THEORY OF MOLECULAR RYDBERG STATES

Molecular Rydberg states have many unusual properties, lending themselves to a diverse range of experimental applications. This book is designed to unravel the mysteries of molecular Rydberg states that lie beyond the scope of accepted spectroscopic theories. It is the first single-authored text to focus on the application of multi-channel quantum defect theory (MQDT) and *ab initio* theory to this special class of molecular systems, introducing readers to novel theoretical techniques. The scattering techniques of MQDT are examined, along with a unified description of bound states and fragmentation dynamics. Connections with established spectroscopic theory are also described. The book concludes with an account of the spherical tensor and density matrix theories required for the interpretation of multiphoton experiments. While the main text focuses on physical principles and experimental applications, appendices are used to handle advanced mathematical detail. This is a valuable resource for researchers in chemical, atomic and molecular physics.

MARK CHILD is a distinguished theoretical chemist and internationally recognised authority on quantum defect theory and its applications to molecular systems. He was Coulson Professor of Theoretical Chemistry at the University of Oxford, a post from which he recently retired.

'This excellent book is ripe with insights and practical methods, and it will be indispensable for anyone interested in learning the theory of molecular Rydberg states.'

Christopher H. Greene, Professor of Physics,
Fellow of JILA, University of Colorado

'In this book, Mark Child presents the crucial ideas, techniques, and surprises of Rydberg states with authority, clarity, and glorious attention to interconnections. The physically sensible approximations upon which MQDT is based are explained and illustrated, both pictorially and rigorously: why MQDT works so well to describe many things that the Born–Oppenheimer approach cannot; the power of MQDT to deal in a unified manner with all aspects of molecular structure and dynamics; and the extraordinary compactness of infinite-member channels rather than individual electronic states as fundamental building blocks . . . Theorists and experimentalists ignore MQDT at their peril.'

Robert Field, Haslam and Dewey Professor of Chemistry,
Department of Chemistry, Massachusetts Institute of Technology

'Mark Child's monograph is not only comprehensive and authoritative but also delightfully readable, teaching clearly the subtleties of how to describe molecules in which one electron has been excited to near the ionization limit. Moreover, a unifying description is developed based on the ideas of electron-molecule scattering (multichannel quantum defect theory), a description that shows a seamless transition between bound Rydberg states and the unbound ionization continuum. I enthusiastically recommend this book to anyone desiring to understand the nature and dynamics of molecular Rydberg states. It is the starting place for all serious students of this topic.'

Richard N. Zare, Chair, Marguerite Blake Wilbur
Professor in Natural Science, Department of Chemistry,
Stanford University

'This book fills a gap, and will be of great value to graduate students and researchers interested in highly excited molecular systems.'

Christian Jungen, Directeur de Recherche au CNRS,
Université de Paris-Sud

Cambridge Molecular Science

As we move further into the twenty-first century, chemistry is positioning itself as the central science. Its subject matter, atoms and the bonds between them, is now central to so many of the life sciences on the one hand, as biological chemistry brings the subject to the atomic level, and to condensed matter and molecular physics on the other. Developments in quantum chemistry and in statistical mechanics have also created a fruitful overlap with mathematics and theoretical physics. Consequently, boundaries between chemistry and other traditional sciences are fading and the term *Molecular Science* now describes this vibrant area of research.

Molecular science has made giant strides in recent years. Bolstered both by instrumental and theoretical developments, it covers the temporal scale down to femtoseconds, a timescale sufficient to define atomic dynamics with precision, and the spatial scale down to a small fraction of an Angstrom. This has led to a very sophisticated level of understanding of the properties of small molecule systems, but there has also been a remarkable series of developments in more complex systems. These include: protein engineering; surfaces and interfaces; polymers; colloids; and biophysical chemistry. This series provides a vehicle for the publication of advanced textbooks and monographs introducing and reviewing these exciting developments.

THEORY OF MOLECULAR RYDBERG STATES

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Contents

Preface

My initial aim was to introduce the powerful but relatively under-used techniques of multichannel quantum defect theory (MQDT) to graduate students in atomic and molecular physics. The methods are particularly attractive in two ways. They provide an elegant, computationally tractable approach to the treatment of molecular Rydberg states, which invalidate the normal molecular assumption that the electronic motion is overwhelmingly rapid compared with other degrees of freedom. In addition the theory offers a unified description of the discrete molecular states below an ionization limit and those above in the ionization continuum. At the same time the novelty of the MQDT method makes it essential to point to the links with the familiar techniques of 'normal' molecular physics.

While writing, I realized that workers in two other fields would benefit from a more general treatment of molecular Rydberg states. In the first place there is a huge literature on electronic structure theory or 'quantum chemistry', which can, however, handle only the very lowest Rydberg states, owing to the very long range of the excited orbitals. A chapter has been written to show how the familiar quantum chemical techniques can be adapted to handle arbitrary members of the infinite Rydberg series. Secondly, to meet the demands of modern experiments, the chapters involving interaction with radiation take account of developments in the theoretical description of coherent multiphoton excitation and resonant multiphoton ionization.

The book is primarily written for graduate students in atomic and molecular physics. Many will have seen and admired the striking success of the theory. My hope is that the book will enable them to apply it for themselves. To avoid undue mathematical complexity, the main text focuses on physical principles and illustrative applications, leaving technical details to be covered in the appendices. Knowledge of scattering theory will be helpful but not essential for the early chapters, while the later ones require familiarity with angular momentum algebra.

I myself was introduced to the mysteries of quantum defect theory at a lecture by Ugo Fano. I later had the benefit of working with Christian Jungen and Chris Greene and, of course, learned much from my own collaborators, notably Rick Gilbert, Colin Batchelor, Miyabi Hiyama and Adam Kirrander. I am particularly indebted to Christian Jungen for constant advice and encouragement during the preparation of the book. It is also a pleasure to acknowledge the hospitality of the Chemistry Department of ETH in Zurich and Laboratoire Aimé Cotton at Orsay. Discussions with Mireille Aymar and Frederik Merkt were particularly helpful. I also owe debts to Oxford colleagues, John Brown, John Eland, Brian Howard, David Manolopoulos and Tim Softley for expertise and advice. In addition thanks are due to John Freeman and Yuan-Pin Chang for assistance in the preparation of various diagrams. Financial support by the Leverhulme Trust during the early stages of writing is gratefully acknowledged.

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