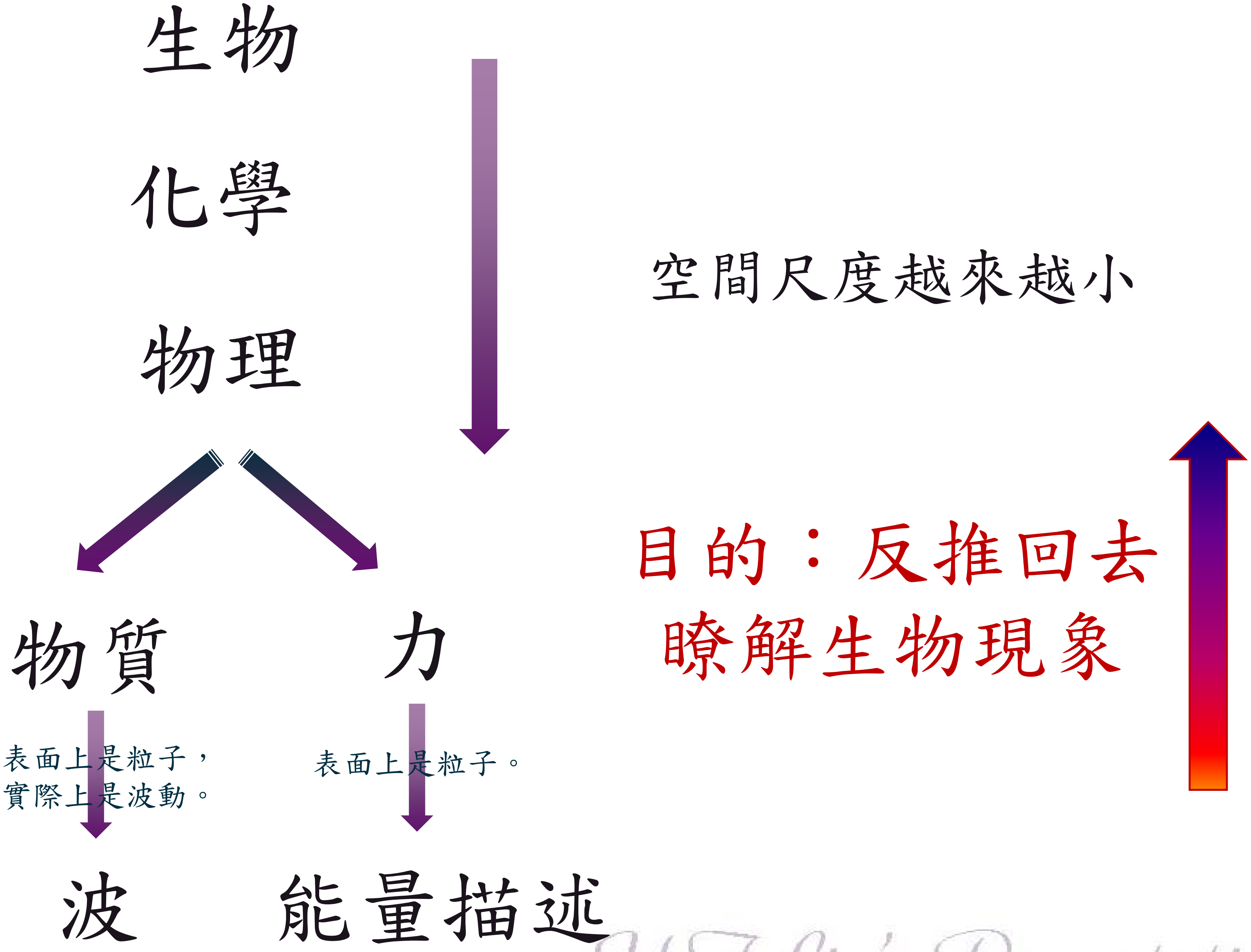
林盈廷

高雄醫學大學
生命科學院
生物科技學系 助理教授

第一教學大樓 N1038 室
校內分機：2792
ytlin@kmu.edu.tw

Reference Books

- Physical Chemistry for the Life Sciences
  (Engel, Drobny and Reid)
- Biophysical Chemistry
  (James P. Allen)



生物

化學

物理

空間尺度越來越小

物質

力

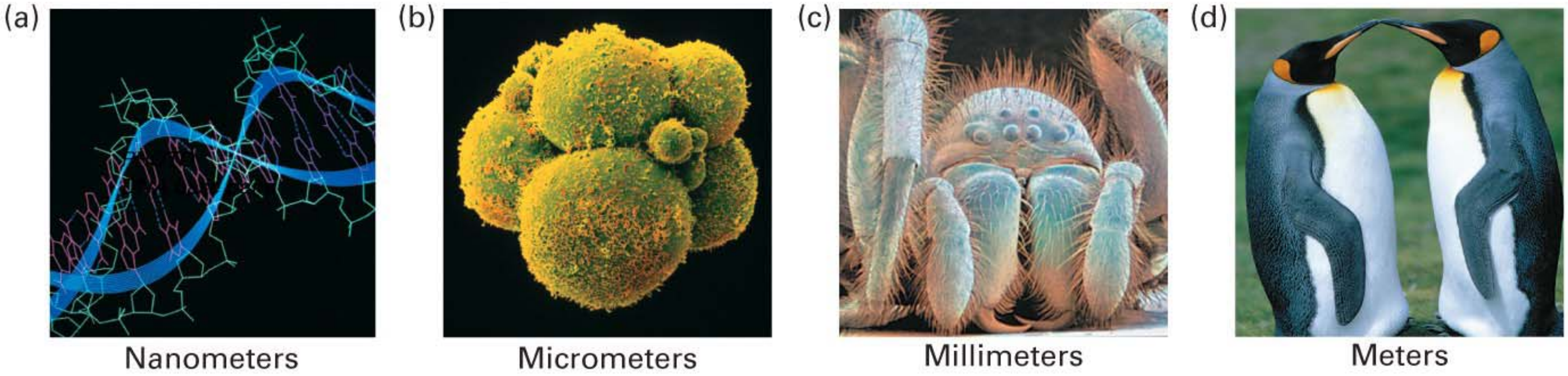
表面上是粒子，
實際上是波動。

表面上是粒子。

波

能量描述

目的：反推回去
瞭解生物現象

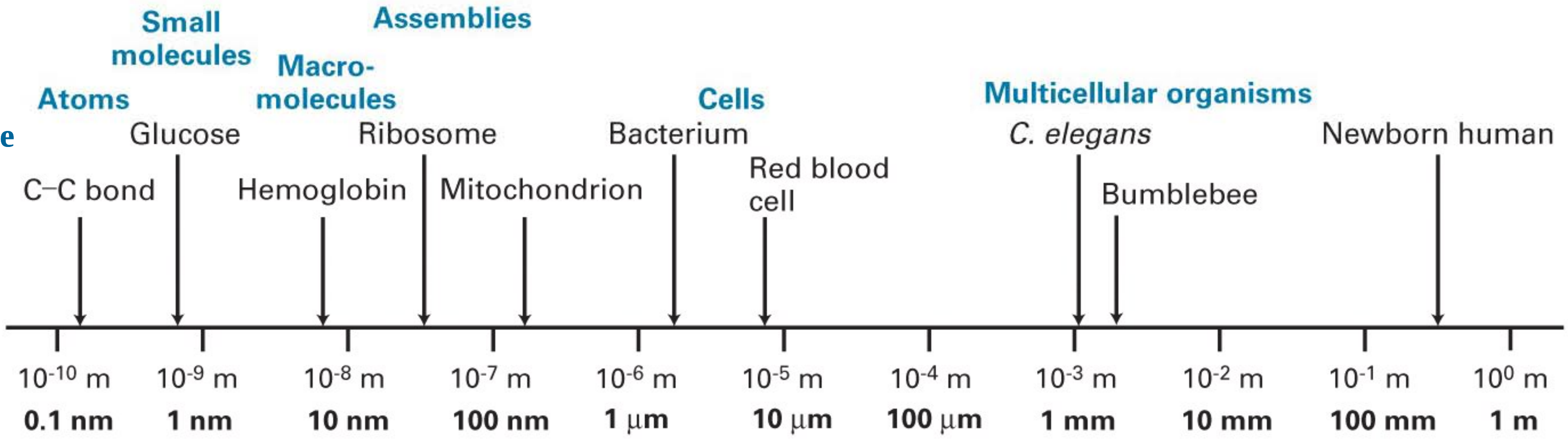


(a) Nanometers

(b) Micrometers

(c) Millimeters

(d) Meters



Atoms

Small molecules

Macro-molecules

Assemblies

Cells

Multicellular organisms

C–C bond

Glucose

Hemoglobin

Ribosome

Mitochondrion

Bacterium

Red blood cell

C. elegans

Bumblebee

Newborn human

10^{-10} m	10^{-9} m	10^{-8} m	10^{-7} m	10^{-6} m	10^{-5} m	10^{-4} m	10^{-3} m	10^{-2} m	10^{-1} m	10^{0} m
0.1 nm	**1 nm**	**10 nm**	**100 nm**	**1 μm**	**10 μm**	**100 μm**	**1 mm**	**10 mm**	**100 mm**	**1 m**

Wave

法則

- 科學研究邏輯有歸納法及什麼法？
- 牛頓定律三大法則為何？
- 量子力學的七個法則為何?
- 熱力學四個法則為何？

Lecture

Quantum Chemistry and Spectroscopy (II)

把物質切到最小，我們知道：
它表面上是粒子，實際上是波動。

Tiny Particle Wave equation

- Wind wave
- Airy wave theory
- Wave equation
- Acoustic wave equation
- Vibrations of a circular drum
- Standing wave
- Electromagnetic wave equation
- Schrödinger equation

Schröedinger equation

Figure 10.4 Erwin Schrödinger (1887–1961). Schrödinger proposed an expression of quantum mechanics that was different from but equivalent to Heisenberg's. His expression is useful because it expresses the behavior of electrons in terms of something we understand—waves. The Schrödinger equation is the central equation of quantum mechanics.

Schröedinger equation

Total energy

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}+V\psi=E\psi$$

Kinetic energy

Potential energy

$$\hbar=\frac{h}{2\pi}=1.054\times10^{-34}\ Js$$

Chapter 13, Physical Chemistry for the Life Sciences (Engel, Drobny and Reid)

把物質切到最小，我們知道：
它表面上是粒子，實際上是波動。

Tiny Particle Wave equation

- Wind wave
- Airy wave theory
- Wave equation
- Acoustic wave equation
- Vibrations of a circular drum
- Standing wave
- Electromagnetic wave equation
- Schrödinger equation

Schröedinger equation

CORBIS-Bettmann

Figure 10.4 Erwin Schrödinger (1887–1961). Schrödinger proposed an expression of quantum mechanics that was different from but equivalent to Heisenberg's. His expression is useful because it expresses the behavior of electrons in terms of something we understand—waves. The Schrödinger equation is the central equation of quantum mechanics.

Schröedinger equation

Total energy

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}}+\boxed{V}\psi=\boxed{E}\psi$$

Potential energy

Kinetic energy

$$\hbar=\frac{h}{2\pi}=1.054\times10^{-34}\ Js$$

Chapter 13, Physical Chemistry for the Life Sciences (Engel, Drobny and Reid)

Quantum Chemistry 的七個法則

➔用來形成 Schröedinger equation

（也就是可用來描述粒子的波動方程式）

Quantum Mechanics 的七個法則

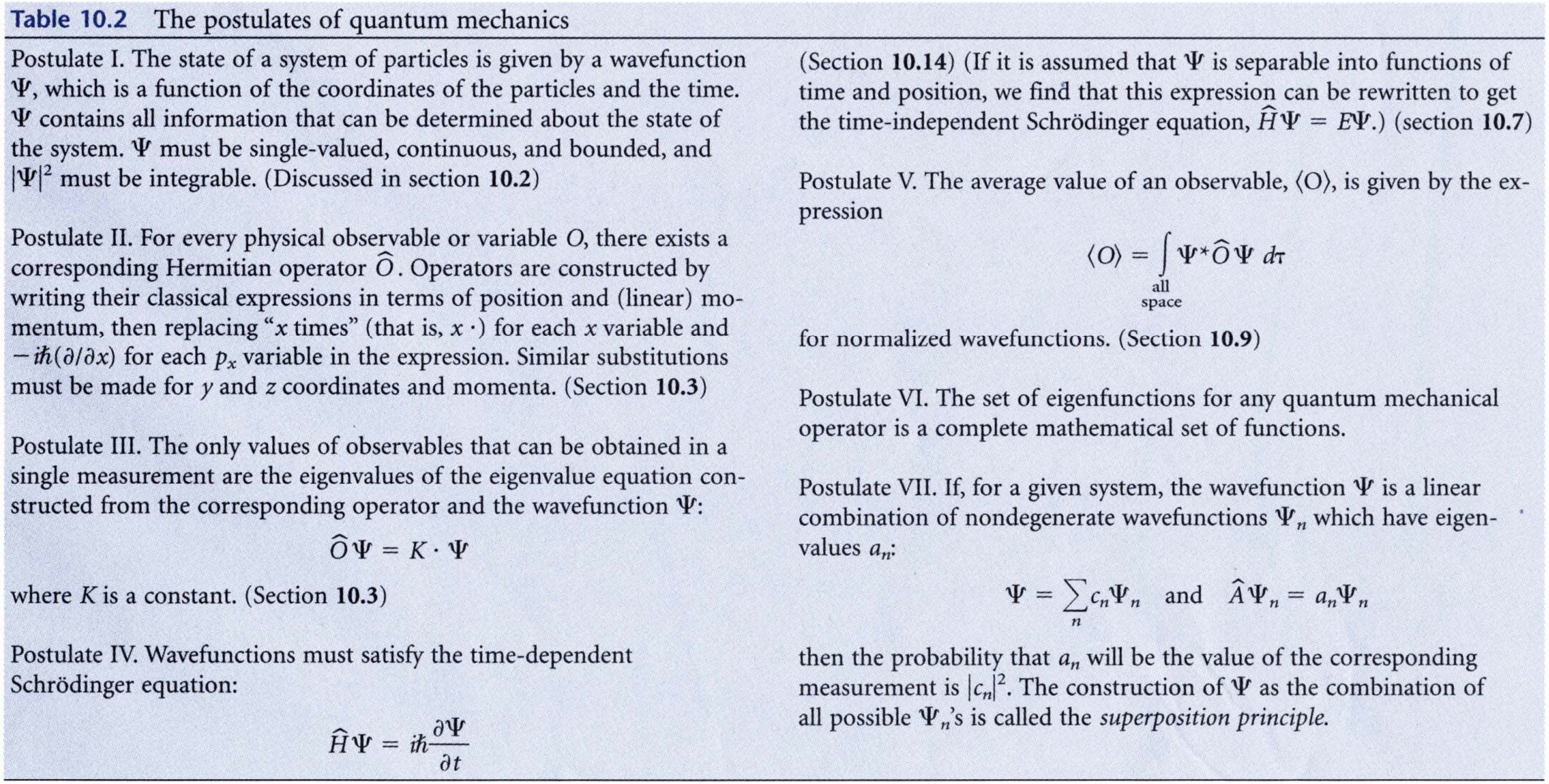


Table 10.2 The postulates of quantum mechanics

Postulate I. The state of a system of particles is given by a wavefunction Ψ, which is a function of the coordinates of the particles and the time. Ψ contains all information that can be determined about the state of the system. Ψ must be single-valued, continuous, and bounded, and $|\Psi|^2$ must be integrable. (Discussed in section **10.2**)

Postulate II. For every physical observable or variable O, there exists a corresponding Hermitian operator $\widehat{O}$. Operators are constructed by writing their classical expressions in terms of position and (linear) momentum, then replacing "x times" (that is, $x\,\cdot$) for each x variable and $-i\hbar(\partial/\partial x)$ for each p_x variable in the expression. Similar substitutions must be made for y and z coordinates and momenta. (Section **10.3**)

Postulate III. The only values of observables that can be obtained in a single measurement are the eigenvalues of the eigenvalue equation constructed from the corresponding operator and the wavefunction Ψ:

$$\widehat{O}\Psi = K \cdot \Psi$$

where K is a constant. (Section **10.3**)

Postulate IV. Wavefunctions must satisfy the time-dependent Schrödinger equation:

$$\widehat{H}\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

(Section **10.14**) (If it is assumed that Ψ is separable into functions of time and position, we find that this expression can be rewritten to get the time-independent Schrödinger equation, $\widehat{H}\Psi = E\Psi$.) (section **10.7**)

Postulate V. The average value of an observable, $\langle O\rangle$, is given by the expression

$$\langle O\rangle = \int_{\substack{\text{all}\\ \text{space}}} \Psi^* \widehat{O}\Psi \, d\tau$$

for normalized wavefunctions. (Section **10.9**)

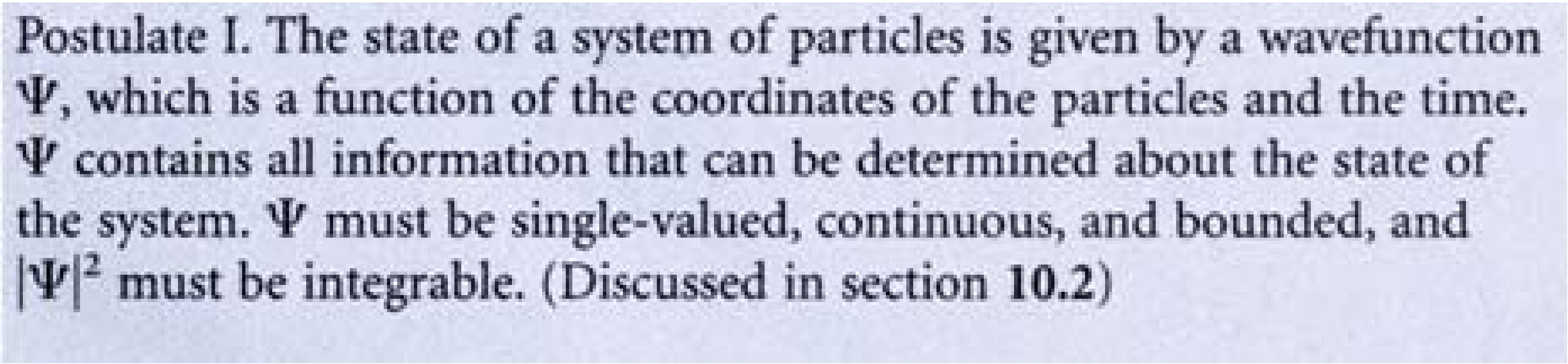
Postulate VI. The set of eigenfunctions for any quantum mechanical operator is a complete mathematical set of functions.

