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Series on wave phenomena in the physical sciences

What's the Matter with Waves

An introduction to techniques and applications of quantum mechanics

William Parkinson

IOP ebooks

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Series Editor

Sanichiro Yoshida

Southeastern Louisiana University

About the series

The aim of this series is to discuss the science of various waves. It consists of several books, each covering a specific subject known as a wave phenomenon. Each book is designed to be self-contained so that the reader can understand the gist of the subject. From this viewpoint, the reader can read any book as a stand-alone article. However, it is beneficial to read multiple books as it would provide the reader with the opportunity to view the same aspect of wave dynamics from different angles.

The targeted readership is graduate students of the field and engineers whose background is similar but different from the subject. Throughout the series, it is intended to help students and engineers deepen their fundamental understanding of the subject as wave dynamics. An emphasis is laid on grasping the big picture of each subject without dealing with detailed formalism, and yet understanding the practical aspects of the subject. To this end, mathematical formulations are simplified as much as possible and applications to cutting edge research are included. The reader is encouraged to read books cited in each book for further details of the subject.

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This book is dedicated to the most important people in my life—my family, especially my wife Bonnie.

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Author biography

Bill Parkinson

Bill Parkinson attended California University of Pennsylvania, receiving a BS in chemistry in 1977. This was followed with stints as an environmental engineer, a construction worker, marine biologist, and high school physics and mathematics teacher. He obtained his PhD from the University of Florida's Quantum Theory Project in 1989, where he had the great fortune of rubbing elbows with the world's leading experts in computational chemistry during some of the field's most formative years. After postdoctoral positions at Odense University (now Syddansk Universitet, the University of Southern Denmark) and Texas A&M, he joined the faculty of Southeastern Louisiana University in 1991. His pastimes and passions include yard work, biking, volleyball, the beach, and Pittsburgh Steeler football.

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Chapter 1

Introduction

Everyday experience is a helpful guide as we attempt to model the physical world around us. For example, interpreting wave motion is aided by noting the movement of a bobber on the ripples of a pond. Anticipating trajectories resulting from colliding bodies may be facilitated from observation of a pool table cue ball. Understanding action at a distance from a force field is furthered by participating in a game of catch. With regard to the subject at hand, observing ocean water crashing into a rock jetty, listening to sound echoing through a mountain valley, or locating a penny on the bottom of a fountain provides a basis of comprehension for wave–matter interaction.

By contrast attempts to phenomenologically model a chemical process in which matter undergoes a transformation of constitution present daunting challenges. Ignoring for a moment the fact that reaction rates commonly occur in a time frame that render them humanly imperceptible, a more fundamental impediment is the scale of matter dimensionally. We cannot 'see' the system interacting, we may only verify the occurrence of chemistry from observing affects on its surroundings: heat evolution, a phase change, a flash of light, a smell, a puff of smoke. In fact, the only 'illuminating' probe at these dimensions is a light wave. Suppose then that we are somehow magically able to ride a light beam, as if it allows us to don nanoscopes for the purpose of observing matter in action during a chemical process. Even with this advantage, we would quickly find that attempts to utilize rules for cue balls or other projectile motions do not apply. We would also learn the light itself is not just a casual observer in this environment, but is an intimate part of the system dynamics.

Ultimately would come to the realization that an entirely new set of principles and guidelines, far outside the box of those ingrained from familiar observation, are required to correctly model and predict events. The approach taken here will then be to review our understanding of the behavior of macroscopic matter. Particular focus will be given to instances where the governing rules hold fast, and where there is a disconnect. This is facilitated by reviewing experimental evidence that could not be

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explained away by accepted guidelines. We will then introduce the necessary modifications to allow matter's description at the atomic and molecular level.

While navigating this course, the advantage taken from tangible connection with everyday experience must unfortunately be abandoned. We will in fact find it necessary to incorporate some facets of our common understanding of wave behavior into the model of matter. This seems counterintuitive. Even to the most casual observer, there are obvious differences between matter and waves. Though each takes a variety of distinguishable forms, matter and waves are ultimately differentiated by a single criterion. Waves uniquely have the capability of occupying the same space at the same time. For example consider four individuals simultaneously conducting two separate conversations as depicted in figure 1.1. Everyday experience tells us that opposing pairs can communicate, even though sounds from their voices are somewhere intersecting. In addition, light reflecting off any one of them can be detected by the remaining three, even though these waves must also inhabit the same space along their journey. This property, known as *superposition*, allows waves to exhibit constructive and destructive interference, which for sound results in phenomena such as piano chords and devices like noise-cancelling headphones.

By distinct contrast, one of the two fundamental characteristics of matter is that it 'takes up space' (the other, according to any physical science primer, being that it has mass. This is technically saying the same thing actually, but I digress…). Of course the implication of matter occupying space is that it must exclude other matter from that space. Despite this very fundamental of differences, matter and waves are intimately related. Most waves are actually disturbances of matter. Sound, water, and string waves cannot move through space without matter acting as a *medium* to

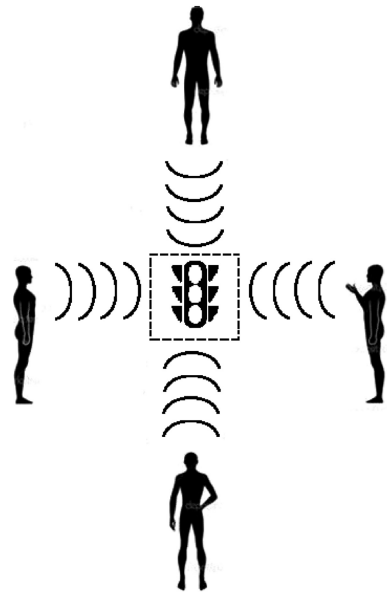

Figure 1.1. Superposition of propagating waves.

enable their propagation. In fact for quite some time it was believed waves and matter had an inextricable relationship. With Huygens' introduction of the wave theory of light, it presupposed the requirement of a support medium. The search ensued for the so-called *aether*, until its existence was debunked as a result of experiments performed by Michelson and Morley.

