CHEMICAL BONDING

AUDREY L. COMPANION

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SECOND EDITION

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PREFACE

When the first edition of *Chemical Bonding* appeared in 1964, its major purpose was clear: to correct a deficiency in orbital theory in most general chemistry textbooks. Since most textbooks today are more than adequate in treatment of atomic and molecular structure, obviously a remedial supplement is no longer needed. The audience for the book has for some years now included advanced high school students who wish more detail, freshman college students seeking a "how-to-do-it" approach, and upper-level students wanting a broad qualitative overview of bonding theory before plunging into quantum-mechanical treatments.

In this edition there is virtually no change in the level of presentation of the material. After many years of teaching bonding theory to freshman students I believe that explicit discussions of the characteristics of wave functions, flooded-planet models, signs of *LCAOMO*s, etc., are not understood by the average student. An instructor with better-than-average students can easily expand such topics in lecture.

The first two chapters, covering the experimental background and history of quantum theory, are purposely brief and may be omitted. Large portions of Chapter 3 on atoms and Chapter 4 on molecules have been rewritten, and most

diagrams are new. In Chapter 4 I have retained the mixed *VB–MO* approach of the first edition primarily because it works well with students. Chapter 5 has been expanded, particularly in sections on metals and semiconductors, and a new section on silicates and glasses has been added to demonstrate materials science applications of the theory. More advanced concepts on transition-metal chemistry, such as the Jahn-Teller effect, have been removed from Chapter 6 in this edition.

Other general changes include: incorporation of certain topics (such as dative bonding), previously developed in the text, into problems at the chapter ends; an increase in the number of problems and revision of most of the old ones; use of SI units throughout; and an increase in the number of journal references.

Through the years the suggestions and criticisms offered by friends at many universities have led to what I hope now is a better book. In particular I wish to thank my former colleague Kenneth Schug for his help both in the early years and in the development of the materials science ideas included in this edition, my present colleague Paul Corio for his witch hunt on Pennsylvania Duchisms and for other comments, and Mary and Martin Kilpatrick for their encouragement over many years. I am grateful to the following reviewers for their helpful comments upon reading the manuscript: Professor David L. Adams, North Shore Community College; Professor Frank O. Ellison, University of Pittsburgh; Professor Gil Haight, University of Illinois at Urbana-Champaign; Professor Robert M. Kren, University of Michigan-Flint; Dr. Conrad Stanitski, Randolph-Macon College; and Professor Duane D. Swank, Pacific Lutheran University. All errors remaining are my own.

Audrey L. Companion

THE BEGINNINGS OF QUANTUM THEORY

QUANTUM THEORY

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CONTENTS

Frustration and rebellion, though of a quiet sort, abounded in **1-1** science in the early twentieth century, particularly among those concerned with the nature of matter and energy. Many new ideas were born, and many promptly buried; many old and established laws of physics were shaken. Out of this chaotic period emerged the modern theory of the structure of atoms, molecules, and solids, a theory virtually unchallenged today. A rigorous discussion of its basis requires at least a sound understanding of calculus, a tool usually not at the fingertips of beginners in chemistry. Yet even without the underlying mathematics we can describe quite well the nature of atoms and molecules, since the physical theory is rich in pictures and rules which are usually easily accepted. These we shall lean upon heavily in this text. Frequently, though, we shall encounter concepts which seem unpalatable, for they defy the rules governing events occurring in everyday life. Yet accept them we must, for they are supported by unequivocal experimental evidence. One of these unusual concepts involves the dual life led by the phenomenon called light, with which we begin.

THE NATURE OF LIGHT

Largely because of the impact of the creative genius of Sir **1-2** Isaac Newton (1642–1727), who advocated a corpuscular

(particle-like) model, the wave theory of light propagation was not really accepted until about 1850, despite the accumulation of experimental evidence supporting it. At that time the experiments finally overwhelmed the particle model, and until the turn of the century the wave theory was undisputed. Many scientists felt that the corpuscular model had been properly and permanently put to rest.

Even now it is believed that light is *propagated through space* in the form of a wave motion, somewhat like ripples on a pond at the drop of a pebble. Figure 1-1 illustrates a representation of such a wave. The distance A is the maximum *amplitude* of the disturbance; the distance from crest to crest (or valley to valley) is its *wavelength* λ (Greek lambda), a distance quite large in a pond but very small when the wave motion describes light. For example, for visible light λ ranges from 400 to 700 nm.

Light travels through space with a velocity c of approximately 3×10^8 m/s; i.e., the peaks and valleys of Fig. 1-1 move in the direction of the light beam with a velocity c. In 1 sec a stationary microcosmic observer of a light beam of wavelength λ would count c/λ peaks passing by or would observe a frequency of peaks ν (Greek nu) of c/λ cycles per second associated with the wave. Thus, for *light*, wavelength and

FIGURE 1-1
Representation of a light wave.