Postulate VII. If, for a given system, the wavefunction Ψ is a linear combination of nondegenerate wavefunctions Ψ_n which have eigenvalues a_n:

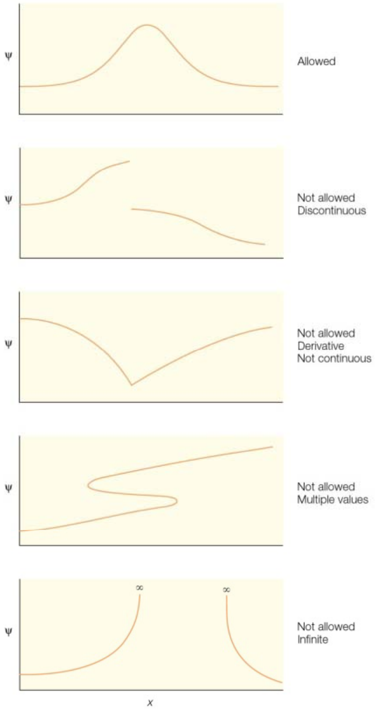
$$\Psi = \sum_n c_n \Psi_n \quad \text{and} \quad \widehat{A}\Psi_n = a_n \Psi_n$$

then the probability that a_n will be the value of the corresponding measurement is $|c_n|^2$. The construction of Ψ as the combination of all possible Ψ_n's is called the *superposition principle.*

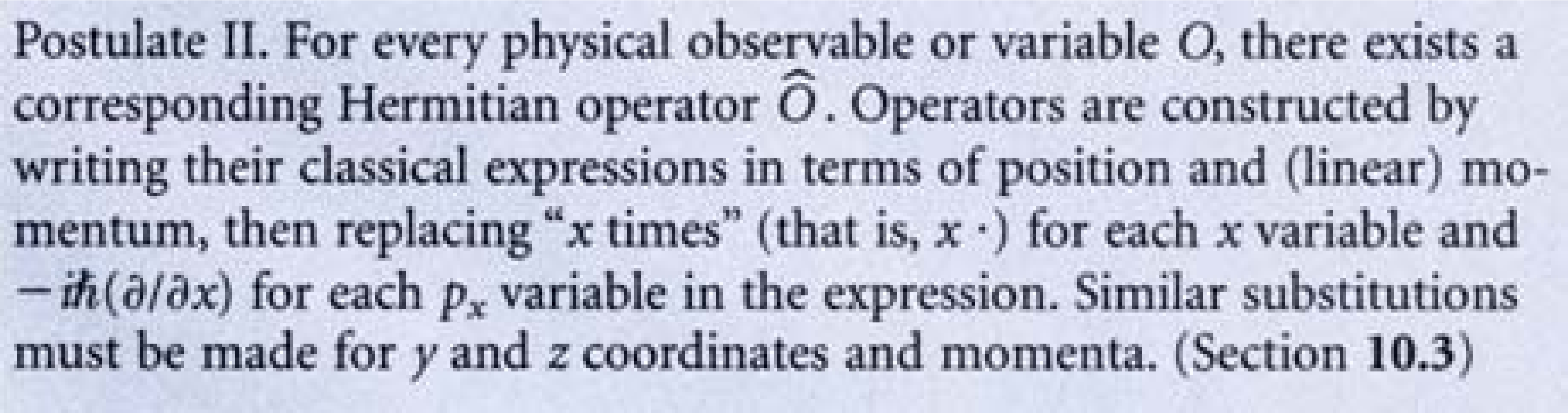
Quantum Mechanics 法則 1



Postulate I. The state of a system of particles is given by a wavefunction Ψ, which is a function of the coordinates of the particles and the time. Ψ contains all information that can be determined about the state of the system. Ψ must be single-valued, continuous, and bounded, and $|\Psi|^2$ must be integrable. (Discussed in section **10.2**)



Quantum Mechanics 法則 2



Postulate II. For every physical observable or variable O, there exists a corresponding Hermitian operator $\hat{O}$. Operators are constructed by writing their classical expressions in terms of position and (linear) momentum, then replacing "x times" (that is, $x\cdot$) for each x variable and $-i\hbar(\partial/\partial x)$ for each p_x variable in the expression. Similar substitutions must be made for y and z coordinates and momenta. (Section **10.3**)

$$p_x$$

$$\hat{O} = -i\hbar\left(\frac{\partial}{\partial x}\right)$$

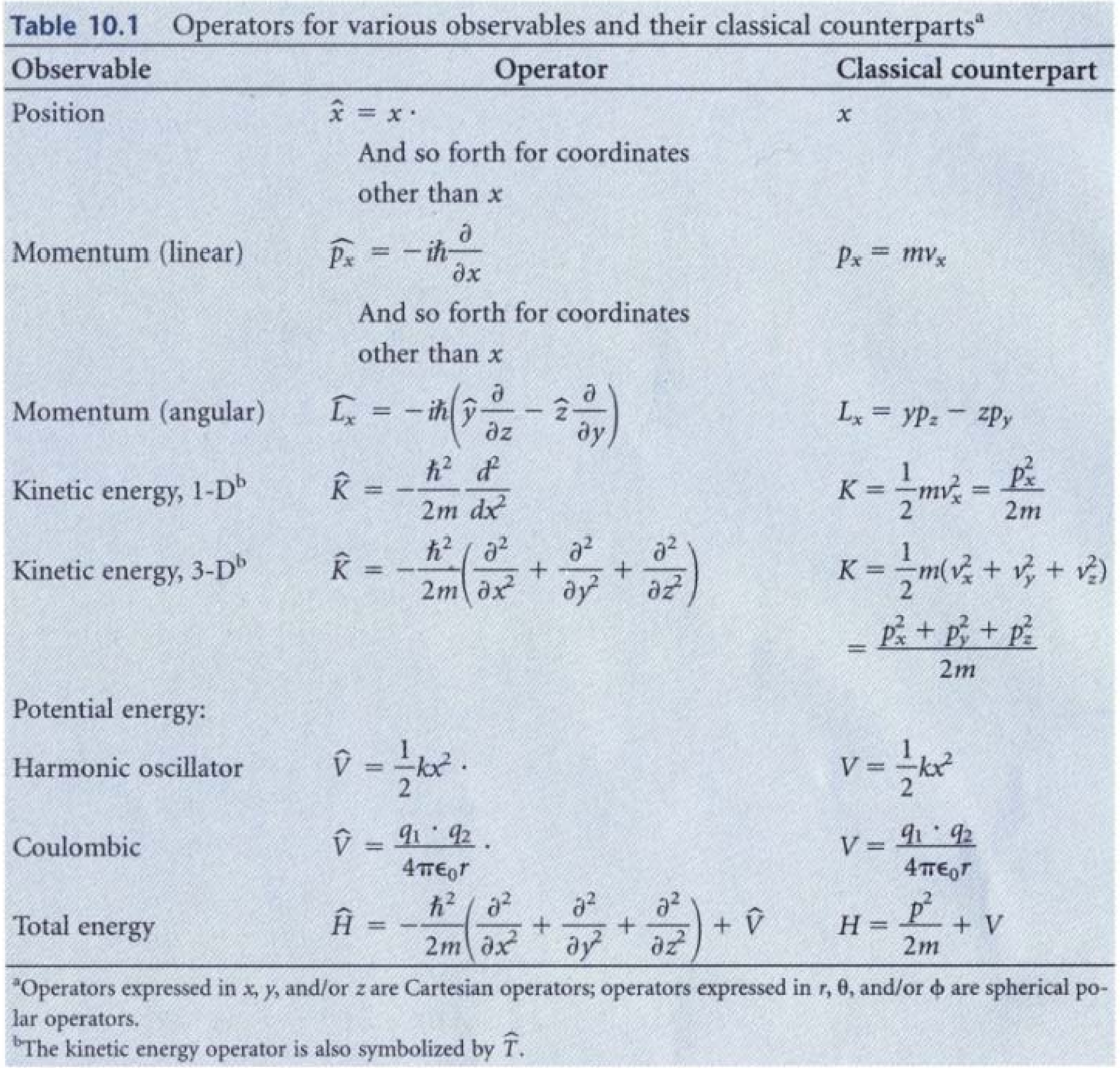


Table 10.1 Operators for various observables and their classical counterparts[a]

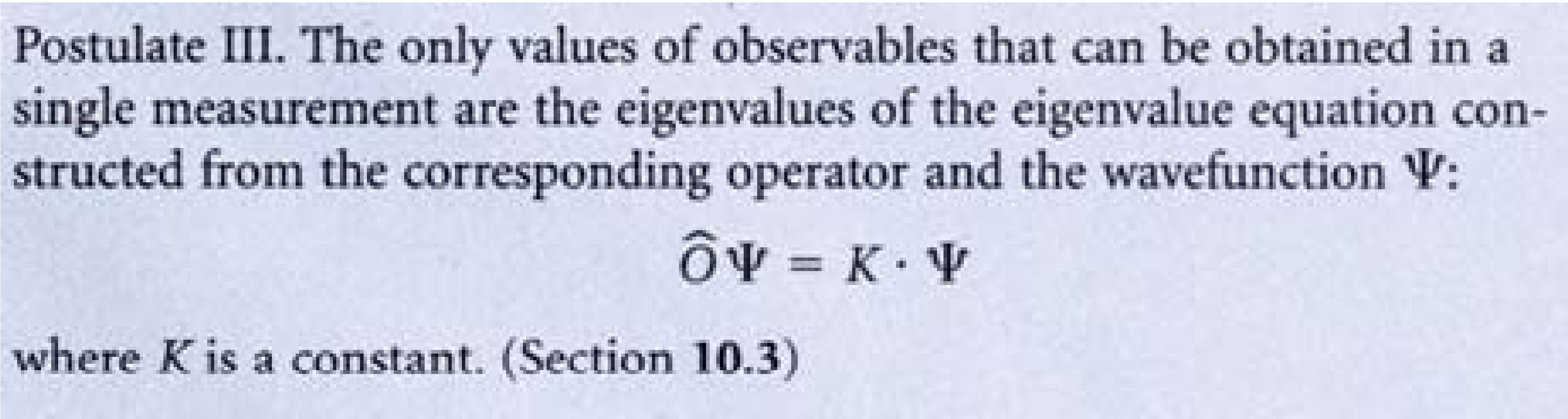
Observable	Operator	Classical counterpart
Position	$\hat{x} = x\cdot$ And so forth for coordinates other than x	x
Momentum (linear)	$\widehat{p_x} = -i\hbar\dfrac{\partial}{\partial x}$ And so forth for coordinates other than x	$p_x = mv_x$
Momentum (angular)	$\widehat{L_x} = -i\hbar\left(\hat{y}\dfrac{\partial}{\partial z} - \hat{z}\dfrac{\partial}{\partial y}\right)$	$L_x = yp_z - zp_y$
Kinetic energy, 1-D[b]	$\hat{K} = -\dfrac{\hbar^2}{2m}\dfrac{d^2}{dx^2}$	$K = \dfrac{1}{2}mv_x^2 = \dfrac{p_x^2}{2m}$
Kinetic energy, 3-D[b]	$\hat{K} = -\dfrac{\hbar^2}{2m}\left(\dfrac{\partial^2}{\partial x^2} + \dfrac{\partial^2}{\partial y^2} + \dfrac{\partial^2}{\partial z^2}\right)$	$K = \dfrac{1}{2}m(v_x^2 + v_y^2 + v_z^2)$ $= \dfrac{p_x^2 + p_y^2 + p_z^2}{2m}$
Potential energy:		
Harmonic oscillator	$\hat{V} = \dfrac{1}{2}kx^2\cdot$	$V = \dfrac{1}{2}kx^2$
Coulombic	$\hat{V} = \dfrac{q_1 \cdot q_2}{4\pi\epsilon_0 r}\cdot$	$V = \dfrac{q_1 \cdot q_2}{4\pi\epsilon_0 r}$
Total energy	$\hat{H} = -\dfrac{\hbar^2}{2m}\left(\dfrac{\partial^2}{\partial x^2} + \dfrac{\partial^2}{\partial y^2} + \dfrac{\partial^2}{\partial z^2}\right) + \hat{V}$	$H = \dfrac{p^2}{2m} + V$

[a] Operators expressed in x, y, and/or z are Cartesian operators; operators expressed in r, θ, and/or ϕ are spherical polar operators.

