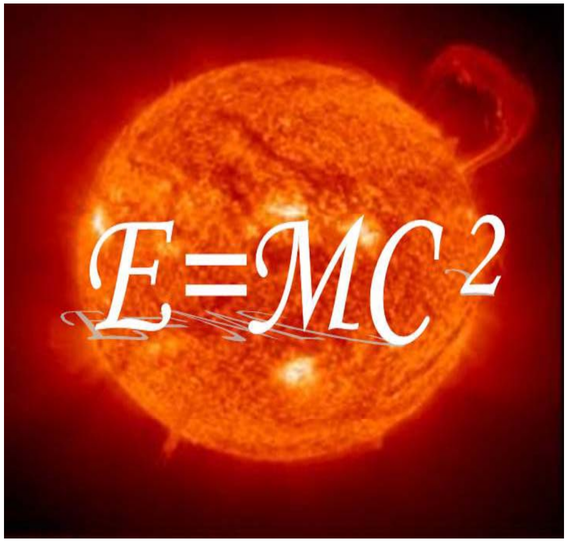
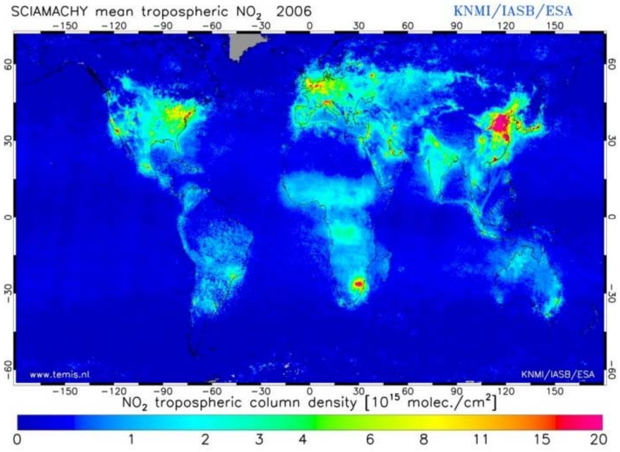
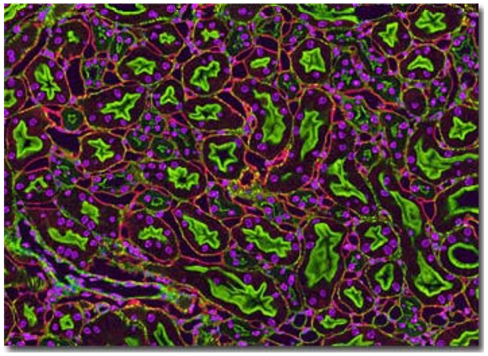
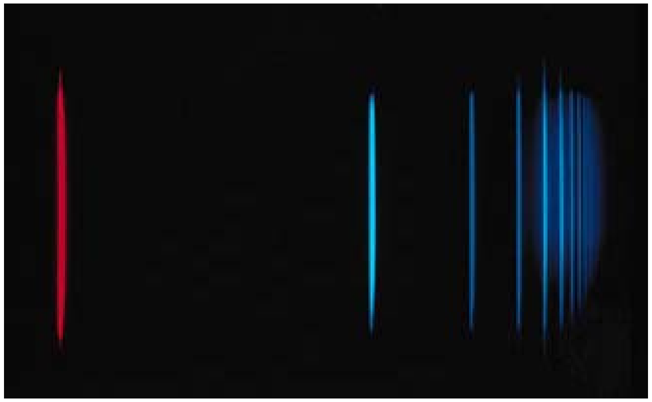
Interaction of Light with Matter









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CHEM 5161

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Wave Particle Duality

- Huygens “planar wavefront” vs Newtons “Corpuscular Theory”, 1600’s

- Young and Fresnel, early 1800s “Double slit experiment”
  - Maxwell, late 1800s “Maxwell equations”

wave

- Max Planck, 1901 “Black body radiation”
- Albert Einstein, 1905 “Photoelectric effect”, $E = h\nu$

