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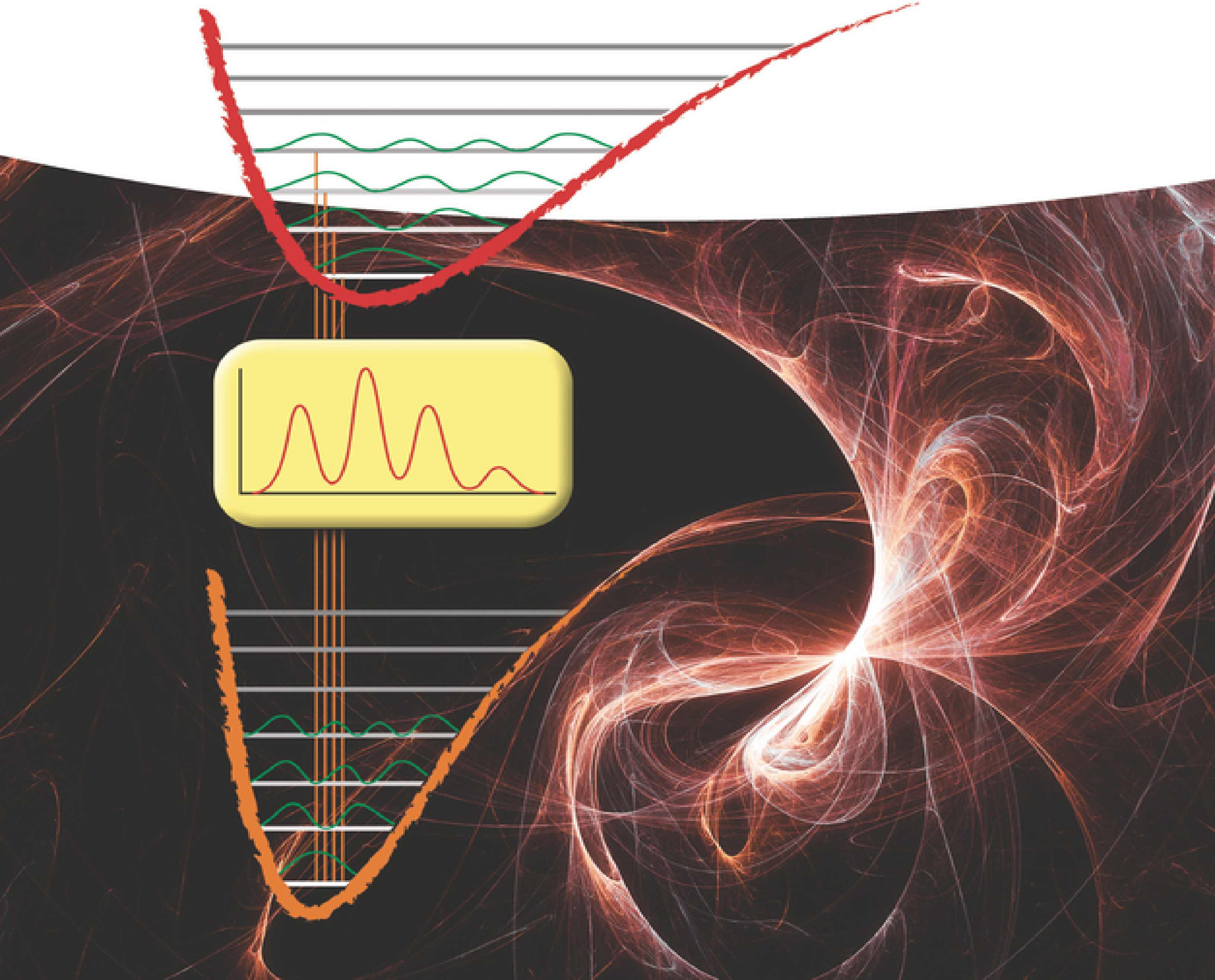
Max Diem