In contrast to other wave forms, electromagnetic radiation creates a disturbance in *space*. This effect is described in physics as being generated by a *field*, or interacting fields as is the case here. In fact, electromagnetic radiation prefers an absence of matter. As evidenced by gazing upward towards the nighttime sky, electromagnetic radiation continuously self-generates and propagates through space when unimpeded by matter. When electromagnetic radiation of a particular type does encounter matter it may pass through, be diffracted, refracted, reflected, scattered, or absorbed. Matter and its interaction with light and other portions of the electromagnetic spectrum is the basis of a wide variety of qualitative and quantitative analytical chemistry techniques.

The arrival of spectroscopy as a characterizing tool for the composition of substances was paralleled by the fundamental questions light–matter interaction posed. By the late nineteenth and early twentieth centuries, instrumentation had achieved levels of resolution revealing information that could not be explained by contemporary theories. Attempts to formalize the mechanism of light–matter energy transfer blurred their fundamental distinction. As an initial explanation, light waves were re-imagined to possess matter-like characteristics. Eventually viewpoints shifted to treating matter from a wave perspective. In this way many experimental inconsistencies could be resolved. Ultimately, we should be resigned to the fact that both light or matter can individually exhibit wave- or particle-like characteristics. The circumstances dictating their behavior ultimately depend on the situation, but invariably occur at the atomic and molecular level. Our purpose in subsequent sections is therefore to take a nanoscopic view of matter behaving as a wave in order to gain insight into its macroscopic properties.

As a prelude to the tale of matter and waves and its timeline, we must begin two centuries beforehand, to properly acknowledge antecedent milestones. The eighteenth century is appropriately known as the 'Age of Enlightenment' or 'Age of Reason.' With apology to the scientific and engineering accomplishments of the period, an incredible array of mathematical techniques and advancements were introduced by Gauss, Euler, Fourier, LaPlace, Maclaurin, LaGrange, Taylor, Leibnitz, Bernoulli, Legendre, Newton and others. At the time much of this probably seemed no more than academic indulgence with little or no connection to the real world. However a century later these techniques were essential to formulation of thermodynamics and electrodynamics by individuals including Ampere, Faraday, Maxwell, Clausius, Joule, Helmholtz, Boltzmann, Thompson (Lord Kelvin), and Gibbs.

These achievements marked a seminal moment in the annals of scientific accomplishment. After a lengthy gestation, a coming of age was signaled. With roots in human curiosity, fear, and superstition followed by a lengthy infancy of straightforward phenomenological modeling, science now embraced a new,

fundamental purpose. Interpreting the workings of the everyday world was no longer the be-all and end-all. Scientists pushed the envelope of human experience to dimensions beyond what could be seen by a telescope or microscope. The frontiers of science were inextricably dependent on abstract mathematical techniques, culminating in more versatile, robust, and predictive scientific models. Theory now blazed a trail for experimental investigation.

Throughout this time, both the interpretation of matter as well as the properties and behavior of waves were thought to be on firm theoretical ground. However, evidence which emerged in the late nineteenth and early twentieth centuries blurred the lines between matter and waves. After much consternation, reflection, and debate among scientists, a blended behavior of light and matter emerged known as *wave–particle duality*. Much of the same mathematics, that by then had served theoreticians so well for over a century, again proved crucial and indispensable.

Quantum mechanics, the consummation of wave–matter interaction, marked a paradigm shift in more ways than the radical departure of its physics. It did not congeal from the singular ruminations or epiphany of any one individual. Quantum mechanics was an evolution of thought and philosophy coalesced from decades of work, culminating from efforts of an unprecedentedly-large collection of vital contributors. Previous landmark events in science could almost invariably be attributed to efforts of a single individual. The global effort that quantum mechanics represented was a testament to evolving human connectivity. By the twentieth century, scientists were taking full advantage of information sharing from advances in communication and experiencing an increased mobility attributable to ease of travel.

Quantum mechanics refined our understanding of matter to the point that its profound impact now demarcates the advent of 'modern physics.' Within a brief period of time it reverberated across chemistry and molecular biology as well. Subsequent to its introduction several of the leading scientists of the day, most familiarly Einstein, took on worldwide celebrity status. Nobel prizes were awarded to a variety of its principal contributors over a broad span of the twentieth century. These include prizes in physics to Planck in 1918, Einstein in 1921, Bohr in 1922, de Broglie in 1929, Heisenberg in 1932, Schrödinger in 1933, Pauli in 1945, and Born in 1954. Awards for contributions of quantum mechanics in chemistry were given to Pauling in 1954, Mullikan in 1966, and Pople and Kohn in 1998. Many other recipients in both fields were either guided in their experiments or directly impacted in their theoretical developments by quantum mechanics. It is somewhat unsettling to read the press release accompanying Mullikan's 1966 prize which points out the overwhelmingly complex nature of the discipline, essentially stating that quantum mechanics was inaccessible to the layperson. One of the main goals of this work is to help allay such predispositions or trepidations.

To punctuate the human interest aspect, no other image heralds the arrival of quantum mechanics or underscores the collective effort behind it quite like figure 1.2, a photograph of participants in the 1927 Solvay Conference. These invitation-only events feature varying focus topics that to this day they are intermittently held in Brussels, having been instituted by Belgian industrialist Ernest Solvay in 1911. The

