Chapter 1

Introduction

1.1 Historical foreword to positron physics research

One of the biggest unsolved puzzles in physics is the origin of the process known as baryogenesis, through which the apparent asymmetry between matter and antimatter that is currently observable in the visible cosmos developed in the very first stages of the early universe (Kolb and Turner, 1994). According to the Big Bang theory, in fact, equal amounts of particles and antiparticles should have created at the time of the primordial expansion of the universe (Kolb and Turner, 1994). Since antimatter and matter annihilate when they interact, a self-destruction of the young universe shortly after its early development should have occurred. However, as this was clearly not the case, some physical laws must have acted in an unknown way to produce the predominance of particles over antiparticles in the present universe, as we know it.

The major subject of interest in the present thesis, namely the positron, is the most simple and most abundant example of such rare antiparticles. The positron is the antimatter counterpart of the electron, as they share the same mass, spin (½) and magnitude of the electric charge, but have opposite signs on the charge: the positron is positively charged, whereas the electron is negative. When an electron and a positron collide with each other, they may mutually annihilate and the result of this impact is the emission of two gamma ray photons, each with an energy equal to the electron or positron rest energy (i.e. 511 keV). Despite this very close similarity in the physical properties between the electron and the positron, their behaviour in their interaction with matter can be very different. This soon became pretty clear to the scientists who started the very first experiments of modern positron atomic physics, in between the late 1940s and early 1950s (Shearer and Deutsch, 1949; Deutsch, 1951), and thereby discovered a new bound state made up of a positron and an electron, the so-called positronium atom.

To really highlight the exceptional role played by positrons in the development of physics, we have to go further back in time by some 20 additional years when the existence of the antimatter counterpart of the electron was first postulated by Paul Dirac. At that time Dirac was trying to develop a relativistic theory of quantum mechanics and, in an effort to derive the relativistic version of the Schrödinger quantum mechanical equation of motion for the wavefunction of the electron, he found that the expected solution to that system of equations was not unique. Indeed the solution envisaged the possibility of electrons having either positive energy (as the electron does) or negative energy (Dirac, 1928). However, the existence of another electron-like particle, although with opposite charge, was explicitly predicted by Dirac only in the following year (Dirac, 1930). In the beginning he proposed the proton as the potential candidate of such a particle (Dirac, 1930), notwithstanding the fact that the proton was known to have a much greater mass than the electron. Later on, however, possibly following Robert Oppenheimer's contrary arguments to this picture (Close, 2009), Dirac revised his view and ultimately predicted the existence of a particle with the same properties of an electron, but with a positive charge, that had not been observed yet and that he called the "anti-electron" (Dirac, 1931). This particle is of course what we now refer to as a positron.

In the decades after the existence of the positron was postulated, as an obvious progression to Dirac's outstanding result, it became clear that for every known particle there is a corresponding anti-particle with equivalent physical properties, like the mass, spin and the lifetime, but with exactly opposite charge (Close, 2009). This fact is now a well-known implication of the CPT theorem, a fundamental property that requires the conservation of symmetry by all physical phenomena undergoing a simultaneous inversion of charge, parity and time. In fact, the possibility of charge inversion inevitably involves the existence of the matter-antimatter duality in the universe, as a consequence of the preservation of CPT symmetry (Griffiths, 1987).

Since then, it has been demonstrated experimentally that every known kind of particle has a corresponding anti-particle. However, the first anti-particle to have ever been observed was, again, the positron and, like many other findings in the history of physics, this happened almost by chance. The discovery of the positron is commonly attributed to the American physicist Carl Anderson, who, only a few years after Dirac's prediction, detected a track of positively charged particles passing through a cloud chamber and emerging from a lead plate when trying to observe gamma radiation in cosmic rays (Anderson, 1933) (see Fig. 1.1). As the Wilson chamber was immersed in a uniform magnetic field, the curvature radius of the particle trail could be measured and was found to match the mass-to-charge ratio of an electron, even though the particle was bending in the opposite direction owing to its positive charge. Anderson denoted this new particle "positron" and in 1936 he gained the Noble Prize in Physics for the first experimental evidence of antimatter. However, the positron had actually already been observed before independently by the Russian physicist Dmitri Skobeltsyn in 1923 (Close, 2009) and by Chung-Yao Chao, one of Robert Millikan's students at the California Institute of Technology, in 1929 (Mehra and Rechenberg, 2001). This was achieved in two experiments similar to that of Anderson, although without knowing at all that positrons were involved. Skobeltsyn and Chao were, in fact, so puzzled by their results that they remained unexplained until years later when the positron was eventually properly discovered by another of Millikan's students at Caltech, namely Anderson.

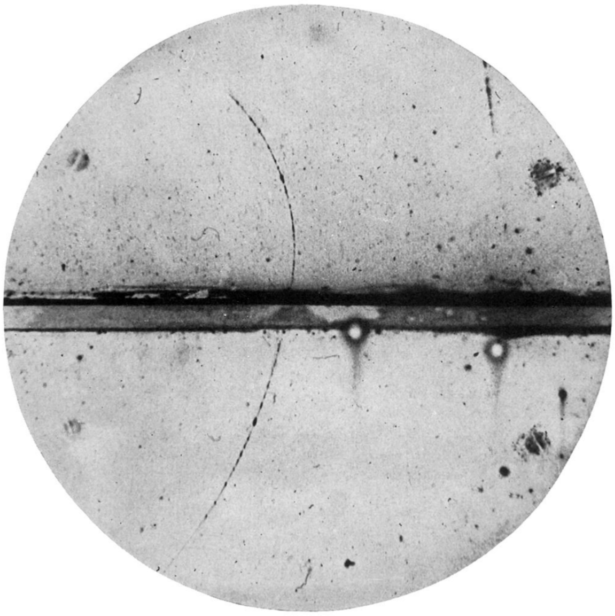

Fig. 1.1. Photograph by Carl Anderson of a track of one of the first positrons ever observed originating from cosmic radiation and passing through a lead plate in a cloud chamber (Anderson, 1933).

