

Preface

Research on processes which occur when electrons, positrons and photons collide with atoms, ions and molecules has seen a rapid increase in interest, both experimentally and theoretically, in recent years. This is partly because these processes provide an ideal means of investigating the dynamics of many-particle systems at a fundamental level and partly because a detailed understanding of these processes is required in many fields, particularly in the analysis of astronomical observations, in plasma physics including controlled thermonuclear fusion, in the interaction of super intense lasers with atoms and molecules, in atmospheric physics and chemistry including global warming, in isotope separation, in electrical discharges in gases and in electron surface interaction processes.

In recent years a number of important advances have been made in both experiment and theory. On the experimental side these advances include the absolute measurement of cross sections, the development of coincidence techniques, the use of polarized beams and targets, the development of very high resolution electron beams, the application of new light sources, the development of femtosecond and attosecond laser beams and a rapidly increasing number of studies using high-resolution positron and positronium beams. On the theoretical side these advances include the development of methods which allow highly accurate excitation and ionization cross sections to be calculated at intermediate energies, the increasing ability to determine accurate low-energy cross sections for electron and positron collisions with complex atoms and molecules and the development of non-perturbative approaches for studying multiphoton processes for many-electron targets. Many of these theoretical advances have been made possible by the increasing availability of high-performance parallel computers and the development of general computer programs which can take advantage of these facilities.

This monograph describes a generalized *R*-matrix theory of atomic collisions and its application to the *ab initio* study of atomic, molecular and optical collision processes. *R*-matrix theory was first introduced by Wigner and Eisenbud in the late 1940s in an analysis of nuclear resonance reactions. These resonances were described in terms of temporary compound states formed by the colliding nuclei, which were contained in an internal region of configuration space. The *R*-matrix, which represents the complexity of the compound states, relates the radial components of the wave function to their derivatives on the boundary of the internal

region. In the external region it was assumed that the colliding nuclei were weakly interacting and hence the complexity of the collision process was represented by the R -matrix. In early work the R -matrix was represented by a few parameters used to fit the experimental observations and in later work it was calculated directly using nuclear model potentials. This theory has been widely used in nuclear physics and developments have been reviewed by many authors.

The realization that R -matrix theory could be developed and applied as an *ab initio* approach to study atomic, molecular and optical collision processes began to emerge in the 1960s as a result of new resonance phenomena observed using high-resolution electron spectrometers and synchrotron radiation sources. In the analysis of these experiments it became clear that processes such as resonant electron – atom collisions and photoionization could be understood and predicted using R -matrix theory. Following the ideas introduced by Wigner and Eisenbud, configuration space describing the collision process is partitioned into three regions by spheres of radii a_0 and a_p . In the internal region, where the colliding atomic or molecular systems interact strongly, the resulting compound system behaves in a similar way to a bound state. Consequently, configuration interaction approaches, developed over many years to study bound-state problems, can often be extended to provide an *ab initio* treatment of the compound system yielding the R -matrix on the boundary of the internal region. In the the external and asymptotic regions, where the colliding systems are weakly interacting, the solution of the coupled equations describing their relative motion can be rapidly obtained using standard methods, yielding the scattering amplitudes and cross sections.

The monograph commences by presenting an overview of collision theory in Part I. As well as giving a self-contained summary of this theory it also provides an introduction to the basic concepts and notation required in Part II. After an introductory chapter on potential scattering, Chap. 2 presents an overview of multichannel collision theory with emphasis on electron collisions with atoms and atomic ions. Chapter 3 then provides an overview of resonance theory and threshold behaviour. In these chapters quantities such as the K -matrix, S -matrix, scattering amplitudes and cross sections, as well as resonance and threshold behaviour, are introduced.

Part II then turns to a detailed discussion of R -matrix theory of atomic, molecular and optical collisions and its applications. It commences in Chap. 4 with a review of R -matrix theory in potential scattering which sets the scene for the later chapters which develop and apply multichannel R -matrix theory to a wide range of collision processes. One of the first detailed applications of R -matrix theory in atomic, molecular and optical physics, in the early 1970s, was to electron collisions with atoms and atomic ions, which is reviewed in Chap. 5. More general aspects of R -matrix theory are also presented in this chapter including multichannel variational principles for the R -matrix and the inclusion of relativistic effects. Then in subsequent chapters the theory and application of R -matrix theory to a wide range of collision processes are discussed including electron collisions at intermediate energies, positron collisions with atoms and ions, photoionization, photorecombination and atoms in fields, multiphoton processes using Floquet and time-dependent theory, electron, positron and photon collisions with molecules and electron collisions with transition metal

oxides and electron transport in semiconductor devices. For all of these applications general computer programs have been developed and those that have been published or are generally available are briefly reviewed.

The monograph concludes with six appendices which summarize basic mathematical results and computational methods which are used in Parts I and II.

Finally, I wish to recognize my great indebtedness to Sir Harrie Massey and Richard Buckingham who introduced me to collision theory and the crucial role of scientific computing when I was a graduate student at University College London in the 1950s. Also, this monograph could not have been written without the inspiring atmosphere that Sir David Bates established in the Department of Applied Mathematics and Theoretical Physics at the Queen's University of Belfast where I have been privileged to work for the last 43 years. I also wish to take this opportunity to acknowledge two leading scientists and friends who made crucial contributions to the research discussed in this monograph. First, Ugo Fano for his incisive comments and encouragement over many years, particularly in the 1960s when it was clear there was a need for an *ab initio* theory which could accurately describe and predict the wide range of atomic, molecular and optical resonance phenomena being observed. Second, Mike Seaton for his support and encouragement over many years and for showing that the *R*-matrix approach could be used to calculate the vast amount of data required in the analysis of astronomical observations. I would also like to acknowledge long-term collaborations with Cliff Noble, Jonathan Tennyson, Klaus Bartschat and Charles Joachain. Throughout my years at Queen's University, in addition to many collaborators worldwide, I have been fortunate to interact and to work with many outstanding members of staff and graduate students. In particular it is a pleasure to mention Alan Hibbert, Derek Robb, Donald Allison, John Mitchell, Keith Berrington, Ken Taylor, Arthur Kingston, Ken Bell, Stan Scott, Penny Scott, Kevin Dunseath, James Walters, Robin Reid, Patrick Norrington, Charles Gillan, Katrina Higgins, Hugo van der Hart, Cathy Ramsbottom, David Glass and James Colgan who played a major role in the development of the theory, computational methods and computer programs and in the calculations discussed in this monograph.

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