particle

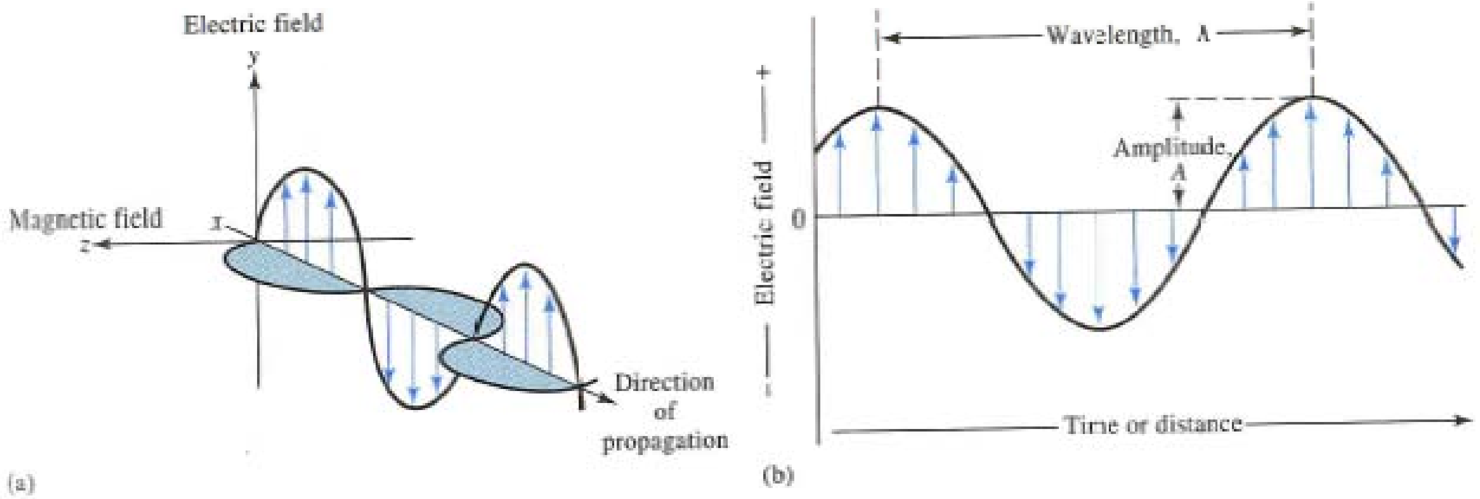
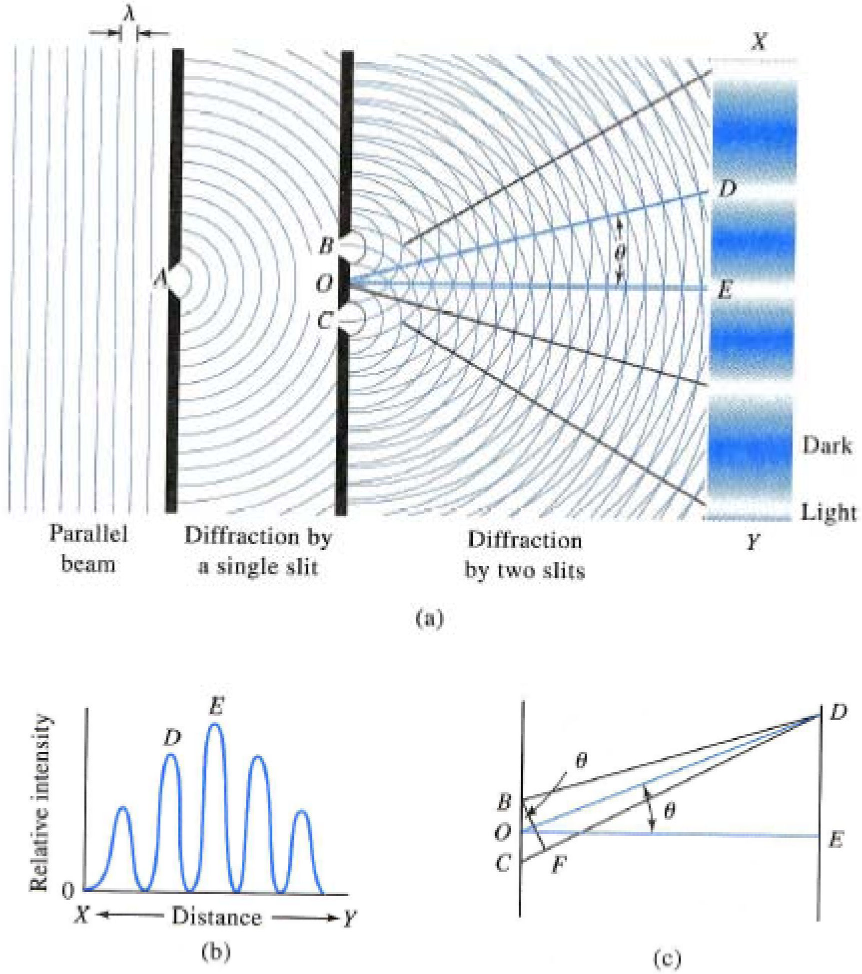


FIGURE 6-1 Wave nature of a beam of single-frequency electromagnetic radiation. In (a), a plane-polarized wave is shown propagating along the x-axis. The electric field oscillates in a plane perpendicular to the magnetic field. If the radiation were unpolarized, a component of the electric field would be seen in all planes. In (b), only the electric field oscillations are shown. The amplitude of the wave is the length of the electric field vector at the wave maximum, while the wavelength is the distance between successive maxima.

Young and Fresnel, 1803
“Double slit experiment”



(a)

(b)

(c)

FIGURE 6-8 Diffraction of monochromatic radiation by slits.

