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.

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