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:

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

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

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 $s^{-1} = Hz$. 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):

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

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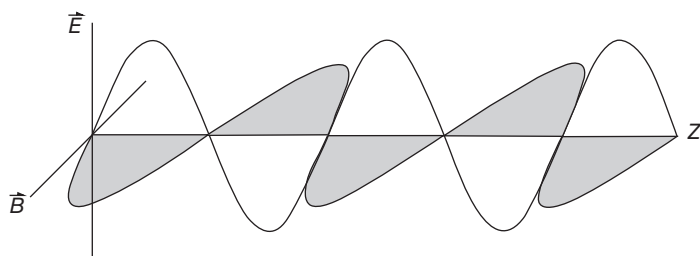
Figure 1.1 Description of the propagation of a linearly polarized electromagnetic wave as oscillation of electric ($\vec{E}$) and magnetic ($\vec{B}$) fields.

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 between well-defined stationary states. This view obviously does not include the creation of radio waves or other long-wave phenomena, for example, in standard antennas in radio technology, but describes ultraviolet, visible, and infrared radiation, which are the main subjects of this book. The atomic line spectra that are employed in analytical chemistry, for example, in a hollow cathode lamp used in atomic absorption spectroscopy, are due to transitions between electronic energy states of gaseous metal atoms.

The light created by the hot filament in a standard light bulb is another example of light emitted by (metal) atoms. However, here, one needs to deal with a broad distribution of highly excited atoms, and the description of this so-called blackbody radiation was one of the first steps in understanding the quantization of light.

Any material at a temperature T will radiate electromagnetic radiation according to the blackbody equations. The term "blackbody" refers to an idealized emitter of electromagnetic radiation with intensity $I(\lambda, T)$ or radiation density $\rho(T, \nu)$ as a function of wavelength and temperature. At the beginning of the twentieth century,
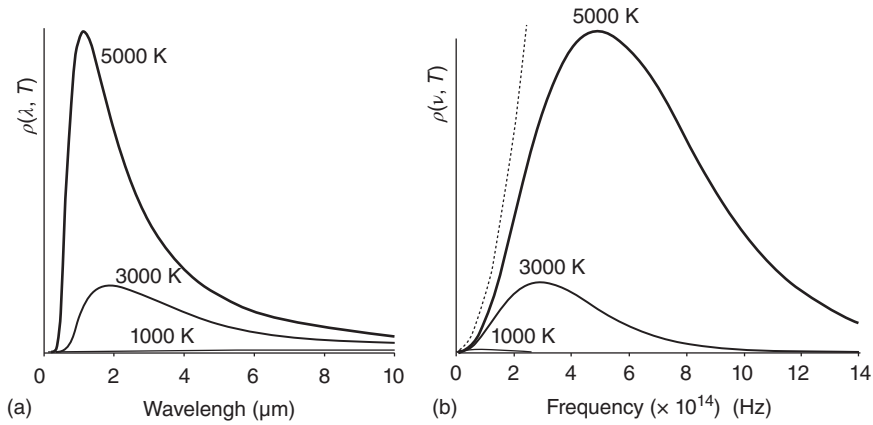
Figure 1.2 (a) Plot of the intensity I radiated by a blackbody source as a function of wavelength and temperature. (b) Plot of the radiation density of a blackbody source as a function of frequency and temperature. The dashed line represents this radiation density according to Eq. (1.5).

it was not possible to describe the experimentally obtained blackbody emission profile by classical physical models. This profile was shown in Figure 1.2 for several temperatures between 1000 and 5000 K as a function of wavelength.