Today, it is well known that positrons are generated by β^+ emission radioactive decays (through the weak interaction), or by pair production from a sufficiently energetic photon (that is with an energy > 1.022 MeV, i.e. twice the electron or positron rest energy). However, in the years immediately after the prediction and experimental discovery of the positron, the research on low-energy positron atomic physics progressed quite slowly (Surko *et al.*, 2005), mainly owing to the non-trivial experimental task (for that time) of finding an appropriate positron source and producing a low-energy beam of sufficient positron intensity. In the decades following Anderson's discovery of the positron, the first artificially irradiated radioactive isotopes, like ^{13}N and ^{64}Cu and now the more common ^{22}Na, started to become more readily available for use as efficient positron emitters (Dahl, 2002). Nevertheless, even when these sources had become available, the energy spectrum of the emitted positrons was found to be pretty broad, varying from 0 up to and above hundreds of keV (Mills, 1995). This prevented for some time the possibility of studying low energy positron interactions with matter.

It was only after the discovery of the moderating property of some materials, that low energy beams eventually became available. First W. Cherry (Cherry, 1958) and subsequently, in the late 1960's, D. Groce (Groce *et al.*, 1968) and J. Madey (Madey, 1969), separately found out that low energy positrons would be re-emitted from the surface of some solid materials as the result of the fast incident positrons rapidly slowing down in collisions with the atoms of the material (Coleman, 2000). These results stimulated further interest and research into the thermalizing and surface emitting properties of various materials, and their applications in positron moderating techniques (Tong, 1972; Costello *et al.*, 1972a). Low energy positron beams of sufficient intensity and relatively narrow energy resolution were soon obtained by employing moderators with an efficiency of ~10^{-5}, and in 1972 the first positron total cross section (TCS) measurements of the modern era were ultimately carried out (Canter *et al.*, 1972; Costello *et al.*, 1972b). The first targets to be investigated in these early experiments were simple atomic systems, mainly the noble gases (Bransden and Hutt, 1975; Brenton *et al.*, 1978; Kauppila *et al.*, 1976; Sinapius *et al.*, 1980). The reason these species were examined first is that they represented the relatively easiest system for theoretical modelling, owing to their closed electronic shell structures.

Since then, many other groups in the world have undertaken research on cross section measurements of low-energy positron scattering. We mention the historic groups at the University College London (Canter *et al.*, 1972), Wayne State University (Kauppila *et al.*, 1976), Bielefeld University (Sinapius *et al.*, 1980), University of Texas (Coleman and Hutton, 1980), University of Tokyo (Sueoka and Mori, 1984), Yamaguchi University (Sueoka and Hamada, 1993), University of California (Surko, 2001), University of Trento (Zecca *et al.*, 2005) and, most recently, the research team at the Australian National University (Sullivan *et al.*, 2008c). Over the years, interest on total cross section measurements has moved from the simple atoms to bigger scattering systems like complex molecules (Kauppila and Stein, 1990) and, recently, also bio-molecules (Brunger *et al.*, 2009). At the same time, the experimental techniques have evolved from electrostatic beams based on linear particle accelerators, time of flight methods and magnetically guided linear transmission to buffer-gas trap-based beams in strong magnetic fields (Surko *et al.*, 2005). This development in the experimental configurations has lately allowed the carrying out of very accurate low-energy positron scattering studies, with statistical uncertainties becoming comparable to those typically achievable in experiments involving the commonly much brighter-source electron beams. Positron beam intensities have, in fact, improved from ~1-2 counts per second in the early experiments (Costello *et al.*, 1972b) to ~10^4 counts per second with the introduction of the buffer-gas trap (Surko *et al.*, 2005). This is basically a consequence of the dramatic enhancement in moderator efficiencies from 10^{-7} in the first moderators (Groce *et al.*, 1968), to 10^{-3} with the mono-crystal metals like tungsten (Lynn *et al.*, 1985) and on to more than 1% with the introduction of the solid noble-gas moderators (Mills and Gullikson, 1986; Greaves and Surko, 1996). The energy resolution of the positron beams has also improved from the initial modest ~1-1.5 eV (Canter *et al.*, 1972; Costello *et al.*, 1972b) down now to as low as ~18-25 meV (Surko *et al.*, 2005). As a result of this experimental progress in positron technology, a whole new research avenue of precise measurements for state-specific collision processes (elastic scattering, excitation, ionization, positronium formation, vibrations, rotations), and for differential scattering distributions, has been undertaken in recent years. Note that this has not been restricted to positrons only, but has involved also positronium as the investigation probe (Surko *et al.*, 2005).

At present, positrons are not only used to investigate their basic interactions with matter and its constituents, although these kind of studies remain the key research topic in positron physics, they are also currently exploited in a series of diverse scientific and technological applications, with both fundamental and practical implications. Among the examples of positrons important role in understanding the fundamentals of atomic physics, we mention their application in creating anti-hydrogen atoms (Andresen *et al.*, 2010), which might possibly help our understanding for the baryon asymmetry in the universe. Amongst the numerous technological applications of positrons we cite the relevance of positron lifetime measurements in annihilation studies on solid material surfaces, in order to characterize the materials at the nanoscale and detect the presence of any defects or cavities in their microscopic structure (Schultz and Lynn, 1988). These kind of studies, in fact, can have significant practical applications in nanotechnology and medicine. Finally, another relevant positron-based technique that is now well-established and extensively employed as a clinical tool, is positron emission tomography (PET) for imaging of the metabolic processes occurring in the human body and also for the diagnosis of certain types of tumours (Wahl and Buchanan, 2002).