[b] The kinetic energy operator is also symbolized by $\hat{T}$.

ation

Quantum Mechanics 法則 3



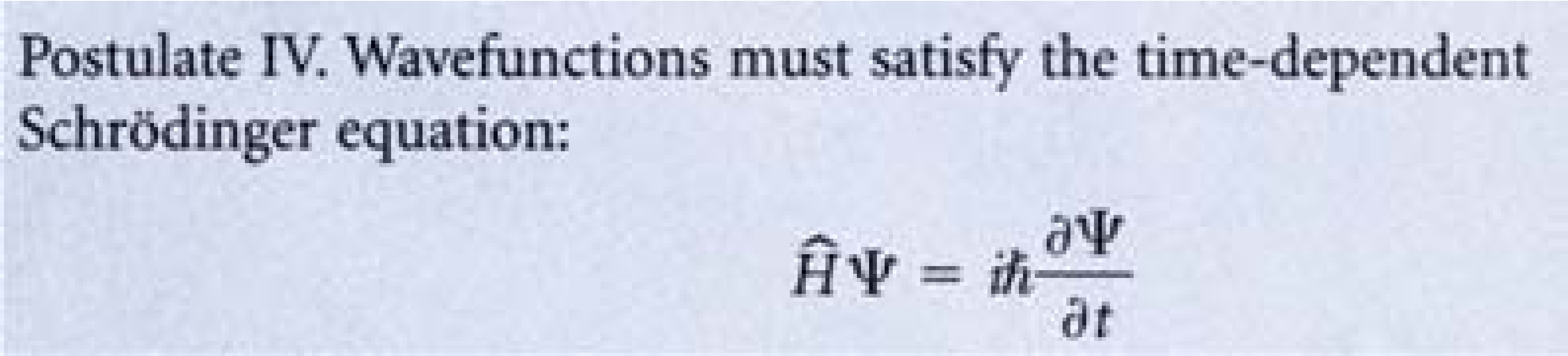
Postulate III. The only values of observables that can be obtained in a single measurement are the eigenvalues of the eigenvalue equation constructed from the corresponding operator and the wavefunction Ψ:

$$\hat{O}\Psi = K \cdot \Psi$$

where K is a constant. (Section 10.3)

observables

Quantum Mechanics 法則 4

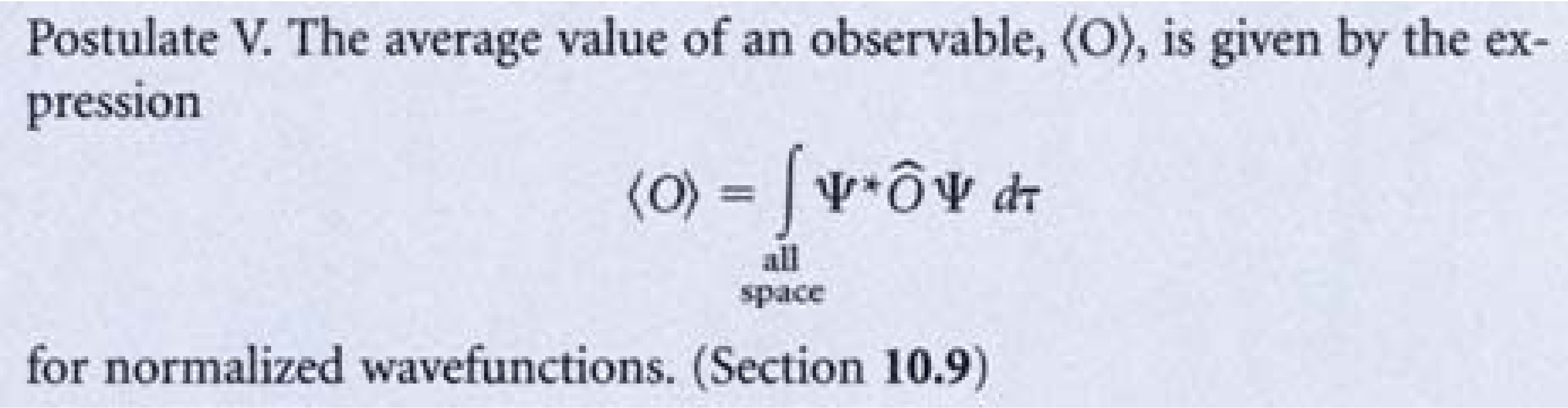


Postulate IV. Wavefunctions must satisfy the time-dependent Schrödinger equation:

$$\hat{H}\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

time dependent

Quantum Mechanics 法則 5



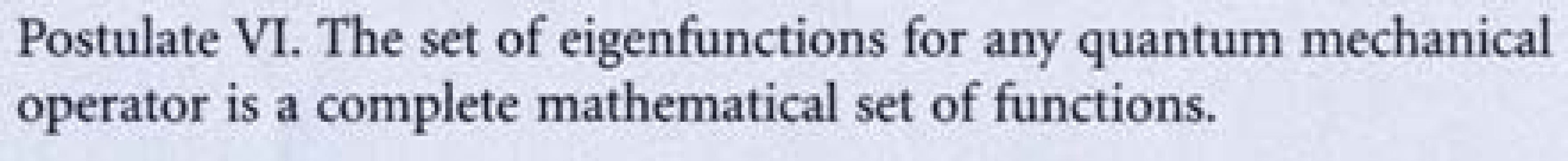
Postulate V. The average value of an observable, $\langle O \rangle$, is given by the expression

$$\langle O \rangle = \int_{\substack{\text{all}\\ \text{space}}} \Psi^* \hat{O} \Psi \, d\tau$$

for normalized wavefunctions. (Section **10.9**)

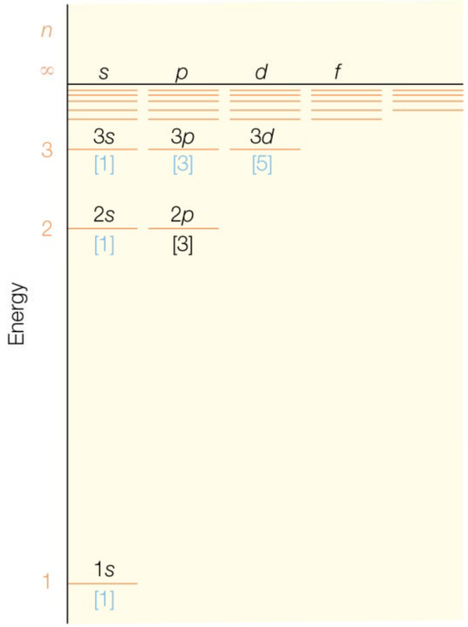
average observables

Quantum Mechanics 法則 6



Postulate VI. The set of eigenfunctions for any quantum mechanical operator is a complete mathematical set of functions.

$$\int_{-\infty}^{\infty}\psi_i^*(x)\psi_j(x)dx=\begin{cases}0, i\neq j\\1, i=j\end{cases}\qquad(13.21)$$



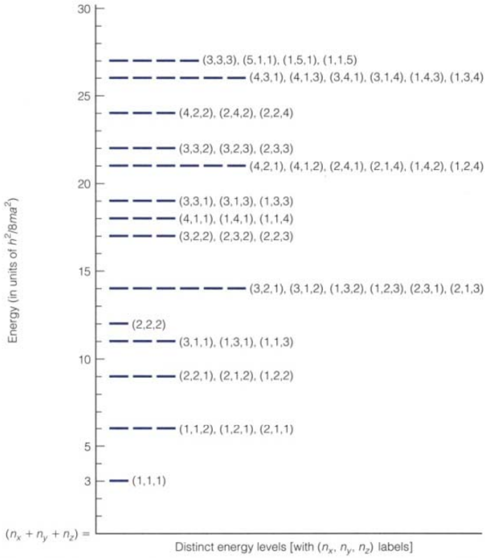


Figure 10.13 The energy levels of the 3-D particle-in-a-(cubical)-box. In this system, different wavefunctions can have the same energy. This is an example of degeneracy.

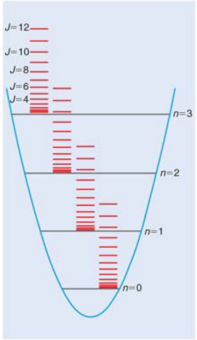
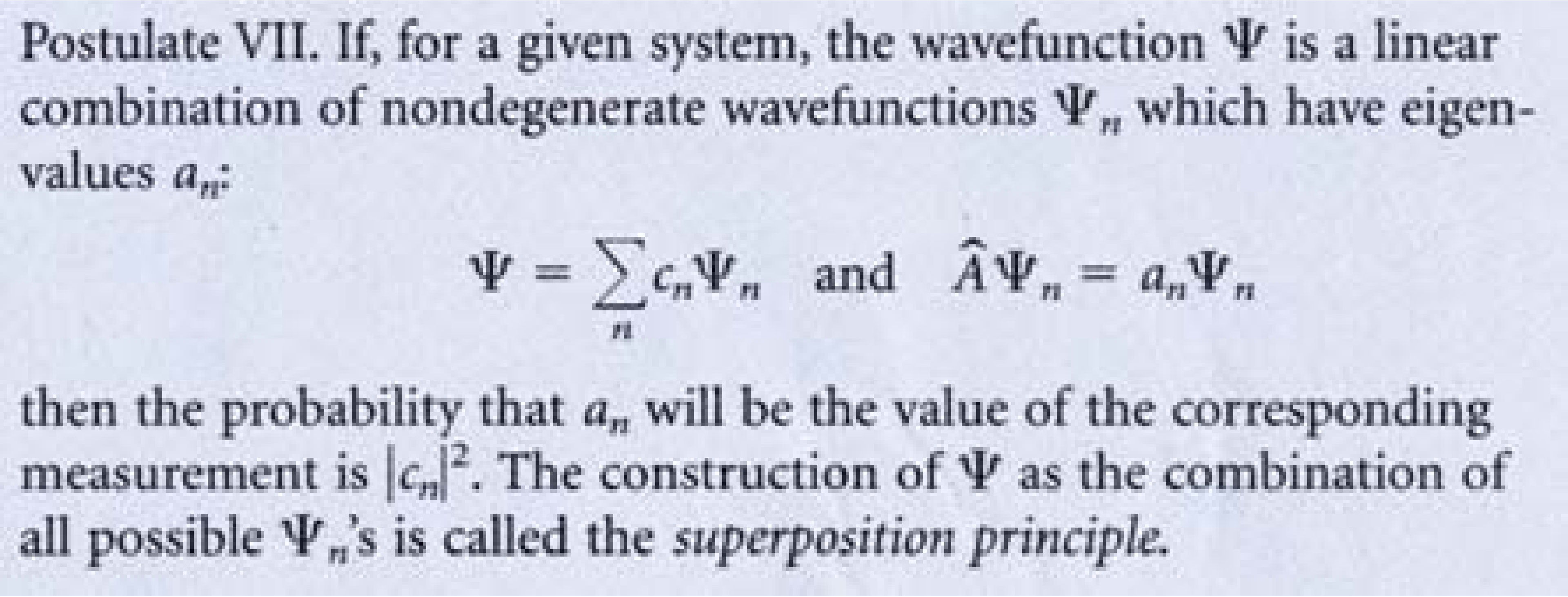


Figure: 18-08

Quantum Mechanics 法則 7



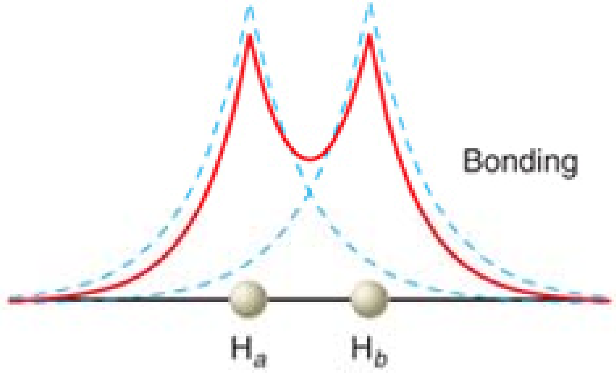
Postulate VII. If, for a given system, the wavefunction Ψ is a linear combination of nondegenerate wavefunctions Ψ_n which have eigenvalues a_n:

$$\Psi = \sum_n c_n \Psi_n \quad \text{and} \quad \hat{A}\Psi_n = a_n \Psi_n$$

then the probability that a_n will be the value of the corresponding measurement is $|c_n|^2$. The construction of Ψ as the combination of all possible Ψ_n's is called the *superposition principle.*

波

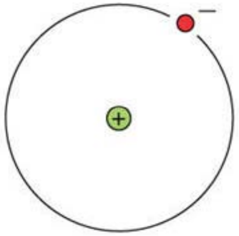
可以相加減



Different Systems

(Chapter 14 ~ Chapter 18)

- 不同的系統，
  有不同的 Schröedinger equation 的解



Schröedinger equation for hydrogen atom

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}}\psi+\boxed{V}\psi=\boxed{E}\psi$$

E

ψ

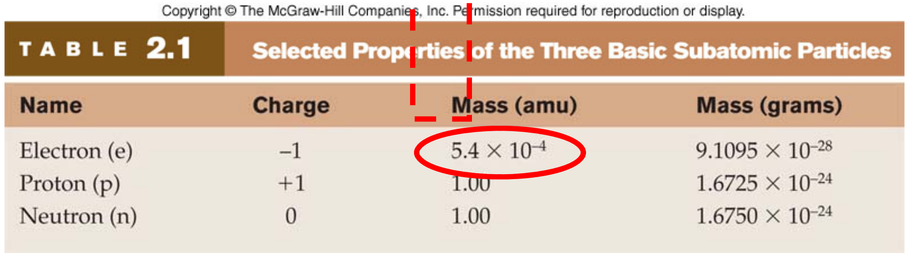
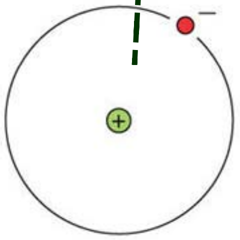


TABLE 2.1 Selected Properties of the Three Basic Subatomic Particles

Name	Charge	Mass (amu)	Mass (grams)
Electron (e)	–1	5.4×10^{-4}	9.1095×10^{-28}
Proton (p)	+1	1.00	1.6725×10^{-24}
Neutron (n)	0	1.00	1.6750×10^{-24}



Chapter 13, Physical Chemistry for the Life Sciences (Engel, Drobny and Reid)

Different Systems

(Chapter 14 ~ Chapter 18)

- 不同的系統，
  有不同的 Schröedinger equation 的解

Schröedinger equation 的解，是 Orthogonal。

$$\int_{-\infty}^{\infty} \psi_i^*(x)\psi_j(x)dx = \begin{cases} 0, i \neq j \\ 1, i = j \end{cases} \qquad (13.21)$$