M. Planck attempted to reproduce the observed emission profile using classical theory, based on atomic dipole oscillators (nuclei and electrons) in motion. These efforts revealed that the radiation density ρ emitted by a classical blackbody into a frequency band $d\nu$ as function of ν and T would be given by Eq. (1.5):

$$\rho(T, \nu) = \frac{8\pi k T \nu^2}{c^3} \tag{1.5}$$

where the Boltzmann constant $k = 1.381 \times 10^{-23}$ [J/K]. This result indicated that the total energy radiated by a blackbody according to this "classical" model would increase with ν^2 as shown by the dashed curve in Figure 1.2b. If this equation were correct, any temperature of a material above absolute zero would be impossible, since any material above 0 K would emit radiation according to Eq. (1.5), and the total energy emitted would be unrestricted and approach infinity. Particularly, toward higher frequency, more and more radiation would be emitted, and the blackbody would cool instantaneously to 0 K. Thus, any temperature above 0 K would be impossible. (For a more detailed discussion on this "ultraviolet catastrophe," see Engel and Reid [2].)

This is, of course, in contradiction with experimental results and was addressed by M. Planck (1901) who solved this conundrum by introducing the term $1/(e^{h\nu/kT} - 1)$ into the blackbody equation, where h is Planck's constant:

$$\rho(T, \nu) = \frac{8\pi\, h\nu^2}{c^3} \frac{1}{\left(e^{\frac{h\nu}{kT}} - 1\right)} \approx \frac{8\pi\, h\nu^2}{c^3} e^{-\frac{h\nu}{kT}} \qquad \text{for } \frac{h\nu}{kT} \gg 1 \tag{1.6}$$

The shape of the modified blackbody emission profile given by Eq. (1.6) is in agreement with experimental results. The new term introduced by Planck is

basically an exponential decay function, which forces the overall response profile to approach zero at high frequency. The numerator of the exponential expression contains the quantity $h\nu$, where h is Planck's constant ($h = 6.626 \times 10^{-34}$ Js). This numerator implies that light exists as "quanta" of light, or light particles (photons) with energy E:

$$E_{\text{photon}} = h\nu \tag{1.7}$$

This, in itself, was a revolutionary thought since the wave properties of light had been established more than two centuries earlier and had been described in the late 1800s by Maxwell's equations in terms of electric and magnetic field contributions. Here arose for the first time the realization that two different descriptions of light, in terms of waves and particles, were appropriate depending on what questions were asked. A similar "particle–wave duality" was later postulated and confirmed for matter as well (see below). Thus, the work by Planck very early in the twentieth century is truly the birth of the ideas resulting in the formulation of quantum mechanics.

Incidentally, the form of the expression $\frac{1}{\left(e^{\frac{h\nu}{kT}}\right)}$ or $e^{\frac{-h\nu}{kT}}$ is fairly common-place in classical physical chemistry. It compares the energy of an event, for example, a molecule leaving the liquid for the gaseous phase, with the energy content of the surroundings. For example, the vapor pressure of a pure liquid depends on a term $e^{\frac{-\Delta H_{\text{vap}}}{RT}}$, where ΔH_{vap} is the enthalpy of vaporization of the liquid, and $RT = NkT$ is the energy at temperature T, R is the gas constant, and N is Avogadro's number. Similarly, the dependence of the reaction rate constant and the equilibrium constant on temperature is given by equivalent expressions that contain the activation energy or the reaction enthalpy, respectively, in the numerator of the exponent. In Eq. (1.6), the photon energy is divided by the energy content of the material emitting the photon and provides a likelihood of this event occurring.

Figure 1.2 shows that the overall emitted energy increases with increasing temperature and that the peak wavelength of maximum intensity shifts toward lower wavelength (Wien's law). The total energy W radiated by a blackbody per unit area and unit time into a solid angle (the irradiance), integrated over all wavelengths, is proportional to the absolute temperature to the fourth power:

$$\int_{0}^{\infty} W \, d\lambda = \sigma T^4 \tag{1.8}$$

(Stefan–Boltzmann law)

The irradiance is expressed in units of $\left[\frac{W}{m^2 s\ sr}\right]$ or $\left[\frac{\text{photons}}{m^2 s\ sr}\right]$.

The implication of the aforementioned wave–particle duality will be discussed in the next section.