Direction of propagation
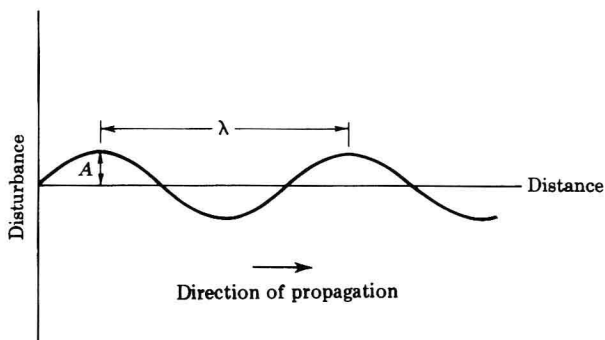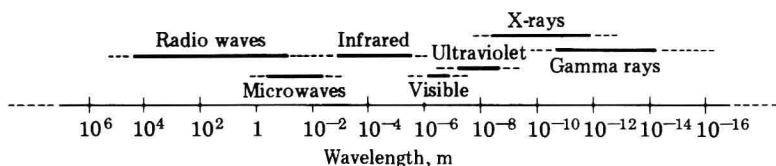
FIGURE 1-2
The electromagnetic spectrum.

frequency, both convenient descriptions of the wave property, are related by the equation

$$\lambda \nu = c$$

That which we call visible light is but a very narrow part of a large group of radiation types comprising the *electromagnetic spectrum* (Fig. 1-2), which includes very-long-wavelength radio waves and very-short-wavelength gamma rays. All these radiation types are the same phenomenon; the basis for the classification shown in Fig. 1-2 is largely the experimental means of detection or generation.

The human eye is tuned to interpret only radiation of wavelength 400 to 700 nm (where 1 nm $= 10^{-9}$ m), and these numbers are thus the limits of the visible portion of the electromagnetic spectrum.

There are many experimental "proofs" of the wave nature of light. One, which will be of particular use to us later, involves the reflection or diffraction of x-rays by orderly stacks of atoms in a crystal. Figure 1-3 shows in cross section two x-rays of wavelength λ impinging at an angle θ on the surface of a crystal in which atoms are arrayed in planes separated by a distance d. Both rays are associated with waves traveling in phase, so that their amplitudes maximize and minimize together and they reinforce one another (point A), at least up to the line BE, after which the rays undergo reflections from different planes. Now unless the distance BCD is equal to λ or to some integral multiple n of λ, the two emerging rays will be out of phase and may cancel one another. Through simple geome-
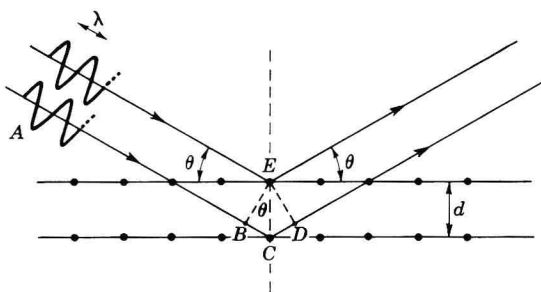
FIGURE 1-3
Diffraction of x-rays by a
crystal lattice.

try BCD is $2d \sin \theta$, so that the condition for getting strong reflections from the crystal is

$$n\lambda = 2d \sin \theta \quad \text{where } n = 0, 1, 2, 3, \dots$$

the Bragg diffraction law. Experimentally, if the angle of incidence of x-rays on a crystal surface is varied, strong reflections are observed at just the angles predicted, with blackness or grayness in between. Such an experiment could not be explained by a particle model of light.

However, in 1900 the German scientist Max Planck reintroduced the concept of corpuscular light while presenting a theory explaining blackbody radiation. If the radiation emerging from a pinhole in a very hot closed furnace, a "black body," is passed through a prism and a graph of amount of energy emitted versus wavelength is constructed for a given temperature, a curve like one of those in Fig. 1-4 is obtained. Explanations of these curves based on all the rules and regulations of physics known at the time (classical physics) failed to explain the shapes and temperature dependence of the curves.

Planck attacked this problem by searching for a formula connecting radiant energy, temperature, and wavelength, guessing different functions and adjusting them with numerical constants until he found the correct *empirical* relationship between the variables. Armed with this, he then searched for a

hypothetical "model" for the furnace system from which he could derive theoretically his empirical formula. Success came rapidly when he compared the atoms constituting the walls of the furnace to a large assembly of oscillators of all vibrational frequencies absorbing and emitting energy. One of the assumptions of his analysis was startling: the oscillators could change their energy by absorbing or emitting only spurts or bundles of energy, which he called *quanta*. Furthermore, a quantum of energy was related to the oscillator frequency ν by the equation $E = h\nu$, where h is a proportionality constant, Planck's constant. When the absorption and emission probabilities of the group of oscillators were counted, radiant energy distributions like those of Fig. 1-4 resulted. Such distributions could not be obtained without these assumptions.