Quantum Mechanical Foundations of Molecular Spectroscopy



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Preface

When the author took courses in quantum mechanical principles and chemical bonding in graduate school in the early 1970s, the course materials seldomly covered the fascinating interplay between spectroscopy and quantum mechanics, and textbooks of these days devoted the majority of space to derivations and mathematical principles and the discussion of the hydrogen atom and chemical bonding. While an understanding of these subjects is, of course, a necessity for further study, this book emphasizes a slightly different approach to quantum mechanics, namely, one from the viewpoint of a spectroscopist. In this approach, the existence of stationary energy states – either electronic, vibrational, rotational, or spin states – is considered the fundamental concept, since spectroscopy exists because of transitions between these states. Quantum mechanics provides the theoretical framework for the interpretation of experimental data. On the other hand, spectroscopic results provide the impetus for refining theories that explain the results. Classical physics cannot provide this framework, since the idea of stationary energy states violates the laws of classical physics.

Thus, the approach taken here in this book is to present early on, in Chapter 2, how the application of quantum mechanical principles leads necessarily to the existence of stationary energy states using the particle-in-a box model system. The third chapter then introduces the concept of spectroscopic transitions between these stationary states, using time-dependent perturbation theory.

The following chapters are presented in order of mathematical complexity of the Schrödinger equation that describes the problem. The simplest case, the particle in a box, is discussed in Chapter 2. The next subject is the simple harmonic oscillator, for which the eigenfunctions resemble those of the particle in a box, and transitions can be visualized in terms of the discussion in Chapters 2 and 3. In the following discussions (Chapters 5–10), vibrational, rotational, atomic, molecular electronic, and spin spectroscopies will be introduced. These discussions, if possible, start with a classical description, followed by the quantum mechanical equations for wavefunctions and eigenvalues, and the derivation of the selection rules. These selection rules determine the form and information content of the respective spectroscopic techniques. Although space limitations prevent in-depth discussions of spectroscopic applications to complex molecular systems, all efforts have been made to include molecular systems larger than diatomic molecules (the level of molecular complexity where many textbooks capitulate), since the world we live in mostly consists of more complicated molecules than diatomics.

Thus, in Chapter 5, the concept of the harmonic oscillator (Chapter 4) will be extended to vibrational (infrared and Raman) spectroscopy of polyatomic molecules. This chapter introduces concepts of band shapes, lifetimes, and a quantum mechanical description of molecular polarizability. Next in complexity are the differential equations for a rotational molecule that leads to rotational spectroscopy (Chapter 6). These equations will introduce the quantum mechanical description of the angular momentum and the energy levels of simple and more complicated molecules. The results from the rotational Schrödinger will also be used to solve the radial part of the hydrogen atom Schrödinger equation (Chapter 7). The principles learned from the rotational Schrödinger equation will also be used to introduce the spin eigenfunctions and eigenstates, a subject that leads directly to spin spectroscopy such as nuclear magnetic resonance (NMR), which is discussed in Chapter 8.

Next, the structure of atoms and ions containing more than one electron will be presented. This discussion includes an introduction to atomic spectroscopy and term symbols of electronic states. However, since the main theme of this book is molecular spectroscopy, this chapter only serves as an introduction to these subjects.

Chapter 10 is devoted to electronic spectroscopy of di- and polyatomic molecules. Again, as in previous chapters, it is necessary to define the states between which electronic transitions occur. This leads necessarily to the discussion of chemical bonding in terms of molecular orbital theory. Chemical bonding will be discussed to the level that electronic spectra of simple molecules can be explained, but the interaction between vibrational and electronic wavefunctions to produce vibronic states will be discussed in more detail to explain fluorescence phenomena as well as some Raman effects that rely on transitions into vibronic energy levels. Finally, Chapter 11 introduces group theory and the symmetry properties of molecules and the influence of symmetry on the appearance of molecular spectra.

The approach taken here in this book was strongly influenced by an excellent textbook *Physical Chemistry* by Engel and Reid [1] that was used as a required text in undergraduate physical chemistry courses at Northeastern University. This book emphasizes the unconventional approach taken by the early theorists who are responsible for the field of quantum mechanics as we know it. I gained substantial understanding of the philosophical background of quantum mechanics from this book. What is presented here in Quantum Mechanical Foundations of Molecular

Spectroscopy is a similar approach but with much more emphasis on molecular spectroscopy.