Albert Einstein, 1905
“Photoelectric effect”

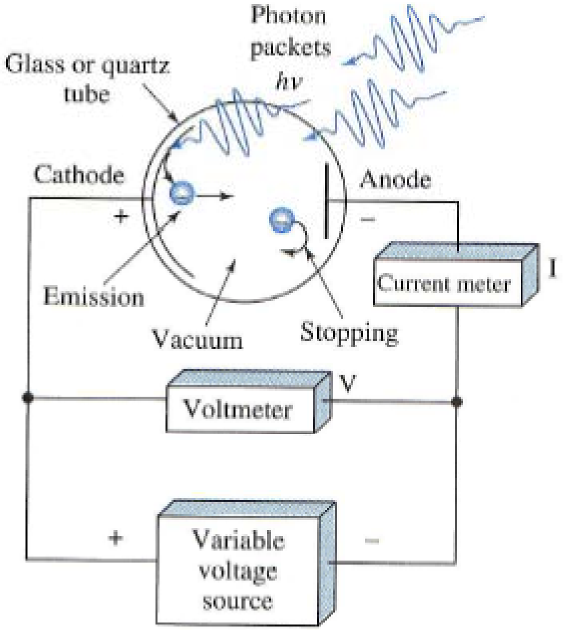


FIGURE 6-13 Apparatus for studying the photoelectric effect. Photons enter the phototube, strike the cathode, and eject electrons. The photoelectrons are attracted to the anode when it is positive with respect to the cathode. When the anode is negative as shown, the electrons are “stopped,” and no current passes. The negative voltage between the anode and the cathode when the current is zero is the stopping potential.

Photoeffect cont.

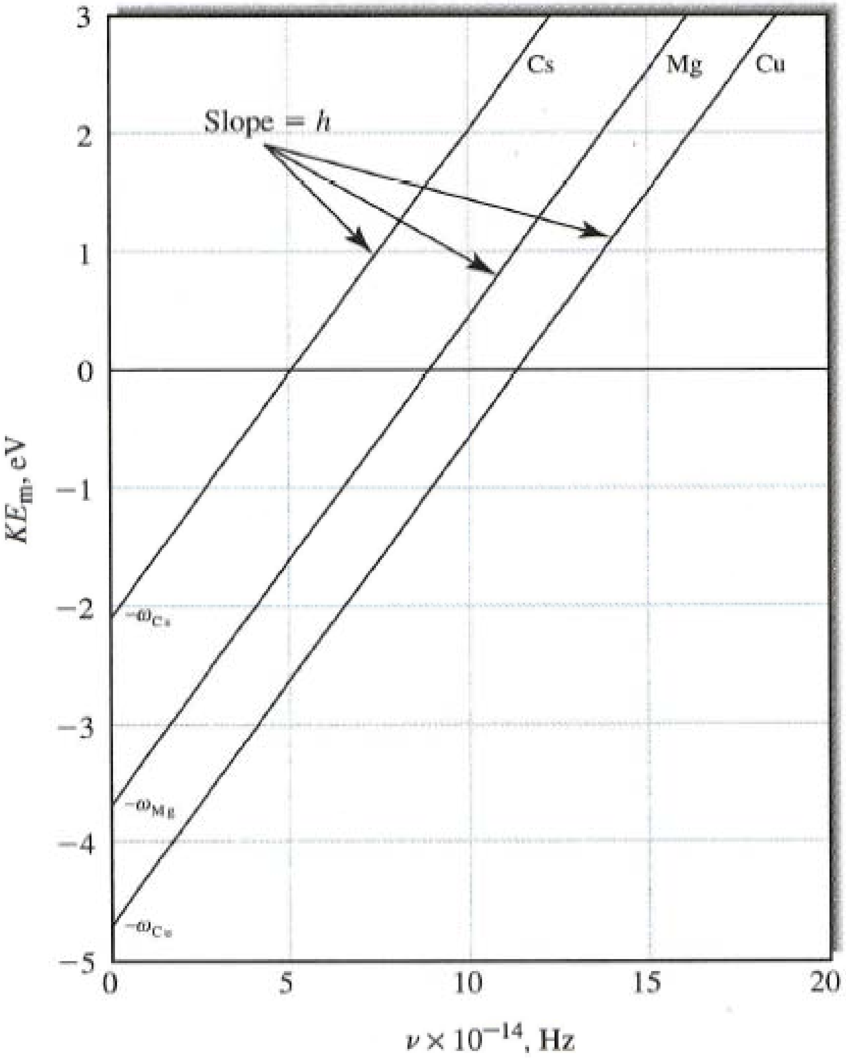


FIGURE 6-14 Maximum kinetic energy of photoelectrons emitted from three metal surfaces as a function of radiation frequency. The y-intercepts ($-\omega$) are the work functions for each metal. If incident photons do not have energies of at least $h\nu = \omega$, no photoelectrons are emitted from the photocathode.