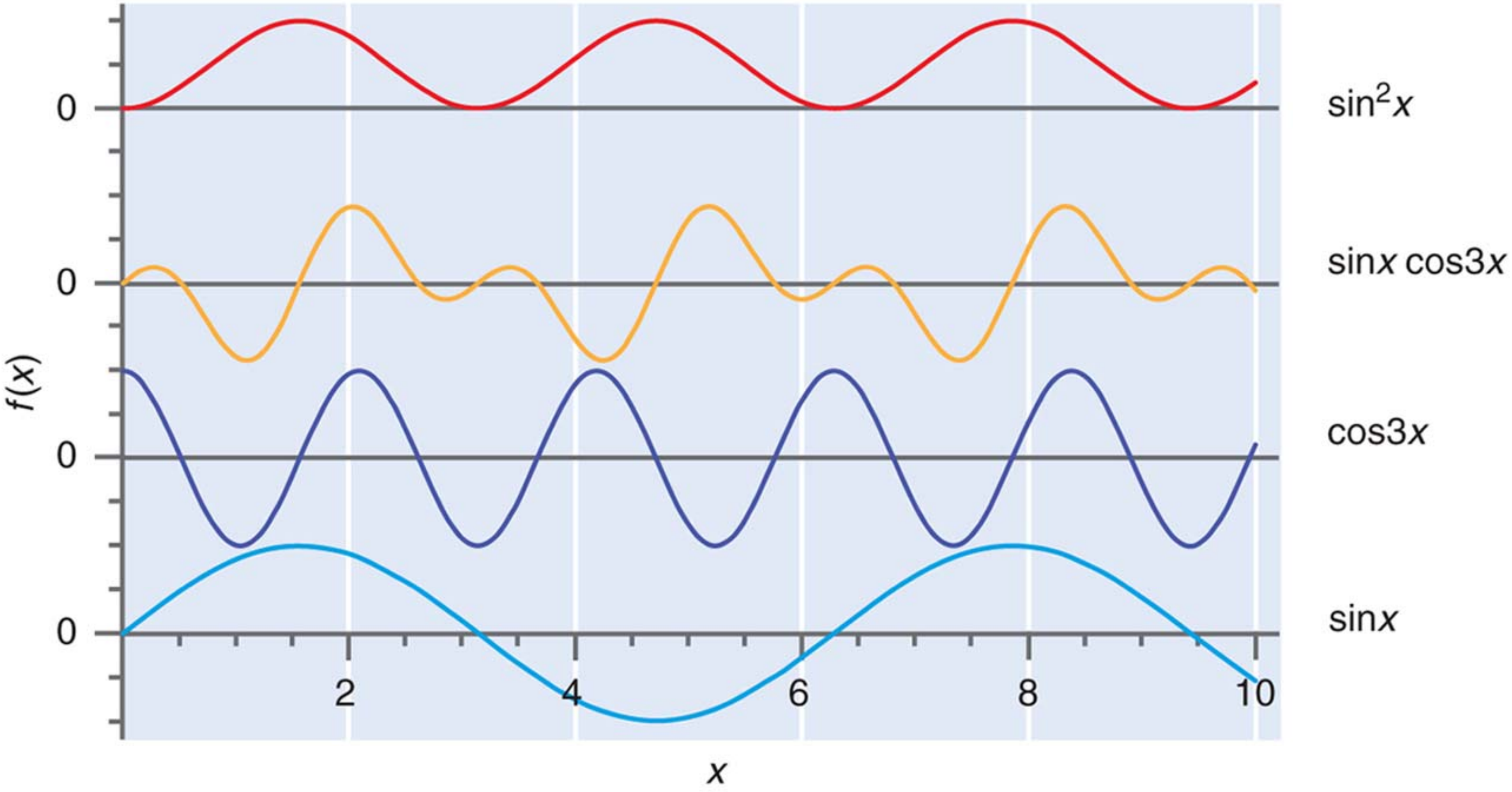


Figure: 13-02EP

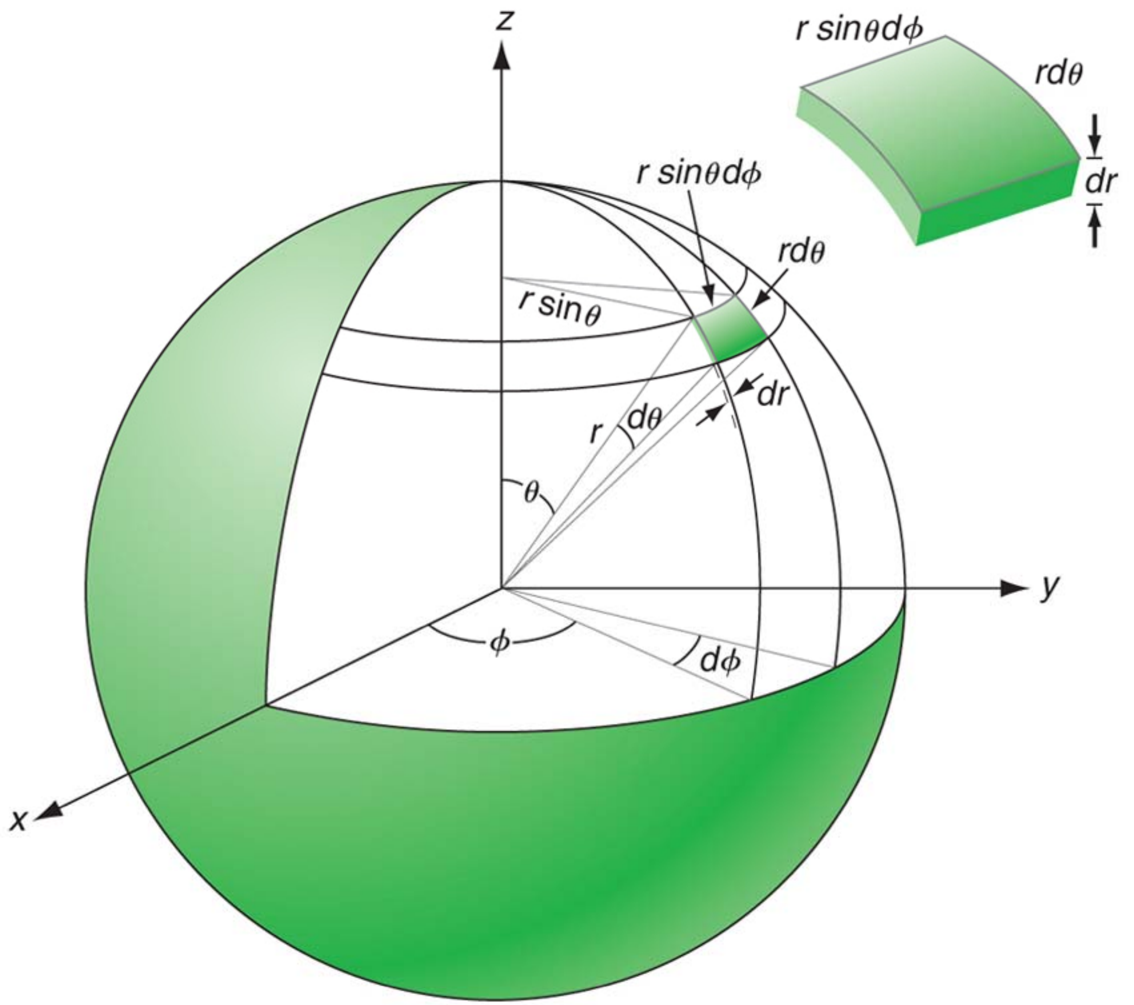
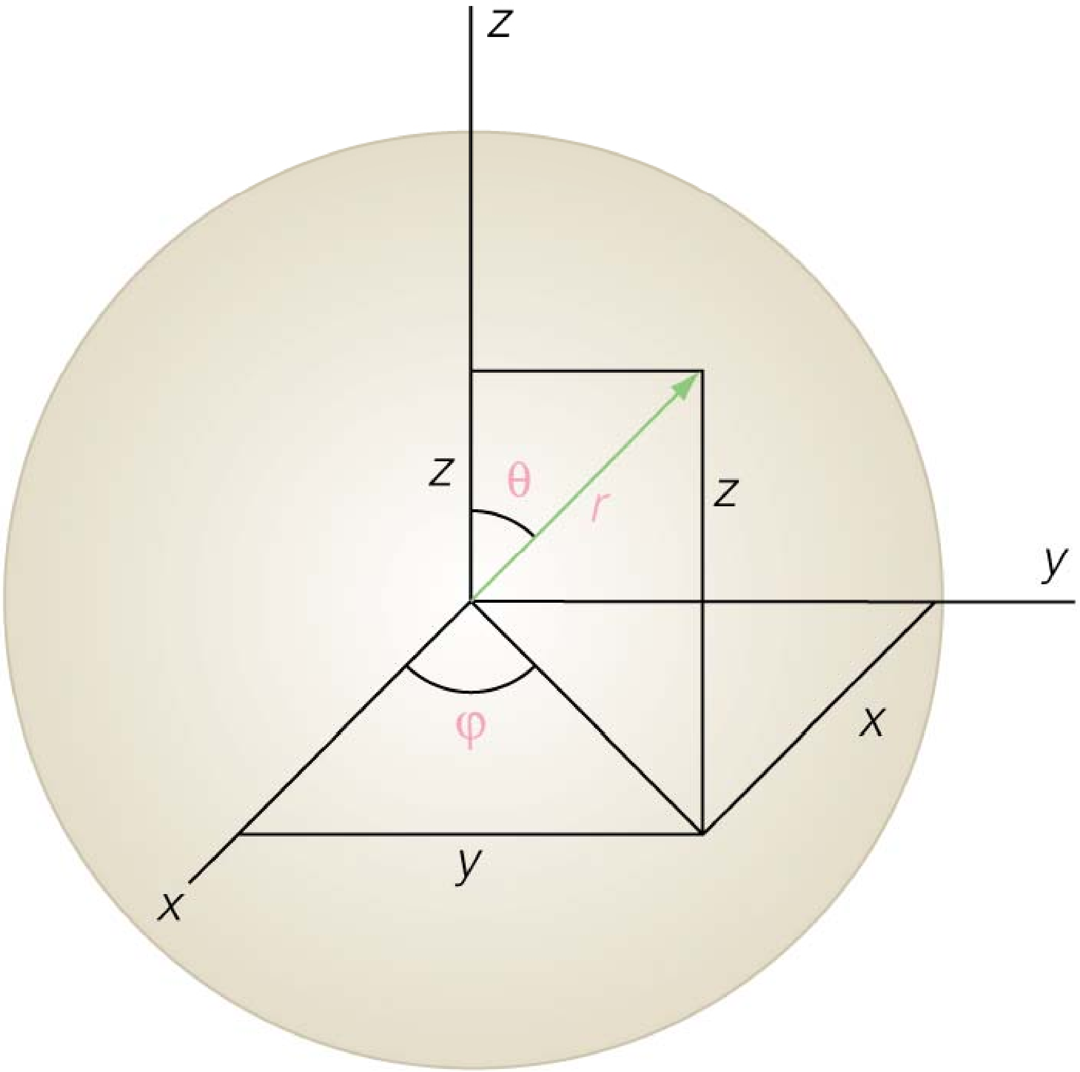
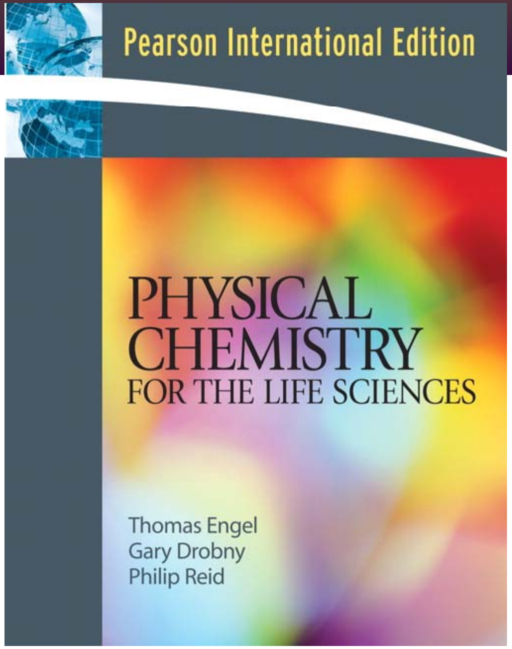


Figure: 13-07


z
z
θ
r
z
y
φ
x
y
x

Physical Chemistry

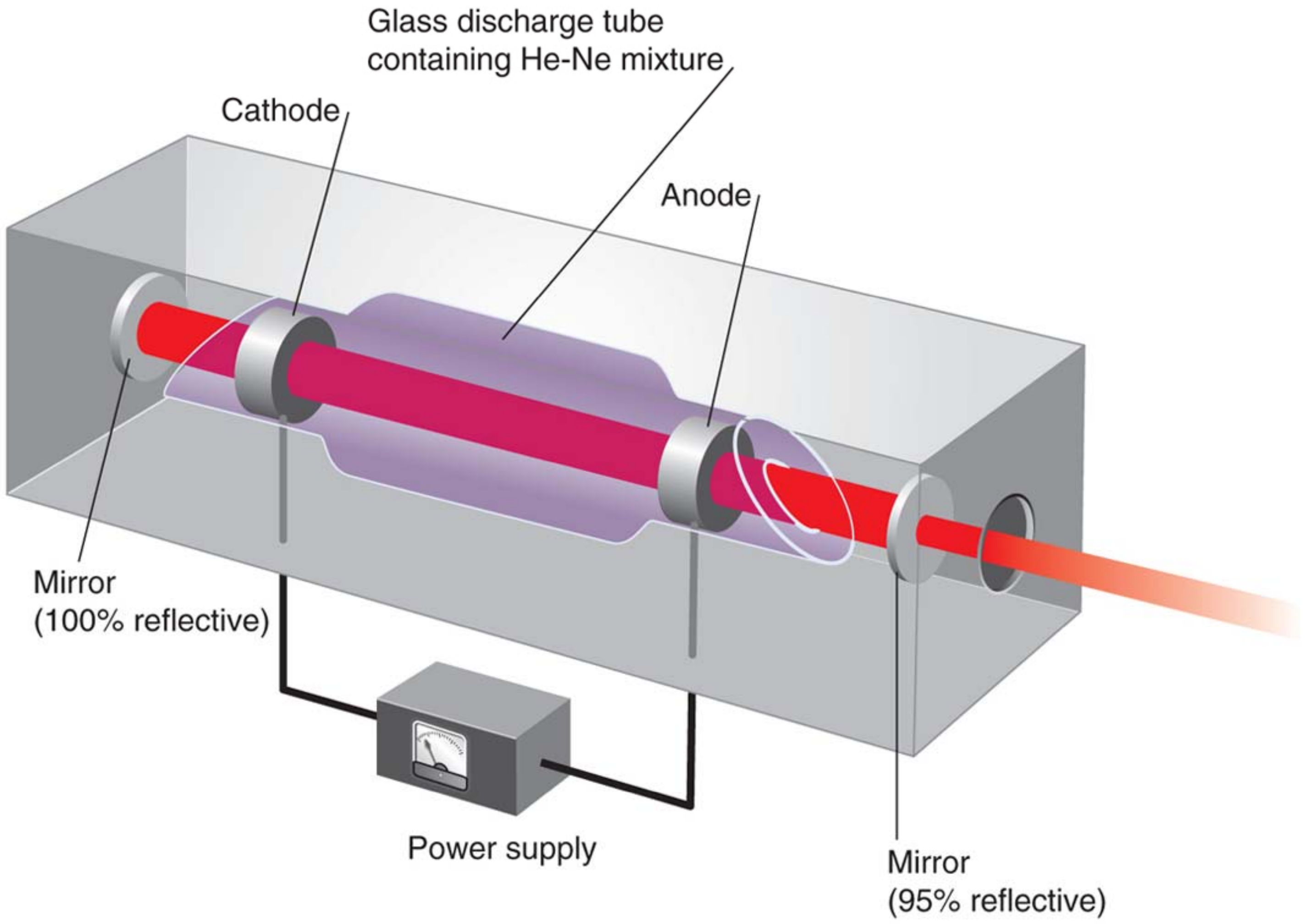
For the Life Sciences



CHAPTER 19

Electronic Spectroscopy

The Helium-Neon laser



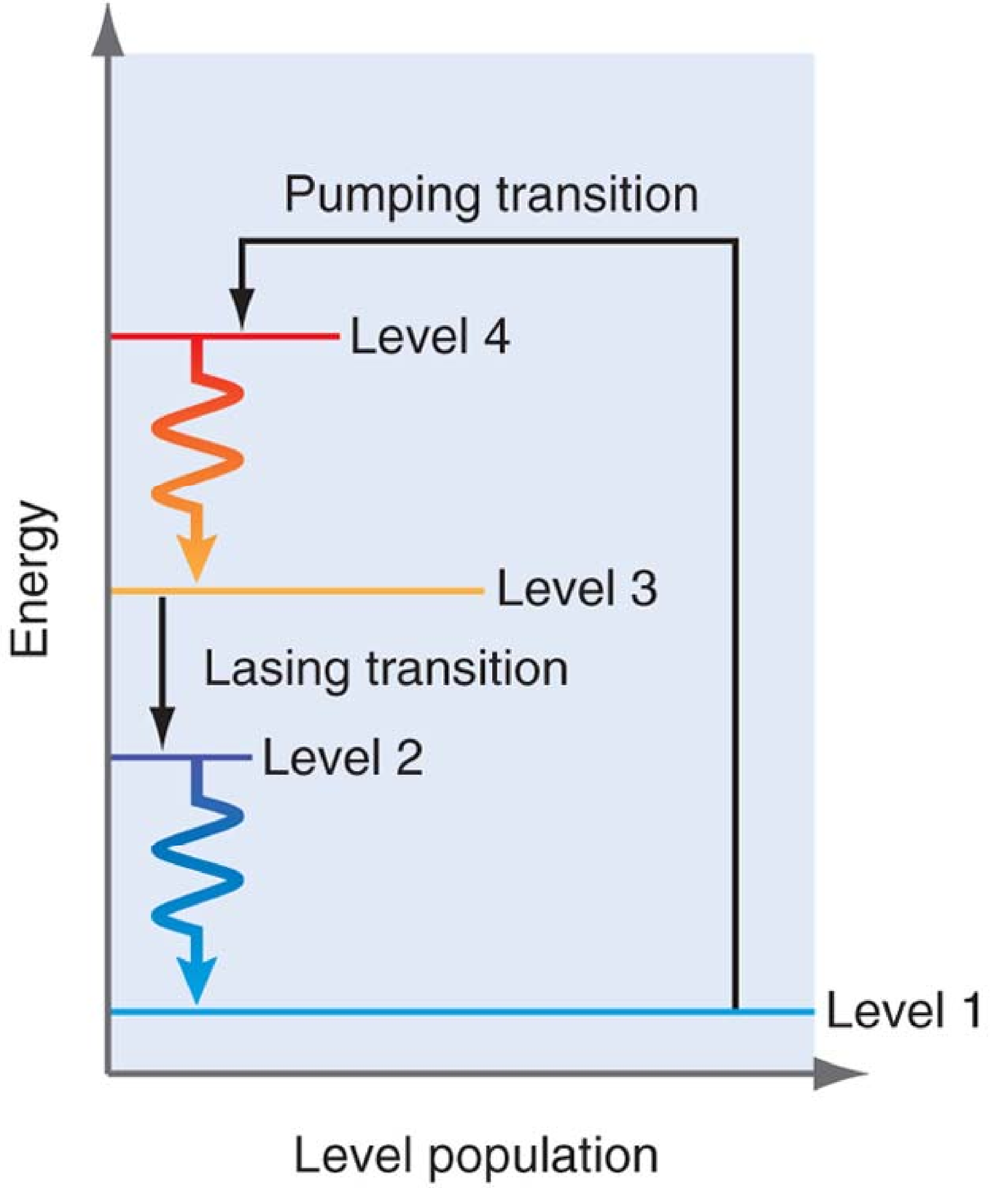


FIGURE 19.4

Schematic representation of a four-state laser. The energy is plotted vertically, and the level population is plotted horizontally.

