CHAPTER 1 THE EMERGENCE OF QUANTUM MECHANICS

1.1 INTRODUCTION

We live in a mysterious world. Microwave ovens heat food in minutes, yet the interior of the oven remains cool to the touch. We have light emitting diodes, polarized screens, and mega-pixel displays in our pockets and on our watches. Our atmosphere contains spectral windows that let visible light in and infrared light (heat) out. These atmospheric windows can be closed by some molecules but not others. Lasers have been added to weapons, range finders, barcode scanners, and thermometers. None of these phenomena or products can be understood without spectroscopy—the mother of quantum mechanics.

The aim of this book is to teach you spectroscopy, and in so doing, quantum mechanics.

Spectroscopy is the study of light interacting with matter through absorption, emission, and scattering. Learning spectroscopy will lead to an understanding of the main features of quantum theory. This book takes the unique approach of presenting the whole theory in one dimension. Understanding this one-dimensional approach will give intuition into three-dimensional atomic and molecular spectroscopy by analogy. Specifically, the responses of one-dimensional quantum systems to changes in mass, size, and temperature are very similar to the responses of actual 3D atomic and molecular systems.

1.1.1 Useful modes of thought

Before quantum theory, before physics, and before mathematical science, people lived in a world of vital forces, formal causes, and ethereal vortices propelling the planets through the heavens. Algebra slowly emerged in the work of Diophantus (Encyclopædia Britannica, 2022a) and al-Khwarizmi (Encyclopædia Britannica, 2022b), and math took a prominent position in René Descartes' (1596–1650) 1629 manuscript *Rules for the Direction of the Mind* (René Descartes, 1990). His Rule IV states plainly that "*There is need of a method for finding out the truth*." In his exposition on this rule, he spoke of seed-like epiphanies in the mind, or "*germs of useful modes of thought.*" His new mode of thought was the awareness that mathematics was a method of finding out the truth about the world.

> For the human mind has in it something that we may call divine, wherein are scattered the first *germs of useful modes of thought*. (René Descartes, 1990)

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Spectroscopy Theory in One Dimension, Darren L. Williams and Victoria S. Jackson

Over the remaining centuries to our present day, these mathematical "*germs of useful modes of thought*" have become calculus, physics, quantum mechanics, and symmetry. They directed the mind of humanity toward scientific discoveries and technological advancements that continue to astonish and amaze.

1.1.2 Newton triumphant

It was Descartes' *Geometry* published in 1637 that inspired a young Isaac Newton (1642–1727) to embark on original mathematical work. In a few short years "Newtonian Physics" would describe the motions of the planets and the paths of cannon balls (Newton, 1990). The world-changing consequences cannot be overstated. Knowing the trajectory of a moving object yielded predictive abilities of Biblical proportion, as Alexander Pope quipped.

> Nature and Nature's Laws lay hid in night,
> God said, Let Newton be, and all was light. (Alexander Pope quoted by Adler MJ, 1990)

The mathematics Newton developed for his work on gravitation led to successful mathematical descriptions of electric and magnetic forces by Fourier, Faraday, and Maxwell. A great hubris developed. It was believed (then and now) that a mechanistic and mathematical description was possible in all areas of study, including economics, sociology, and psychology (Adler, 1990b).

However, protruding through the topsoil of this lush valley of discovery were hints of another structure of nature. There was trouble in paradise.

1.1.3 Darkness in the light

The fundamental nature of light was an enigma. Newton imagined light as a corpuscle (particle), while Huygens imagined an oscillating wave (Adler, 1990a). The reputation of Newton made the particulate view unassailable for over a century. In fact, Thomas Young's Bakerian Lectures to the Royal Society on the nature of light revealed by diffraction patterns in 1801 and 1803 were harshly criticized as being "destitute of every species of merit" for suggesting that Huygens was correct about light's wavelike nature (Young, 1802, 1804; and Baggott, 2016).

Over the years, data piled up supporting both views. The conservation of kinetic energy of light-ejected (photo-) electrons clearly suggested that light was a particle (photon) and that electrons were particles as well.

In contrast, the diffraction patterns of light described by Thomas Young suggested that the light was a wave. Strangely, even electrons, which were clearly particles with a measurable charge and mass, produced the same types of diffraction patterns (behaving like waves) when they interacted with a crystalline substance (Thomson and Reid, 1927).