1.2 Motivations behind this thesis

The recent progress achieved in the research field of positron physics has been impressive, thanks to both important developments in the experimental techniques employed to study the scattering dynamics between positrons and atoms or molecules and also the advances in scattering theory towards an understanding of the fundamental interactions driving the various collisional processes (Surko *et al.*, 2005). Nevertheless there is still a lot of scope for further development, as there are some unclear points and many open questions regarding the interaction of positrons with matter. The plan of the present thesis was to undertake low energy cross section measurements for positron scattering from atoms and molecules, with the aim of trying to shed light on some of those subjects. In order to achieve that, low energy positron collision experiments were carried out with two different beamlines, the positron spectrometer at the University of Trento in Italy and the apparatus for atomic and molecular positron collisions at The Australian National University in Canberra. In the following we briefly summarise the most important rationales behind the work presented in this thesis.

First of all, from a fundamental perspective, it is very interesting to study the basic forces driving the process of an incoming positron scattering off target atoms or molecules at very low energy. Information about those interactions can be precisely inferred from the magnitude and energy dependence of the total cross section measured in that energy range. In this respect, it was a particular motivation to investigate the role that the relevant physico-chemical properties of the target might play in driving the main collisional interactions and how they are reflected in the measured cross sections. The target properties are expected to affect especially the very low energy total cross section, i.e. below the positronium formation threshold, and that is why the present measurements focus on gathering data to energies below about 1 eV. In the past, this low energy range has rarely been experimentally investigated, if not at all in many cases (Kauppila and Stein, 1990; Surko *et al.*, 2005). The reason for this is that the earlier experimental techniques were often not capable of going down so low in energy, whereas the apparatus at the University of Trento was developed precisely to perform those very low energy measurements. Moreover, scattering theory calculations are usually available at these low energies, but because of the lack of experimental data, it was not possible to validate those theory results. Therefore, another of the motivations for the present measurements is to provide the very first experimental data in this very low energy range, in order to check for the validity of the existing computations.

The availability of experimental cross section results is important at all energies in order to support the development of positron scattering theory. However, mainly owing to the different experimental effects that inevitably affect the measurements (e.g. the forward angle scattering effect – see Chapter 2) and sometimes also because of a discrepancy in the techniques employed in the various experiments, a large scatter is often present among the existing experimental data sets on a given target. This, of course, somewhat complicates the interpretation of the results of the theoretical calculations, as it is not clear exactly what experimental data the model should attempt to reproduce. Therefore, an important rationale behind the present measurements is also to provide very accurate total cross sections, which can eventually be considered as experimental benchmark results, against which scattering models can be tested rigorously with high confidence.

A particularly intriguing reason for undertaking positron scattering experiments, is to compare those results with the available corresponding cross sections for electron collisions on the same target. From this comparison, in fact, additional information about the different behaviour of the two conjugated particles and their somewhat diverse interactions with matter can be inferred. At low energy the differences in positron collisions, with respect to those involving electrons, include the repulsive mean static field for the positron-target interaction, opposite to the attractive electron-target potential, the absence of an exchange interaction and the presence of an additional scattering channel, namely positronium formation (either virtual or real). The latter process leads to stronger correlation effects in positron scattering, as compared to electron scattering, owing to the attractive electron-positron Coulomb interaction (Surko *et al.*, 2005).

Finally, a very recent research avenue for which positron scattering has become of real importance is the study of the effects of radiation damage on biomolecular systems. Since the discovery almost a decade ago that low energy secondary electrons, emitted by primary ionising radiation entering the human body, can attach to and cause single and double-strand breaks in the structure of the nucleic acids, as well as the fragmentation of their various components (Boudaiffa *et al.*, 2000), the availability of cross sections for either positron or electron scattering off biologically relevant molecules has become crucial. These, in fact, represent the essential input data for the codes simulating low-energy particle tracks in biological matter (Fuss *et al.*, 2010; Muñoz *et al.*, 2008). However, unfortunately, cross sections for the relevant biomolecules are typically unavailable, because of the difficulty in working with targets that are often solid at room temperature and are also thermally instable, as they tend to decompose with increasing temperature. Hence, the need for investigating smaller but related species of biological interest has now become of almost primary importance in the field.

1.3 Overview of positron scattering theory

In order to set the positron cross section measurements presented in this thesis into a general theoretical frame, we now briefly review the concepts for scattering of a particle off matter, with a particular focus on positrons colliding with atoms and molecules. We first outline the fundamental forces behind the low-energy interaction between the incident positrons and the atoms or molecules, of which the target is composed, and the various possible events that may occur as an outcome of the collisional process. Then we provide a précis of the non-relativistic quantum-mechanical description of the process of elastic scattering of a particle (the probe) impinging on another particle, or aggregate of particles (the target), and interacting with each other via a central potential. From this formulation we subsequently derive the theoretical expressions for the total cross section and the differential cross section (DCS), which are two of the main quantities that are actually measured in a “real” scattering experiment. Finally we provide a very brief overview of a selected set of the most relevant currently existing models, as used to calculate the scattering cross sections of interest, both for the case of atoms and molecules as the component units of the target.

1.3.1 Low-energy interactions and scattering channels

First of all, let us describe the fundamental forces responsible for the process of a low-energy positron interacting with an atom or molecule. To this end, we refer to the review paper by Surko *et al.* (2005) and to the lecture notes of McEachran (2011).

The two main interactions that drive the physical dynamics of an incoming positron colliding with a target atom or molecule at very low energy, i.e. below the positronium formation threshold, are the static and the dipole interaction. The static potential derives from the mean static field of the target, which in turn is due to the short-range repulsive Coulomb interaction $V_C(r)$ between the positively charged positron and the positive charge q of the nucleus:

$$V_C(r) = k_e \frac{q}{r}, \tag{1.1}$$

where r is the separation distance and k_e is the Coulomb constant. As a consequence, the incident positron does not penetrate far inside the atomic or molecular charge cloud. Note that this is a major difference in comparison to the way electrons interact with matter, as electrons have a negative charge and thus the static potential is negative (i.e. attractive) in that case.