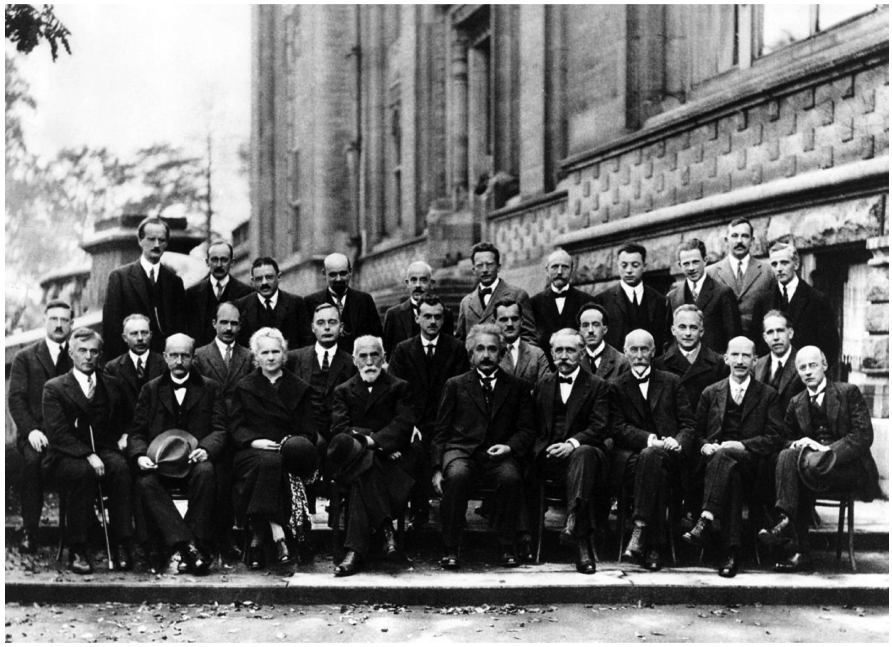

Figure 1.2. Participants of the 1927 Solvay Conference.
Row 1: I Langmuir, M Planck, M Sklodowska-Curie, H Lorentz, A Einstein, P Langevin, C Guye, C Wilson, C Richardson
Row 2: P Debye, M Knudsen, W Bragg, H Kramers, P Dirac, A Compton, L de Broglie, M Born, N Bohr
Row 3: A Piccard, E Henriot, P Ehrenfest, E Herzen, T de Donder, E Schrödinger, J Verschaffelt, W Pauli, W Heisenberg, R Fowler, L Brillouin

1927 meeting, fifth in the series, featured lectures and discussions focused on the title subject: 'Electrons and Photons,' and a conference theme parallel to the topics of this book. Lewis once wrote, 'Science has its cathedrals, built by the efforts of few architects and of many workers.' The 1927 Solvay Conference validated one's standing as an architect to the sanctum of quantum mechanics. Essentially everyone who was anyone relevant to its development was present, a contingent in some ways analogous to the 1992 US men's Olympic basketball 'Dream Team.' Even those with no more than a passing knowledge of science will recognize several names. Those with a passion for it should particularly appreciate the special nature of the moment.

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Chapter 2

Motion in matter

We begin the study with a discussion of classical mechanics, developed using the approach introduced by Hamilton. Similar to Lagrangian mechanics, it is a re-formulation of the traditional Newtonian approach. In certain physical situations these alternatives provide insight that Newton's kinematics lack. Hamilton's formulation is of particular utility, as it lends itself seamlessly as we transition to quantum mechanics. The central feature of this approach is the Hamiltonian H. This function contains information describing the energy content of a particle or system of particles for all times. As is the case in most physical situations, the Hamilton can be partitioned into kinetic (T) and potential (V) energy components such that:

$$H = T + V \tag{2.1}$$

Time evolution of a system's ith particle is given by Hamilton's equations:

$$\frac{\mathrm{d}p_i}{\mathrm{d}t} = -\frac{\partial H}{\partial q_i} \tag{2.2}$$

$$\frac{\mathrm{d}q_i}{\mathrm{d}t} = \frac{\partial H}{\partial p_i} \tag{2.3}$$

In equations (2.2) and (2.3), p and q are the momentum and generalized position coordinates, respectively.

We shall begin by considering two objects of mass m_1 and m_2 in motion through space with trajectory vectors $\vec{r}_1$ and $\vec{r}_2$, respectively (see figure 2.1). We make the assumption that the particles experience no external potential ($V = 0$). With momentum defined as $p = mv$, the scalar kinetic energy of each particle is:

$$T_i = \frac{|\vec{p}_i|^2}{2m_i} \tag{2.4}$$

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Hamilton's equations are consistent with the system's kinematics. According to equation (2.3), the velocity of each particle is:

$$v_i = \frac{\mathrm{d}r_i}{\mathrm{d}t} = \frac{\partial H}{\partial p} = \frac{p_i}{m_i} \tag{2.5}$$

This two body system has six *degrees of freedom*. Either particle can independently translate in any of three Cartesian directions of motion: x, y, or z or, from the perspective of spherical polar coordinate system, independently in components: r, θ, or ϕ. We assume the motion of each mass is constrained by a binding force. Referring to figure 2.1, three degrees of freedom describe the unit vector components of $\vec{R}$ for translation of the center of mass M $(= m_1 + m_2)$. The magnitude of $\vec{R}$ is determined from the mass-weighted averages of $\vec{r}_1$ and $\vec{r}_2$:

$$\vec{R} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2} \tag{2.6}$$

The remaining three degrees of freedom express components of $\vec{r}$, the internal motion vector (a chemist would call its magnitude the 'bond length'). From figure 2.1, vector addition gives: $\vec{r}_2 = \vec{r}_1 + \vec{r}$. When substituted into equation (2.6) with rearrangement, $\vec{r}_1$ can be expressed in terms of $\vec{r}$ and $\vec{R}$:

$$\vec{r}_1 = \vec{R} - \frac{m_2}{m_1 + m_2}\vec{r} \tag{2.7}$$

Similarly, from figure 2.1 we note that: $\vec{r}_1 = \vec{r}_2 - \vec{r}$. Substituting this into equation (2.6) gives:

$$\vec{r}_2 = \vec{R} + \frac{m_1}{m_1 + m_2}\vec{r} \tag{2.8}$$

Equations (2.7) and (2.8) are substituted into the kinetic energy expression:

$$T = \frac{\left|\vec{p}_1\right|^2}{2m_1} + \frac{\left|\vec{p}_2\right|^2}{2m_2} = \frac{1}{2}\left[m_1\left|\frac{\mathrm{d}\vec{r}_1}{\mathrm{d}t}\right|^2 + m_2\left|\frac{\mathrm{d}\vec{r}_2}{\mathrm{d}t}\right|^2\right] \tag{2.9}$$

Expanding the dot products leads to:

$$\begin{aligned} T = {} & \frac{1}{2}m_1\left[\left|\frac{\mathrm{d}\vec{R}}{\mathrm{d}t}\right|^2 - 2\frac{m_2}{m_1 + m_2}\frac{\mathrm{d}\vec{R}}{\mathrm{d}t}\cdot\frac{\mathrm{d}\vec{r}}{\mathrm{d}t} + \frac{m_2^2}{(m_1 + m_2)^2}\left|\frac{\mathrm{d}\vec{r}}{\mathrm{d}t}\right|^2\right] \\ & + \frac{1}{2}m_2\left[\left|\frac{\mathrm{d}\vec{R}}{\mathrm{d}t}\right|^2 + 2\frac{m_1}{m_1 + m_2}\frac{\mathrm{d}\vec{R}}{\mathrm{d}t}\cdot\frac{\mathrm{d}\vec{r}}{\mathrm{d}t} + \frac{m_1^2}{(m_1 + m_2)^2}\left|\frac{\mathrm{d}\vec{r}}{\mathrm{d}t}\right|^2\right] \end{aligned} \tag{2.10}$$