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particle

The birth of quantum mechanics

- Niels Bohr, 1913 “Explanation for the Balmer Series of the hydrogen atom”

- De Broglie, 1924 “all matter has wave like properties“, $\lambda = h/p$

- Erwin Schroedinger, 1926 “theoretical framework of quantum mechanics”

- Werner Heissenberg, 1927 “uncertainty principle”, $\Delta E \, \Delta t \geq h/2\pi$

The hydrogen atom - Balmer Series

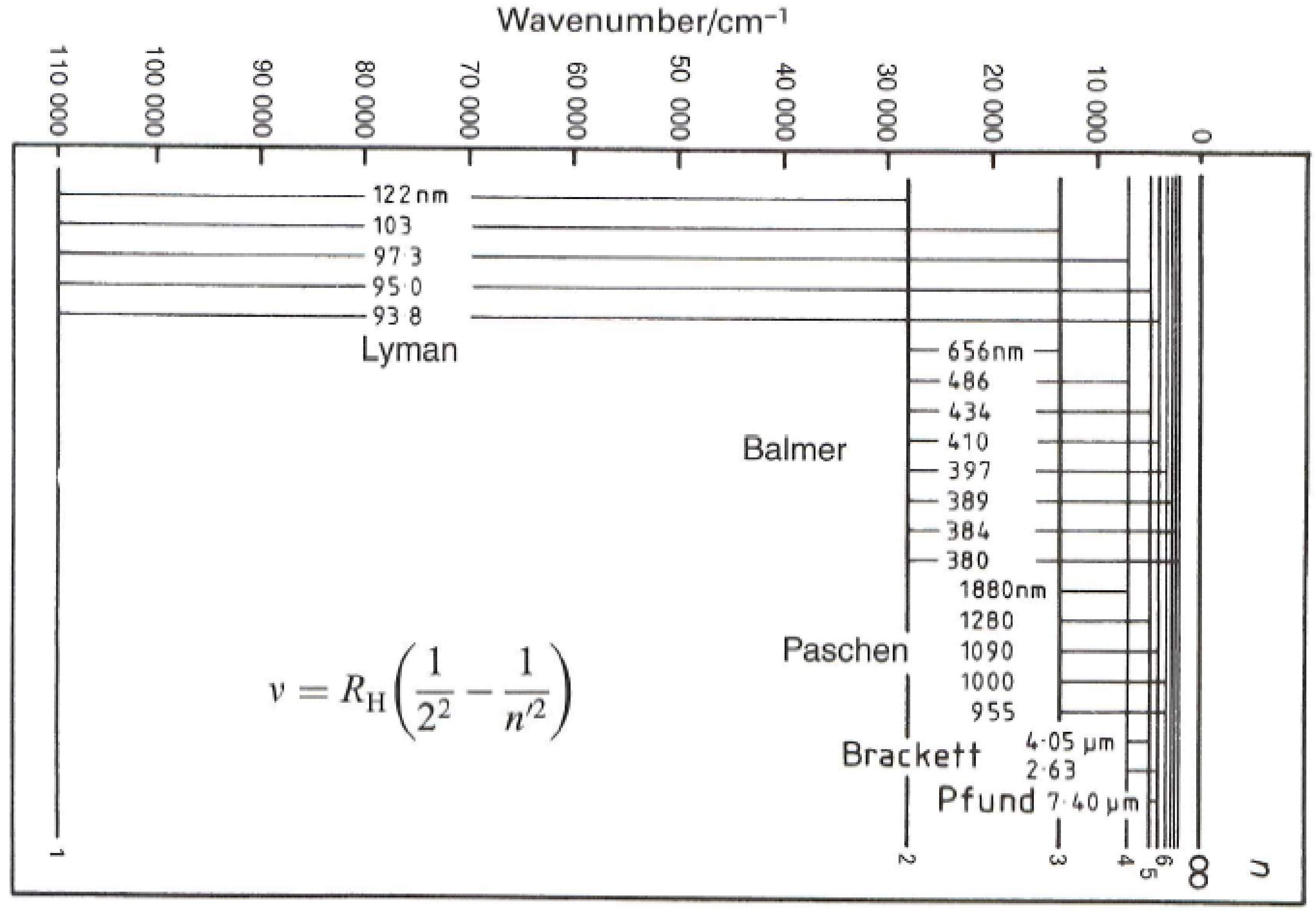


Figure 1.1 Energy levels (vertical lines) and observed transitions (horizontal lines) of the hydrogen atom, including the Lyman, Balmer, Paschen, Brackett and Pfund series

Examples de Broglie

- What is the momentum and the de Broglie wavelength associated with a human weighing 70kg and running at 20 km/hr ?
- What is the momentum and the de Broglie wavelength of an electron accelerated through a voltage of 100 V ?