Although the present book emphasizes the relationship between spectroscopy and quantum mechanics more than other texts, the author wishes to point out the importance of following up on some proofs and derivations (omitted here) by studying books on “real” quantum mechanics or quantum chemistry. In particular, the one- and two-volume treatments by I. Levine [2, 3] are highly recommended, as well as many other old and new books [4, 5].

The mathematical requirements for understanding this book do not exceed the level achieved after a three-semester sequence of calculus, and all efforts have been made to provide examples and problems that will illuminate the mathematical steps. Most importantly, although some derivations are presented, the goal is not to lose sight of what quantum mechanics does for spectroscopy in the mathematical complexities.

Boston, August 2019

Literature references for the Preface are at the end of the Introduction.

Introduction

This book, *Quantum Mechanical Foundations of Molecular Spectroscopy*, is based on a graduate-level course by the same name that is being offered to first-year graduate students in chemistry at the Department of Chemistry and Chemical Biology at Northeastern University in Boston. When I joined the faculty there in 2005, I revised the course syllabus to emphasize the philosophical underpinnings of quantum mechanics and introduce much more of the quantum mechanics of molecular spectroscopy, rather than atomic structure, chemical bonding, and what is commonly referred to as "quantum chemistry."

As my own appreciation of many aspects of quantum mechanics evolved, I found it useful to start my lectures in this course with a quote from a famous researcher and Nobel laureate (1995, for his work on quantum electrodynamics), the late Professor Richard Feynman, which – taken slightly out of context – reads [6]:

> I think I can safely say that nobody understands quantum mechanics.

This rather discouraging statement has to be seen from the viewpoint that, when studying quantum mechanics, one realizes that this theory is not based on axioms, but on *postulates* – a very unusual fact in the sciences. Furthermore, it replaced deterministic results with probabilistic answers. When exposed to these conundrums, students will naturally ask the question: "Why bother studying quantum mechanics, if I will not understand it anyway?" or worse, "Is quantum mechanics for real, or is it the brainchild of some far-out mad scientists?" The answer here is also contained in a quote by Feynman:

> It doesn't matter how beautiful a theory is, …. If it doesn't agree with experiment, it's wrong.

This statement could also be formulated to imply that a theory that consistently provides answers that agree with the experiment most likely is correct. Thus, although nobody may understand quantum mechanics in its entirety, it gives answers that – over and over – agree with experiments and in fact provides a mechanism and framework for explaining the experimental results.

Quantum mechanics originated in the early decades of the twentieth century, when it was found that some experiment results just could not be explained by existing laws of physics and, in fact, violated established physical dogmas. It was these results that gave rise to the emergence of quantum mechanics that grew out of a patchwork of ideas aimed at explaining these hitherto unexplainable experimental results. These ideas coalesced into the field we now refer to as quantum mechanics. This newly formulated theory was wildly successful in explaining a myriad of physical and chemical observations – from the shape and meaning of the periodic chart of elements to the subject of this book, namely, the interaction of light with matter that is the basis of spectroscopy.

While many aspects of molecular spectroscopy, such as the rotational or vibrational energies of a molecule, can be described in classical terms, the idea that atoms and molecules can exist in quantized, stationary energy states is a direct result of the postulates of quantum mechanics. Furthermore, application of the principles of time-dependent quantum mechanics explains how electromagnetic radiation of the correct energy may cause a transition between these stationary energy states and produce observable spectra. Thus, the entire field of molecular spectroscopy is a direct result of quantum mechanics and represents the experimental results that confirms the theory. The phenomenal growth of all forms of spectroscopy over the past eight decades has contributed enormously to our understanding of molecular structure and properties. What started as simple molecular spectroscopy such as infrared and Raman vibrational spectroscopy, (microwave) rotational spectroscopy, ultraviolet–visible absorption, and emission spectroscopy has now bloomed into a very broad field that includes, for example, the modern magnetic resonance techniques (including medical magnetic resonance imaging); nonlinear, laser, and fiber-based spectroscopy; surface and surface-enhanced spectroscopy; pico- and femtosecond time-resolved spectroscopy, and many more. Spectroscopy is embedded as a major component in material science, chemistry, physics, and biology and other branches of scientific and engineering endeavors. Thus, the quantum mechanical underpinnings of spectroscopy are a major subject that need to be understood in the pursuit of scientific efforts.