Equation (2.10) is simplified by noting the cross-term derivatives involving $\vec{r}$ and $\vec{R}$ cancel, and that:

$$\frac{1}{2}m_1\frac{m_2^2}{(m_1 + m_2)^2} + \frac{1}{2}m_2\frac{m_1^2}{(m_1 + m_2)^2} = \frac{1}{2}\frac{m_1m_2}{m_1 + m_2} = \frac{1}{2}\mu \tag{2.11}$$

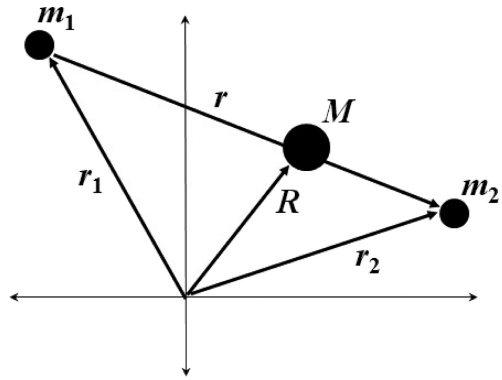

Figure 2.1. Coordinate system of a two-body problem.

Equation (2.11) introduces the *reduced mass* of the two-body system μ, which can alternatively be defined:

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \tag{2.12}$$

Note from either equation (2.11) or (2.12), as: $m_1 \to m_2$, $\mu \to \frac{1}{2}m_1$, and as $m_1 \to 0$, $\mu \to m_1$. Equation (2.10) expressed as a function of the center of mass M, the center of mass vector $\vec{R}$, the reduced mass μ, and the internal motion vector $\vec{r}$ is thus:

$$T = \frac{1}{2}M\left|\frac{\mathrm{d}\vec{R}}{\mathrm{d}t}\right|^2 + \frac{1}{2}\mu\left|\frac{\mathrm{d}\vec{r}}{\mathrm{d}t}\right|^2 \tag{2.13}$$

The interpretation of equation (2.13) is as follows. For a two-body system, three of the six possible degrees of freedom result from changes in the Cartesian components of $\vec{R}$. This is the kinetic energy due to translation of the center of total mass M (and inherently properties such as the kinetic temperature and pressure of a bulk sample of these systems). The remaining three degrees of freedom are contributions to T due to changes in the Cartesian directions of the internal motion vector $\vec{r}$. It is even more instructive when these degrees of freedom are connected to the rate of change of $\vec{r}$, which occur in either one of two ways. If only the *magnitude* of $\vec{r}$ changes with time, the internal motion vector is describing relative *vibrational* motion of the two bodies. Alternatively, as the *direction* of $\vec{r}$ changes, the internal motion vector is undergoing two-body *rotational* motion.

The six independent motions are now constrained to three assigned to translation of the center of mass, and the three that remain representing one vibrational mode (as $\vec{r}$ expands and contracts) and two degenerate rotational modes (as $\vec{r}$ changes direction centered on one of the system's two equivalent moments of inertia). The latter three are independent of the translational degrees of freedom as is evidenced by no change in the center of mass location during these internal motions. As a matter of fact, the center of mass must be invariant to any purely rotational or vibrational mode independent of the number of coupled particles in the system. However, rotation and vibration are not strictly independent of each other.

Vibration results in a changing moment of mass inertia, which to maintain conservation of angular momentum requires an accompanying change in angular rotation speed. Although this complication can be addressed by perturbation theory techniques, we currently hand-wave our way out of this dilemma by assuming a *rigid rotor* approximation, wherein the scalar component of $\vec{r}$ does not change as it changes direction (e.g. a rotating diatomic molecule with fixed bond length).

The reduced mass μ mathematically expresses the mechanics of a two-body system as a one-body system. This simplifies the perspective of vibrational motion from the change in distance between two masses m_1 and m_2 into the movement of a single mass of value μ relative to an infinitely-massive fixed point. Likewise for rotation, instead of thinking about the concerted rotational dance of m_1 with m_2, we can picture mass μ moving circularly relative to an infinitely-massive fixed point in space.

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Chapter 3

Vibrating matter

3.1 Classical vibration

For reasons more pedagogical than pedantic, we begin our discussion of coupled mass motion by considering vibration. In fact, it was during attempts to mathematically model experimentally observed electromagnetic wave generation by vibrating matter that irreparable flaws were exposed in the interpretation of wave matter interaction. In addition solutions to the differential equations of a classically-treated harmonic oscillator serve as a relatively straightforward introduction to many of the mathematical techniques that will be required as we transition to quantum mechanics.

The oscillator is constructed by attaching mass μ to an ideal spring, one which suffers no dissipative loss of energy, that in turn is connected to an infinitely-massive wall. As discussed in chapter 2, μ in this case is exactly m, the mass of the oscillator. Using μ reminds us that the oscillator can indeed be a two-body system. When stretched and released, μ executes 1-dimensional un-damped vibrational motion such that both the amplitude and rate of oscillation are constant with time. This constitutes a *harmonic oscillator* with a pattern of movement known as *simple harmonic motion*. As un-physical as this may seem, it is exhibited by the nuclei of molecules in a variety of modes. Harmonic motion is sustained by the driving force of ambient temperature, and can be stimulated to different oscillations as matter absorbs particular frequencies of electromagnetic radiation. Before we examine the nature of this motion in molecules, it is instructive to first treat a model harmonic oscillator *classically* within Hamilton's framework. Our efforts will not be wasted for two important reasons. First, the exercise will use many of the same mathematical approaches and defining terms that will arise in quantum mechanical systems. More importantly, we will see there is an inconsistency to the energy distribution in a classical oscillator compared to the energy of interaction between electromagnetic waves and vibrating matter.