Schroedinger Equation for the hydrogen atom

$$H = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r} \qquad \nabla^2 = \frac{1}{r^2 \sin\theta}\left[\sin\theta \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial}{\partial\theta}\right) + \frac{1}{\sin\phi}\frac{\partial^2}{\partial\phi^2}\right]$$

Factorization of the wavefunction in polar coordinates:

$$\psi(r, \theta, \phi) = R_{n\ell}(r) Y_{\ell m_\ell}(\theta, \phi) \tag{1.32}$$

$$Y_{\ell m_\ell}(\theta, \phi) = (2\pi)^{-1/2} \Theta_{\ell m_\ell}(\theta) \exp(i m_\ell \phi) \tag{1.35}$$

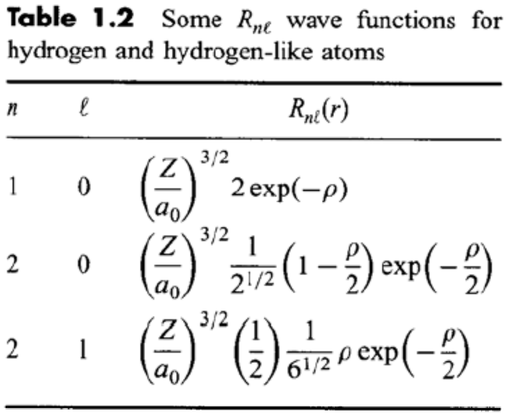


Table 1.2 Some $R_{n\ell}$ wave functions for hydrogen and hydrogen-like atoms

n	ℓ	$R_{n\ell}(r)$
1	0	$\left(\frac{Z}{a_0}\right)^{3/2} 2\exp(-\rho)$
2	0	$\left(\frac{Z}{a_0}\right)^{3/2} \frac{1}{2^{1/2}}\left(1-\frac{\rho}{2}\right)\exp\left(-\frac{\rho}{2}\right)$
2	1	$\left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{1}{2}\right)\frac{1}{6^{1/2}}\rho\exp\left(-\frac{\rho}{2}\right)$

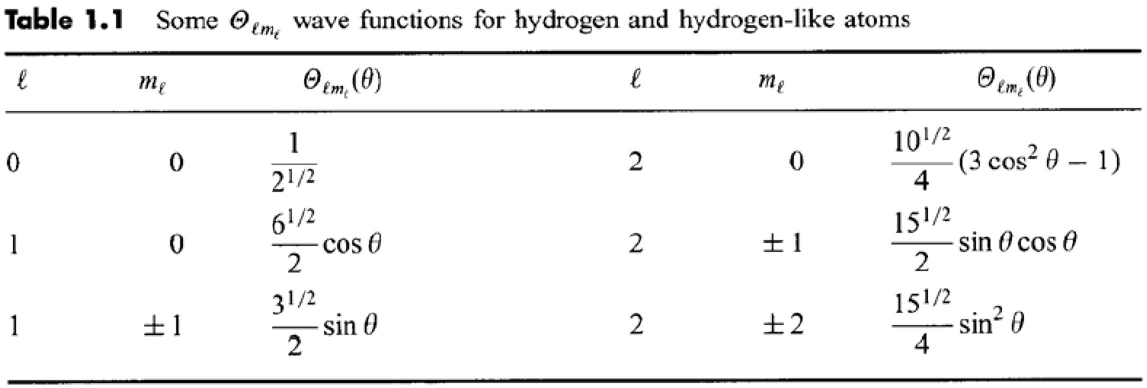
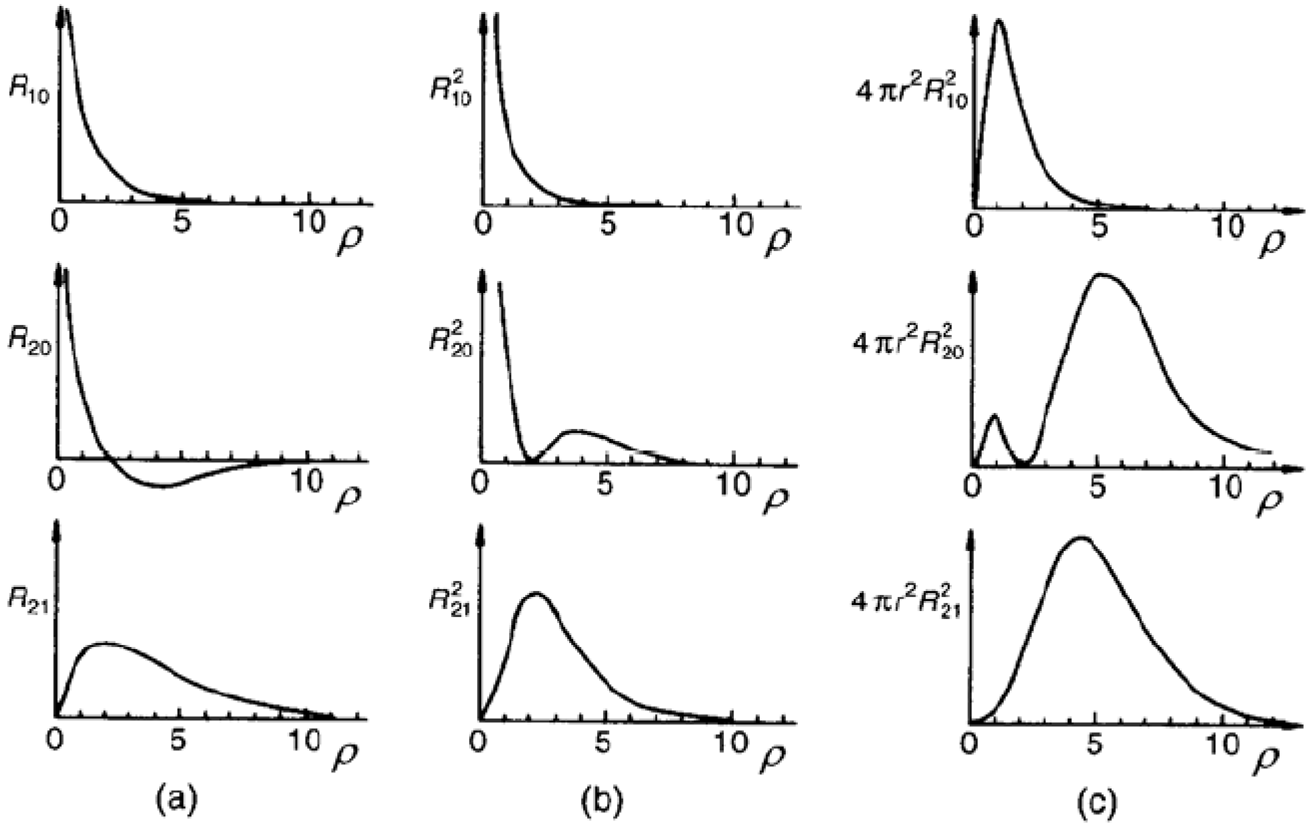