When it is still far away from the target, however, the incident positron can polarise the targets electron cloud and, as a consequence, it interacts with the field of the distorted atom or molecule, giving rise to a long-range attractive polarisation potential $V_P(r)$. This potential depends on the level of polarisation of the electron cloud, which is a quantity precisely represented by the dipole polarisability α of the target:

$$V_P(r) = -\frac{\alpha e^2}{2r^4}, \tag{1.2}$$

where e is the positron charge. We note that the dipole interaction is attractive also for electron scattering, although the extent of the attraction is not necessarily the same as for positrons.

As a consequence of the opposite nature of these two primary electrostatic forces, the nett positron-target potential will be determined by the competition in the strength of the two interactions, which can vary with the energy of the incident positron and depends on the importance of the relevant physico-chemical properties of the target. We note, however, that at very low positron energies, where large separations play a dominant role, the attractive polarisation effect can overcome the repulsive mean static field, leading to an overall negative positron-target potential. This is particularly the case for targets with large dipole polarisabilities and it can result in a rather strong attractive nett potential. This result has the effect of enhancing the scattering probability, which, in turn, is manifested by the typically much higher values of the positron scattering cross section at those low energies, as compared to the higher energies.

The different nature of the static potential for electrons and positrons implies that, at low energy, where only the elastic scattering channel is open in atoms and only elastic, rotational and vibrational channels might be open in molecules, the overall interaction between the target and an electron will be much stronger than it would otherwise be with a positron. This means that, in general, much larger low energy cross sections should be expected for electron scattering with respect to positron collisions on the same species. The opposite sign of the static interaction is not the only feature distinguishing positron from electron scattering. There are other important differences, like the absence of the exchange interaction in positron collisions, as positrons cannot clearly undergo exchange with one of the bound electrons of the target. As the electron exchange interaction is manifest as a somewhat attractive potential, it also contributes to some extent to the anticipated larger magnitude of the low energy electron cross sections as compared to the corresponding cross sections for positrons. However at higher energies, typically between 100-300 eV, the exchange interaction for electron scattering becomes negligible compared to the direct interactions, so that the electron- and positron-target total cross sections might merge.

Two additional inelastic scattering channels are instead exclusive to positron scattering, namely positronium formation and annihilation. Positronium is a bound state of an electron-positron pair, that can be formed during the collision of a positron with an atomic or molecular target, whenever the energy of the incident positron is higher than the difference between the first ionisation energy of the target and the binding energy of the positronium atom (i.e. 6.8 eV). Note that positronium formation leaves the target in a positively ionised state, exactly like another possible scattering process, namely direct ionisation, which is energetically allowed only above the first ionisation potential of the target. However, in the direct ionisation process the incident positron and the ionised electron are free particles, whereas in positronium formation they are bound in an "atom-like" state. This may cause positronium formation to be somewhat difficult to distinguish (experimentally) from the direct ionisation process, while from a theoretical point of view the positronium formation channel is very challenging to incorporate into the scattering models.

Annihilation potentially occurs every time a positron collides with an electron, as the first is the anti-particle of the second. This can occur either with a free electron, or a bound target electron, or after positronium has formed. As a result of an annihilation event, two or more photons are emitted. In the case of two photon emission, two gamma rays are emitted, each with an energy equal to the rest energy of an electron or positron.

At energies below the positronium formation threshold an additional process called virtual positronium formation can still occur. This arises from the possibility of one of the target electrons temporarily joining the incoming positron to form positronium. Virtual positronium formation results in a short-range attractive interaction, which adds to the other attractive positron-target potential, the polarisation effect.

In all cases where the target species is a molecule, another possible positron-molecule interaction has to be taken into account. In addition to the static and polarisation interaction and virtual positronium formation, if the molecule is polar, then another long-range interaction $V_\mathrm{M}(r)$ can play a role in the scattering process. The extent of the effect of this interaction depends on the degree of the polarity of the target, which is accurately represented by the permanent dipole moment μ of the target:

$$V_M(r) \propto \frac{\vec{\mu} \cdot \vec{r}}{r^3}. \tag{1.3}$$

This potential can have a significant attractive effect on the positron, especially if the permanent dipole moment of the target is large.

Moreover, additional inelastic scattering channels even at very low energy, are possible when the target species is a polyatomic molecule. As molecules are structures containing multiple atoms that are "linked" together by different types of bonds, they have several internal degrees of freedom, whose number basically depends on the number of atoms. In general, polyatomic molecules possess vibrational and rotational modes, so that in the process of a positron scattering off a molecular target, a positron with sufficient energy can induce vibrational and rotational excitations. The typical energies required for excitation of molecular vibrations and rotations are very small, so that these processes can take place well below the positronium formation threshold and, thus, represent the first inelastic scattering channels that become open. Note that a vibrational excitation typically occurs simultaneously with the excitation of rotational levels, giving rise to a rovibrational transition. In addition, a vibrational or rovibrational excitation can occur in conjunction with an electronic excitation, leading to a vibronic or a rovibronic transition, respectively.

Electronic transitions can, of course, occur not only in molecules, but also in atoms. Each time the target electrons are excited from an energy level to another one with higher energy, provided that the positron incident on the atom is sufficiently energetic to induce that transition between the two states, electronic excitation might occur. However, note that for atoms the lowest electronic excitation threshold energy is higher than that for the ground state of positronium formation, whereas for molecules it is lower. The energy interval in-between these two thresholds is known as the Ore gap region, where the only two processes energetically allowed for positron-atom scattering are the elastic and the positronium formation channels.

Summarising all the potential pathways for the scattering of a low energy positron off an atom or molecule, we can split them into two main groups, depending on the nature of the collision: elastic and inelastic reactions. Elastic scattering happens whenever the states of the positron and target are left unchanged by the collision and, as a result, the kinetic energy of the scattered positron is the same as that of the incident positron. However, when the incoming positron and the target undergo a change of their initial quantum state during the scattering process, so that the initial positron energy gets in part or entirely lost, the collision then becomes inelastic. Inelastic scattering includes a wide variety of possible outcomes, with the various fundamental scattering processes being listed in Table 1.1.

