

# Chapter 1

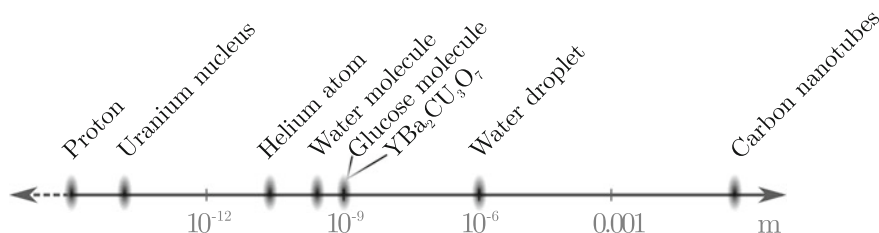
## New Ideas for Solving Old Problems - An Introduction

**Abstract** In this introductory chapter, a general view on the field of molecular dynamics and the main ideas of this book are presented. Furthermore, an outline of the rest of the book is shown by describing the contents of the three different parts.

If one sets up a length scale diagram for objects studied in the different fields of physics, molecules are located somewhere in between the single particle scales of nuclei or elementary particles and the macroscopic length scales of condensed matter (see Fig. 1.1). Correspondingly, this line of objects with increasing size can also be followed in the sense of an evolution: Elementary particles clump together to form nuclei, which together with electrons subsequently can form molecules. An aggregation of molecules can consequently be viewed as either forming liquids or, depending on structural properties, crystalline solids and other macroscopic forms of matter. Zooming into the length scales of single molecules, already there, notifiable differences occur. On the one hand side we find small molecules like the prominent water molecule,  $\text{H}_2\text{O}$ , and on the other hand there are all kinds of sugars, acids, or even DNA and proteins. A detailed understanding of the properties of single molecules of all sizes is obviously of great interest to the research community with influences on very different fields like organic and inorganic chemistry as well as biochemistry.

In this work, the main focus is on small molecules with at most ten nuclei. Apart from being the building blocks also for larger molecules, they are special in many different senses: First, they are found literally everywhere, in the human body, in earth's atmosphere as well as in the surrounding of the center of our galaxy. Secondly and maybe a little surprisingly, even though the number of particles is small, we find an enormous variety of dynamical properties. The latter are nowadays explored by spectroscopic techniques that reach astonishingly high resolutions. Experiments on diatomic molecules have shown that electric dipole transitions between molecular states can be recorded with an accuracy of  $\Delta f/f \approx 10^{-9}$  [10, 11]. Therefore, theoretical models for the description of the internal dynamics must be extremely accurate in predicting these transitions and a lot of computational effort is required to accomplish this task.

Such highly precise measurements and accurate models are used not only to predict the dynamics of molecules in the laboratory but also in other environments with very different and even unknown conditions. One prominent respective example is the aforementioned interstellar space, where, e.g., temperature, densities, and



**Fig. 1.1** Typical length scales of some of the objects studied in physics. Molecules, the topic of the present book, are located between the single particle scale of nuclei or atoms and the macroscopic length scales of long nanotubes or the unit cell diameter of crystalline superconductors like  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . Already here, the difference in the dimensions of the water and the glucose molecule indicates the wide variety of objects of molecular spectroscopy

time-scales are much different from those in experiments. Nevertheless, by using observational studies, one tries to unambiguously identify certain molecules in various regions in space, where, e.g., astrochemical networks afterwards are used to explain the evolution of galaxies, planets or even exoplanetary atmospheres. These identification procedures need extremely precise predictions since the observed spectra are mostly extremely dense and slight changes in molecular parameters would lead to large uncertainties in the identification. Due to large efforts in high-resolution spectroscopy in the laboratories, astronomical observations were able to find (to date) about 180 molecules in very different conditions in space. The largest found molecules were recently the fullerenes  $\text{C}_{60}$  and  $\text{C}_{70}$  in young planetary nebula [12]. On the way to more complex molecules, molecules like ethanol [13] and, more recently, ether methyl ether,  $\text{C}_2\text{H}_5\text{OCH}_3$ , have been detected already but the search for larger and more complex molecules is still ongoing and a ‘hot topic’ in the astrophysical community.

In addition to the study of single molecules, molecular spectroscopy is also used to record reactions of molecules. In general, knowing reaction rates for small molecules are of large interest again in the astrochemical community, since respective reaction networks strongly depend on the accuracy of these parameters. Again using high-resolution methods, it is nowadays possible to follow the reaction processes on a quantum state resolved level. In particular, measurements are made to explain features of, e.g., reactive collisions in interstellar space, where very cold molecules collide and at most exchange a small portion of energy. Nevertheless, in this process, the internal properties of the colliding particles can change when concerning, e.g., their intrinsic spins.