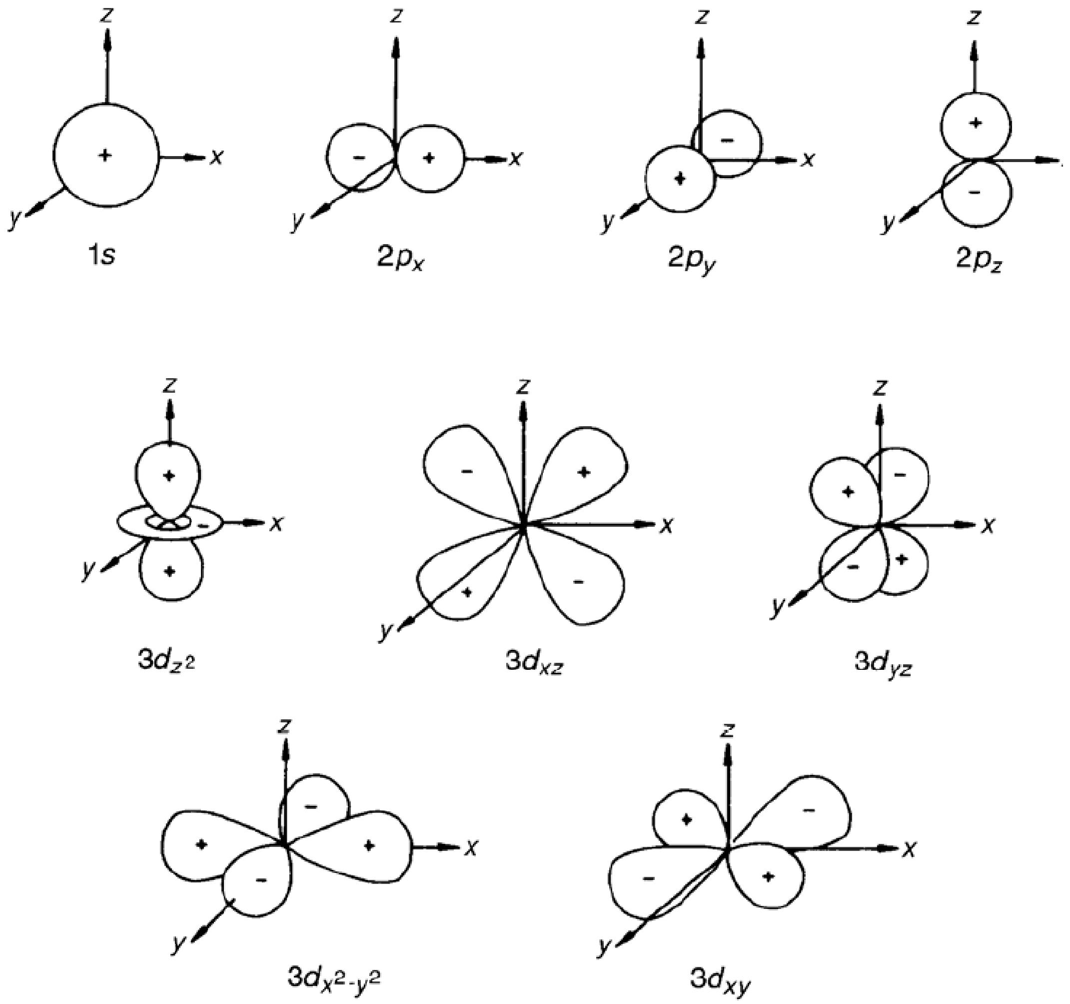
Table 1.1 Some $\Theta_{\ell m_\ell}$ wave functions for hydrogen and hydrogen-like atoms

