

Springer Series on Atomic, Optical, and Plasma Physics

Volume 97

Editor-in-chief

Gordon W.F. Drake, Windsor, Canada

Series editors

James Babb, Cambridge, USA

Andre D. Bandrauk, Sherbrooke, Canada

Klaus Bartschat, Des Moines, USA

Philip George Burke, Belfast, UK

Robert N. Compton, Knoxville, USA

Tom Gallagher, Charlottesville, USA

Charles J. Joachain, Bruxelles, Belgium

Peter Lambropoulos, Iraklion, Greece

Gerd Leuchs, Erlangen, Germany

Pierre Meystre, Tucson, USA

The Springer Series on Atomic, Optical, and Plasma Physics covers in a comprehensive manner theory and experiment in the entire field of atoms and molecules and their interaction with electromagnetic radiation. Books in the series provide a rich source of new ideas and techniques with wide applications in fields such as chemistry, materials science, astrophysics, surface science, plasma technology, advanced optics, aeronomy, and engineering. Laser physics is a particular connecting theme that has provided much of the continuing impetus for new developments in the field, such as quantum computation and Bose-Einstein condensation. The purpose of the series is to cover the gap between standard undergraduate textbooks and the research literature with emphasis on the fundamental ideas, methods, techniques, and results in the field.

More information about this series at <http://www.springer.com/series/411>

Hanno Schmiedt

Molecular Symmetry, Super-Rotation, and Semiclassical Motion

New Ideas for Solving Old Problems

 Springer

Hanno Schmiedt
Institute of Physics I
University of Cologne
Cologne
Germany

ISSN 1615-5653 ISSN 2197-6791 (electronic)
Springer Series on Atomic, Optical, and Plasma Physics
ISBN 978-3-319-66070-7 ISBN 978-3-319-66071-4 (eBook)
DOI 10.1007/978-3-319-66071-4

Library of Congress Control Number: 2017949496

© Springer International Publishing AG 2017

This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.

The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

The publisher, the authors and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, express or implied, with respect to the material contained herein or for any errors or omissions that may have been made. The publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Printed on acid-free paper

This Springer imprint is published by Springer Nature
The registered company is Springer International Publishing AG
The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

Preface

Describing molecules with mathematical methods has fascinated the scientific community for a long time. Nowadays, large computing facilities are available, and they are used for extremely precise calculations of molecular properties that can be investigated in experiments. Nevertheless, developments in experimental techniques are still challenging the theoretical predictions by their overwhelming accuracy. This book is at first place intended to show that away from an extensive use of computational techniques, the reflection onto the most fundamental property of many-body physics, namely symmetry, still leads to new insights into the wide field of molecular dynamics. The beauty of using simple algebraic methods even for the description of some of the most challenging problems in recent molecular research has excited me from the first day on. With this book, I hope to transfer this excitement to the reader and show that the theoretical work also on the foundations of molecular dynamics is still far from being completed.

Recent developments in experimental high-resolution spectroscopy have opened up very many new routes for the study of molecules [1]. For instance, ion-trap spectroscopy has become a versatile tool in studying ion–molecule reactions in a quantum-state resolved manner (see, e.g., [2] and references therein). This is used to analyze the reactions themselves but it also facilitates the characterization of molecular states of single ions, which are inaccessible to traditional spectroscopic methods. With this, the famous protonated methane, an “enfant terrible” ([3], p. 1) of molecular spectroscopy, has been precisely characterized only a few years ago [4]. Traditional theories encounter major problems in describing the respective dynamics since its extreme floppiness even at low temperatures makes it impossible to define any structure, which is traditionally the inevitable starting point for theories of molecular dynamics.

In addition to the above-described techniques, where stored ions are actually cooled to temperatures of a few Kelvin, other technologies have emerged to study molecules at the opposite side of energetic excitation: Optical centrifuges allow to control and study molecules in extremely high excited rotational states. For those states, quantum chemical calculations even with the most advanced algorithms are faced again with serious computing-time problems.

All these improvements brought up the question if using larger and larger computing facilities is in fact the “golden way” to tackle the problems of molecular theory. Or is it possible to step back and use the most fundamental properties of molecular dynamics to answer at least some of the questions arising from modern-day molecular spectroscopy?

This book is intended to review some of these questions and actually presents a clear answer to this question: We can in fact use basic symmetry considerations to achieve new answers to the questions of modern-day molecular spectroscopy. Reviewing and renewing parts of the foundations of molecular physics is worthwhile and can be used to circumvent—at least in a first step—the use of large computing facilities, even though the latter are still needed for more exact studies.