There are potentially other inelastic processes, originating from the combination of those listed in Table 1.1 and occurring simultaneously. We cite, for instance, rotational and vibrational excitations, vibrational and electronic excitations, rotational plus vibrational and electronic excitations. In addition, direct ionisation can take place together with electronic excitation, whereby the atomic or molecular ion is created in an excited state. Similarly, the positronium atom can also be formed in either its ground state or in one of its excited states.

Table 1.1. A list of the most important scattering processes for a low-energy positron (e^+) colliding with an atom or molecule (A).

Reaction	Scattering channel
$e^+ + A \rightarrow e^+ + A$	Elastic collision
$e^+ + A \rightarrow e^+ + A_r^*$	Rotational excitation (molecules only)
$e^+ + A \rightarrow e^+ + A_v^*$	Vibrational excitation (molecules only)
$e^+ + A \rightarrow e^+ + A_e^*$	Electronic excitation
$e^+ + A \rightarrow A^+ + \mathrm{Ps}(e^+e^-)$	Positronium formation
$e^+ + A \rightarrow e^+ + A^+ + e^-$	Direct ionisation
$e^+ + A \rightarrow A^+ + 2\gamma$	2-photon direct annihilation

We note that the cross section for the 2-photon direct decay scattering channel is typically much smaller than that of the other processes which leave the target in an ionised state, so that the sum of the positronium formation and direct ionisation cross sections basically constitutes the total ionisation cross section. The grand total cross section, which is the primary quantity measured in the experiments described in this thesis, is simply given by the sum of the integral cross sections (ICSs) of the individual scattering channels listed in Table 1.1.

1.3.2 Basics of scattering theory and scattering cross sections

We now briefly summarise the fundamentals of the non-relativistic quantum mechanical theory of elastic scattering of a particle from a target (Fig. 1.2), by making reference to the work of McEachran (2011) and Dalfovo (1995). Our aim is to derive a quantum mechanical analytic expression for the elastic differential cross section, the elastic integral cross section and the total cross section by solving the equation governing the evolution of the wavefunction of a particle, the positron in our case. For ease, we limit the discussion to the case in which the incident particle and the target interact via a constant (as a function of time) central potential.

The starting point for the non-relativistic quantum mechanical description of a particle-target scattering process is the time-independent Schrödinger equation:

$$H\psi(r) = E\psi(r), \tag{1.4}$$

where H is the total Hamiltonian of the particle-target system, ψ is the wavefunction of the system, r is the radial distance in a spherical coordinate reference frame (r, θ, φ) and $E = \hbar^2 k^2/2m$ is the particle incident energy (with $\vec{k}$ the momentum vector of the system). The Hamiltonian H of the system, in turn, is given by:

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(r), \tag{1.5}$$

where $\hbar$ is the reduced Planck constant $(\hbar = h/2\pi)$, m is the mass of the incident particle, ∇^2 is the Laplace operator and V is the interaction potential that depends only upon the relative coordinate r, i.e. it is a central potential.

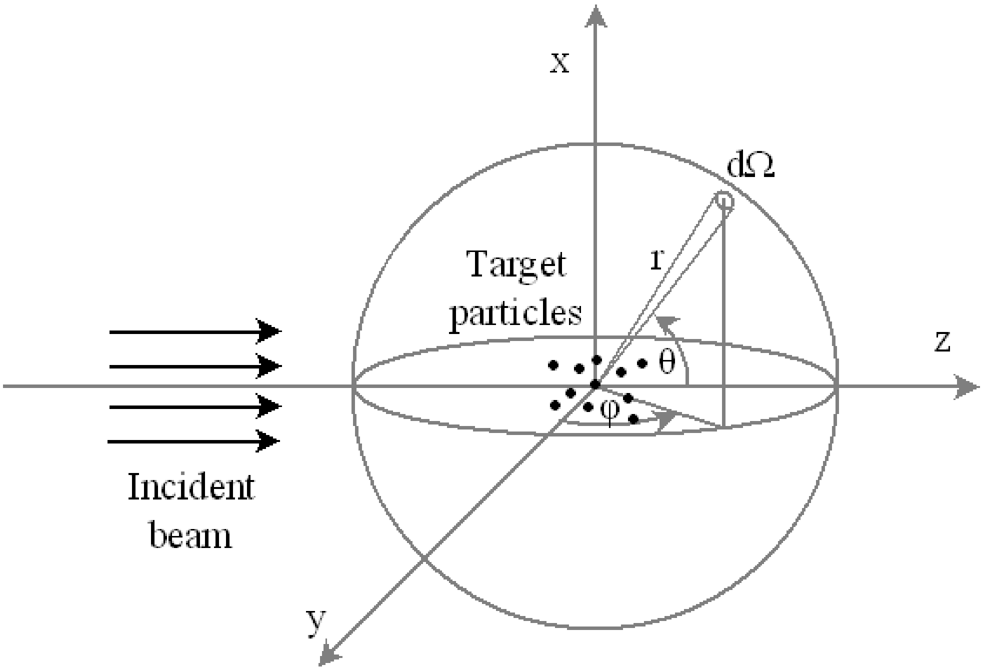

Fig. 1.2. Schematic diagram of a typical differential scattering geometry.

The scattering problem can be solved by finding the exact solution of Eq. (1.4). However, we can expect the asymptotic form of the wavefunction ψ after the scattering, i.e. far away from the central potential of the target, to be that of a free particle with proper boundary conditions. This is a reasonable assumption in the limit of a short-range interaction potential, i.e. a potential such that $V(r) \to 0$ faster than $\sim 1/r$ as $r \to \infty$. In this case, the solution of Eq. (1.4) is a wavefunction $\psi(\vec{k}, \vec{r})$, whose behaviour must satisfy the asymptotic condition:

$$\psi(\vec{k}, \vec{r}) \xrightarrow[r\to\infty]{} A(k) \left[e^{i\vec{k}\cdot\vec{r}} + f(\theta, \varphi) \frac{e^{ikr}}{r} \right], \tag{1.6}$$

where $A(k)$ represents a normalisation constant that does not depend on the coordinate r. Eq. (1.6) indicates that, at large distances, the wavefunction $\psi(\vec{k}, \vec{r})$ can be described by the superposition of an incoming plane wave, corresponding to the incident positron beam, and an outgoing spherical wave, the scattered beam, with an amplitude f that depends on the angular coordinates (θ, φ), as the scattering is in general not isotropic (Fig. 1.3). The function $f(\theta, \varphi)$, is called the scattering amplitude and is related to the differential and the total cross sections, two of the quantities of interest in a scattering experiment. Let us now see why and how.