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The attached spring supplies *a restoring force* relative to the direction of motion of the mass, according to the empirical rule known as Hooke's Law:

$$\vec{F}_x = -k\vec{x} \tag{3.1}$$

The minus sign of equation (3.1) indicates the direction of the restoring force, hence the acceleration experienced by the object, is in opposition to the mass displacement. The scalar proportionality factor k is known as the *spring constant*, which by dimensional analysis must possess units: $\mathrm{N} \cdot \mathrm{m}^{-1}$ or the SI form: $\mathrm{kg} \cdot \mathrm{s}^{-2}$. The magnitude of k describes the spring 'stiffness'. Equation (3.1) demonstrates that a spring with large k requires a large applied force to achieve small displacement, while a spring with small k will exhibit substantial displacement with small applied force. In ballpark terms, a Slinky has spring constant of roughly $k = 0.5\ \mathrm{N} \cdot \mathrm{m}^{-1}$, contrasted by a car shock absorber with $k \approx 50\ 000\ \mathrm{N} \cdot \mathrm{m}^{-1}$. Bond strengths of molecules are inferred from their gas phase spring constants (referred to by chemists as bond force constants). Representative examples are provided by the relatively weakly-bound hydrogen chloride (HCl): $k = 480\ \mathrm{N} \cdot \mathrm{m}^{-1}$ in contrast to carbon monoxide (CO): $k = 1860\ \mathrm{N} \cdot \mathrm{m}^{-1}$.

The oscillator's kinetic energy is related to the momentum of mass μ. Its potential energy is dependent on the displacement of μ, and is symmetric independent of the type of displacement (whether the spring is stretched or compressed). The system Hamiltonian takes the following form:

$$H = T(p) + V(x) \tag{3.2}$$

From chapter 2, equation (2.2) relates the rate of change of momentum and potential:

$$\frac{\mathrm{d}p}{\mathrm{d}t} = -\frac{\partial H}{\partial x} = -\frac{\partial V(x)}{\partial x} \tag{3.3}$$

Using the momentum expression $p = mv$, and Newton's Second Law written in terms of rate of change of momentum, we have:

$$F = -\frac{\partial V(x)}{\partial x} \tag{3.4}$$

Equation (3.4) is true of any *conservative force* like an ideal spring, or a conservative field, such as those generated by gravity, point charges, or magnets. Equation (3.1) is inserted in equation (3.4), rearranged and integrated over definite limits to give:

$$V(x) = k\int_0^x x'\,\mathrm{d}x' = \frac{1}{2}kx^2 \tag{3.5}$$

The spring stores no potential energy at zero displacement (the bottom limit of the left-hand side of equation (3.5) integrates to $V(0) = 0$), and at other values is parabolic (see figure 3.1). The 'steepness' of the parabolic potential is directly proportional to the spring constant k. Stiff springs exhibit sharply increasing potential energy with displacement while floppy springs have relatively shallow potential curves.

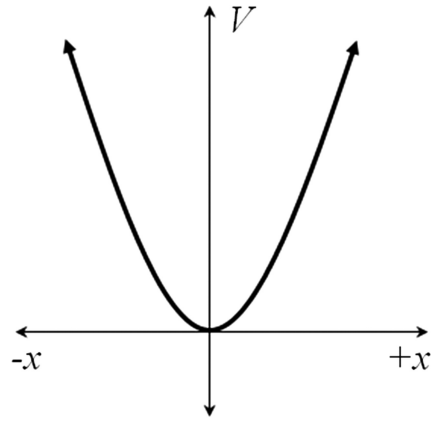

Figure 3.1. The potential energy curve of a harmonic oscillator.

An analytical expression for the displacement x is found by solving the differential equation that arises from applying Newton's Second Law:

$$F_x = \frac{\mathrm{d}p_x}{\mathrm{d}t} = \mu a_x = \mu \frac{\mathrm{d}v_x}{\mathrm{d}t} = \mu \frac{\mathrm{d}^2 x}{\mathrm{d}t^2} \tag{3.6}$$

and equation (3.1):

$$\frac{\mathrm{d}^2 x}{\mathrm{d}t^2} = -\frac{k}{\mu} x \tag{3.7}$$

Expressions in the form of equation (3.7), known as *eigenvalue problems*, play an important role in applied physics and mathematics in general. Variable x, *the eigenfunction*, is subjected to a mathematical action known as an *operator*, which in this case is the process of taking a second derivative: $\mathrm{d}^2/\mathrm{d}t^2$. In fact, this action can be viewed as sequential applications of a first derivative: $\mathrm{d}^2/\mathrm{d}t^2 = \mathrm{d}/\mathrm{d}t(\mathrm{d}/\mathrm{d}t)$. As seen in equation (3.7), the operator acts on an eigenfunction, and returns the eigenfunction along with its *eigenvalue*, in this case: $-k/\mu$. Eigenvalue equations are central to quantum mechanics, but as this example shows also have practical utility across physics and applied mathematics.

The solution to equation (3.7) requires an eigenfunction which upon taking its second derivative returns the negative of that eigenfunction. Both a real and imaginary general solution can be proposed:

$$x = \begin{array}{c} A \sin \omega t + B \cos \omega t \\ \text{or} \\ Ce^{+i\omega t} + De^{-i\omega t} \end{array} \tag{3.8}$$

The solutions in equation (3.8) include pre-factors A, B, C, and D that for now must only meet two stipulations, they are: (1) time independent and (2) have dimension of SI length units: m. The eigenfunctions also contain imaginary factor $i = \sqrt{-1}$, and define a quantity known as the *angular speed* ω of the harmonic oscillator

(SI unit: rad · s^{-1}). Inserting either of the solutions from equation (3.8) into equation (3.7) shows the angular speed to be a function of the spring constant and the reduced mass:

$$\omega = \sqrt{\frac{k}{\mu}} \tag{3.9}$$

The solutions in equation (3.8) can also be written in forms such as: $x = A \sin 2\pi ft + B \cos 2\pi ft$ with the definition of frequency f (SI unit: s^{-1} or Hertz):

$$f = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{3.10}$$

The functions in equation (3.8) are the only valid solutions for eigenvalue equations with an operator involving second differentiation. The exponential and trigonometric forms can be inter-converted by expanding each in power series, which show that: $e^{\pm i\theta} = \cos\theta \pm i \sin\theta$. Only the exponential forms would be valid for operators involving first differentiation. We will later see these are required in certain quantum mechanical cases, particularly for eigenfunctions of both linear and angular momentum. But for now let us focus upon the real solution containing trigonometric functions. Its form is a natural description of vibrating matter in a wavelike fashion. It also seems that this solution is a combination of two independent sine and cosine waves. To borrow a term from chapter 1, the general solution for vibrating matter is a *superposition* of waves.