References

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1

Transition from Classical Physics to Quantum Mechanics

At the end of the nineteenth century, classical physics had progressed to such a level that many scientists thought all problems in physical science had been solved or were about to be solved. After all, classical Newtonian mechanics was able to predict the motions of celestial bodies, electromagnetism was described by Maxwell's equations (for a review of Maxwell's equations, see [1]), the formulation of the principles of thermodynamics had led to the understanding of the interconversion of heat and work and the limitations of this interconversion, and classical optics allowed the design and construction of scientific instruments such as the telescope and the microscope, both of which had advanced the understanding of the physical world around us.

In chemistry, an experimentally derived classification of elements had been achieved (the rudimentary periodic table), although the nature of atoms and molecules and the concept of the electron's involvement in chemical reactions had not been realized. The experiments by Rutherford demonstrated that the atom consisted of very small, positively charged, and heavy nuclei that identify each element and electrons orbiting the nuclei that provided the negative charge to produce electrically neutral atoms. At this point, the question naturally arose: Why don't the electrons fall into the nucleus, given the fact that opposite electric charges do attract? A planetary-like situation where the electrons are held in orbits by centrifugal forces was not plausible because of the (radiative) energy loss an orbiting electron would experience. This dilemma was one of the causes for the development of quantum mechanics.

In addition, there were other experimental results that could not be explained by classical physics and needed the development of new theoretical concepts, for example, the inability of classical models to reproduce the blackbody emission curve, the photoelectric effect, and the observation of spectral “lines” in the emission (or absorption) spectra of atomic hydrogen. These experimental results dated back to the first decade of the twentieth century and caused a nearly explosive reaction by theoretical physicists in the 1920s that led to the formulation of quantum mechanics. The names of these physicists – Planck, Heisenberg, Einstein, Bohr, Born, de Broglie, Dirac, Pauli, Schrödinger, and others – have become indelibly linked to new theoretical models that revolutionized physics and chemistry.

This development of quantum theory occupied hundreds of publications and letters and thousands of pages of printed material and cannot be covered here in this book. Therefore, this book presents many of the difficult theoretical derivations as mere facts, without proof or even the underlying thought processes, since the aim of the discussion in the following chapters is the *application* of the quantum mechanical principles to molecular spectroscopy. Thus, these discussions should be construed as a guide to twenty-first-century students toward acceptance of quantum mechanical principles for their work that involves molecular spectroscopy.

Before the three cornerstone experiments that ushered in quantum mechanics – Planck's blackbody emission curve, the photoelectric effect, and the observation of spectral “lines” in the hydrogen atomic spectra – will be discussed, electromagnetic radiation, or light, will be introduced at the level of a wave model of light, which was the prevalent way to look at this phenomenon before the twentieth century.

1.1 Description of Light as an Electromagnetic Wave

As mentioned above, the description of electromagnetic radiation in terms of Maxwell's equation was published in the early 1860s. The solution of these differential equations described light as a transverse wave of electric and magnetic fields. In the absence of charge and current, such a wave, propagating in vacuum in the positive *z*-direction, can be described by the following equations:

$$\vec{\mathbf{E}} = E_0 \sin(\boldsymbol{k} \times \boldsymbol{z} - \omega t) = E_0 \sin(2\pi z/\lambda - 2\pi \nu t) \tag{1.1}$$

$$\vec{\mathbf{B}} = B_0 \sin(\boldsymbol{k} \times \boldsymbol{z} - \omega t) = B_0 \sin(2\pi z/\lambda - 2\pi \nu t) \tag{1.2}$$

where the electric field $\vec{\mathbf{E}}$ and the magnetic field $\vec{\mathbf{B}}$ are perpendicular to each other, as shown in Figure 1.1, and oscillate in phase at the angular frequency