1.3 The Photoelectric Effect

In 1905, Einstein reported experimental results that further demonstrated the energy quantization of light. In the photoelectric experiment, light of variable color

(frequency) illuminated a photocathode contained in an evacuated tube. An anode in the same tube was connected externally to the cathode through a current meter and a source of electric potential (such as a battery). Since the cathode and anode were separated by vacuum, no current was observed, unless light with a frequency above a threshold frequency was illuminating the photocathode. Einstein correctly concluded that light particles, or photons, with a frequency above this threshold value had sufficient kinetic energy to knock out electrons from the metal atoms of the photocathode. These "photoelectrons" left the metal surface with a kinetic energy given by

$$E_{\text{kin}}(\text{photoelectron}) = E_{\text{photon}} - \phi = h\nu - \phi \qquad (1.9)$$

where ϕ is the work function, or the energy required to remove an electron from metal atoms. This energy basically is the atoms' ionization energy multiplied by Avogadro's number. Furthermore, Einstein reported that the photocurrent produced by the irradiation of the photocathode was proportional to the intensity of light, or the number of photons, but that increasing the intensity of light that had a frequency below the threshold did not produce any photocurrent. This provided further proof of Eq. (1.9).

This experiment further demonstrated that light has particle character with the kinetic energy of the photons given by Eq. (1.7), which led to the concept of wave–particle duality of light. Later, de Broglie theorized that the momentum p of a photon was given by

$$p = h/\lambda \qquad (1.10)$$

Equation (1.10) is known as the de Broglie equation. The wave–particle duality was later (1927) confirmed to be true for moving masses as well by the electron diffraction experiment of Davisson and Germer [3]. In this experiment, a beam of electrons was diffracted by an atomic lattice and produced a distinct interference pattern that suggested that the moving electrons exhibited wave properties. The particle–wave duality of both photons and moving matter can be summarized as follows.

For photons, the wave properties are manifested by diffraction experiments and summarized by Maxwell's equation. As for all wave propagation, the velocity of light, c, is related to wavelength λ and frequency ν by

$$c = \lambda\nu = \nu/\tilde{\nu} \qquad (1.11)$$

with $c = 2.998 \times 10^8$ [m/s] and λ expressed in [m] and ν expressed in [Hz $=$ s^{-1}]. The quantity $\tilde{\nu}$ is referred to as the wavenumber of radiation (in units of m^{-1} or cm^{-1}) that indicates how many wave cycles occur per unit length:

$$\tilde{\nu} = 1/\lambda \qquad (1.12)$$

The (kinetic) energy of a photon is given by

$$E = h\nu = hc/\lambda = \hbar\,\omega \qquad (1.13)$$

with $\hbar = h/2\pi$ and ω, the angular frequency, defined before as $\omega = 2\pi\nu$.

From the classical definition of the momentum of matter and light, respectively,

$$p = m\text{v} \text{ or } p = mc \tag{1.14}$$

it follows that the photon mass is given by

$$m_{\text{photon}} = p/c = h/(c\,\lambda) \tag{1.15}$$

Notice that a photon can only move at the velocity of light and the photon mass can only be defined at the velocity c. Therefore, a photon has zero rest mass, m_0.

Particles of matter, on the other hand, have a nonzero rest mass, commonly referred to as their mass. This mass, however, is a function of velocity v and should be referred to as m_v, which is given by

$$m_v = \frac{m_0}{\sqrt{1 - \left(\frac{v^2}{c^2}\right)}} \tag{1.16}$$

Example 1.1   Calculation of the mass of an electron moving at 99.0 % of the velocity of light (such velocities can easily be reached in a synchrotron).

Answer:
According to Eq. (1.16), the mass m_v of an electron at $v = 0.99\,c$ is

$$m_v = \frac{9.109 \times 10^{-31}}{\sqrt{1 - \left(\frac{0.99\,c^2}{c^2}\right)}} = \frac{9.109 \times 10^{-31}}{\sqrt{1 - (0.990)^2}} = \frac{9.109 \times 10^{-31}}{\sqrt{0.0199}} = \frac{9.109 \times 10^{-31}}{0.141}$$

$$= 6.457 \times 10^{-30} \text{ [kg]} \tag{E1.1.1}$$

The electron at 99 % of the velocity of light has a mass of about seven times its rest mass.