Until this time it was believed that a vibrating body could change its energy by an arbitrary amount (say $0.111\ h\nu$, $0.697\ h\nu$, etc.). Quite possibly Planck's ideas would not have been accepted had it not been for Einstein's use of the quantum concept 5 years later in the explanation of the *photoelectric effect*.

FIGURE 1-4
Blackbody radiation.


1646°K

1449°K

1259°K

Radiant energy ⟶

Wavelength ⟶
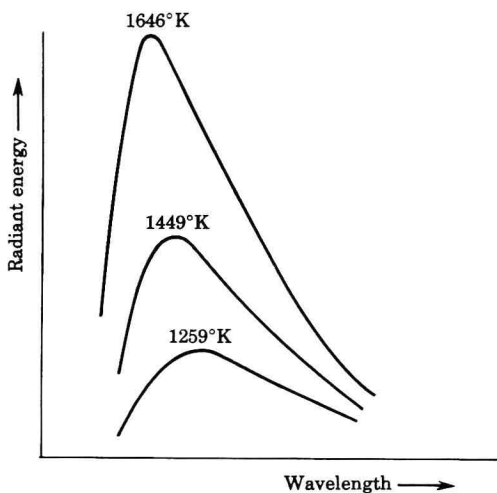
When a clean surface of an alkali metal was irradiated with a light beam, electrons were ejected from the surface. Studies of the kinetic energy ($\frac{1}{2} mv^2$) of the ejected electrons as a function of light frequency ν indicated that below a critical frequency ν_0, characteristic of the metal, no electrons were ejected. For frequencies above ν_0, the kinetic energy of the electrons increased with ν linearly (see Fig. 1-5). These data defied explanation in terms of the wave model. Einstein explained the phenomenon quite simply in terms of collisions between electrons in the metal and bundles of light of energy $E = h\nu$ which he called *photons*. When a bombarding photon hits the surface it collides with and transfers its energy to an electron. The electron expends some of this energy in work (W) to escape the metal, retaining the rest as kinetic energy. Einstein's equation for the process was:

$$\underbrace{h\nu}_{\text{photon}} = \underbrace{W + \tfrac{1}{2}mv^2}_{\text{electron}}$$

For photon energies below the constant work term $W = h\nu_0$, no electrons can escape the metal. Photon energies in excess of W appear as kinetic energy of the electron ejected after the collision. A collision process is a corpuscular phenomenon!

FIGURE 1-5
Data from observations of the photoelectric effect.
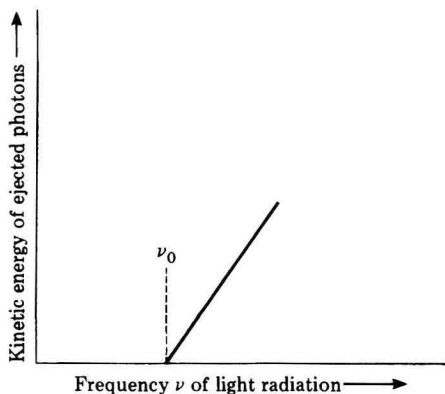
Both models, corpuscular and wave, seem here to stay. Light, as it is propagated through space, is distinctly wavelike and, when it interacts with matter in energy-exchange processes, sometimes assumes a corpuscular nature.

We shall meet the important proportionality constant h again in the Bohr model of the atom (Chap. 2) and in the Schrödinger equation (Chap. 3), on which we base the modern theory of atoms and molecules and solids. h is now regarded as a fundamental constant of nature, particularly appropriate to systems of atomic size. In SI units h is 0.6626×10^{-33} J/s.

With the relation $E = h\nu$, we can now discuss the electromagnetic spectrum in terms of energy. Since $\nu\lambda = c$, $E = hc/\lambda$, and since both h and c are constants, the energy of a photon is inversely proportional to its wavelength. Radio waves are of low energy, gamma rays of high energy; near and within the visible range, infrared (IR) and red are of lower energy, violet and ultraviolet (UV) of higher energy.

The spectrum emitted by a furnace (Fig. 1-4) is a *continuum*, a display of *all* wavelengths, with no detectable gaps. Many heated solids, for example, a tungsten filament in an electric bulb, emit such a continuum. This smear of all wavelengths appears as white light to an observer.

THE DUAL NATURE OF MATTER

1-3

The notion of the electron as a particle is commonly accepted and has been for a long time now. Its wavelike character is less easily conceived.

Basing his arguments on the symmetry of nature, the French physicist de Broglie postulated that, if light has both particlelike and wavelike character, a similar duality must exist for matter, and he proceeded to show that a definite wavelength could be associated with the movement of bodies of matter.

Previously Einstein had proved theoretically that mass and energy were interconvertible quantities (a theory later proved experimentally by nuclear physicists and chemists) and had shown that associated with a photon of energy E was an equivalent mass of E/c^2. The momentum p (mass × velocity) of a