ℓ	m_ℓ	$\Theta_{\ell m_\ell}(\theta)$	ℓ	m_ℓ	$\Theta_{\ell m_\ell}(\theta)$
0	0	$\frac{1}{2^{1/2}}$	2	0	$\frac{10^{1/2}}{4}(3\cos^2\theta - 1)$
1	0	$\frac{6^{1/2}}{2}\cos\theta$	2	±1	$\frac{15^{1/2}}{2}\sin\theta\cos\theta$
1	±1	$\frac{3^{1/2}}{2}\sin\theta$	2	±2	$\frac{15^{1/2}}{4}\sin^2\theta$

Copenhagener Interpretation
Radial component of the wavefunction



Copenhagener Interpretation cont
Angular component of the wavefunction



Quantum numbers of atoms

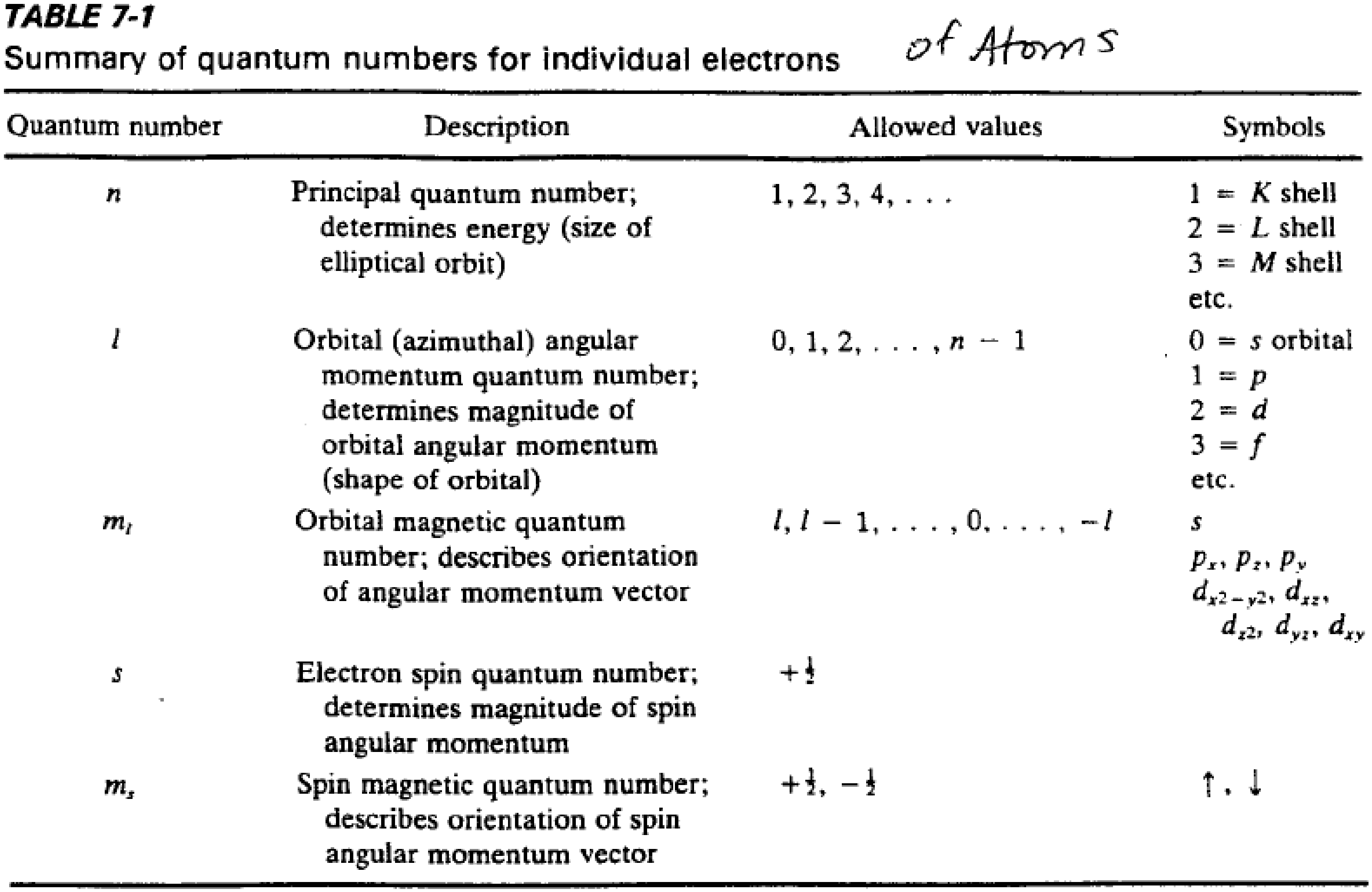
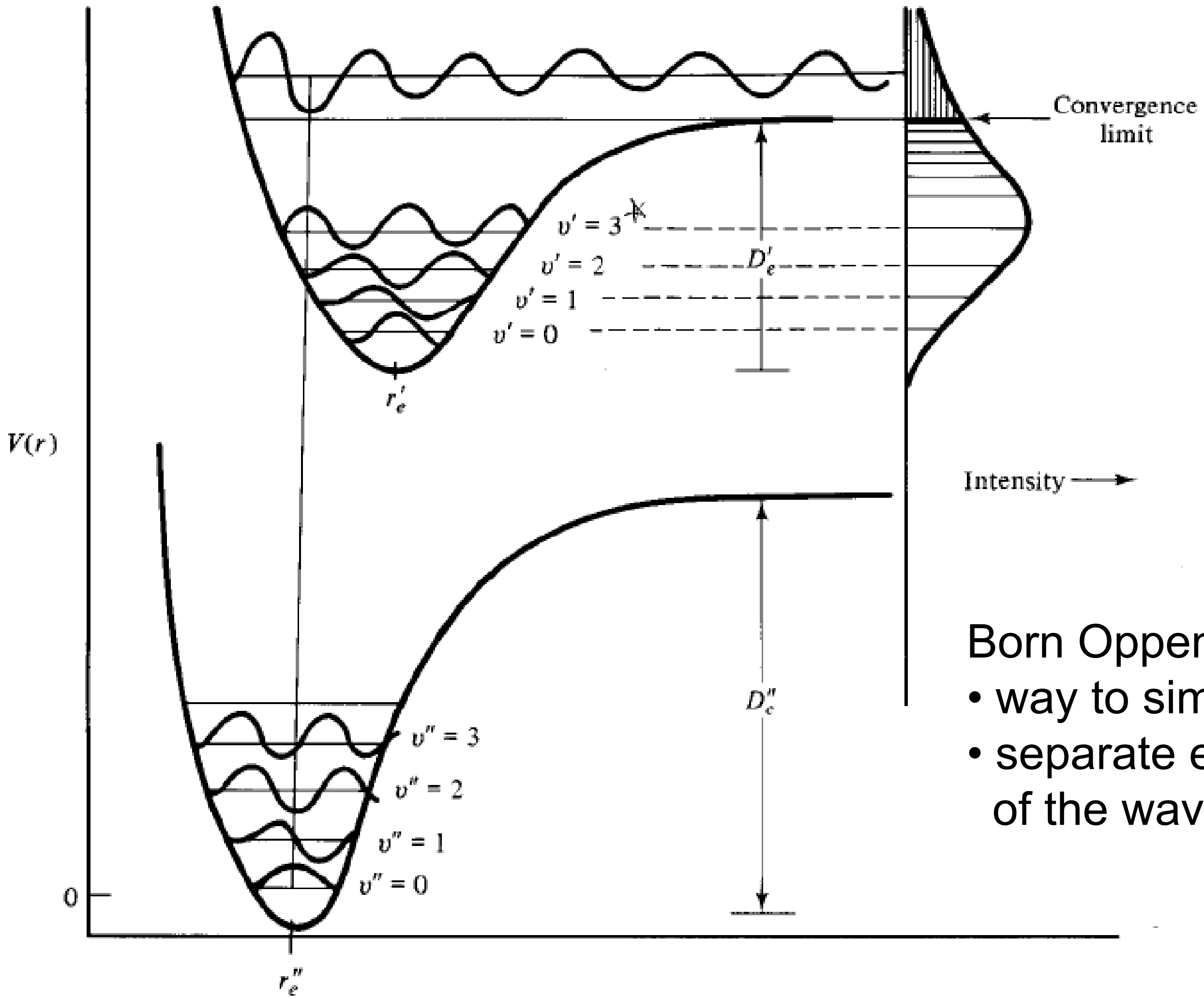