There seemed to be a world of mystery surrounding spectroscopy—light interacting with matter. There were four experiments that Newtonian physics could not explain.

1. Hydrogen (and other atoms) emitted discrete spectral lines when excited.
2. The emission spectrum of a hot object (blackbody radiation) depended upon temperature and not on the identity of the substance.
3. Photoelectrons streamed off a surface with a kinetic energy that was directly proportional to the frequency of the incident light as long as the light frequency was above a material-dependent threshold (work function).
4. The heat capacity of diamond and other substances seemed to go to zero as the temperature went to zero.

Hot hydrogen atoms in an electric discharge or flame produced emissions that appeared as very narrow lines when dispersed by a grating or prism onto a photographic plate (Fig. 1.1). Peaks in a spectrum are still called "spectral lines" today. Balmer and Rydberg showed that these *spectral emission lines* of the hydrogen atom could be aligned with an integer series. These integers eventually became known as *quantum numbers*, but the meaning of these integers was unclear (Baggott, 2016).

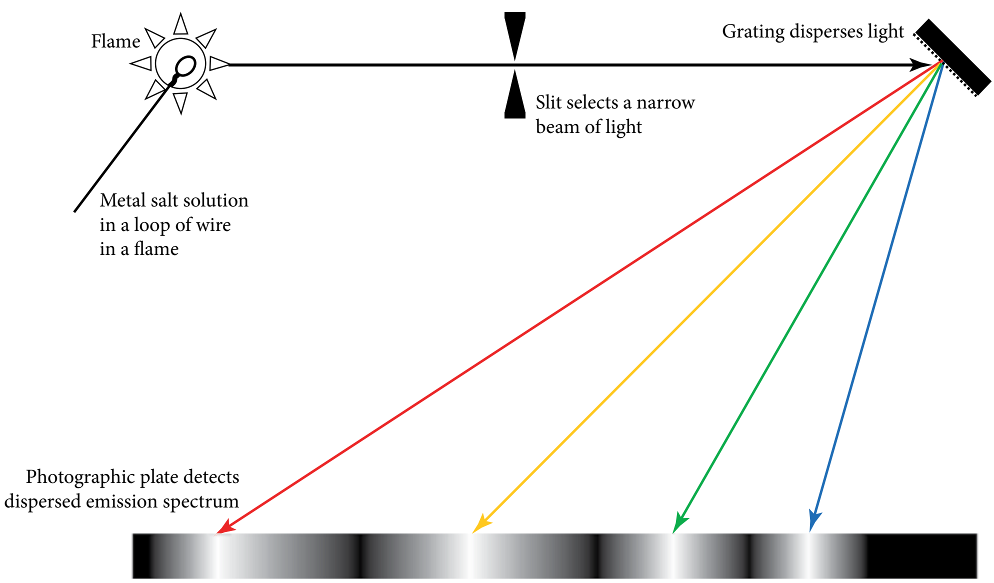

FIG. 1.1
The historical way of collecting emission spectra involved exposing a photographic plate with dispersed light yielding discrete spectral lines when various atoms were introduced into the flame.

1.1.4 The useful germ of quantum thought

The unintentional beginning of quantum theory took place in 1877 with Ludwig Boltzmann. Boltzmann was an atomist and described the statistical emergence of equilibrium in the velocities of individual gas particles. He successfully connected this statistical treatment to the entropy of the gas. In developing his statistical argument, he began with a simple mathematical starting point.

> …to facilitate understanding, I will, as in earlier work, consider a limiting case. [Namely that the] *kinetic energy has discrete values*. … This assumption does not correspond to any realistic mechanical model, but it is easier to handle mathematically… (Sharp and Matschinsky, 2015)

His statistical starting point was with quantized kinetic energy—discrete countable units. Boltzmann quickly pointed out that this was not meant to actually reflect nature, but a *germ of a useful mode of thought* (to use Descartes' words) had been introduced.

This *germ of thought* was picked up by Max Planck in his work on blackbody radiation. The light emitted by hot atoms in a flame or electric discharge (line spectra) is unique to each substance. In contrast to this the light emitted by hot solid objects (blackbody radiation) depends only on the temperature of the object and not the material that makes up the object. The study of this peculiar behavior provided the first breakthrough for Planck and quantum theory.