Further insight comes when the classical harmonic oscillator is treated as a *boundary value problem*, where the solutions in equation (3.8) are subject to constraints, known as *boundary conditions*. Let's suppose that our experiment is designed so that time measurement begins when the oscillator is in motion with the spring neither compressed nor stretched, so that the vibrating mass is at zero displacement. Mathematically this requires at $t = 0$ that $x = 0$. Because $\sin(0) = 0$ and $\cos(0) = 1$, the trigonometric function of equation (3.8) satisfies this boundary condition only if $B = 0$ (and, if we were instead using the imaginary solution, both $C = D = 0$). Under this constraint, the valid solution to the motion of the harmonically oscillating mass reduces to:

$$x = A \sin \omega t \tag{3.11}$$

The pre-factor A may now be given physical interpretation. It scales the sine function beyond its maximum of +1 and minimum of −1. In fact, A is the amplitude of the oscillating mass, or distance from the equilibrium position ($x = 0$) to the turning points at maximum spring stretch ($x = A$) and compression ($x = -A$). On a plot of the oscillator motion, A is the displacement to the positive and negative antinodes of the sine curve.

Philosophically speaking, the problem's general solution provided by equation (3.8) is omnibus, serving the sole purpose of including every viable mathematical solution to the problem. As long as we are not looking, equation (3.8) is throwing

the kitchen sink at the problem in a *superposition of states* form. When boundary conditions are applied, we are taking a peek, with a prejudice that a particular outcome is expected. This causes the destruction of all other possibilities except the most overwhelmingly-likely result. Based on our stipulated requirements, the sine function survives as the only viable representation of the vibrating mass if it is to be located at $x = 0$ when we start our clock. The coefficient B has no possibility other than zero, to meet the constraint.

As a further example, consider the opposing captains of football teams meeting at the 50-yard line for the pre-game coin toss. The referee places a coin on the knuckle of his thumb, and flicks it into the air. As it flips over and over, it is in an indeterminate state—a superposition of both heads *and* tails. Even when trapped on his forearm with the downward-facing palm of his opposite hand, the coin remains in a superposition of states. It is not until he lifts his hand revealing the coin that a specific outcome is obtained. It would seem that events in the Universe are in some way dependent on the action of human observation. A familiar euphemism to this sentiment is the expression: 'if a tree falls in the forest, does it make a sound?'

Philosophical issues such as this fueled a spirited and sometimes contentious debate among some of the most influential physicists of the early 20th century. Much of the discussion focused on the deeper significance of *wavefunctions*, mathematical solutions containing information which determine probabilistic outcomes in the physical universe. These expressions arise as solutions to the differential equations describing the wave-like behavior of matter according to the rules of quantum mechanics. An 'un-observed' wavefunction possesses information for all states and possible outcomes, a condition known as *quantum superposition*. The action of human observation (via measuring properties or specifying boundary conditions) *collapses* the wavefunction to the state of most statistically-likely outcome.

This concept, suggested by Bohr, Born, and Heisenberg, is known as the *Copenhagen Interpretation*. Some scientists, often playing devil's advocate, proposed g*edanken* (*thought*) *experiments* to challenge this premise. The most-familiar of these is 'Schrödinger's Cat', where a feline is sealed in a box along with a radioactive isotope. If the isotope decays it emits lethal radiation, however the cat is in an indeterminate state of life or death unless the box is opened and the outcome is physically observed. A less whimsical challenge was posed in the EPR paradox (so-called after its authors Einstein, Podolsky, and Rosen) which suggested the Copenhagen Interpretation could not justify the limits of accuracy on measurable properties that two simultaneously-formed particles can possess unless they have the ability to communicate information faster than the speed of light. The particles are inextricably wed by what is known as *quantum entanglement*.

So far we have studied the harmonic oscillator for the purpose of introducing commonalities to the classical and quantum mechanical representation of matter, and to point out some of the conundrums that interpreting matter from a wave perspective introduces. We now look at the system energetics, which reveals an

insurmountably fatal flaw in the classical representation of wave motion. Using equation (3.11), the harmonic oscillator kinetic energy is:

$$T = \frac{p^2}{2\mu} = \frac{1}{2}\mu \left|\frac{\mathrm{d}x}{\mathrm{d}t}\right|^2 = \frac{1}{2}\mu\omega^2 A^2 \cos^2 \omega t = \frac{1}{2}kA^2 \cos^2 \omega t \tag{3.12}$$

Here the final identity follows from inserting the definition of angular speed from equation (3.9) into equation (3.12). Using equation (3.5) and equation (3.11) we can also find an expression for the potential energy:

$$V = \frac{1}{2}kx^2 = \frac{1}{2}kA^2 \sin^2 \omega t \tag{3.13}$$

From simple trigonometric relations found in section B.2, the classical harmonic oscillator has total energy:

$$E_{\text{tot}} = T + V = \frac{1}{2}kA^2(\sin^2 \omega t + \cos^2 \omega t) = \frac{1}{2}kA^2 \tag{3.14}$$

The right-hand side of equation (3.14) is time-independent, so the total energy is constant at all times. It is partitioned into kinetic and potential forms that have a relationship expressed in the *virial theorem*, which states a system subjected to potential of the form: $V(r) = c \cdot r^n$ has time-averaged kinetic and potential energies obeying:

$$2\langle T\rangle = n \cdot \langle V\rangle \tag{3.15}$$

Using equation (3.15) and equation (3.5), the harmonic oscillator has average potential and kinetic energy related by: $\langle T\rangle = \langle V\rangle$. Figure 3.2 plots two cycles of the harmonic oscillator subject to boundary conditions $x = 0$ at $t = 0$. The process begins by stretching the mass to store an arbitrary amount of potential energy according to equation (3.5). While holding it stationary there is zero kinetic energy, so $E_{\text{tot}} = V$.

