron, $\gamma = 1/\sqrt{(1-\beta^2)}$, $\beta = v/c$, and v is the speed of the positron relative to the stationary electron. Of most relevance for our discussion is annihilation at low positron energies, where $v \ll c$, so that equation (1.2) reduces to the familiar form

$$\sigma_{2\gamma} = 4\pi r_0^2 c/v. \tag{1.3}$$

Note that $\sigma_{2\gamma} \to \infty$ as $v \to 0$, although the annihilation rate, which is proportional to the product $v\sigma_{2\gamma}$, remains finite. At low incident positron energies the two gamma-rays are emitted almost collinearly, the energy of each being close to mc^2 (= 511 keV). Annihilation of a small fraction of the positrons emanating from the radioactive source can occur at relativistic speeds and then it is necessary to use the full equation (1.2).

Annihilation can also occur with the emission of three (or more) gamma-rays, and Ore and Powell (1949) calculated that the ratio of the cross sections for the three- and two-gamma-ray cases is approximately 1/370. Higher order processes are expected to be further depressed by a similar factor. A case in point is the four-gamma-ray mode, for which the branching ratio with the two-gamma-ray mode was shown by Adachi *et al.* (1994) to be approximately 1.5×10^{-6}, in accord with QED calculations.

The two other processes shown in Figure 1.1 are the radiationless and single quantum annihilations (RA and SQA respectively), and both need to involve the nucleus or the entire atom in order to conserve energy and momentum simultaneously. As such, they are much less probable than the two-gamma-ray process and have been much less studied. Both processes are expected to involve mainly inner shell electrons. In the RA case shown here the energy released in the annihilation of the positron with a bound electron is transferred to another bound electron, which is then liberated with a kinetic energy of $E + mc^2 - 2E_\mathrm{b}$, where E is the total energy of the positron as defined in equation (1.1) and E_b is the binding energy of each of the two electrons involved (assumed here to be equal). Similarly in SQA, the emitted gamma-ray has an energy of $E + mc^2 - E_\mathrm{b}$.

The Born approximation for the cross section for SQA predicts a Z^5 dependence, where Z is the atomic number of the atom involved in the annihilation (e.g. Bhabha and Hulme, 1934), and its maximum value is approximately 5×10^{-29} m^2 at kinetic energies of the order of a few hundred keV; at these energies the positron can penetrate deep into the electronic core of the atom. The most recent experimental work by Palathingal *et al.* (1995), using a high-energy-resolution gamma-ray detector, has resolved the contributions to SQA from the K-, L- and M-shells for a number of targets. They found that the annihilation cross section for the K-shell scaled as $Z^{5.1}$, whereas the L-shell had a characteristic exponent of 6.4. Further details on the theoretical and experimental situation are given by Palathingal *et al.* (1995) and Bergstrom, Kissel and Pratt (1996).

The experimental evidence for radiationless annihilation is not very convincing and, indeed, the only claim to have observed this phenomenon is that of Shimizu, Mukoyama and Nakayama (1965, 1968), who used a β-ray spectrometer to fire 300 keV positrons into a lead foil. The emitted electrons were recorded using a silicon detector which allowed some energy selection. An excess of measured counts was found in the energy region to be expected for the target, and the derived cross section was approximately 10^{-30} m^2. According to theoretical work on radiationless annihilation by Mikhailov and Porsev (1992), in which the strong Coulomb repulsion experienced by the positron was taken into account, the cross section should scale as Z^8, with a value of approximately 10^{-32} m^2 at a positron kinetic energy of 500 keV and for a target with $Z = 80$. This is nearly two orders of magnitude lower than the value obtained by Massey and Burhop (1938), the discrepancy being attributed to the use of a plane wave representation of the electron state by Massey and Burhop. In the light of the more recent theoretical value, the experimental result appears too high, and further investigations are required.