Equation (1.16) demonstrates that the mass of any matter particle will reach infinity when accelerated to the velocity of light. Their kinetic energy at velocity v (far from the velocity of light) is given by the classical expression

$$E_{\text{kin}} = \tfrac{1}{2}\,mv^2 = p^2/2m \tag{1.17}$$

The discussion of the last paragraphs demonstrates that at the beginning of the twentieth century, experimental evidence was amassed that pointed to the necessity to redefine some aspects of classical physics. The next of these experiments that led to the formulation of quantum mechanics was the observation of "spectral lines" in the absorption and emission spectra of the hydrogen atom.

1.4   Hydrogen Atom Absorption and Emission Spectra

Between the last decades of the nineteenth century and the first decade of the twentieth century, several researchers discovered that hydrogen atoms, produced in gas discharge lamps, emit light at discrete colors, rather than as a broad continuum
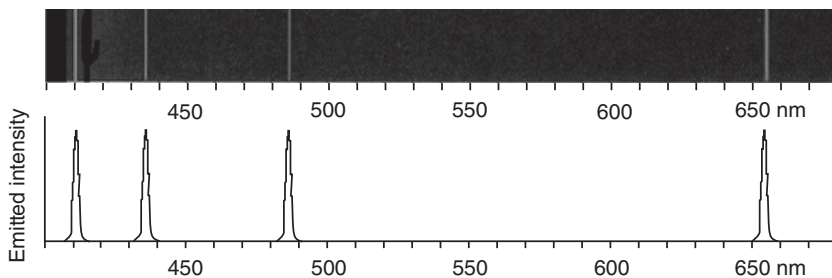
Figure 1.3 Portion of the hydrogen atom emission in the visible spectral range, represented as a "line spectrum" and schematically as an emission spectrum.

of light as observed for a blackbody (Figure 1.2a). These emissions occur in the ultraviolet, visible, and near-infrared spectral regions, and a portion of such an emission spectrum is shown schematically in Figure 1.3. These observations predate the efforts discussed in the previous two sections and therefore may be considered the most influential in the development of the connection between spectroscopy and quantum mechanics.

These experiments demonstrated that the H atom can exist in certain "energy states" or "stationary states." These states can undergo a process that is referred to as a "transition." When the atom undergoes such a transition from a higher or more excited state to a lower or less excited state, the energy difference between the states is emitted as a photon with an energy corresponding to the energy difference between the states:

$$\Delta E_{\text{molecule}} = E_f - E_i = E_{\text{photon}} = h\nu = hc/\lambda \tag{1.18}$$

where the subscript f and i denote, respectively, the final and initial (energy) state of the atom (or molecule). Such a process is referred to as a "emission" of a photon. Similarly, an absorption process is one in which the atom undergoes a transition from a lower to a higher energy state, the energy difference being provided by a photon that is annihilated in the process. Absorption and emission processes are collectively referred to as "transitions" between stationary states and are directly related to the annihilation and creation, respectively, of a photon.

The wavelengths or energies from the hydrogen emission or absorption experiments were fit by an empirical equation known as the Rydberg equation, which gave the energy "states" of the hydrogen atom as

$$E(n) = -R_y/n_2 \tag{1.19}$$

In this equation, n is an integer (>0) "quantum" number, and R_y is the Rydberg constant, ($R_y = 2.179 \times 10^{-18}$ J). This equation implies that the energy of the hydrogen atom cannot assume arbitrary energy values, but only "quantized" levels, $E(n)$. This observation led to the ideas of electrons in stationary planetary orbits around the nucleus, which – however – was in contradiction with existing knowledge of electrodynamics, as discussed in the beginning of this chapter.