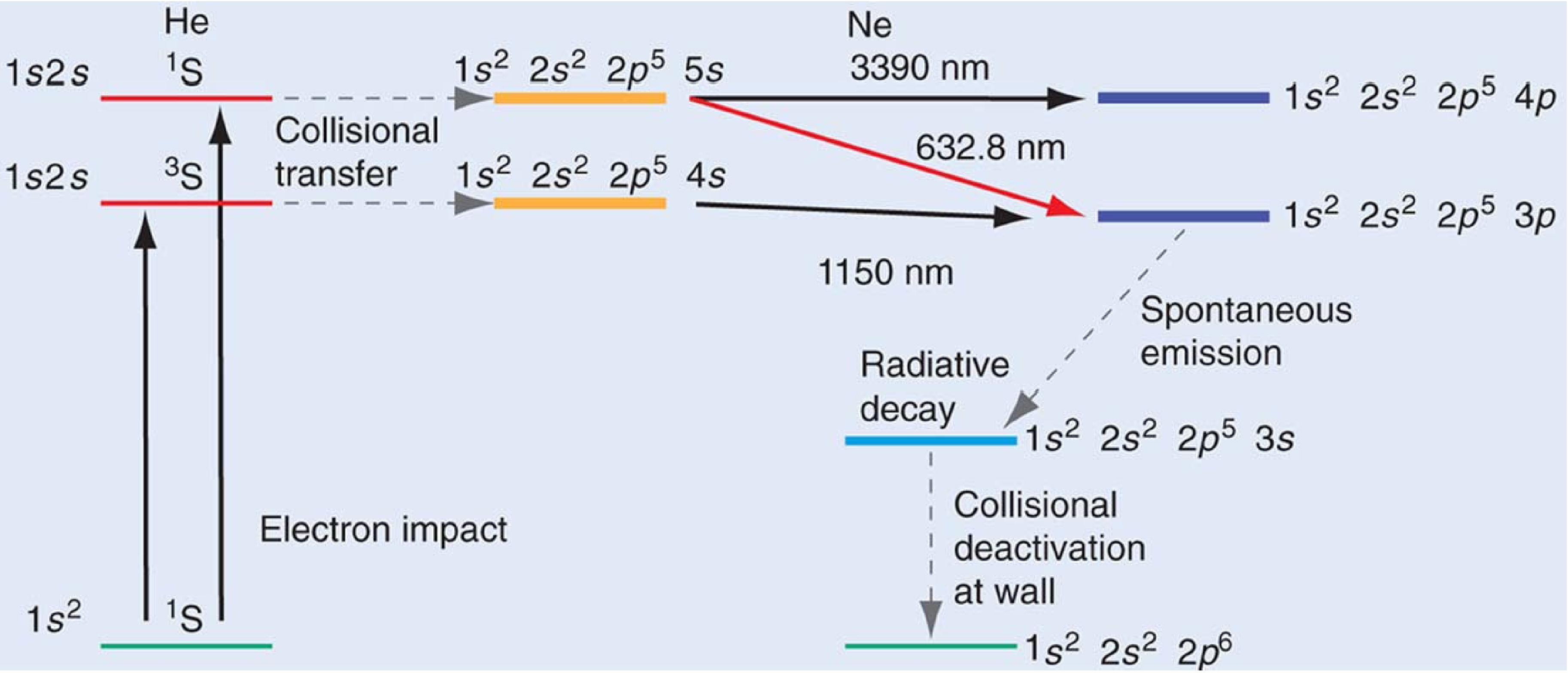


FIGURE 19.8

Transitions in the He-Ne laser. The slanted solid show three possible lasing transitions.

The energy of electronic transitions in molecules

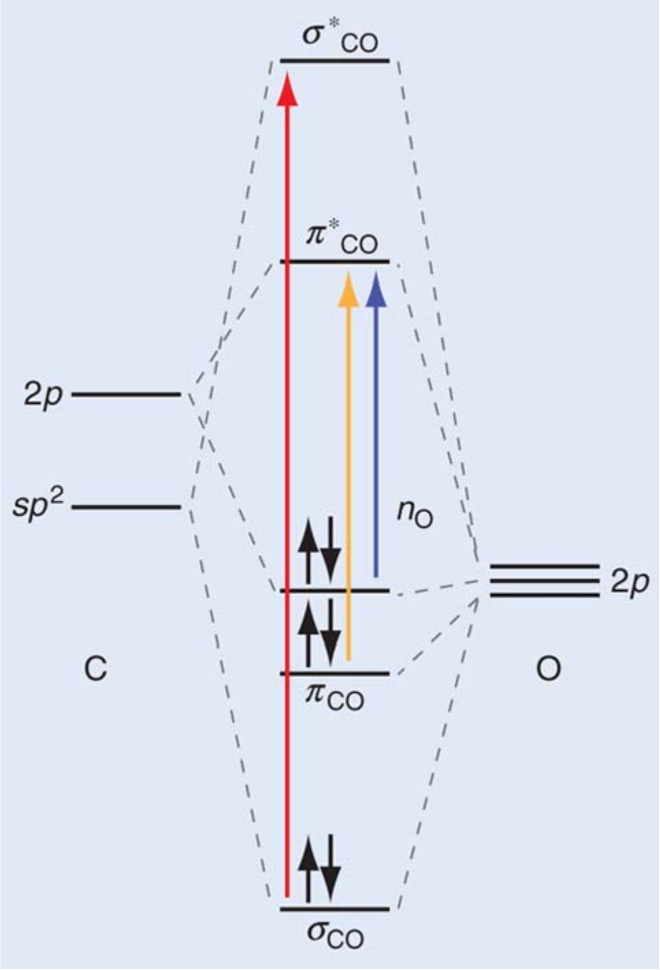
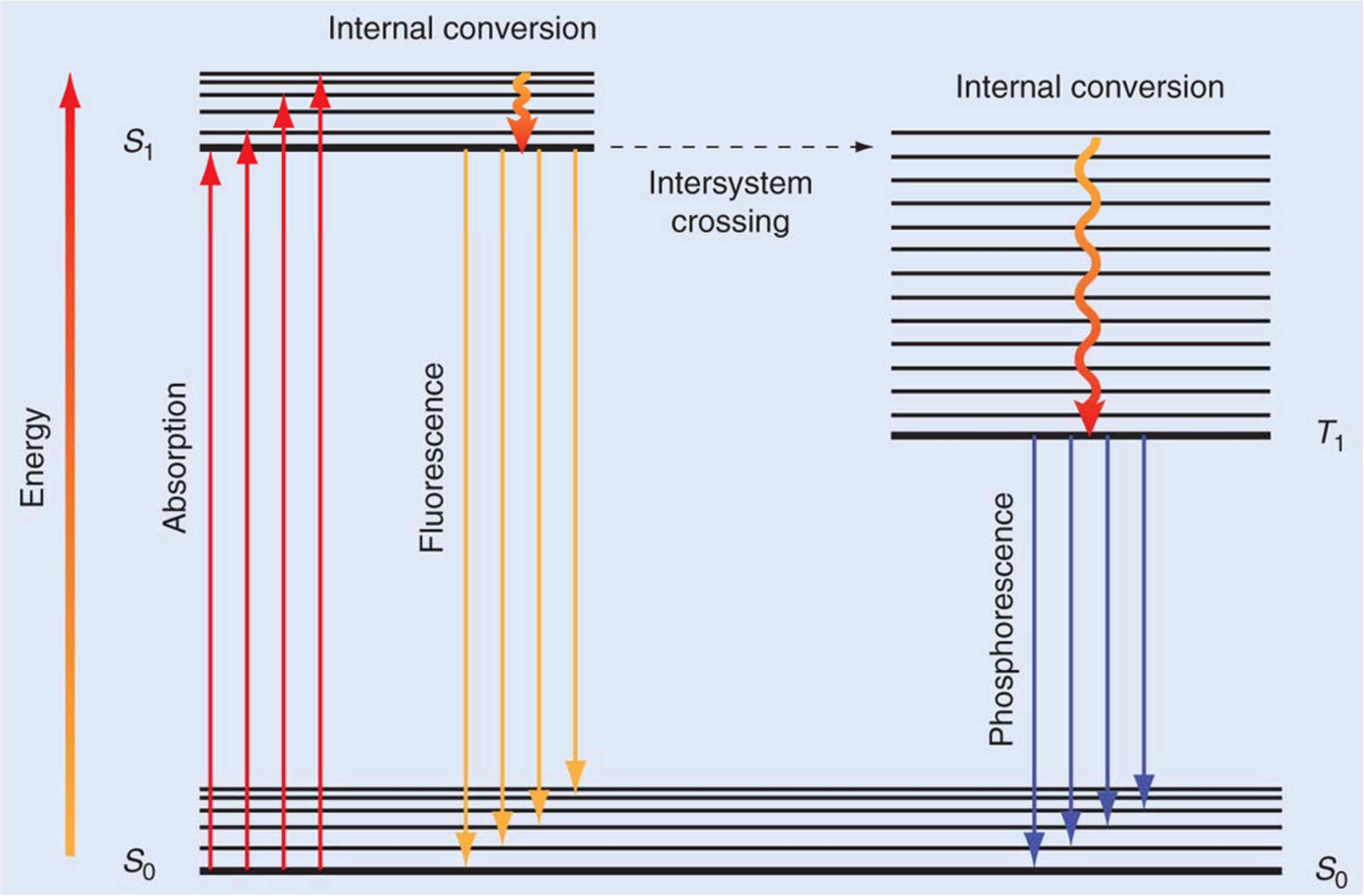


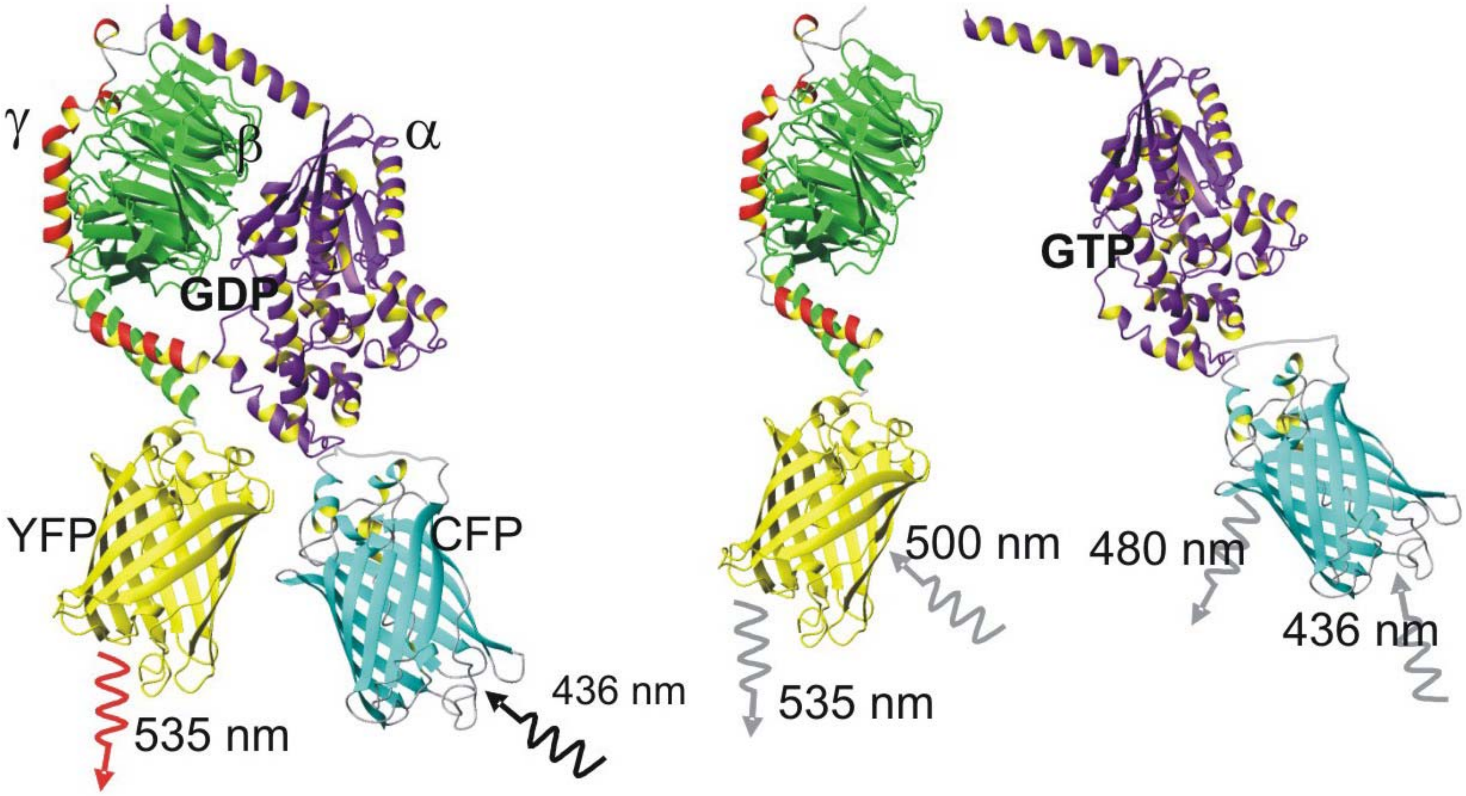
FIGURE 19.14

A simplified MO energy diagram is shown for the C—O bonding interaction in formaldehyde. The most important allowed transitions between these levels are shown. Only one of the *sp*^{2} orbitals on carbon is shown because the other two hybrid orbitals form σ_{CH} bonds.

Fluorescence and Phosphorescence



FRET: Fluorescence Resonance Energy Transfer



circular dichroism

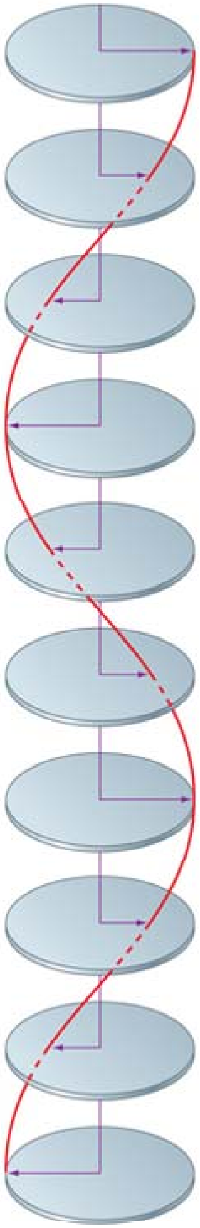


FIGURE 19.28

The arrows in successive images indicate the direction of the electric field vector as a function of time or distance. For linearly polarized light, the amplitude to the electric field vector changes periodically, but is confined to the plane of polarization.