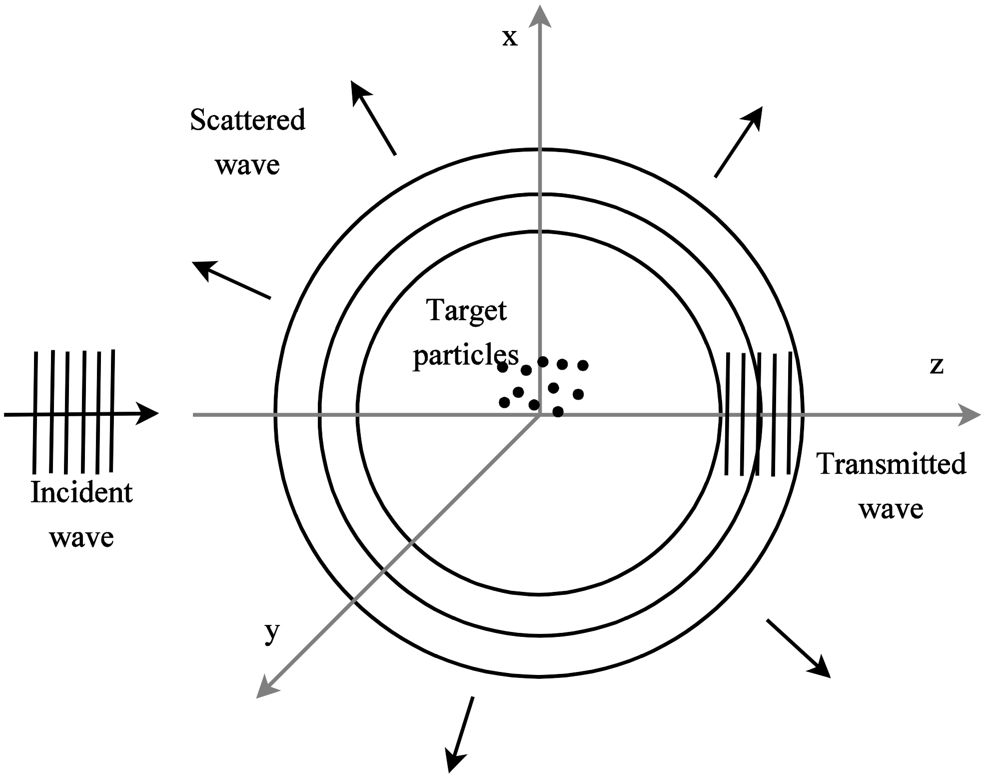

Fig. 1.3. Schematic diagram representing a scattering experiment. An incident plane wave represents the incoming beam, while a spherical wave represents the scattered particles of the beam after collision. The superposition of the scattered and incoming waves forms the transmitted beam in the forward direction.

In general, a cross section is a measure of the effective scattering area of the target intercepted by the incident beam and, therefore, has the dimensions of a surface. The cross section related to a scattering process is, in fact, defined as the ratio of the number of particles of the incident beam that undergo a scattering event of a specific type per unit time and per unit scatterer of the target, to the flux of incoming particles incident onto the target. The incident flux I_0 is given by the number of incident particles per unit time crossing a unit surface area perpendicular to the direction of motion of the beam. Note that the cross section depends exclusively on the intrinsic properties of the probe-target system.

One can select only the particles elastically scattered per unit time, per unit scatterer across a solid angle $d\Omega$ in the direction $\Omega = (\theta, \varphi)$. Their number dN_{el} will then be proportional to both I_0 and $d\Omega$:

$$dN_{\mathrm{el}} = I_0 \sigma_{\mathrm{el}}(\theta, \varphi) d\Omega. \quad (1.7)$$

The constant of proportionality σ_{el} here represents exactly the elastic differential cross section for scattering into the angle (θ, φ):

$$\sigma_{\mathrm{el}}(\theta,\varphi) \equiv \frac{d\sigma_{\mathrm{el}}}{d\Omega}(\theta,\varphi). \tag{1.8}$$

By deriving the quantum-mechanical expression of the probability density current associated to the wavefunction $\psi(\vec{k},\vec{r})$, given in Eq. (1.6), in the asymptotic region $r \to \infty$, one can show that the outgoing flux of particles passing through the surface area $r^2 d\Omega$, for very large r, is given by:

$$dN_{\mathrm{el}} = |f(\theta,\varphi)|^2 I_0 d\Omega. \tag{1.9}$$

Therefore, by substituting Eq. (1.9) into Eq. (1.7), the elastic differential cross section is:

$$\frac{d\sigma_{el}}{d\Omega}(\theta,\varphi) = |f(\theta,\varphi)|^2. \tag{1.10}$$

The scattering amplitude is, thus, related to the probability of elastic scattering at an angle (θ,φ) and connects the differential cross section to the asymptotic form of the wavefunction $\psi(\vec{k},\vec{r})$, which is a solution of the Schrödinger equation (Eq. 1.4). Eq. (1.10) is a fundamental result, because, in principle, it provides a relationship between the information gathered from the scattering experiments and the theoretical calculations of scattering theory.