The energy level diagram described by Eq. (1.19) is depicted in Figure 1.4. Here, the sign convention is as follows. For $n = \infty$, the energy of interaction between nucleus

Figure 1.4 Energy level diagram of the hydrogen atom. Transitions between the energy levels are indicated by vertical lines.
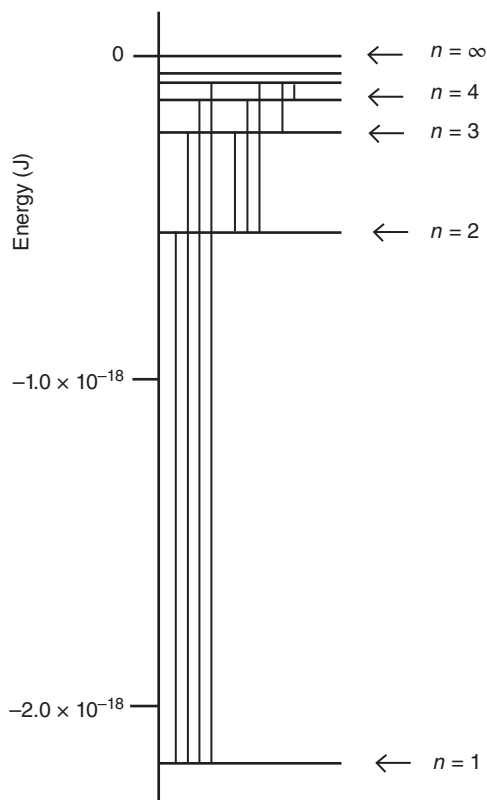
and electron is zero, since the electron is no longer associated with the nucleus. The lowest energy state is given by $n = 1$, which corresponds to the H atom in its ground state that has a negative energy of 2.179×10^{-18} J.

Equation (1.19) provided a background framework to explain the hydrogen atom emission spectrum. According to Eq. (1.19), the energy of a photon, or the energy difference of the atomic energy levels, between any two states n_f and n_i can be written as

$$E_{\text{photon}} = \Delta E_{\text{atom}} = E_f - E_i = -R_y \left[\frac{1}{n_f^2} - \frac{1}{n_i^2} \right] \tag{1.20}$$

At this point, an example may be appropriate to demonstrate how this empirically derived equation predicts the energy, wavelength, and wavenumber of light emitted by hydrogen atoms. This example also introduces a common problem, namely, that of units. Although there is an international agreement about what units (the système international, or SI units) are to be used to describe spectral transitions, the problem is that few people are using them. In this book, all efforts will be made to use SI units, or at least give the conversion to other units.

The sign conventions used here are similar to those in thermodynamics where a process with a final energy state lower than that of the initial state is called an "exothermic" process, where heat or energy is lost. In Example 1.2, the energy is

lost as a photon and is called an emission transition. When describing an absorption process, the energy difference of the atom is negative, $\Delta E_{atom} < 0$, that is, the atom has gained energy ("endothermic" process in thermodynamics). Following the procedure outlined in Example 1.2 would lead to a negative wavelength of the photon, which of course is physically meaningless, and one has to remember that the negative ΔE_{atom} implies the absorption of a photon.

Example 1.2 Calculation of the energy, frequency, wavelength, and wavenumber of a photon emitted by a hydrogen atom undergoing a transition from $n = 6$ to $n = 2$.

Answer:
The energy difference between the two states of the hydrogen atom is given by

$$\Delta E_{atom} = E_f - E_i = -R_y \left[\frac{1}{6^2} - \frac{1}{2^2} \right] = R_y \left[\frac{1}{4} - \frac{1}{36} \right] = 0.22222 \, R_y \qquad (E1.2.1)$$

Using the value of the Rydberg constant given above, $R_y = 2.179 \times 10^{-18}$ J, the energy difference is

$$\Delta E_{atom} = 4.842 \times 10^{-19} \, J. \qquad (E1.2.2)$$

Using Eq. (1.12), $\Delta E = E_{photon} = h\nu = hc/\lambda$, the frequency ν is found to be

$$\nu = \frac{\Delta E}{h} = \frac{4.842 \times 10^{-19}}{6.626 \times 10^{-34}} = 7.308 \times 10^{15} \left[\frac{J}{Js} = s^{-1} \right] = [Hz] \qquad (E1.2.3)$$