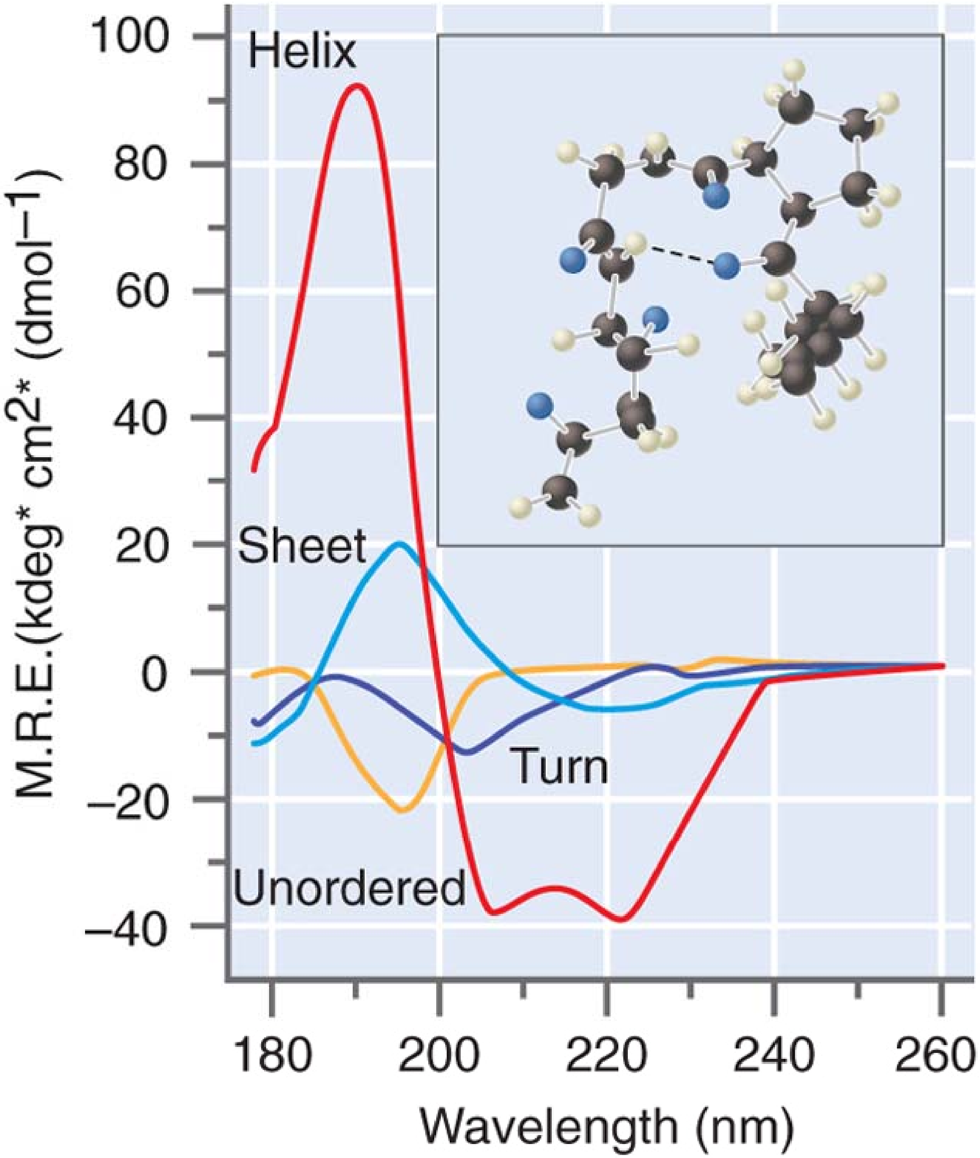
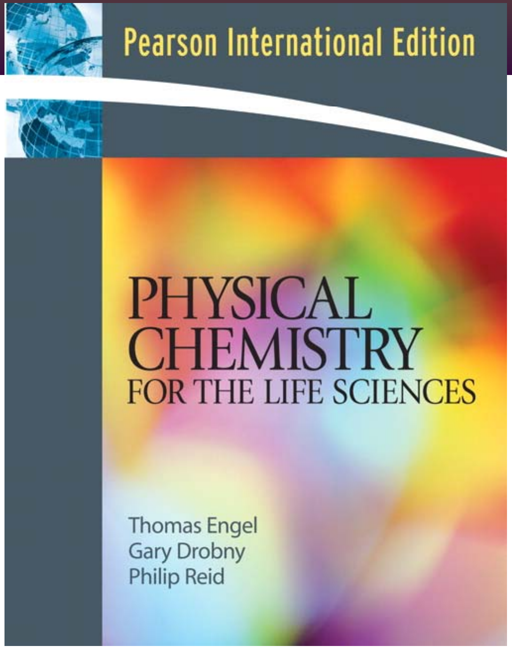


FIGURE 19.32

The rotation angle θ is shown as a function of wavelength for biomolecules having different secondary structures. Because the curves are distinctly different, circular dichroism spectra can be used to determine the secondary structure for optically active molecules. The inset shows the hydrogen bonding between different amide groups that generates different secondary structures.

Physical Chemistry

For the Life Sciences



Pearson International Edition

PHYSICAL
CHEMISTRY
FOR THE LIFE SCIENCES

Thomas Engel
Gary Drobny
Philip Reid

CHAPTER 20

Nuclear Magnetic Resonance Spectroscopy

Y.T.Lin's Presentation

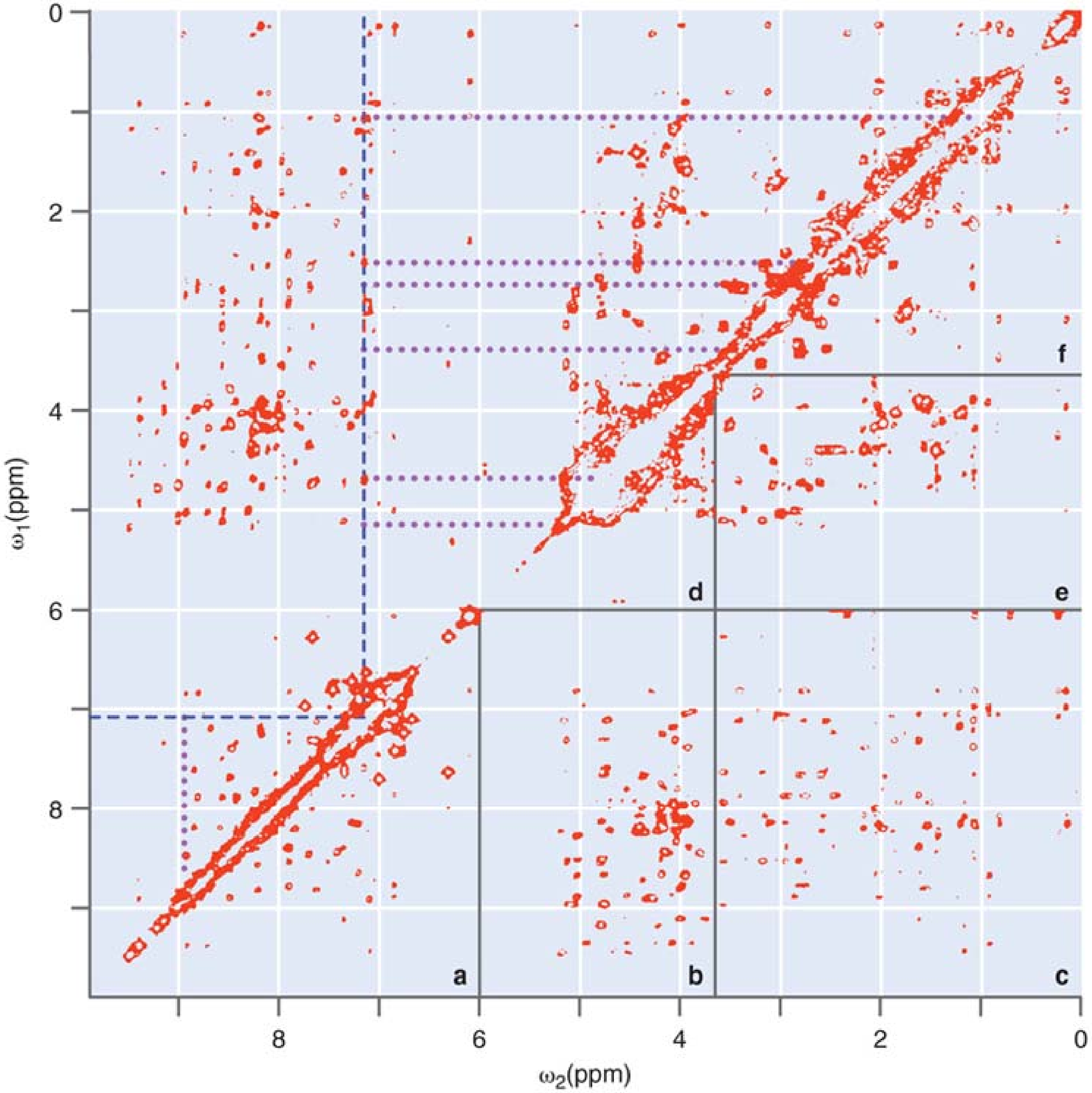


FIGURE 20.35

The proton NOESY spectrum of the proteinase inhibitor BUSI II. The spectrum below the diagonal is divided into six regions a through f that denote cross peaks between distinct proton types (see text). Above the diagonal, the vertical dotted line identifies cross peaks, between an amide proton at 7.2 ppm to six other types of protons, indicated by horizontal dotted lines. The amide proton at 7.2 ppm also has an NOE cross peak to another proton at 8.9 ppm.

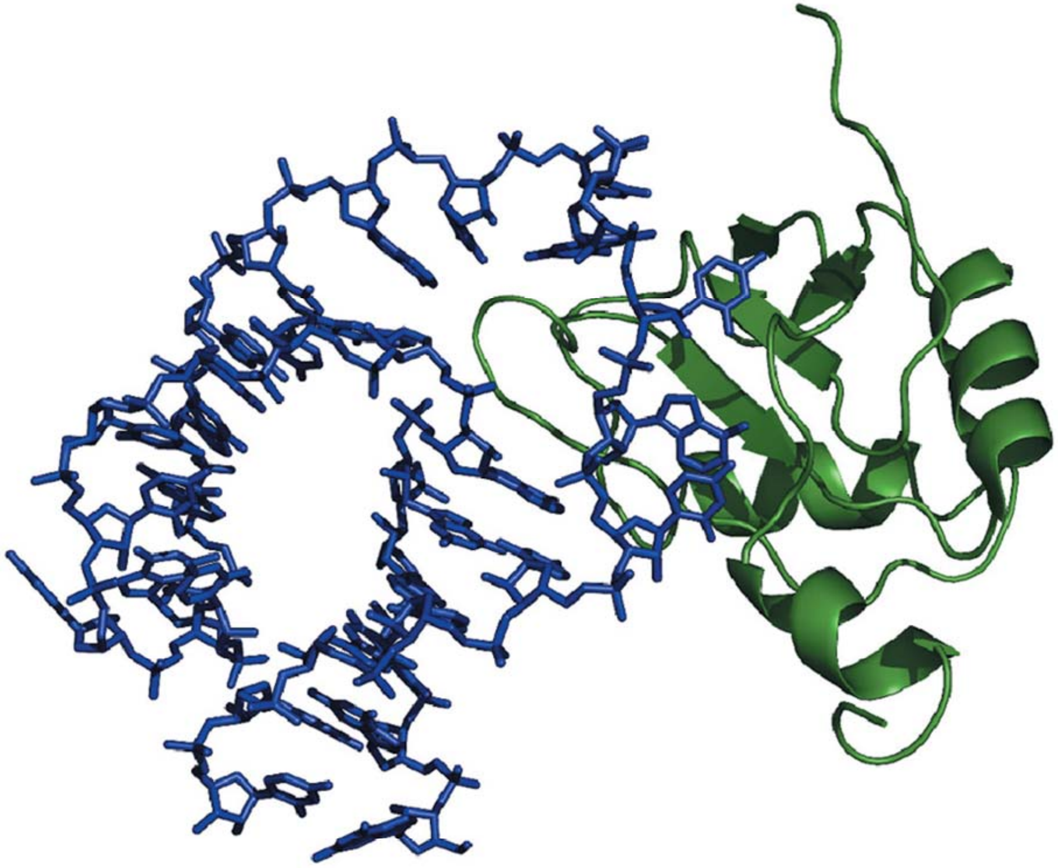


FIGURE 20.37

The structure of the complex formed between UTR RNA (shown in blue) and the U1A protein (show in green).

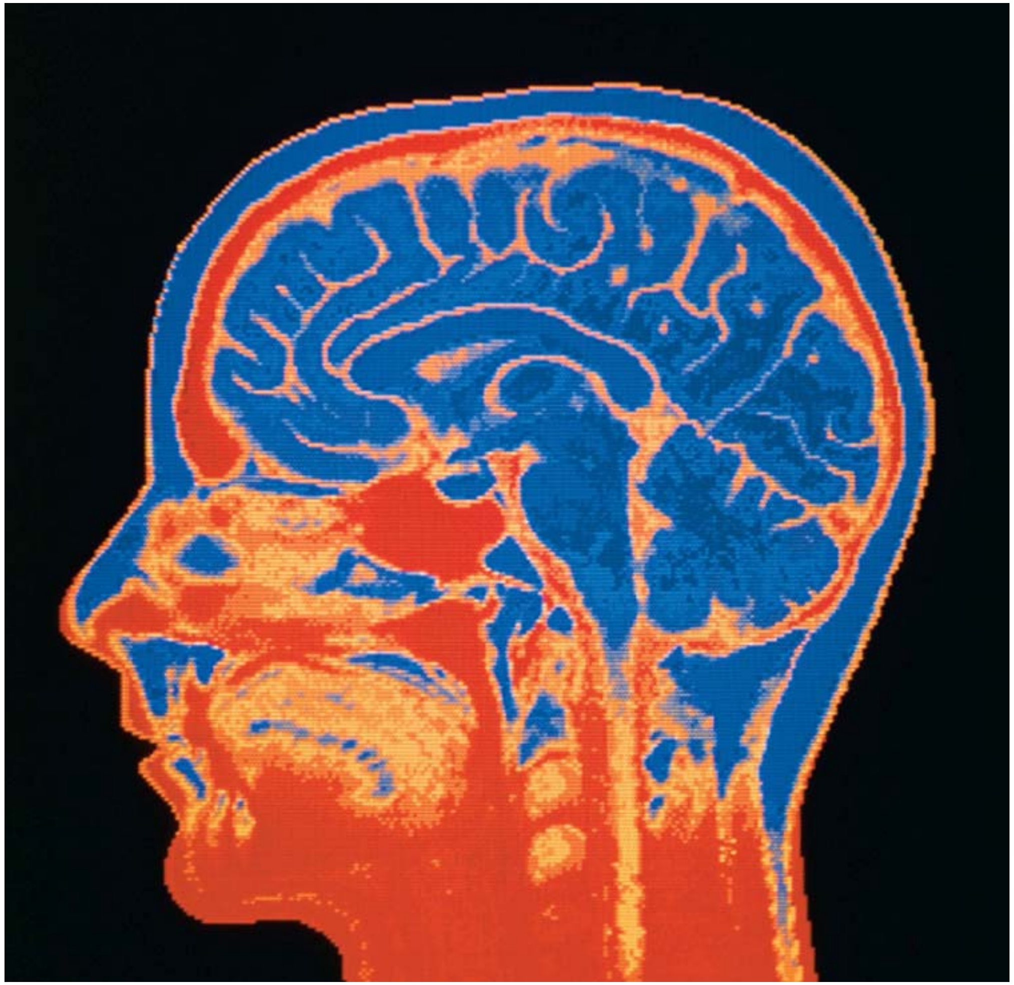
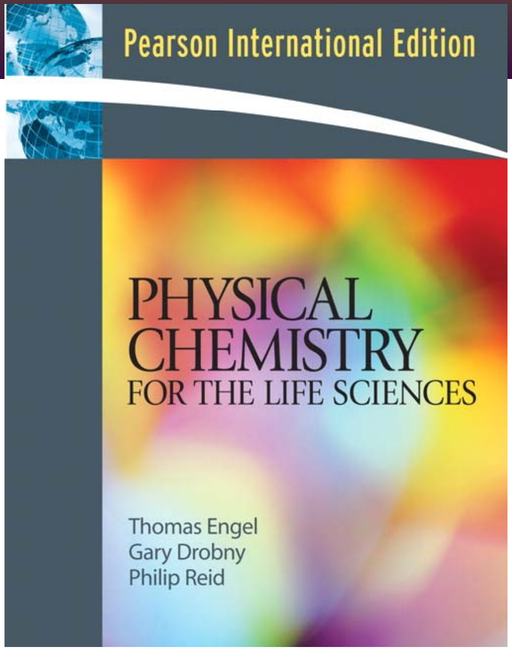


FIGURE 20.45

This figure shows an NMR image taken of a human brain. The section shown is obtained from a noninvasive scan of the patient's head. The contrast has its origin in the dependence of the relaxation time on the strength of binding of the water molecule to different biological tissues.

