

Spectroscopy Theory in One Dimension

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13 July 2024 10:37:44



AIP Publishing Books

A publication of AIP Publishing

Melville, New York

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First edition, published 2022.

Library of Congress Control Number: 2022943598

ISBN: 978-0-7354-2564-4 (Softcover)

ISBN: 978-0-7354-2566-8 (Online)

ISBN: 978-0-7354-2567-5 (ePub)

ISBN: 978-0-7354-2565-1 (ePDF)

Set in 10/13pt MinionPro by Nova Techset Private Limited, Bengaluru & Chennai, India, and bound by The Sheridan Group, USA

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Published by AIP Publishing

1305 Walt Whitman Road, Suite 110, Melville, NY 11747-4300, USA

To the creator of all things visible and invisible... *Soli Deo Gloria*

ACKNOWLEDGMENTS

This project was completed by my father Darrell Williams' wise words, "the measured task gets done." I passed this wisdom on to my Master of Science student and co-author Victoria Spenn Jackson when she completed much of the mathematics in this book during her graduate work in the Chemistry Department at Sam Houston State University.

Our work has been questioned, challenged, and honed by the Physical Chemistry I Quantum Mechanics and Spectroscopy students at SHSU over the past 18 years. Their successes in industry and graduate schools across the country speak to the usefulness of teaching spectroscopy theory in one dimension.

Victoria's work on the material in this text was supported by the Welch Foundation Departmental Development Grant X011, and we are grateful for their generous support of the Chemistry Department over many decades.

The Professional and Academic Center for Excellence directed by Dr Todd Primm at SHSU sponsored the Faculty Writing Circles. The writing circles encouraged and aided the writing process with their writing retreats, weekly writing meetings, and instruction in sustained-effort tools such as pomodoro timing.

I thank my book team: colleague David Thompson Ph.D., former students Ashley Williams, Heather Coats M.S., Joe Treviño M.S., Nilan Kamathewatta Ph.D., my sister Patti J. Brown M.S., and current students Andrea Martinez, Brodin Huse, Marie Hailey, Makaul Barbaree, Micaela Badger, and Tommy Gilpin for their constructive comments and reviews.

I am especially grateful to my Ph.D. advisor Dr. Joseph W. Nibler for his in-depth review of the science, for his insightful corrections, and for his informative Foreword.

I thank the many employees and regulars at Sipsy's coffeehouse in Huntsville, TX. They were the first coffeehouse to open after COVID, and I wrote most of this manuscript over two years sitting in their "good chair."

I acknowledge the active support of my wife Jennifer M. Williams, who frequently told me to "go write" while she finished tasks without me. I have many fond memories of her driving us all over Texas while I wrote on my laptop in the passenger seat.

FOREWORD

One of the joys of an academic career is the opportunity to work with creative and interesting students. Over the last 60 years in the Chemistry Department at Oregon State University, I have had the privilege to interact with many such individuals. Not the least of these was Darren Williams, whose intellect and infectious enthusiasm as a student, as a teaching assistant, and as a person were evident from the beginning of his doctoral studies with me. Darren has a quirky sense of humor, an aspect I enjoyed immensely. Once, while serving as a teaching assistant in an advanced Chemistry lab I was teaching, he was asked to obtain photos of all the graduating seniors. He did so, but brought a Groucho Marx nose, moustache, and glasses for each student to wear for the occasion, something each did with delight. Another time, at a Western Spectroscopy Association meeting in Asilomar, CA, he and two other students presented in a poster session their research obtained in our lab using Coherent Anti-Stokes Raman Spectroscopy (CARS). But, they asked me at the last minute if they could bring an additional poster they were preparing with their very latest results. I said OK if it is good science and there is room at the session. Darren assured me that the poster “LOOKS very good.” Turns out it was a bogus poster that mocked the use of acronyms such as CARS, by claiming the development of new spectroscopic techniques (PLANES, TRAINS, and AUTOMOBILES) to detect the delivery of anti-cancer drugs in mice. Replete with spectra, very linear graphs, and complex statistical analysis, only slowly did viewers realize that it was a total spoof. Recognition brought smiles and laughter, results that invariably followed a number of other such Williams’s pranks.

Many students have been fortunate to enjoy Darren as a teacher at Sam Houston University, where he is a Professor of Chemistry. This book offers clear evidence of his ability to make complex topics clear and accessible to all. Most physical chemistry and quantum mechanics courses briefly discuss one-dimensional problems such as the particle in a box and on a ring. The focus is usually on the mathematical form of the energy levels and wave functions. In this book, Darren and his co-author, Victoria Jackson, go much further. They discuss in detail the calculation of transition probabilities using the one-dimensional dipole and polarizability operators. The results lead naturally to selection rules and to predicted spectral intensities. Explicit examples are given for electronic, infrared, and Raman spectroscopies, as well as for Rayleigh light scattering. The authors also show how the same selection rules can be derived from symmetry and group theoretical arguments. The result is an exposition that ties many aspects of quantum mechanics together and allows extension to 2- and 3-dimensional problems. This book will be especially helpful to undergraduates taking Physical Chemistry and to beginning graduate students interested in spectroscopy. I heartily recommend it.

Joseph Nibler
Emeritus Professor of Chemistry
Oregon State University

PREFACE

“Quantum is kicking my butt. ☹” she wrote on social media.