The total number of particles elastically scattered out of the incident beam per unit time and per unit scatterer is obtained by integrating Eq. (1.7) over the full solid angle:

$$N_{\mathrm{el}} = I_0 \sigma_{\mathrm{el}}. \tag{1.11}$$

Similarly, the elastic integral cross section can be calculated by integrating the elastic differential cross section of Eq. (1.8) throughout the entire solid angular range, i.e.

$$\sigma_{\mathrm{el}} = \int_0^{4\pi} \frac{d\sigma_{\mathrm{el}}}{d\Omega}(\theta,\varphi)\, d\Omega = \int_0^{2\pi} \mathrm{d}\varphi \int_{-\pi/2}^{\pi/2} \frac{d\sigma_{\mathrm{el}}}{d\Omega}(\theta,\varphi) \sin\theta\, d\theta\,. \tag{1.12}$$

Substituting Eq. (1.10) into Eq. (1.12), we obtain:

$$\sigma_{\mathrm{el}} = \int_0^{4\pi} |f(\theta,\varphi)|^2\, d\Omega = \int_0^{2\pi} \mathrm{d}\varphi \int_{-\pi/2}^{\pi/2} |f(\theta,\varphi)|^2 \sin\theta\, d\theta\,. \tag{1.13}$$

Depending on the specific type of scattering event, different kinds of cross sections can be defined: the elastic integral cross section, the positronium formation cross section, the direct ionisation cross section, and so on (see Section 1.3.1). Thus, similar to the results we have outlined for elastic scattering, one can define also the differential and the integral cross sections for all the individual inelastic processes that may occur, when more than one scattering channel is open. The total cross section at each energy will then be simply obtained by summing up the integral cross sections of the various individual processes that are energetically allowed at that energy:

$$\sigma_{\text{tot}} = \sigma_{\text{el}} + \sigma_{\text{Ps}} + \sigma_{\text{ion}} + \dots \tag{1.14}$$

Finally, the total number of particles scattered out of the incident beam per unit time and per unit scatterer is related to the total cross section in the following way:

$$N_{\text{tot}} = I_0 \sigma_{\text{tot}}. \tag{1.15}$$

We have observed that the scattering amplitude is related to the scattering cross sections. To obtain the scattering amplitude, in principle, we do not need to know the wavefunction $\psi(\vec{k},\vec{r})$, but it is enough to find out its asymptotic form, i.e. Eq. (1.6). However, in practice, the full wavefunction $\psi(\vec{k},\vec{r})$ has to be known, in order to determine its asymptotic form. Now, let us briefly summarize how a solution $\psi(\vec{k},\vec{r})$ of the Schrödinger equation (Eq. 1.4) and an explicit expression for the scattering amplitude can be obtained in the particular case in which the interaction potential is central. In this case, in fact, it is possible separate the radial and angular coordinates in the Schrödinger equation (Eq. 1.4). By expressing the Laplace operator in Eq. (1.5) in spherical coordinates, the Hamiltonian of the system assumes the following form:

$$H = -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{l^2}{\hbar^2 r^2}\right] + V(r), \tag{1.16}$$

where l^2 is the total orbital angular momentum operator:

$$l^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]. \tag{1.17}$$

We can take advantage of the fact that the angular momentum operator l^2 and its projection l_z along the z-axis, commute with the Hamiltonian H, i.e. $[l^2, H] = [l_z, H] = 0$, to expand the wavefunction $\psi(\vec{k},\vec{r})$ in terms of partial waves. In addition, as we expect $\psi(\vec{k},\vec{r})$ to be symmetric about the z-axis, i.e. to be independent of the coordinate φ, we can write:

$$\psi(\vec{k},\vec{r}) = \sum_{l=0}^{\infty} a_l(k)\frac{u_l(k,r)}{r}P_l(\cos\theta). \tag{1.18}$$

In Eq. (1.18), $a_l(k)$ are coefficients to be determined, $u_l(k,r)$ are the radial functions and the angular functions $P_l(\cos\theta)$ are the Legendre polynomials of degree l. Note that the wavefunction does not depend on the quantum number m, the eigenvalues of the l_z operator with the spherical harmonics as the associated eigenfunctions. The radial partial waves $u_l(k,r)$ must satisfy the Schrödinger equation:

$$\left[\frac{d^2}{dr^2} + k^2 - \frac{l(l+1)}{r^2} - U(r)\right] u_l(k,r) = 0, \tag{1.19}$$

where $U(r) = 2mV(r)/\hbar^2$.
If the following condition holds:

$$\lim_{r\to\infty} r u_l(r) = 0, \tag{1.20}$$

the spectrum for the solutions of the Schrödinger equation (Eq. 1.19) is split into two parts:

$$E < 0 \qquad u_l(r=0) = 0, \tag{1.21}$$

$$E > 0 \qquad \lim_{r\to\infty} u_l(r) = A_l(k)\sin\left[kr - \frac{l\pi}{2} + \delta_l(k)\right]. \tag{1.22}$$

We are interested in the non-trivial solutions with $E > 0$. These solutions contain the terms $\delta_l(k)$, called phase shifts, defined for each partial-wave of angular momentum $l = 0, 1, 2, ...$ and often referred to as the s-wave, p-wave, d-wave, etc. phase shifts. The quantities $\delta_l(k)$ basically represent the overall effect of the scattering by the interaction potential, which is manifested as shifts in the phase of each l^{th} partial wave.