The wavelength of such a photon is given by Eq. (1.7) as

$$\lambda = \frac{h \, c}{E} = \frac{6.626 \times 10^{-34} \times 2.998 \times 10^8}{4.842 \times 10^{-19}} = 4.102 \times 10^{-7} \left[\frac{Js \, m}{J \, s} = m \right] = 410.2 \, [nm] \qquad (E1.2.4)$$

that is, a photon in the ultraviolet wavelength range. Finally, the wavenumber of this photon is

$$\widetilde{\nu} = \frac{1}{\lambda} = \frac{1}{4.102 \times 10^{-7}} = 2.438 \times 10^6 \, [m^{-1}] \qquad (E1.2.5)$$

This is a case where the SI units are used infrequently, and the results for the wavenumber are usually given by spectroscopists in units of cm^{-1}, where $1 \, m^{-1} = 10^{-2} \, cm^{-1}$. Accordingly, the results in Eq. E1.5 is written as
$\widetilde{\nu} = 2.438 \times 10^4 \, [cm^{-1}]$ or about $24\,380 \, cm^{-1}$.

1.5 Molecular Spectroscopy

Example 1.2 in the previous section describes an emission process in *atomic spectroscopy*, a subject covered briefly in Chapter 9. Molecular spectroscopy is a branch of science in which the interactions of electromagnetic radiation and molecules are studied, where the molecules exist in quantized stationary energy states similar to those discussed in the previous section. However, these energy states may or may not be due to transitions of electrons into different energy levels, but due to vibrational,

Table 1.1 Photon energies and spectroscopic ranges[a].

	ν_{photon}	λ_{photon}	E_{photon} [J]	E_{photon} [kJ/mol]	E_{photon} [m^{-1}]	Transition
Radio	750 MHz	0.4 m	5×10^{-25}	3×10^{-4}	2.5	NMR[b]
Microwave	3 GHz	10 cm	2×10^{-24}	0.001	10	EPR[b]
Microwave	30 GHz	1 cm	2×10^{-23}	0.012	100	Rotational
Infrared	3×10^{13} Hz	10 μm	2×10^{-20}	12	10^5	Vibrational
UV/visible	10^{15}	300 nm	6×10^{-19}	360	3×10^6	Electronic
X-ray	10^{18}	0.3 nm	6×10^{-16}	3.6×10^5	3×10^9	X-ray absorption

a)   For energy conversions, see Appendix 1.
b)   The resonance frequency in NMR and EPR depends on the magnetic field strength.

rotational, or spin energy levels. Thus, molecular spectroscopy often is classified by the wavelength ranges of the electromagnetic radiation (for example, microwave or infrared spectroscopies) or changes in energy levels of the molecular systems. This is summarized in Table 1.1, and the conversion of wavelengths and energies were discussed in Eqs. (1.11)–(1.15) and are summarized in Appendix 1.

In this table, NMR and EPR stand for nuclear magnetic and electron paramagnetic resonance spectroscopy, respectively. In both these spectroscopic techniques, the transition energy of a proton or electron spin depends on the applied magnetic field strength. All techniques listed in this table can be described by absorption processes although other descriptions, such as bulk magnetization in NMR, are possible as well. As seen in Table 1.1, the photon energies are between 10^{-16} and 10^{-25} J/photon or about 10^{-4}–10^5 kJ/(mol photons). Considering that a bond energy of a typical chemical (single) bond is about 250–400 kJ/mol, it shows that ultraviolet photons have sufficient energy to break chemical bonds or ionize molecules. In this book, mostly low energy photon interactions will be discussed, causing transitions in spin states, rotational, vibrational, and electronic (vibronic) energy levels.