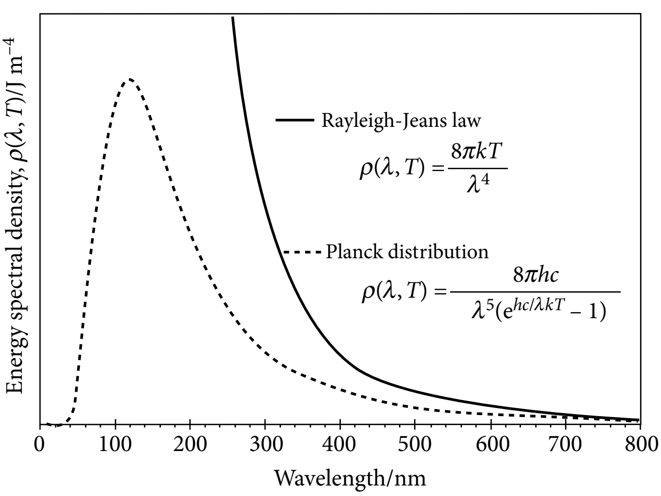

FIG. 1.2
Comparison of the Rayleigh–Jeans law derived from classical physics and the Planck distribution that incorporated the elementary quantum of action (h).

Planck was not an atomist but was being pulled inexorably toward atomism by Boltzmann's ideas. Instead of quantized energies, Planck introduced the idea that light emitted and absorbed by individual oscillators in a black body could only be emitted or absorbed in discrete energy packets characterized by the elementary quantum of action h [Eq. (1.1)]. The Rayleigh–Jeans' law matched the blackbody emission spectrum at long wavelengths, but Planck's distribution law matched the experimental spectrum over the entire range (Fig. 1.2). The crucial feature of Planck's work was his use of the atomistic Boltzmann distribution [$\exp(hc/\lambda kT)$] which contains h—the elementary quantum of action.

Planck knew that this was an important advancement in science.

> While the significance of the quantum of action (h) for the interrelation between entropy and probability was thus conclusively established, the part played by this new constant in the uniformly regular occurrence of physical processes still remained an open question. I, therefore, tried immediately to weld the elementary quantum of action h somehow into the framework of the classical theory. … The failure of every attempt to bridge this obstacle soon made it evident that the elementary quantum of action plays a fundamental part in atomic physics, and that its introduction opened up a new era in natural science (Planck, 1990).

This elementary quantum of action, introduced by Planck, became what we call Planck's constant, h [$6.626\ 070\ 040(81) \times 10^{-34}$ J s] (Fundamental Constants Data Center of the NIST Physical Measurement Laboratory, 2022), and the Planck equation [Eq. (1.1)] was quickly verified by the photoelectron experiment as the slope of the plot of electron kinetic energy vs illumination frequency,

$$E = h\nu = \frac{hc}{\lambda}. \tag{1.1}$$

The emission of all black body irradiators was solved, but the emission lines of the simplest atom—hydrogen—were still a problem for classical physics. The integers of Balmer and Rydberg were a mystery. Bohr proposed that these emission lines represent quantized electron jumps between discrete orbits similar to planetary orbits in a solar system. This was problematic primarily because charged particles spinning in a circle would emit electromagnetic radiation continuously as they spiraled into the nucleus. What kept the electrons in specific orbits around an attractive nucleus?

1.1.5 Standing waves

De Broglie (2021) (pronounced De Broy) was the first to connect the discrete orbit idea to *standing waves* in his thesis dissertation in 1924. He loved music and the wave behavior of stringed instruments produced in him a *germ of a useful mode of thought*, namely that the electron orbits might consist of discrete standing waves (de Broglie, 2021).

De Broglie was able to combine Planck's equation $E = hc/\lambda$ and Einstein's equation $E = mc^2$ to relate wavelength to momentum ($\lambda = h/mc$), and the aforementioned electron diffraction experiments validated this relationship (de Broglie, 2021). Einstein acknowledged de Broglie's idea in a paper that was later read by Erwin Schrödinger. The quantized standing wave *germ of thought* passed from de Broglie to Einstein to Schrödinger, and two years later, Schrödinger's *wave mechanics* burst onto the scene.