My heart sank and a knot developed in my stomach. I wondered to myself, “I hope it isn’t my fault.”

So I reached out to her with a direct message. She had graduated from SHSU the previous May and is now enrolled in a Chemistry Ph.D. program at a top-tier research institution. I was worried that my method of teaching quantum mechanics had not prepared her for graduate school.

She quickly responded and put me at ease. She said all of the students from both large and small universities were struggling with the multivariable calculus. Then, she said, “at least I know where these problems are going,” and that put me at ease.

I have been teaching spectroscopy in one dimension from the wave function to the full simulated spectrum for 18 years and teaching the students to apply their knowledge to three-dimensional systems by analogy. This text was written to document this method of teaching quantum mechanics and spectroscopy.

I hope that this text will serve many roles: (a) as a text for motivated chemistry majors to read prior to (or during) their quantum mechanics and spectroscopy course, (b) as a lecture preparation text for professors giving them many one-dimensional examples of the math of spectroscopy, and (c) as a refresher text for professional spectroscopists who want to resharpen their theoretical understanding of the tools of their trade.

Paul Adrien Maurice Dirac, who shared the 1933 Nobel Prize with Schrödinger, made his now-famous statement in his 1929 paper *Quantum Mechanics of Many-Electron Atoms*:

“The underlying physical laws necessary for the mathematical theory for a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.”

In his next sentence, Dirac clearly states the purpose and motivation of this book:

“It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to *an explanation of the main features of complex atomic systems without too much computation.*”

That is why this book exists—to explain the main features of spectroscopy without too much computation. With these simple models, we discuss why the daytime sky is blue, why the sunsets are red, why diamonds sparkle, and how lasers work.

With this book, we hope you gain a working knowledge of the forest by focusing on one species of tree—the one-dimensional wave function.

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August 2022



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13 July 2024 10:37:44

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BRIEF CONTENTS

- Chapter 1 The Emergence of Quantum Mechanics**
A brief history contrasting Newtonian or classical physics with quantum physics.
- Chapter 2 Managing the Messy Mathematics**
The *mathematical road map* for the whole book. The equations are presented but not solved.
- Chapter 3 Energy and the Transition Equations**
This chapter shows how the Hamiltonian, the wave function, and the Schrödinger equation are combined to obtain the energy levels of the 1D particle in a box and particle on a ring systems. The transition equations are also computed showing the transition energies or spectral lines in traditional units of wavenumbers and wavelength.
- Chapter 4 Into the Spectroscopic Weeds—Absorption and Emission Intensities**
The transition probabilities are computed analytically for absorption and emission yielding the selection rules $\Delta n = \{\pm 1, \pm 3, \pm 5, \dots\}$ for the 1DPB. For the 1DPR system, the electric dipole is mapped onto the ring coordinate system, which yields the dipole operator $\cos \theta$, for absorption and emission and the well-known rotational selection rules of $\Delta n = \{\pm 1\}$ only.
- Chapter 5 Rayleigh and Raman Scattering Intensities**
For elastic (Rayleigh) and inelastic (Raman) scattering, the polarizability operator is represented by the x -axis squared (x^2). The selection rules for the scattering transitions yield non-zero results for the transition probability integrals, $\Delta n = \{0, \pm 2, \pm 4, \dots\}$.

For the 1DPR system, the polarizability operator (x^2) is mapped onto the ring coordinate system, yielding a $\cos^2 \theta$ operator for scattering phenomena. The scattering moment integral solutions yield the Rayleigh and rotational Raman selection rules of $\Delta n = \{0, \pm 2\}$.

Chapter 6 The Big Picture

Several stick spectrum examples are plotted for the 1DPB and 1DPR systems for absorption, emission, Rayleigh and Raman scattering.

Chapter 7 Why Symmetry?

The zero and non-zero properties of the integrals of even and odd functions are emphasized because this is the foundation of the symmetry-derived selection rules. What took *pages of calculus* to determine analytically in Chapters 4 and 5 can be performed on a *Post-it-Note*[®] if the symmetries of the wave functions are known.

Chapter 8 Symmetry Selection Rules for the 1D Particle in a Box

The point group (C_i) and the Mulliken symmetries (A_g or A_u) of the wave functions are assigned. The transition moment integrals for absorption/emission, Rayleigh scattering, and Raman scattering are presented. The direct product table for the C_i point group is used to determine the symmetry selection rules for the 1DPB system.

Chapter 9 Symmetry Selection Rules for the 1D Particle on a Ring

The $D_{\infty h}$ point group and the Mulliken symmetries of the wave functions are assigned to the 1DPR system. The transition moment integrals for absorption/emission, Rayleigh scattering, and Raman scattering are presented. The direct product table for the point group is used to determine the symmetry selection rules for the 1DPR system.

Chapter 10 Is Symmetry Enough? What's Missing?

This chapter shows the power of symmetry to assign and interpret spectra. Several examples are given of real 3D systems. However, the symmetry selection rules are not able to produce spectral intensities.

Chapter 11 Failures of Classical Physics Revisited, and Understood

This chapter demonstrates that even a one-dimensional understanding of quantum mechanics can be used to fully explain the four failures of classical physics commonly presented in physical chemistry textbooks. This chapter ends the book with a list of main take-aways from the text.