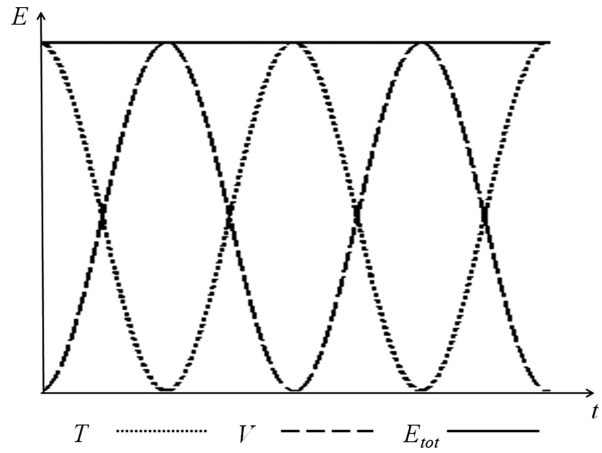

Figure 3.2. Plots of kinetic, potential, and total energy for the first two cycles of a classical harmonic oscillator.

The spring is released and the clock started when the mass is at its equilibrium position ($x = 0$). At this point (see equation (3.13)), the spring stores no potential energy so $E_{tot} = T$ and the system is at maximum velocity. As the mass drives past equilibrium, the spring compresses as the system slows and its kinetic energy is converted back to the stored form. This continues until all kinetic energy is converted to potential at the negative turning point and the cycle repeats.

The total energy being a function of the square of the oscillator amplitude does not clash with everyday experience. For instance, the energy (loudness) of sound is a function of the sound wave amplitude (the degree of compression and rarefication that the medium experiences). Another example is supplied by a pendulum, which uses gravity to supply the restoring force instead of a spring. We can envision a child on a swing, whose energy depends on the height she reaches above the ground at her turning points. An additional conclusion drawn from equation (3.14) is that the energy of the classical harmonic oscillator is *continuous*. Since the oscillator's amplitude A is allowed to take any real value desired (we can in theory pull the ideal spring out to any distance we wish), the energy E_{tot} can therefore have any real value.

3.2 Planck's approach to vibration

Now that we have a clear picture of the behavior of classical oscillation within the framework of Hamiltonian mechanics we turn to its shortcomings, particularly with regard to the ability of charges in vibrating matter to produce electromagnetic waves. If we enter this prejudiced by analysis of the last section, we would expect from equation (3.14) that matter would generate light with energy related to the magnitude of the oscillator force constant and the square of the oscillation amplitude. It would also seem this energy would have a continuous range. Both conjectures prove to be incorrect. The mathematics that resolved these issues posed an even more intriguing question. Were the shortcomings attributable to our understanding of waves or to our perception of matter?

At the turn of the 20th century, Rayleigh and Jeans used the results that we have so far proposed—a continuous energy harmonic oscillator model—to describe electromagnetic waves radiating from a black body. Their development relied upon classical thermodynamic arguments. According to the *principle of equipartition of energy*, temperature T produces an average energy of $\frac{1}{2}kT$ each for kinetic and potential contributions to the oscillator energy. The physical constant k used here is unfortunately not the spring force constant, but is now Boltzmann's constant, the ideal gas constant per particle (see the unit definitions of appendix A). The total energy per unit area is either referred to as the black body energy density or the *spectral brightness* (B). If the surface area is taken as the square of an oscillator's wavelength, then using $\lambda = c/\nu$:

$$B \propto kT\frac{\nu^2}{c^2} \tag{3.16}$$

From dimensional analysis, B has units of $\mathrm{N} \cdot \mathrm{m}^{-1}$ $(\mathrm{kg} \cdot \mathrm{s}^{-2})$ which is the dimensionality of an oscillator's force constant (unfortunately also represented by

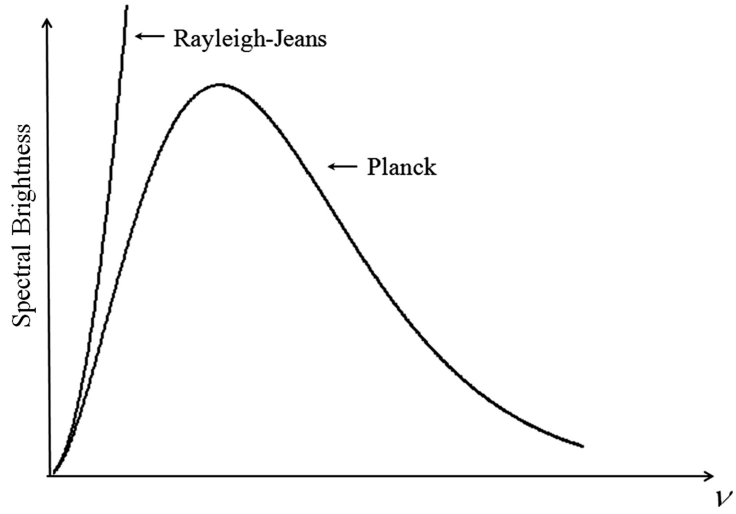

Figure 3.3. Comparing the Planck and Rayleigh–Jeans formulations of spectral brightness.

the symbol k). Multiplying B by the dimensionality of square amplitude does in fact give energy units as equation (3.14) stipulates. Equation (3.16) reproduces experimental results very accurately at low frequency (long wavelength), but as is depicted in figure 3.3 infinitely diverges beyond the visible range. Scientists therefore melodramatically referred to this as the *ultraviolet catastrophe*.

Around about the same time (actually, a little before) Max Planck studied the same problem but employed a *statistical* rather than classical thermodynamic treatment. He required oscillator energies distributed in *discrete*, evenly-spaced levels with values proportional to integer multiples of the *frequency* of oscillation:

$$E_n = nh\nu \quad n = 0, 1, 2, \ldots \tag{3.17}$$

The proportionality constant h in equation (3.17) has units of angular momentum, and is now known as Planck's constant. This value, which turns out to be inherent to all quantum mechanical phenomena, is often referred to as the *quantum of action*.

As we will ultimately learn in chapter 9, evenly-spaced vibrational energy levels are only strictly valid for parabolic potentials like that shown in figure 3.2. Real systems such as diatomic molecules have anharmonic potentials (see section 9.2) in which subsequent energy levels become increasingly closer in energy until reaching their dissociation limit. Typical spacing between vibrational energy levels is on the order of 10^{-20} J. Although this seems an inconsequential if not negligible amount of energy, it is actually intermediate in the quantum hierarchy. For instance, quantized rotational level spacings are on the order 10^{-21} J, while electronic levels: 10^{-19} J. Borrowing from statistical mechanics Planck's oscillators are summed into a vibrational partition function Z^V in the following fashion:

$$Z^V = \sum_{n=0}^{\infty} e^{-nh\nu/kT} \tag{3.18}$$

The nth energy level is called a *microstate* of the system, and its exponential term is a *Boltzmann factor*, representing the population of that state relative to the zeroth-level state. As equation (3.18) shows, Boltzmann factors are summed to give the partition function.