Physical Chemistry

For the Life Sciences



Pearson International Edition

PHYSICAL CHEMISTRY
FOR THE LIFE SCIENCES

Thomas Engel
Gary Drobny
Philip Reid

CHAPTER 21

Y.T.Lin's Presentation

X-ray structure

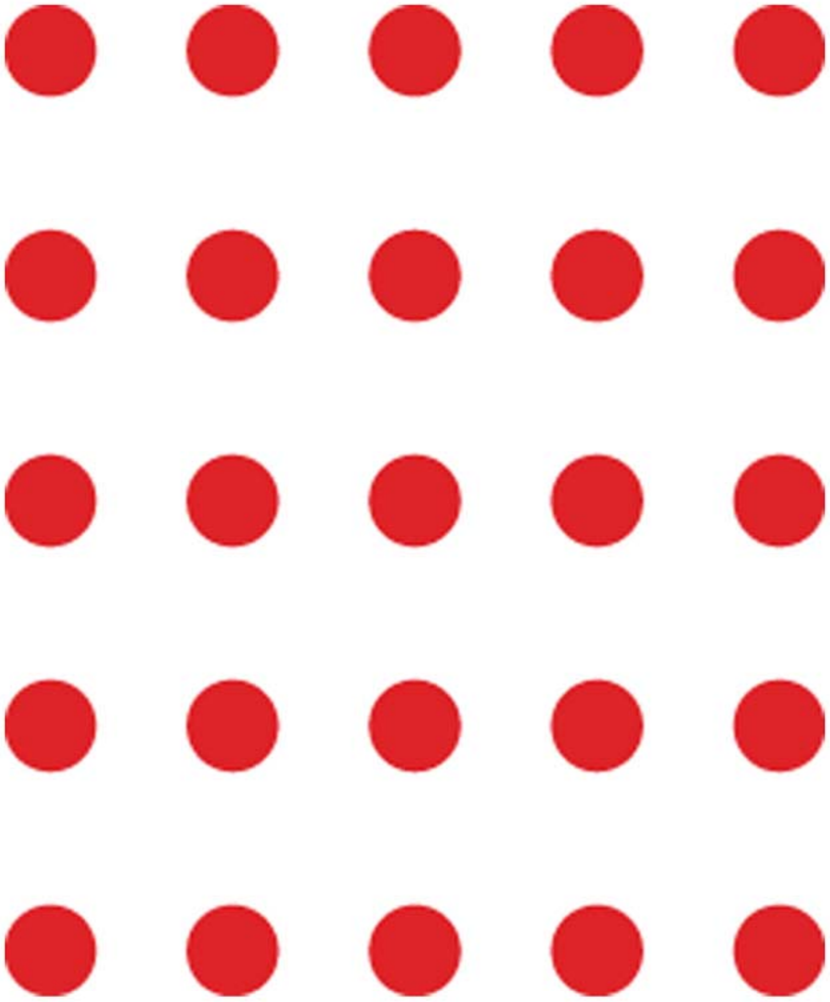


FIGURE 21.13

The diffraction pattern of a two-dimensional crystal, the axes of which are perpendicular, is a rectangular array of points that we call diffraction spots.

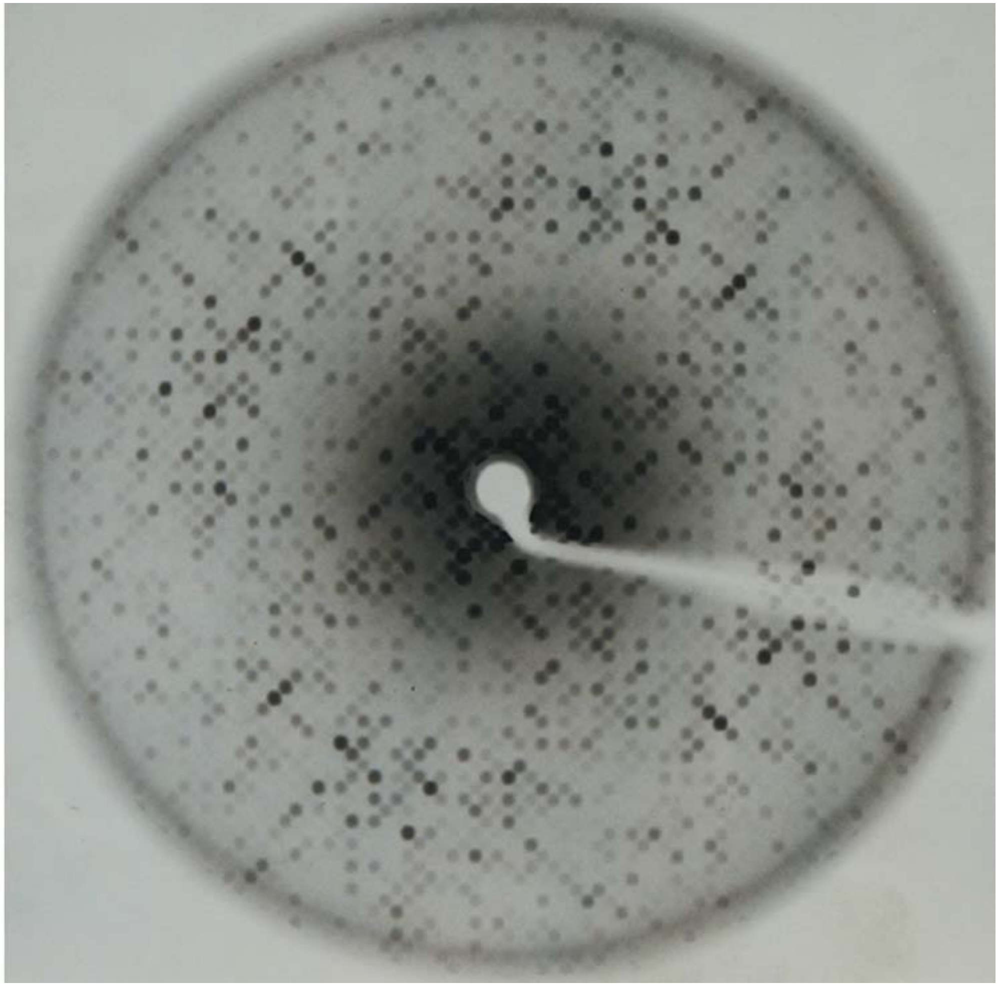


FIGURE 21.14

A diffraction image taken using the precession method is shown for the metalloprotein hemerythrin. All of the diffraction spots can be assigned indices *h* and *k* and *l* = 0.

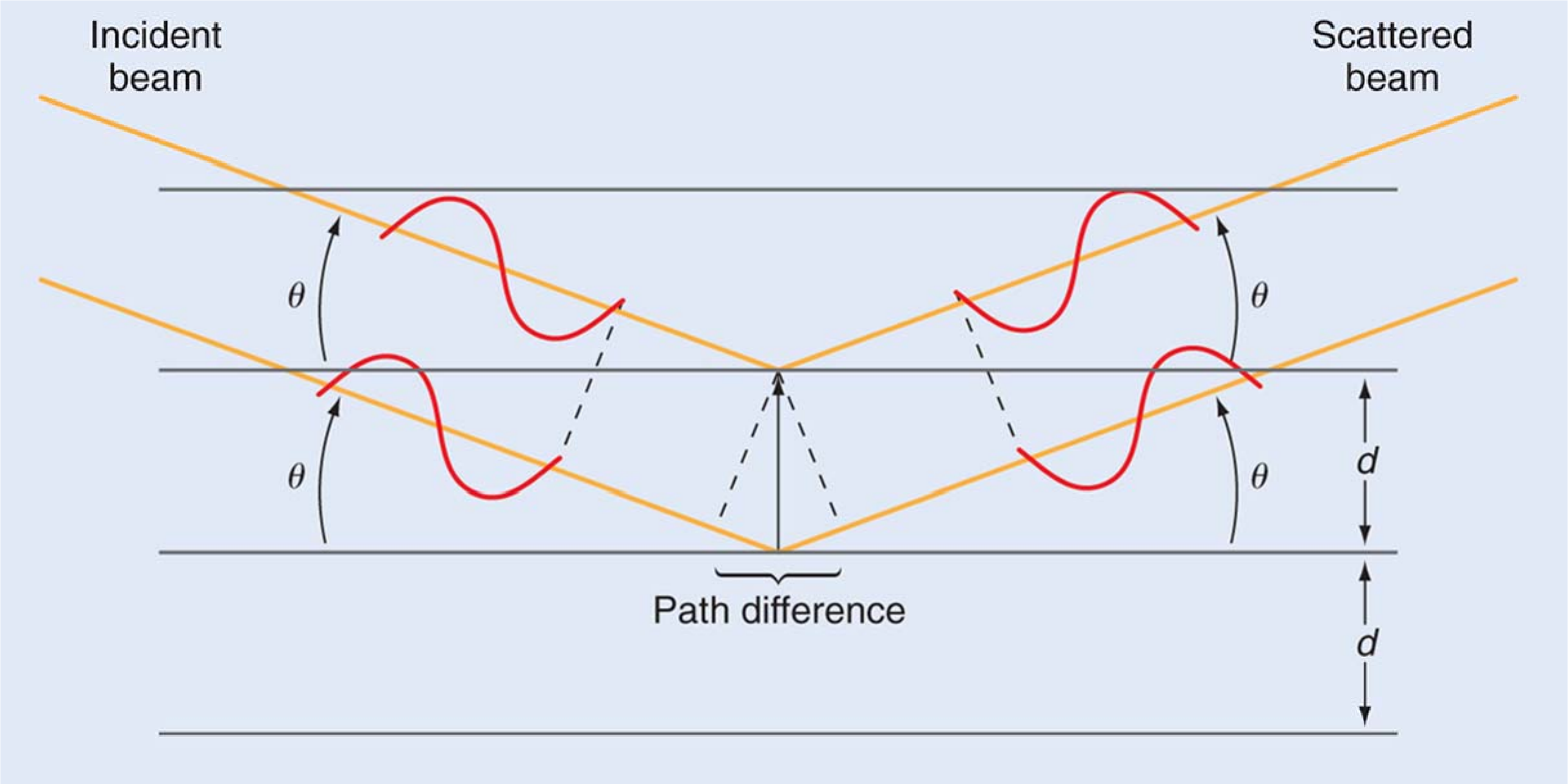


FIGURE 21.15

Diffraction from a set of parallel crystal planes is depicted. To simplify the drawing, the lattice motif is not shown. Diffraction or constructive interference is observed if the path difference between adjacent planes is an integral multiple of the X-ray wavelength.

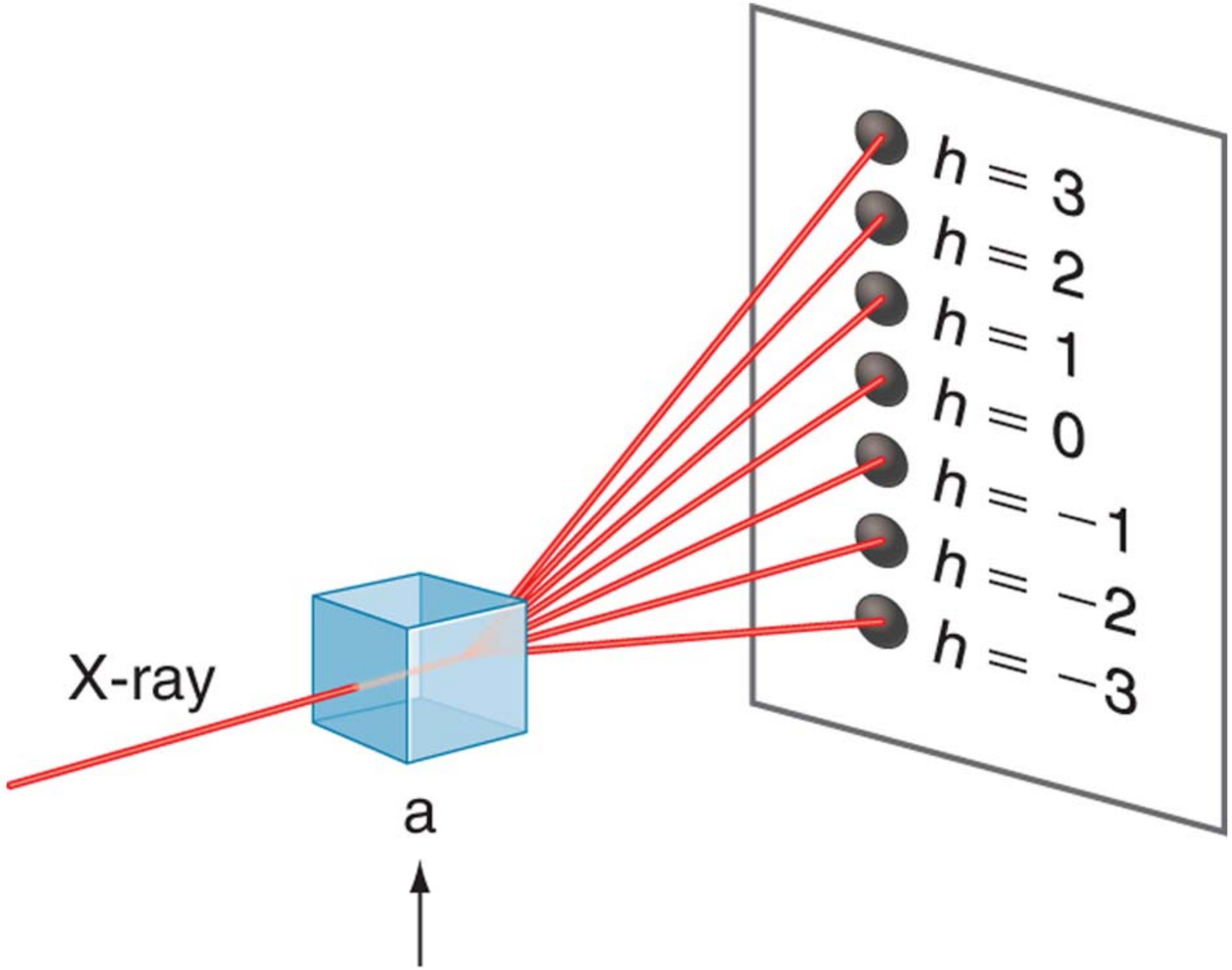


FIGURE 21.16

The diffraction pattern from the set of (100) planes is shown. Each spot corresponds to a different diffraction order.

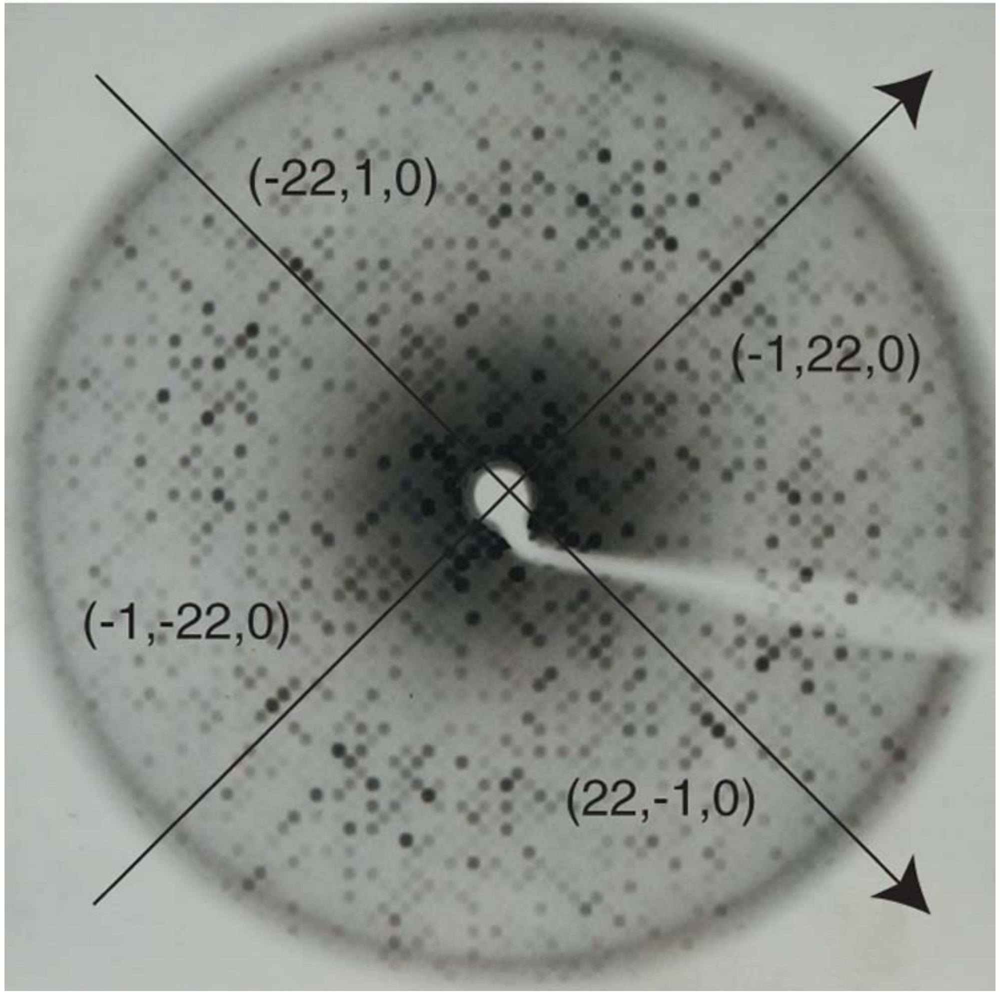


FIGURE 21.17

The diffraction pattern of Figure 21.14 with the indices of four planes giving rise to the diffraction spots is shown. On the basis of this indexing, the unit cell for hemerythrin has the dimensions $a = b = 8.66$ nm. The diffraction pattern obtained by rotating the crystal by 90° gives $c = 8.08$ nm.