$$\omega = 2\pi \nu \tag{1.3}$$

where ν is the frequency of the oscillation, measured in units of $s^{-1} = \mathrm{Hz}$. In Eqs. (1.1) and (1.2), $\mathbf{k}$ is the wave vector (or momentum vector) of the electromagnetic wave, defined by Eq. (1.4):

$$k = |\vec{\boldsymbol{k}}| = 2\pi/\lambda \tag{1.4}$$

Here, λ is the wavelength of the radiation, measured in units of length, and is defined by the distance between two consecutive peaks (or troughs) of the electric or magnetic fields. Vector quantities, such as the electric and magnetic fields, are indicated by an arrow over the symbol or by bold typeface.

Since light is a wave, it exhibits properties such as constructive and destructive interference. Thus, when light impinges on a narrow slit, it shows a diffraction pattern similar to that of a plain water wave that falls on a barrier with a narrow aperture. These wave properties of light were well known, and therefore, light was considered to exhibit wave properties only, as predicted by Maxwell's equation.

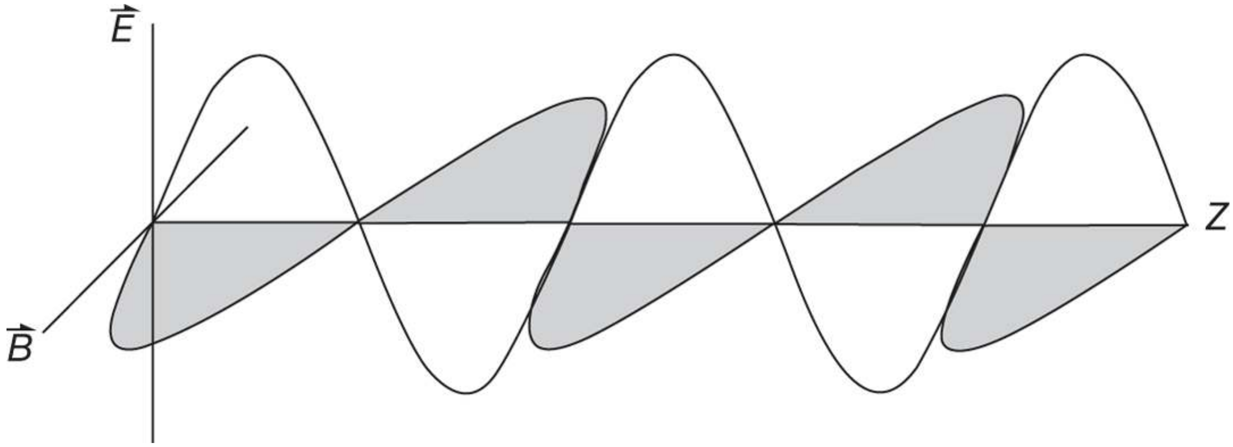

Figure 1.1 Description of the propagation of a linearly polarized electromagnetic wave as oscillation of electric ($\vec{E}$) and magnetic ($\vec{B}$) fields.

In general, any wave motion can be characterized by its wavelength λ, its frequency ν, and its propagation speed. For light in vacuum, this propagation speed is the velocity of light c ($c = 2.998 \times 10^8$ m/s). (For a list of constants used and their numeric value, see Appendix 1.) In the context of the discussion in the following chapters, the interaction of light with matter will be described as the force exerted by the electric field on the charged particles, atoms, and molecules (see Chapter 3). This interaction causes a translation of charge. This description leads to the concept of the "electric transition moment," which will be used as the basic quantity to describe the likelihood (that is, the intensity) of spectral transition.

In other forms of optical spectroscopy (for example, for all manifestations of optical activity, see Chapter 10), the magnetic transition moment must be considered as well. This interaction leads to a coupled translation and rotation of charge, which imparts a helical motion of charge. This helical motion is the hallmark of optical activity, since, by definition, a helix can be left- or right-handed.

1.2 Blackbody Radiation

From the viewpoint of a spectroscopist, electromagnetic radiation is produced by atoms or molecules undergoing transitions