In general, this book has three parts: It aims to show how basic symmetry considerations help in (i) understanding selection rules in molecular reactions but also (ii) in the characterization of exotic molecules. Furthermore, ideas of classical mechanics are reformulated and attached to advanced quantum mechanical models to understand (iii) ultrafast rotating molecules. During the course of this work, various basic ideas of molecular symmetry and semi-classical treatments are presented. And, as a final goal, the book shows these basic concepts to answer some of the challenging problems of molecular spectroscopy. As one example of these answers, it shows the advent of a fundamentally new way of studying molecular rotation, the super-rotor model, which successfully describes the protonated methane molecule, which has been tackled by traditional theories for over 30 years. As a new model, it led to many controversial debates in the past few years, and this book is meant to set the stage for even more such discussions and, hopefully, for future work.

The results presented in this book are based on my Ph.D. work in the group of Stephan Schlemmer and on recent publications together with him, Per Jensen, and some of the people from the ExoMol group in London [5–9]. I want to thank all of them, especially Stephan Schlemmer, who was the most supportive Ph.D. supervisor one could imagine. In addition, I would like to thank his awesome group; without the numerous discussions with, e.g., the experts on ion-trap spectroscopy, this work would have been impossible. A very special thanks also to Anni who supported me at all times and cheered me up whenever I needed it. Indeed, I want to thank Monika, Helmut, and Jacob for everything they did for me in the last twenty-nine years. Not to forget all my friends and former colleagues who are playing an important role in getting me out of science from time to time. I must admit that I enjoy that very much.

The work starts with a general introduction, where also the structure of the rest of the book is outlined. Therefore, I postpone this to the first chapter and hope that the reader can enjoy the problems of molecular dynamics with as much fascination and fun as I had by working on them.

Contents

1	New Ideas for Solving Old Problems - An Introduction	1
Part I Group Theory in Molecular Physics		
2	Basic Concepts	9
2.1	Symmetry Groups of the Molecular Hamiltonian	9
2.1.1	General Representation Theory	11
2.1.2	Lie Groups and Permutation Groups	14
2.2	Zero-Order Models in Molecular Theory	18
2.2.1	The Separation of the Molecular Hamiltonian	19
2.2.2	The Zero-Order Models for Nuclear Motion	22
2.3	Connecting Dynamics and Group Theory – Outlook to This Work	25
3	Schur–Weyl Duality in Molecules	27
3.1	Nuclear Spin States in Molecules	27
3.1.1	The Natural Way	31
3.1.2	Unitary Symmetry	35
3.1.3	Permutation Symmetry	37
3.2	Schur–Weyl Duality	39
3.2.1	Application of the Duality Theorem	40
3.3	Conclusion	41
4	Reactive Collisions	45
4.1	Representation Theory in Reactions of Small Molecules	47
4.1.1	Mathematical Preliminaries	47
4.1.2	Single Molecules	49
4.1.3	A First Example	51

4.2	The $H_3^+ + H_2$ Reaction	53
4.2.1	A Restricted Symmetry Group for the Intermediate Complex	56
4.2.2	Implications for Experiments	59
4.2.3	The Deuterated Version	59
4.3	Discussion	62
Part II Extremely Floppy Molecules		
5	Introducing Extreme Floppiness.	67
6	Symmetry Beyond Perturbation Theory	71
6.1	Representation Theory of Molecular Rotation	71
6.1.1	Example: The H_3^+ ion	81
6.2	The Failure of the Subgroup Picture	82
6.3	Concluding Remarks	86
7	The Molecular Super-Rotor	87
7.1	Large Amplitude Motion	87
7.2	Super-Rotation	91
7.2.1	The Energy Expression	93
7.2.2	Degrees of Freedom	94
8	Super-Rotor States and Their Symmetry.	95
8.1	Five-Dimensional Rotor States	95
8.1.1	Parity and Dipole Selection Rules	99
8.2	Permutation-Inversion Symmetry	100
8.2.1	The Permutation Group of Five Identical Particles	102
8.3	Conclusion	105
9	Protonated Methane	107
9.1	The Molecule	107
9.2	The Experiment	109
9.3	The Model	111
9.4	The Discussion	115
10	Refinements and Further Applications.	117
10.1	Beyond Zero-Order	117
10.1.1	Generalized Moments of Inertia	117
10.1.2	Higher-Order Terms	120
10.2	Additional Target Molecules	121
10.3	Concluding Remarks	123

Part III Semi-classical Approach to Rotational Dynamics

11 Ultrafast Rotation	127
11.1 Introduction	127
11.2 The Gutzwiller Trace Formula	129
11.3 The Rotational Energy Surface	136
11.3.1 The Paths on the Rotational Energy Surface	139
11.3.2 The Quantization Conditions	142
11.3.3 Two Approaches to Generate the Rotational Energy Surface	144
12 Application to Sulfur Dioxide	149
12.1 The Molecule	149
12.2 The Comparison	150
13 Discussion	155
13.1 The TROVE - Generated Rotational Energy Surface	155
13.2 Generalization of the Approach	156
14 New Ideas for Solving Old Problems – A Conclusion	159
References	163
Index	169