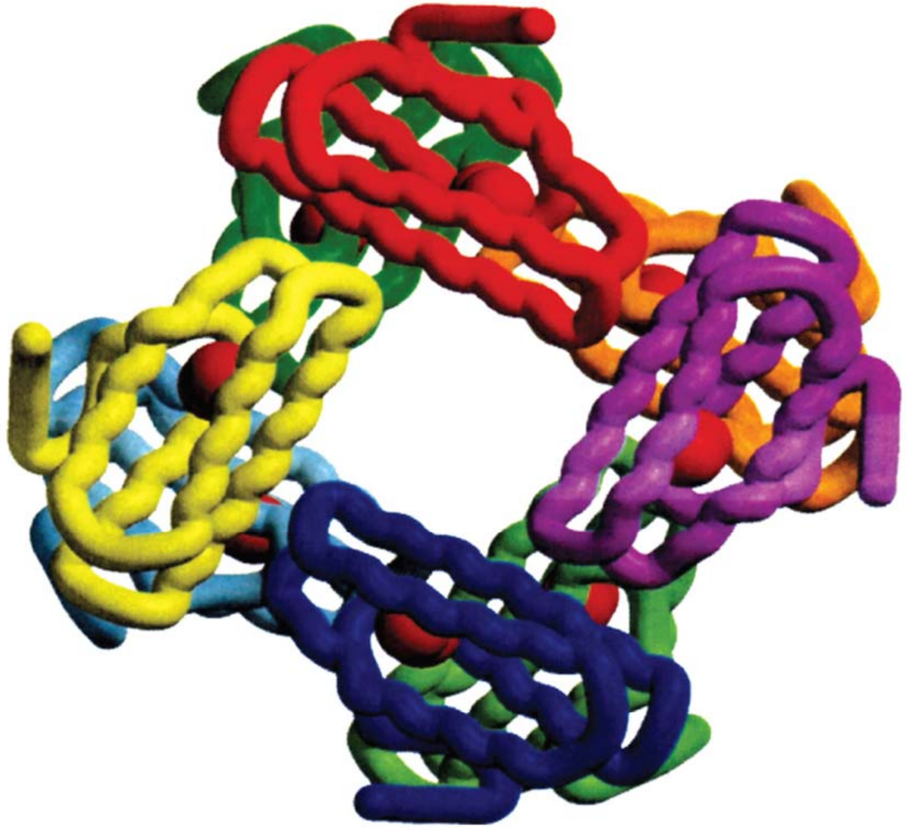


FIGURE 21.18

Hemerythrin consists of eight identical subunits, each of which is made up of a polypeptide containing 113 amino acids, two iron atoms (red spheres), and a single oxygen atom bridging the iron atoms. The polypeptide folds into four α-helices that pack in an antiparallel arrangement forming the tertiary structure of the subunit.

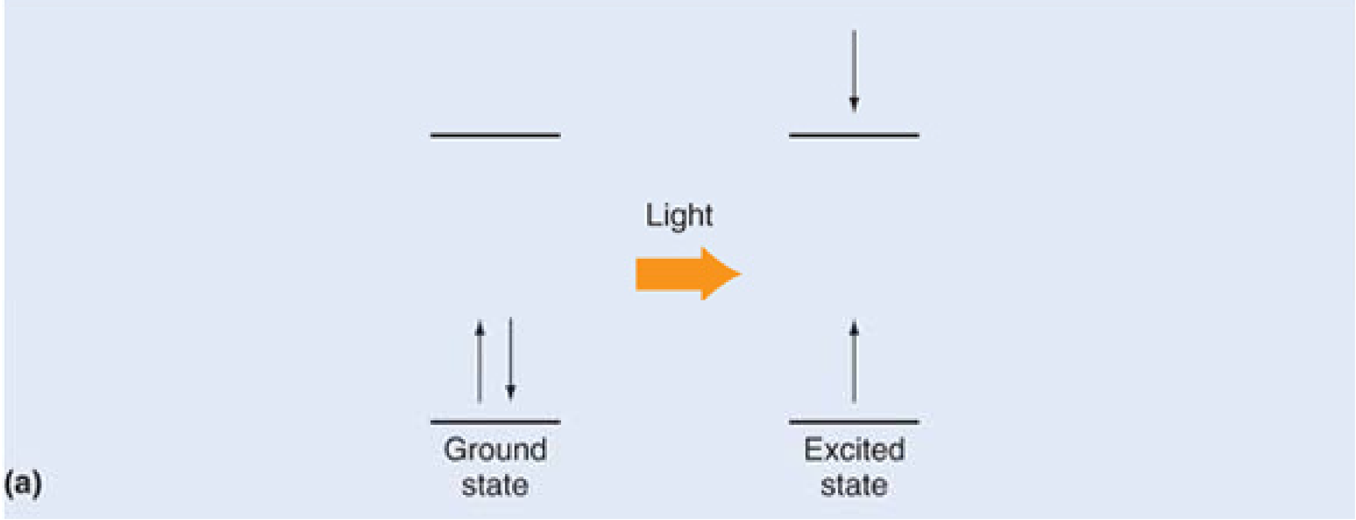


FIGURE 21.25

(a) Light absorption in LH1 and LH2 occurs through electronic excitations.
(b) Energy can also be transferred from one molecule to another through
an electron transfer (redox) reaction.

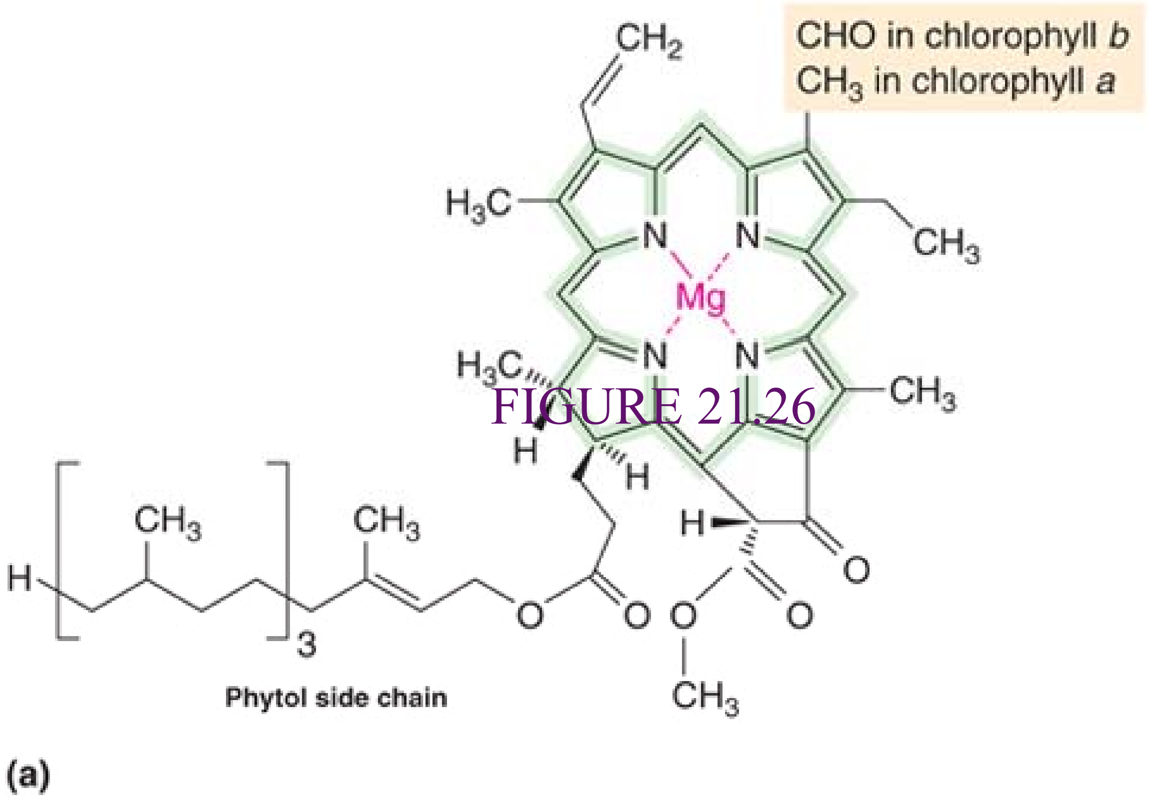


FIGURE 21.26

FIGURE 21.26

(a) Chlorophylls *a* and *b* and bacteriochlorophyll are the primary light absorbers in photosynthesis. The shading indicates the conjugated π-electron network. (b) β-cartene and (c) phycocyamin are examples of additional pigments that also absorb sunlight.

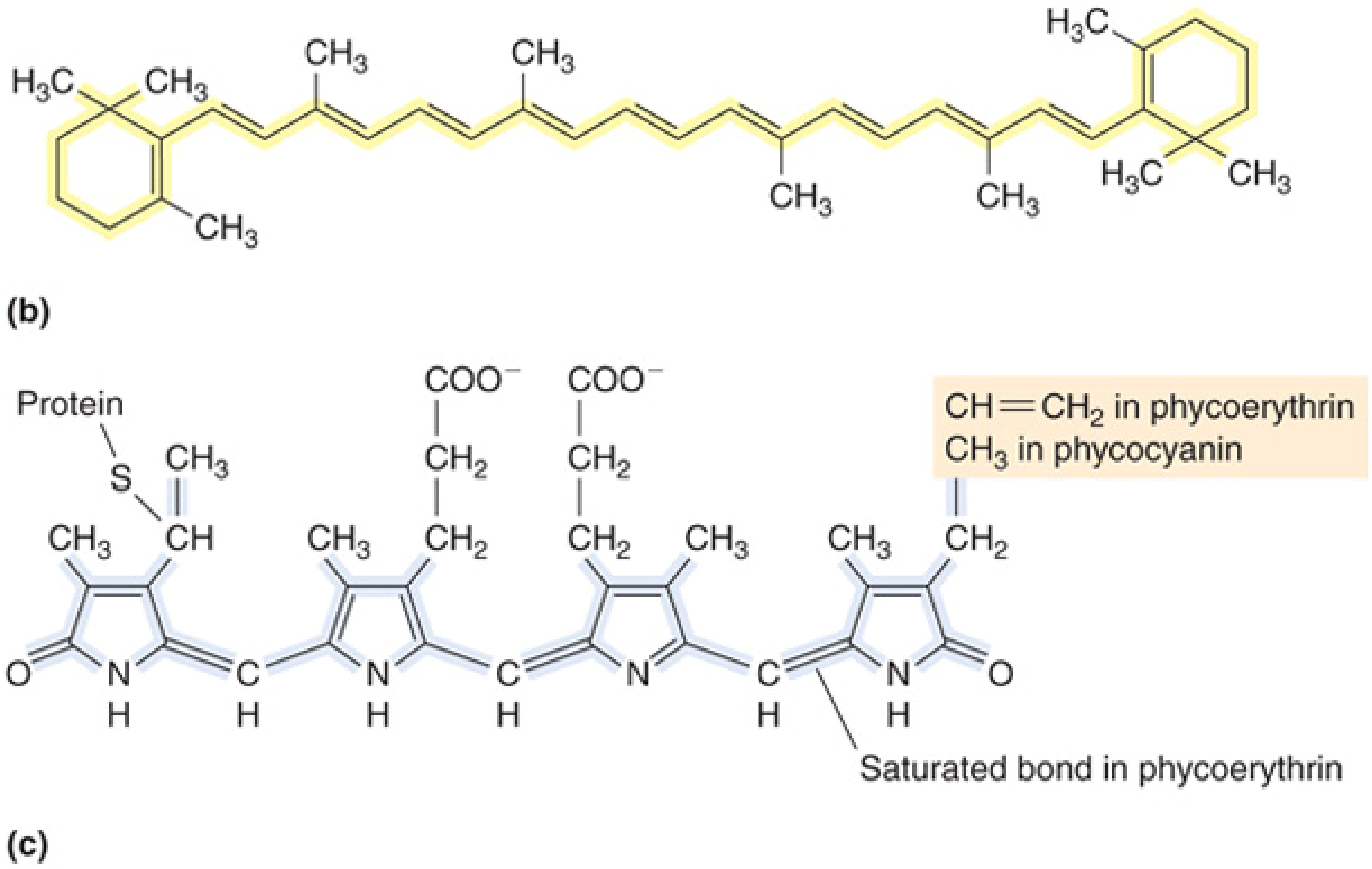


FIGURE 21.26

(continued)

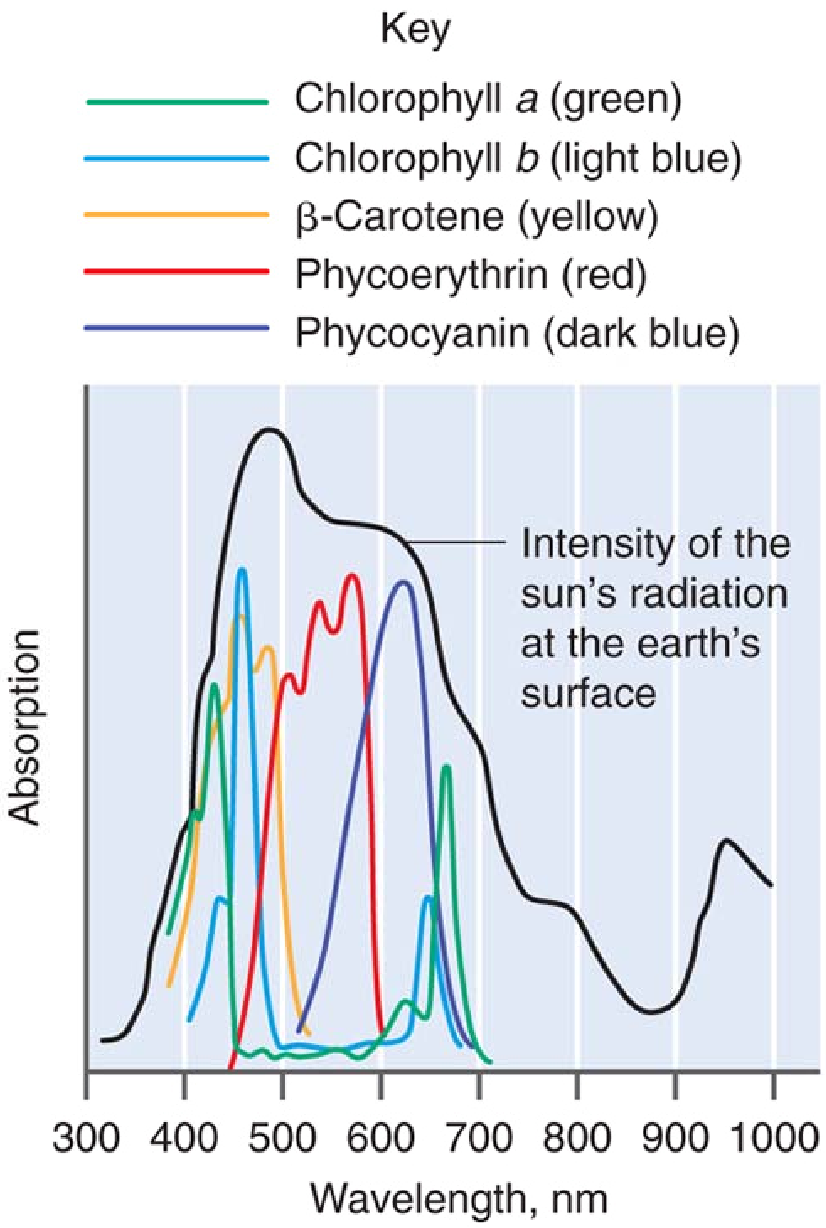


FIGURE 21.27

The colored curves show the absorption spectrum of the light absorbers shown in Figure 21.26. The black curve shows the wavelength distribution in sunlight.

P. 539

End of Lecture

Slide Downloading

http://ytlab.kmu.edu.tw