TABLE 7-1

Summary of quantum numbers for individual electrons of Atoms

Quantum number	Description	Allowed values	Symbols
n	Principal quantum number; determines energy (size of elliptical orbit)	1, 2, 3, 4, . . .	1 = K shell 2 = L shell 3 = M shell etc.
l	Orbital (azimuthal) angular momentum quantum number; determines magnitude of orbital angular momentum (shape of orbital)	$0, 1, 2, \ldots, n-1$	0 = s orbital 1 = p 2 = d 3 = f etc.
m_l	Orbital magnetic quantum number; describes orientation of angular momentum vector	$l, l-1, \ldots, 0, \ldots, -l$	s p_x, p_z, p_y $d_{x^2-y^2}$, d_{xz}, d_{z^2}, d_{yz}, d_{xy}
s	Electron spin quantum number; determines magnitude of spin angular momentum	$+\frac{1}{2}$	
m_s	Spin magnetic quantum number; describes orientation of spin angular momentum vector	$+\frac{1}{2}, -\frac{1}{2}$	↑, ↓

Molecules: Franck Condon Principle (determines line intensity)



Born Oppenheimer approximation:

- way to simplify Schroedinger Equation
- separate electronic and nuclear portion of the wavefunction

Why bother ?

- Quantum mechanics is a theory
- Spectroscopy provides the only (and powerful) means to verify predictions
- Information that can be obtained:
  - Chemical functionality
  - Chemical bonds
  - Potential energy surfaces
  - Reaction dynamics
  - Biological and biomedical applications