An analytical expression for the vibrational partition function results from applying the power series expansion: $1 + x + x^2 \ldots = 1/(1 - x)$ with $x = e^{-h\nu/kT}$:

$$Z^V = \frac{1}{1 - e^{-h\nu/kT}} \tag{3.19}$$

In statistical mechanics, partition functions represent the number of microstates available to be populated subject to available ambient energy kT. Using a typical vibrational spacing of 10^{-20} J, we find from equation (3.19) that $Z^V(100\ \text{K}) = 1.001$, $Z^V(300\ \text{K}) = 1.10$, $Z^V(1000\ \text{K}) = 1.94$, and $Z^V(2000\ \text{K}) = 3.29$. The take-home is that at typical temperatures, only the ground vibrational state is significantly populated. If instead the partition function is numerically summed using equation (3.19) including only the first eight energy levels, we obtain: that $Z^V(100\ \text{K}) = 1.001$, $Z^V(300\ \text{K}) = 1.09$, $Z^V(1000\ \text{K}) = 1.93$, and $Z^V(2000\ \text{K}) = 3.11$. Hence the summations converge very rapidly when $h\nu \ll kT$. The fact that only the first one or two vibrational levels are significant contributors to Z^V is also justification for using a harmonic potential even for real systems at normal temperatures, as the rapid convergence of the sum occurs before anharmonicities become of major importance.

The energy contribution of the oscillators is found from the partition function using the statistical mechanical recipe:

$$E = kT^2 \frac{1}{Z^V} \frac{\partial Z^V}{\partial T} \tag{3.20}$$

It should be noted that equation (3.20) is in actuality an eigenvalue equation: $\hat{O}Z = cZ$ with operator: $\partial/\partial T$ and eigenfunction: Z^V. In a very short period of time we have seen that eigenvalue problems have applications in classical mechanics and statistical mechanics, and will soon enough be used in quantum mechanics as well. From this perspective we can also think of a partition function as a thermodynamic wavefunction. Using equation (3.19) and a little manipulation, it is straightforward to verify that equation (3.20) has solution:

$$E = h\nu \frac{e^{-h\nu/kT}}{1 - e^{-h\nu/kT}} \tag{3.21}$$

Upon multiplying the numerator and denominator above by $e^{+h\nu/kT}$. Planck's spectral brightness formula then results from dividing E by the oscillator surface area:

$$B \propto \frac{h\nu^3}{c^2} \frac{1}{e^{h\nu/kT} - 1} \tag{3.22}$$

As expected, this has the same dimensionality as equation (3.16).

When Planck's constant h was empirically-fit to experimental data, this expression was able to reproduce experimental spectral brightness of a black body radiator for all frequencies. In the visible range and below, both Planck and the Rayleigh–Jeans expressions mimic experiment. Although they appear to be significantly different, it is easy to show that in these frequencies where $h\nu \ll kT$ that expanding the exponential in a power series and neglecting terms quadratic and above, Planck's equation simplifies to the Rayleigh–Jeans form in equation (3.16).

Modeling oscillating matter to produce electromagnetic radiation by employing energy proportional to oscillator frequency instead of amplitude conflicted with classical interpretation. Planck's bold assumption of discrete energy oscillators would quickly be used by the physics community to resolve other troubling experimental–theoretical discrepancies. His approach was seized upon by Einstein to first interpret the heat capacity of low temperature solids. He then applied the same approach to explain the *photoelectric effect*, the phenomenon of shining light on a thin metal foil to cause the ejection of electrons. If electromagnetic radiation interacts with electrons classically, light with energy proportional to wave amplitude (as in equation (3.14)) would eject electrons after reaching a particular level of brightness. It was experimentally determined that, independent of intensity, electrons did not begin to be ejected until the light reached a threshold *frequency*, which Einstein called the *work function* of the material. Increasing light frequency above the threshold caused a linearly proportional increase in the kinetic energy of ejected electrons. Much like he did in resolving the heat capacity issue, Einstein's theoretical model of the photoelectric effect made use of Planck's expression for light energy of equation (3.17).

A couple of decades later, Wolfers and Lewis coined the term *photon* for the frequency-dependent packet of energy carried by light. According to equation (3.17), a green light photon of wavelength 540 nm (frequency 560 THz) possesses energy 3.7×10^{-19} J. It is no wonder this miniscule energy would be hard to detect, and only tangibly influence matter of incredibly small mass or dimension. Light intensity does play a role, but instead of proportionality to photon energy, it is to the *number* of photons a light beam carries, hence the *number* electrons ejected, not their energy. For instance a mole of green light photons have energy 220 kJ, which is the same amount released upon complete combustion of 4 g (≈6 L) of methane gas.

One more point regarding the form of equation (3.17). It can equivalently be represented using the speed of light and its wavelength as: $E = hc/\lambda$, but both c and λ vary depending on the type of matter comprising the medium in which light propagates. As electromagnetic radiation enters matter with index of refraction n, its speed slows and its wavelength shortens according to the expressions $c' = c/n$ and $\lambda' = \lambda/n$. Even though these effects cancel and the photon energy is independent of the medium, it is more satisfactory to express energy in terms of photon frequency, which is invariant to the matter comprising a medium.

In summary, it now seems apparent that light (electromagnetic radiation in general) packs energy proportional to its frequency not its amplitude. Furthermore, this energy does not interact with matter continuously but in discrete bundles referred to as *quanta*. In a variety of examples, with even more to come, modeling

the interaction of matter and electromagnetic waves inevitably involves the quantum of action h. These conclusions initially required our understanding of light to be altered as it encountered matter. However, after a few decades quantum mechanics would flip the perspective. As a consequence, matter exhibited properties previously reserved for light waves. Ultimately, what would evolve is the concept of *wave–particle duality*, in which the role of matter and waves depend on the situation and method of observation.