Erwin Schrödinger combined the integer quantum numbers of Rydberg, the quantized orbits of Bohr, and the standing waves of de Broglie to create a wave mechanical model of the hydrogen atom. Thus, *quantum* theory and wave *mechanics* became *quantum mechanics*.

In wave mechanics, waves are described by wave functions (ψ). These functions are required to be smooth, finite, continuous, and single-valued, as seen in Fig. 1.3. The solutions to Schrödinger's complex differential equations necessitated the use of the eigenvalue equation we call Schrödinger's equation [Eq. (1.2)],

$$\hat{H}\psi = E\psi. \quad (1.2)$$

Developing wave functions for the hydrogen atom and solving for their quantized energies took Schrödinger two months of intense effort. The resulting differential equations were beyond his ability. He reached out to his colleague Hermann Weyl to get help with the solution to the radial wave function (Baggott, 2016). Once solved, the spectroscopic transitions (jumps) between the quantized energy states matched the Balmer rules for the hydrogen atom.

The electrons in their orbits behaved like the violin strings of de Broglie. A violin string can jump an octave from $n = 1$ to $n = 2$ (or higher harmonics with $n > 2$), but it cannot resonate at any other note without changing the length, tension, or mass of the string. This quantum jumping is the expected behavior of standing waves.

What about the intensities of the transitions and the transitions that seemed to have no intensity (a.k.a. *forbidden transitions* and *selection rules*)? This problem was also solved by Schrödinger in his 1926 paper using the total electric moment. If the square of the wave function was interpreted as the

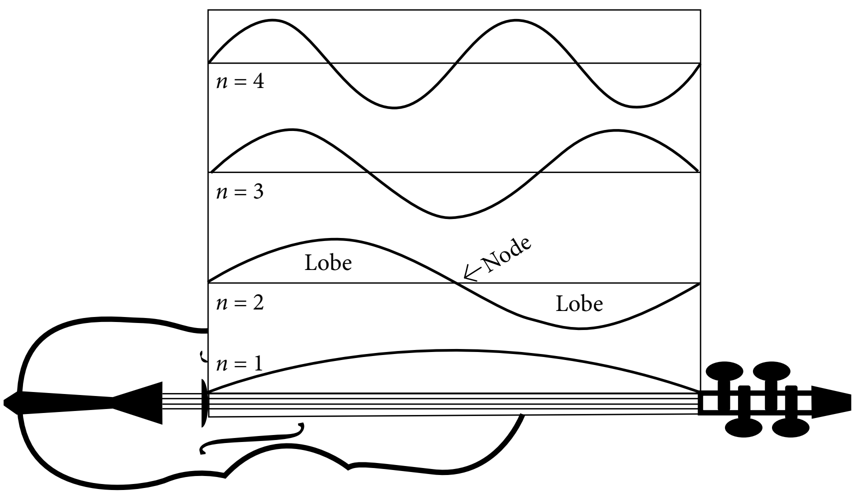

FIG. 1.3
Standing waves are "pinned" to zero at the extremes and have discrete (integer) numbers of oscillating lobes, $n = \{1, 2, 3,\ldots\}$, and fixed places (nodes) where no oscillation occurs.

probability distribution of the particle in all space, then "*the intensity of emitted radiation of a particular frequency is expected to be proportional to the square of the total electric moment*" (Schrödinger, 1926). With this principle in place, Schrödinger was able to produce stick spectra that showed an impressive match between experiment and theory (Fig. 1.4).

The heat capacity experiment was not a spectroscopic phenomenon, but Einstein showed that the heat capacity should go to zero if one uses the same Boltzmann distribution of discrete oscillators that Planck used when solving the blackbody radiation problem (Einstein, 1907).

The new theory matched the experimental data so closely that many felt that wave mechanics could explain everything. For example, Paul Dirac, who shared the 1933 Nobel Prize with Schrödinger, remarked in 1929,

> 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*. (Dirac, 1929)

In the next sentence of his 1929 paper, Dirac calls for approximations that help explain quantum mechanical applications.