Most of the spectroscopic processes discussed are absorption or emission processes as defined by Eq. (1.18):

$$\Delta E_{molecule} = Ef - Ei = E_{photon} = h\nu = hc/\lambda \tag{1.18}$$

However, interactions between light and matter occur even when the light's wavelength is different from the specific wavelength at which a transition occurs. Thus, a classification of spectroscopy, which is more general than that given by the wavelength range alone, would be a resonance/off-resonance distinction. Many of the effects described and discussed in this book are observed as resonance interactions where the incident light, indeed, possesses the exact energy of the molecular transition in question. IR and UV/vis absorption spectroscopy, microwave spectroscopy, and NMR are examples of such resonance interactions.

The off-resonance interactions between electromagnetic radiation and matter give rise to well-known phenomena such as the refractive index of dielectric materials. These interactions arise since force is exerted by the electromagnetic radiation on

the charged particles of matter even at off-resonance frequencies. This force causes an increase in the amplitude of the motion of these particles. When the frequency of light reaches the transition energy between two states, an effect known as anomalous dispersion of the refractive index takes place. This anomalous dispersion of the refractive index always accompanies an absorption process. This phenomenon makes it possible to observe the interaction of light either in an absorption or as a dispersion measurement, since the two effects are related to each other by a mathematical relation known as the Kramers–Kronig relation. This aspect will be discussed in more detail in Chapter 5.

The normal (nonresonant) Raman effect is a phenomenon that also is best described in terms of off-resonance models, since Raman scattering can be excited by wavelengths that are not being absorbed by molecules. A discussion of nonresonant effects ties together many well-known aspects of classical optics and spectroscopy.

1.6 Summary

The observation of the photoelectric effect and the absorption/emission spectra of the hydrogen atom and the modifications required to formulate the blackbody emission theory were the triggers that forced the development of quantum mechanics. As pointed out in the introduction, the development of quantum mechanics is based on postulates, rather than axioms. The form of some of these postulates can be visualized from other principles, but their adoption as "the truth" came from the fact that they produced the correct results.

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Problems

1. What is the maximum wavelength of electromagnetic radiation that can ionize an H atom in the $n = 2$ state?
2. Why is it that any photon with a wavelength below the limiting value obtained in (1) can ionize the H atom, whereas in standard spectroscopy, only a photon with the correct energy can cause a transition?
3. Assume that you carry out the experiment in (1) with light with a wavelength of 10 nm less than calculated in (1). What is the kinetic energy of the photoelectron created?

4. What is the velocity of the electron in Problem 3?
5. Using the de Broglie relation for matter waves, calculate the velocity to which an electron needs to be accelerated such that its wavelength is 10 nm.
6. What percentage of the velocity of light is the velocity in (5)?
7. What is the relativistic mass of this electron?
8. At what velocity is the wavelength of an electron 30 nm?
9. What is the momentum of such the electron in (8)?
10. What is the mass of a photon with a wavelength of 30 nm?
11. What is the momentum of the photon in (10)?
12. Compare and comment on the masses and momenta of the moving particles in Problems (8)–(11).
13. "Frequency doubling" or "second harmonic generation (SHG)" is a little optical trick (Appendix 3) in which two photons of the same wavelength are squashed into a new photon, while the energy is conserved. Calculate the wavelength of the photon created from frequency doubling of two photons with $\lambda = 1064$ nm.
14. "Sum frequency generation (SFG)" is another optical trick (Appendix 3) in which two photons of different wavelengths are squashed into a new photon while the energy is conserved. Calculate the wavelength of SFG photon created from combining two photons with $\lambda_1 = 1064$ nm and $\lambda_2 = 783$ nm.
15. The value of the Rydberg constant, R_y, can be calculated according to $R_y = \frac{m_R \, e'^4}{2 \hbar^2}$ where e' = $e/\sqrt{4\pi\varepsilon_o}$ and where m_R is the reduced mass of electron and proton. Perform an analysis of the units of R_y.
16. Which two experiments demonstrate that light has wave and particle character?
17. Which two experiments demonstrate that moving electrons have wave and particle character?