Additional aspects of positron annihilation, with particular emphasis on the processes of relevance to atomic collisions at low energies, are described in Chapter 6.

2 Positronium

Positronium is the name given to the quasi-stable neutral bound state of an electron and a positron. It is hydrogen-like, but because the reduced mass is $m/2$ the gross values of the energy levels are decreased to half those found in the hydrogen atom, so that the binding energy of ground state positronium is approximately 6.8 eV. An energy level diagram of the ground and first excited states, with principal quantum numbers $n_{\mathrm{Ps}} = 1$ and 2 respectively, is given in Figure 1.2. Note that the fine and hyperfine separations are markedly different from the corresponding values for hydrogen, owing to the large magnetic moment of the positron (658 times that of the proton) and the presence of QED effects such as virtual annihilation (see e.g. Berko and Pendleton, 1980, and Rich, 1981, for summaries).

Positronium can exist in the two spin states, $S = 0$, 1. The singlet state ($S = 0$), in which the electron and positron spins are antiparallel, is termed para-positronium (para-Ps), whereas the triplet state ($S = 1$) is termed ortho-positronium (ortho-Ps). The spin state has a significant influence on the energy level structure of the positronium, and also on its lifetime against self-annihilation.

The need to conserve angular momentum and to impose CP invariance led Yang (1950) and Wolfenstein and Ravenhall (1952) to conclude that positronium in a state with spin S and orbital angular momentum L can only annihilate into n_γ gamma-rays, where

$$(-1)^{n_\gamma} = (-1)^{L+S}. \tag{1.4}$$

This selection rule does not appear to exclude radiationless annihilation and annihilation into a single gamma-ray, but these modes of annihilation are nevertheless forbidden for free positronium.

For ground state positronium with $L = 0$, annihilation of the singlet ($1^1\mathrm{S}_0$) and triplet ($1^3\mathrm{S}_1$) spin states can only proceed by the emission of even and odd numbers of photons respectively. Thus, in the absence of any perturbation the annihilation of para-Ps proceeds by the emission of two, four etc. gamma-rays, and the annihilation of ortho-Ps by the emission of three, five etc. gamma-rays. In both cases the lowest order processes dominate although observation of the five-photon decay of ortho-positronium has been reported (Matsumoto *et al.*, 1996). It is expected from spin statistics that positronium will in general be formed with a population

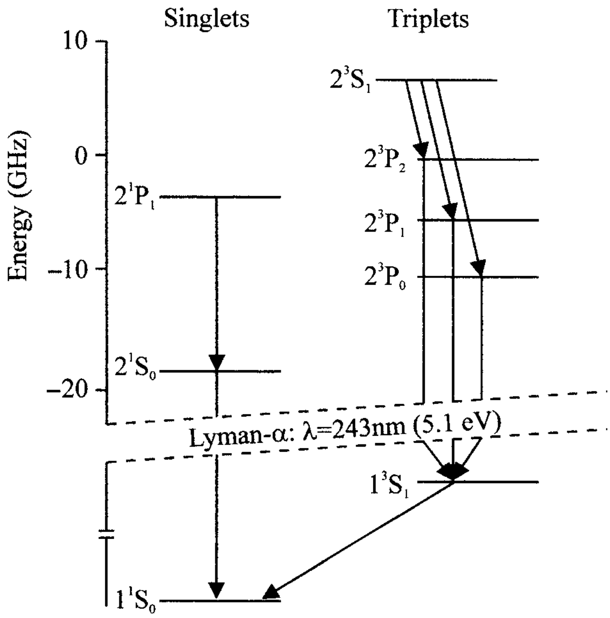

Fig. 1.2. Level diagram of the ground and first excited states of the positronium atom. The splittings are shown for the excited state. The Bohr energy level at $\frac{1}{8}$ ryd is chosen as the arbitrary zero and the 2^3P_2 and 2^1P_1 states are located approximately 1 GHz and 3.5 GHz respectively below that level. The frequencies in GHz are: $2^3S_1 \rightarrow 2^3P_2$, 8.62; $2^3S_1 \rightarrow 2^3P_1, 13.0$; $2^3S_1 \rightarrow 2^3P_0$, 18.5; $2^1P_1 \rightarrow 2^1S_0$, 14.6; $1^3S_1 \rightarrow 1^1S_0$, 203.4.