In conclusion, studying small molecules with high-resolution experiments is obviously contributing a lot to the understanding of astrochemical processes. This is indeed only one of the various applications of molecular spectroscopy but a review of all possible relevant fields is beyond the scope of this work.

However, away from such implications of molecular spectroscopy to other topics of natural sciences, molecular physics itself represents a paradigmatic example of quantum mechanics. As such, molecular dynamics is a playground for testing

predictions from theories which are formed on a very abstract basis initially. One of the most famous examples is the ‘umbrella flipping’ motion in ammonia,  $\text{NH}_3$ , which is predicted and explained by quantum mechanics. Another more recently studied example is protonated methane, where the concept of a classical structure must be abandoned completely since even at zero temperature, its wave function is highly delocalized.

In addition to these examples of how molecular dynamics is influenced by quantum theory, another important issue is the influence of general symmetry properties. The latter is used in both, classical and quantum theories to simplify or explain certain phenomena and again, molecular physics is one of the prototypical examples, where the influence of symmetry is hard to underestimate. In difference to elementary particle and condensed matter theory, molecules are described by the apparatus of representation theory of *finite* groups which is actually itself an active field of study in modern mathematics. Molecules form a formidable testing ground for some of the respective abstract theorems of group theory in general. One very basic example is the ortho- and para-form of molecular hydrogen,  $\text{H}_2$ , the most simple molecule one can imagine. These forms are separable by symmetry: While in para hydrogen the two nuclear spins are coupled anti-symmetrically, in ortho-hydrogen they are interchangeable without any sign change of the molecular wave function. This fundamental difference leads to the strict statement from representation theory that both forms cannot be inter-converted by any electromagnetic radiation. This statement is validated by measurements, where exactly defined ratios of these forms are found. In cold reactions, both forms of molecular hydrogen actually behave as distinct chemical species which has large implications on the related reaction dynamics. Indeed, for larger molecules, the concept of separate spin configurations get more complex but with the help of representation theory is still achievable.

In the course of this work, we will discuss some of the aspects of how representation theory and molecular physics are correlated and find more examples, where influences of quantum mechanics and symmetry are not negligible for the description of molecular dynamics. Before going into the details, we start with formulating some of the fundamental assumptions, molecular physics is based on.

In describing inter- and intra-molecular dynamics, the most convenient starting point is actually to consider an almost static molecular structure, where the nuclei appear as the building parts and the electrons as bonds between them. Nuclear vibrations lead to small displacements of the nuclear coordinates and molecular rotation can be described as that of an almost rigid body. This rather intuitive view is extended by a perturbative approach, where non-rigid terms as well as rotation-vibrational (ro-vibrational) couplings are incorporated into the systems Hamiltonian. With this concept, a large number of molecules can be characterized by structural parameters and higher order equivalents. In particular, these constants give rise to a fingerprint spectrum of individual molecules which is used, e.g., to identify them in radio-astronomical observations of interstellar space.

Experimental laboratory spectroscopy is used to find these structural constants and hence to characterize the molecules as nearly static structures with a well-defined set of numbers indicating the higher order terms in the perturbation series.

However, technical developments have always been a trigger for extending traditional models and often led to the rejection of ideas which were thought to be universal. As experimental spectroscopy reaches higher and higher accuracies in frequency, many different deviations from this ball-and-stick picture emerge: For example, molecules are now known to possibly exhibit distinct low-energy structures that are interconvertible by only a small or even a vanishing portion of energy. Therefore, some molecules must be described in a superposition state of various isomeric geometries. The most renowned example is the aforementioned ammonia molecule, where the nitrogen nucleus is imagined to be located “above” or “below” the plane of the three protons. These two possibilities are indistinguishable and hence the molecule must be described as a quantum object, where both structures are superimposed.

Although ammonia is treatable by an extended ball-and-stick model, [14] where both geometries are treated simultaneously, other molecules and conditions exist, where established molecular theory reaches limits which cannot be solved even by the power of modern computing facilities. If, e.g., the perturbation series converge very slowly, calculations become very expensive and most likely lack a clear physical interpretation. In this work, we discuss two examples of pathological cases where traditional theories tend to fail in a proper description of molecular dynamics:

- In **Part II** of this work, we discuss *extremely floppy molecules* in which the idea of a fixed geometrical structure must be totally abandoned due to numerous large amplitude vibrations. The latter are defined to exhibit nuclear displacements comparable to the linear dimension of the molecular equilibrium structure. One example is the already mentioned tunneling motion in the ammonia molecule. We start that part by a particular discussion of the symmetry of rotational states in molecules, and show certain limits of conventional rotational theory, when it comes to special but still relatively simple molecules [9]. In the subsequent chapters, we review the development of a fundamentally new model for the dynamics of extremely floppy molecules, where internal rotational motion and the overall rotation of the molecule are combined [6, 7]. We call this collective motion *super-rotation* and, in the tradition of theoretical physics, we find an underlying symmetry principle guiding to the formulation of an approximate model for the respective dynamics. It turns out that in contrast to more traditional studies of this class of molecules, this model provides a simple, analytical energy expression as well as the possibility to symmetry classify the according generalized rotational states in the molecular symmetry group. We furthermore show a comparison of this theory to recent experimental results on the dynamics of the prototypical example of extreme floppiness, protonated methane,  $\text{CH}_5^+$  [4, 15]. By fitting a single parameter, our model provides a super-rotational energy spectrum that compares surprisingly well with the experimental results. We retrieve almost all energy levels with an accuracy of a few wave numbers,<sup>1</sup> and find the value of the free parameter close to results of existing ab-initio calculations. These encouraging results are used to outline

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<sup>1</sup>We use the spectroscopic wave number in units of reciprocal centimeters for the unit of energy throughout the text.  $1\text{ cm}^{-1}$  is equivalent to a frequency of about 30 GHz and hence to an energy of approximately  $2 \cdot 10^{-23}\text{ J}$ , the energy of a single photon with a wavelength of one centimeter.

possible extensions of the model, and we discuss potential applications to various kinds of other molecules, summarized in Chap. 10.

- In **Part III**, we consider again rotational dynamics but on a different energy scale. Whereas protonated methane was measured at temperatures of a few Kelvin, rotational dynamics at high temperatures are posing a considerable challenge to traditional quantum mechanical calculations as well. These *ultrafast rotations* involve molecular states with a very large angular momentum quantum number. We demonstrate that they can be described properly in a semi-classical approach [16], where a path-integral based method is used to predict quantized energies without using expensive matrix diagonalization procedures. Once more symmetry is used to determine the paths which the classical rotation “vector” is allowed to follow under the restriction of quantized energies. Based on ideas from the 1990s (see, e.g., [17]), we further develop the theory of semi-classical rotation by applying it to a full quantum mechanical treatment of underlying nuclear vibrations. This induces an intuitive understanding of the rotational dynamics, even at high speed, in terms of a classical rotation. In addition, it provides a relatively fast method to calculate the respective energy levels. As a proof of principle, we use a relatively simple well-known molecule, namely sulfur dioxide,  $\text{SO}_2$ , for testing the method. It turns out that the provided energies are not yet accurate enough for spectroscopic needs, nevertheless, future refinements potentially lead to a better applicability and the possibility to study molecules with more peculiar behavior at these large rotational speeds. The latter includes for instance the coupling of the fast rotations to other degrees of freedom.

In both parts of this work, symmetry is identified to be *the* combining element. We show it to be of crucial importance when traditional approaches reach their limits. Therefore, we start this work with the more general **Part I** on molecular symmetry, where we introduce the basic concepts for the later chapters. The mathematical details are kept at a minimum but sufficient level. We highlight certain parts in boxes and include examples throughout the work to render the text comprehensible also for readers yet unfamiliar with concepts like representation theory, Lie algebras and other parts of mathematical group theory. The more interested reader is referred to textbooks like [18, 19] for the mathematical part and to [14] for the application of group theory to molecules.

As one result of these general symmetry considerations, we show in Chap. 3 of Part I the application of the Schur–Weyl duality theorem, a well-known result of representation theory, to the nuclear spin states in molecules [8]. It enables us to simplify the calculation of the so-called nuclear spin statistical weights, responsible, e.g., for non-observable energy levels, forbidden by Pauli’s well-known exchange principle. Furthermore, the Schur–Weyl duality introduces a new correlation of spin angular momentum and spin permutation symmetry which were yet thought to exist somehow independently. In addition, we show in Chap. 4 how the symmetry of the nuclear spin states in particular influences reactive collisions. We use the famous  $\text{H}_3^+ + \text{H}_2 \rightarrow \text{H}_2 + \text{H}_3^+$  reaction as an illustrative example of formulating selection rules for state-to-state transitions in bi-molecular reactions. They are shown to depend in

particular on the symmetry of an intermediately formed complex. With discussing two respective examples, we are able to show the differences in, e.g., ortho-to-para transition probabilities for the molecular hydrogen under the collisional reaction with  $\text{H}_3^+$ . All the calculations related to the Schur–Weyl duality are done energy- and hence model-independent. Consequently, we put this part ahead of the discussions on the dynamical models for extremely floppy or extremely fast rotating molecules.

In conclusion, this work is intended to show how fundamental symmetry properties and their proper mathematical understanding are essential in the description of molecular dynamics. The semi-classical model of ultrafast rotations as well as the super-rotation model for extremely floppy molecules can serve as a basis for further studies on these pathological cases, where all traditional approaches tend to reach their natural limits. Therefore, ‘old problems’ can be solved by using ‘new ideas’ from basic symmetry considerations.

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Motion

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