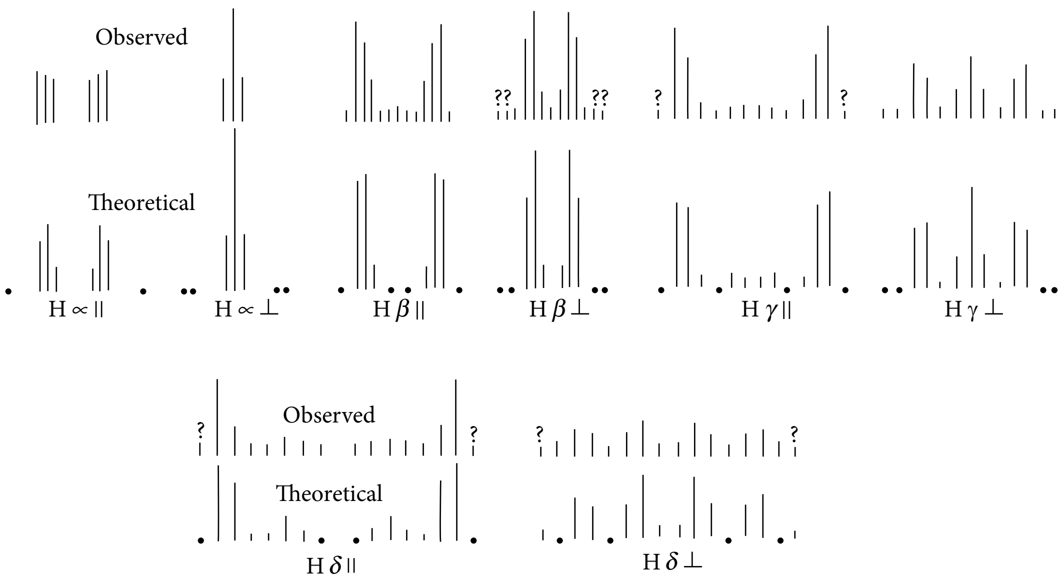

FIG. 1.4
Erwin Schrödinger's comparisons of experimental hydrogen spectral lines to the results of his newly developed quantum mechanics. Reproduced with permission from Schrödinger, E., Phys. Rev. **28**, 1049–1070 (1926). Copyright 1926 American Physical Society.

> 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*. (Dirac, 1929)

That is why this book exists—to explain the main features of spectroscopy without too much computation. In this text, you will find an example of quantum mechanics applied to the simplest computational model—a one-dimensional wave function.

One can understand the whole detailed quantum mechanical explanation of spectroscopy using the *one-dimensional* wave functions of a *particle in a box* (1DPB) and a *particle on a ring* (1DPR). These traditional systems are introduced in most physical chemistry texts, but the texts stop with the solution of the energy levels. This book shows the necessary computations to calculate the intensities and wavelengths of absorption, emission, and scattering spectral transitions as well as the selection rules for both the 1DPB and 1DPR systems.

1.1.6 The symmetry germ of thought

Hermann Weyl, who helped Schrödinger with the eigenvalue problem, caught an idea from his colleague Amalie Emmy Noether that nature possessed a deep symmetry that was reflected in the conservation laws of energy, momentum, charge, etc. Weyl published his group theory of quantum mechanics in 1928, and Eugene Wigner simplified and applied it to atomic spectra in 1931 (Baggott, 2016). The most profound result was the ability to reduce the computation of complex wave equations to simple symmetry relationships that fit on a Post-It Note®. These symmetry-assisted computations of spectroscopic selection rules will be shown in Chaps. 7–10 of this book.

Jumping from this point in history to the present day, we will explore the one-dimensional mathematics of quantum mechanics in two ways, which make up the two major portions of the book:

- Chapters 2–5: Analytical computation of spectroscopic transition wavelengths and intensities
- Chapters 6–10: Group theory computation of allowed and forbidden spectroscopic transitions

A practical application of these mathematical relationships has been developed using spreadsheets, and this will be fully described in a second book—Practical Spectroscopy and Simulation. The second book yields many great insights allowing you to "play" with the numerical solutions to determine the spectral changes that occur with temperature, mass, and size of the quantum system.

The skills developed in the one-dimensional systems may be very effectively applied to three-dimensional systems. The prediction of the selection rules of atomic spectroscopy, molecular vibrational spectroscopy, molecular rotational spectroscopy, molecular ro-vibrational spectroscopy, and electronic spectroscopy of 3D systems are understood through symmetry and by analogy to the behavior of 1D systems.

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