ratio of ortho- to para- equal to 3 : 1, and in the absence of any significant quenching (e.g. via the conversion of ortho-Ps to para-Ps considered in section 7.2), most of the ortho-Ps which is formed will eventually annihilate in this state. Thus, the three-gamma-ray annihilation mode will be much more prolific for positronium than it is for free positron annihilation. The three gamma-rays are emitted in a coplanar fashion, with predicted energy distributions (Ore and Powell, 1949; Adkins, 1983) shown in Figure 1.3(a) along with a recent experimental observation (Chang, Tang and Yaoqing, 1985). The difference between this and the near-monochromatic 511 keV radiation characteristic of the dominant two-gamma-ray annihilation of free positrons provides one way in which to distinguish between these two annihilation modes. This is emphasized in Figure 1.3(b), which shows gamma-ray energy spectra obtained using a high resolution detector under conditions of 0% and 100% positronium formation (Lahtinen *et al.*, 1986).

The lowest order contributions to the annihilation rates for the $n_{\mathrm{Ps}}{}^1S_0$ and $n_{\mathrm{Ps}}{}^3S_1$ states of positronium were first calculated by Pirenne (1946)

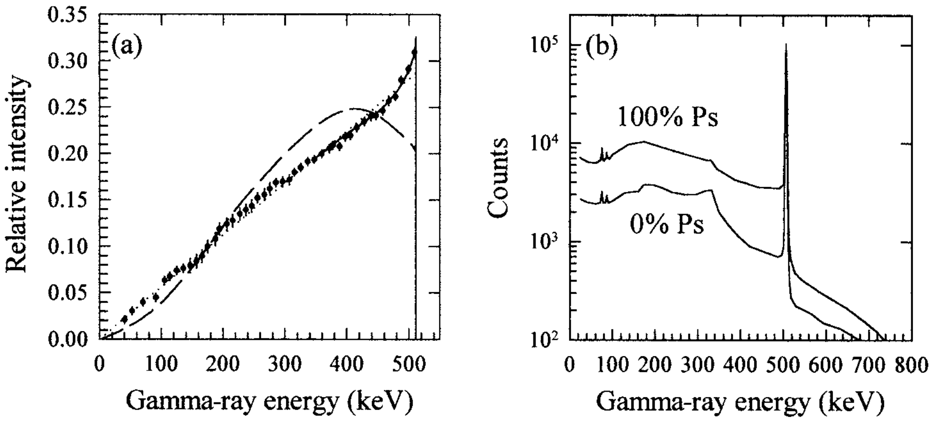

Fig. 1.3. (a) The gamma-ray energy spectrum for the three-photon decay of ortho-positronium. The broken curve is from the theoretical work of Ore and Powell (1949) whilst the dotted line shows the theory of Adkins (1983); the solid line includes an O(α) QED correction. The experimental points are from Chang *et al.* (1985). (b) Schematic gamma-ray energy spectra taken using a high resolution detector under conditions where the fraction of positrons forming positronium is 0% and 100% (e.g. Lahtinen *et al.*, 1986).