Hence, the scattering problem reduces to relating the phase shifts $\delta_l(k)$ to the scattering amplitude $f(\theta,\varphi)$. This is achieved by matching the asymptotic behaviour of the solutions of the Schrödinger equation for the radial partial waves $u_l(k,r)$ (Eq. 1.19), in the limit $r \to \infty$ for $U \neq 0$ (Eq. 1.22) and $U = 0$, and successively substituting then into Eq. (1.18) to get the corresponding expression for the total wavefunction $\psi(\vec{k},\vec{r})$. Then, by comparing with the asymptotic form of the wavefunction $\psi(\vec{k},\vec{r})$ for $r \to \infty$ in Eq. (1.6), the scattering amplitude is obtained:

$$f(\theta,\varphi) = f(\theta) = \frac{1}{k}\sum_{l=0}^{\infty}(2l+1)e^{i\delta_l(k)}\sin\delta_l(k)\,P_l(\cos\theta)\,. \tag{1.23}$$

Substituting Eq. (1.23) into Eq. (1.10), the elastic differential cross section is:

$$\frac{d\sigma_{el}}{d\Omega}(\theta,\varphi) = \frac{1}{k^2}\sum_{l,l'=0}^{\infty}(2l+1)(2l'+1)e^{i(\delta_l-\delta_{l'})} \\ \cdot \sin\delta_l \sin\delta_{l'} P_l(\cos\theta)P_{l'}(\cos\theta)\,. \tag{1.24}$$

The elastic integral cross section is instead obtained by inserting Eq. (1.23) into Eq. (1.13):

$$\sigma_{\mathrm{el}} = \frac{4\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)\sin^2\delta_l(k) \equiv \sum_{l=0}^{\infty}\sigma_l^{\mathrm{el}}(k^2)\,. \tag{1.25}$$

The quantities $\sigma_l^{\mathrm{el}}(k^2)$ are known as the partial wave cross sections and represent the contribution of each partial wave to the total elastic scattering cross section. In conclusion, if we can calculate the phase shifts for a given interaction potential *U*, then we also know the scattering cross sections.

We finally note that matrices are often defined in terms of the phase shifts that describe the scattering process, as the scattering amplitude and thus also the scattering cross sections can then be suitably expressed in terms of their elements. The T-matrix, or transmission matrix, is defined by:

$$T_l(k) = e^{i\delta_l(k)}\sin\delta_l(k)\,, \tag{1.26}$$

while the S-matrix, known as scattering matrix, is given by:

$$S_l(k) = e^{2i\delta_l(k)}. \tag{1.27}$$

Lastly, the K-matrix, often referred to as the reaction matrix, depends on the phase shifts in the following way:

$$K_l(k) = \tan\delta_l(k)\,. \tag{1.28}$$

1.3.3 Positron scattering models

To describe the scattering process outlined in Section 1.3.2 various theoretical approaches have been used in the literature. These methods can be somewhat different from each other, in that they have been developed for solving the scattering problem for different systems. In fact, scattering models turn out to be more complicated to treat when the target is a molecule, as compared to an atom, because of the more difficult task of representing the molecule as a quantum mechanical state due to it possessing many more internal degrees of freedom. Similarly, some interactions or scattering channels can also be rather complicated to include into the calculations (e.g. positronium formation) due to their inherent-multicentre nature. In the following we list and briefly describe the most important models employed in positron scattering theory, that we will encounter in the next chapters when comparing the existing calculations with the present experimental results. In doing so, we make use of the review paper by Surko *et al.* (2005).

Many-body theory provides a method to compare quantitatively the relative importance of various correlation contributions to the positron-atom interaction. One of these techniques, the polarised orbital method (POM), assumes that the incident particle is fixed at a certain position. The effect of the polarisation of the target electron cloud is treated as a polarised orbital potential. This contribution is then added to the static potential and is treated as a perturbation of the atomic wavefunction with respect to the stationary state. The close coupling (CC) approach is based on an expansion of the total wavefunction of the system over a complete set of eigenfunctions separately representing the atomic, ionic and positronium states. The so-called convergent close coupling (CCC) approach is a variant of this method, that includes a direct description of the excited states of the target electrons into the continuum. By employing a properly large set of eigenfunction bases, including pseudostates, it is possible to reach an adequate representation of the scattering system.

The (modified) effective range theory (ERT) provides a simple and accurate estimation of the scattering cross section, by deriving the phase shifts from just two parameters, the scattering length at zero energy and the so-called effective range. These two quantities depend upon the interaction potential between the projectile and the target.

The Kohn variational method (KVM) adopts a few-body approach to the scattering problem. This method consists in using a particular form of the scattering total wavefunction and finding a trial phase shift by varying the so-called Kohn expression representing the scattering process. The R-matrix method is an approach that takes into account the correlation effects of the short-range and long-range interactions, while the Schwinger multichannel (SMC) variational technique uses a particular expression for calculating the scattering amplitude. The advantage of this method is that it uses configuration functions that can be constructed from electron and positron orbitals using a convenient Gaussian basis.

The multicentred nature of the problem of positron-molecule scattering makes it rather difficult to treat ab initio. Despite this complexity, Kohn variational, R-matrix and Schwinger multichannel based calculations have been performed on relatively simple molecules. The Kohn variational and R-matrix methods have in particular successfully been applied to diatomic molecules.

1.4 Outline of the thesis

The present dissertation is structured in the following way.

First of all, the two experimental apparatus used to gather the present cross sections are described in Chapter 2. We first discuss the positron apparatus at the University of Trento and then the positron beamline for atomic and molecular collisions at The Australian National University. The corresponding experimental details, together with the measurement techniques employed in the experiments, are also introduced in this same chapter. The total cross section results for the two atoms investigated in this thesis are also reported in a section of Chapter 2, as a validation of the University of Trento experimental techniques and of the apparatus performance.

The cross section results for positron scattering from all the examined molecules are, instead, presented in the following Chapters 3-6. Total cross sections for positrons impacting on molecular hydrogen are introduced in Chapter 3. The subsequent chapter contains the present total cross section results for positron collisions with a set of isoelectronic molecules, namely molecular nitrogen, carbon monoxide and acetylene. Next, in Chapter 5, we discuss the total cross sections for positron scattering off the primary alcohols methanol and ethanol. In the last results chapter we describe our positron cross section data for some of the important model compounds for individual components of biological macromolecules that we considered. Finally, some general conclusions from the studies conducted as part of the present thesis are drawn in Chapter 7.

Please note that while a literature review of the relevant previous work is often also given in the Introduction of a thesis, here the number and variety of targets investigated has meant that it makes more sense to incorporate that material at the beginning of each particular chapter.