and Ore and Powell (1949) respectively, and are given by

$$\Gamma_{2\gamma}\left(n_{\text{Ps}}{}^1\text{S}_0\right) = \frac{1}{2}\frac{mc^2}{\hbar}\frac{\alpha^5}{n_{\text{Ps}}^3} \tag{1.5}$$

and

$$\Gamma_{3\gamma}\left(n_{\text{Ps}}{}^3\text{S}_1\right) = \frac{2}{9\pi}(\pi^2 - 9)\frac{mc^2}{\hbar}\frac{\alpha^6}{n_{\text{Ps}}^3}, \tag{1.6}$$

where $\alpha \approx 1/137.036$ is the fine structure constant. Inspection of these two expressions reveals that, owing to the extra power of α and to the numerical factor in equation (1.6), the two-gamma-ray annihilation rate is much greater than that for the three-gamma-ray process. For $n_{\text{Ps}} = 1$, it is found that $\Gamma(1^1\text{S}_0) \approx 8$ GHz whereas $\Gamma(1^3\text{S}_1) \approx 7$ MHz. The lifetimes against annihilation of the 1^1S_0 and 1^3S_1 states, being the reciprocals of their annihilation rates, are therefore around 1.25×10^{-10} s and 1.4×10^{-7} s respectively. Further details of higher order contributions to the annihilation rates can be found in the review of Rich (1981) and in Chapter 7, where relevant experimental work is also described.

Considering the $n_{\text{Ps}} = 2$ states (2^1S_0, 2^1P_1, 2^3S_1, and 2^3P_J, with $J =$ 0, 1, 2), the S-state lifetimes display the n_{Ps}^3 scaling law of equations (1.5) and (1.6). For a given value of n_{Ps} the probability that the positron and electron will be found very close together is much lower, and therefore the lifetime against annihilation is much greater for states with $L \neq 0$ than for states with $L = 0$. Alekseev (1958, 1959) calculated the lifetime against annihilation for positronium in the 2P states to be $> 10^{-4}$ s, which is several orders of magnitude greater than the mean life for optical de-excitation. The actual lifetime of an excited state against annihilation may therefore be determined mainly by the lifetime of the atomic transition. As an example, the 2P–1S transition has a characteristic lifetime of 3.2 ns, double the value for the corresponding transition in the hydrogen atom. Therefore, instead of the positronium annihilating directly in a 2P state, it is far more likely to make an optical transition to a 1S state, where annihilation will then take place rapidly at a rate given by either equation (1.5) or equation (1.6), depending on the spin state. Note that the prediction of equation (1.4), that annihilation from the 2^3P and 2^1P states is predominantly into two and three gamma-rays respectively, only applies to direct annihilation. If the positronium first undergoes the optical 2P–1S transition, then the annihilation mode in the lower state is determined by the quantum numbers of that state.

3 Other bound states involving positrons

The next most complex bound state after positronium, and one that has now been observed (Mills, 1981), is the positronium negative ion, Ps^-, which consists of two electrons and a positron. This entity (and its charge conjugate counterpart, the positive ion consisting of two positrons and an electron) has a total spin $S = 1/2$ and a ground state configuration of $^1S^e$. It has no long-lived excited states, but there are several autoionizing resonant states. The most recent calculation of its binding energy with respect to break-up into an electron and positronium gives 0.326 68 eV (Ho, 1993; Frolov and Yeremin, 1989), and Ho (1993) obtained a value of 2.086 1222 ns^{-1} for its annihilation rate, in agreement with the experimental result of Mills (1983b). This value is also close to the spin-averaged annihilation rate of ground state positronium, i.e. one quarter of the rate for the 1^1S_0 state. Further discussion can be found in section 8.1.

Hylleraas and Ore (1947) first showed that the complex involving two electrons and two positrons, the positronium molecule Ps_2, is bound, and this was confirmed by the more accurate work of Ho (1986a), Kinghorn and Poshusta (1993) and Kozlowski and Adamowicz (1993). The later calculations gave the binding energy with respect to break-up into two positronium atoms as 0.435 eV, but a significantly larger value, 0.573 eV, has recently been obtained by El-Gogary *et al.* (1995). The system, with total spin $S = 0$, has no bound excited states, but several autodissociating states have been found (Ho, 1989b). Thus far, Ps_2 has not been observed