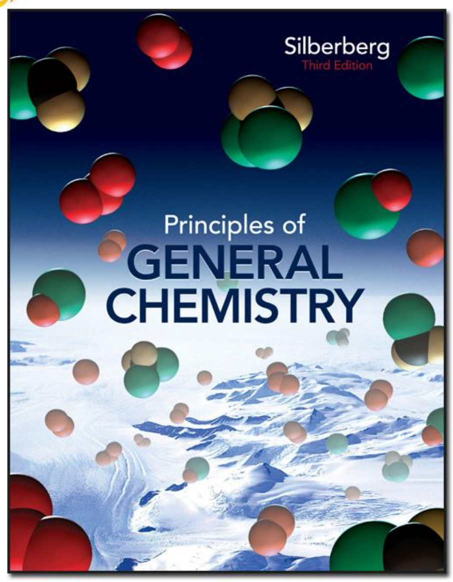


Chapter 07

Lecture Outline

See separate *Image PowerPoint* slides for all figures and tables pre-inserted into PowerPoint without notes.

7-1

Chapter 7

Quantum Theory and Atomic Structure

7-2

Quantum Theory and Atomic Structure

7.1 The Nature of Light

7.2 Atomic Spectra

7.3 The Wave-Particle Duality of Matter and Energy

7.4 The Quantum-Mechanical Model of the Atom

7-3

The Wave Nature of Light

Visible light is a type of ***electromagnetic radiation***.

The wave properties of electromagnetic radiation are described by three variables:

- **frequency (ν)**, cycles per second
- **wavelength (λ)**, the distance a wave travels in one cycle
- **amplitude**, the height of a wave crest or depth of a trough.

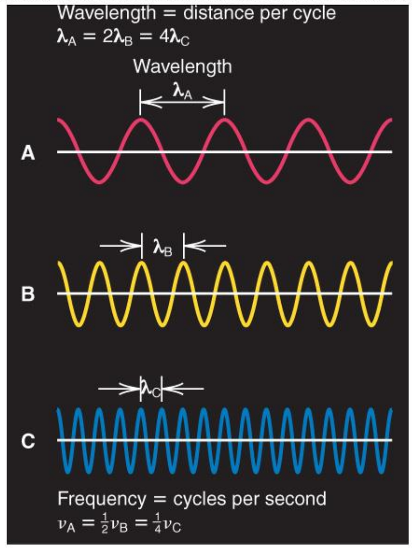
The ***speed of light*** is a constant:

$$c = \nu \times \lambda$$

$$= 3.00 \times 10^8 \text{ m/s in a vacuum}$$

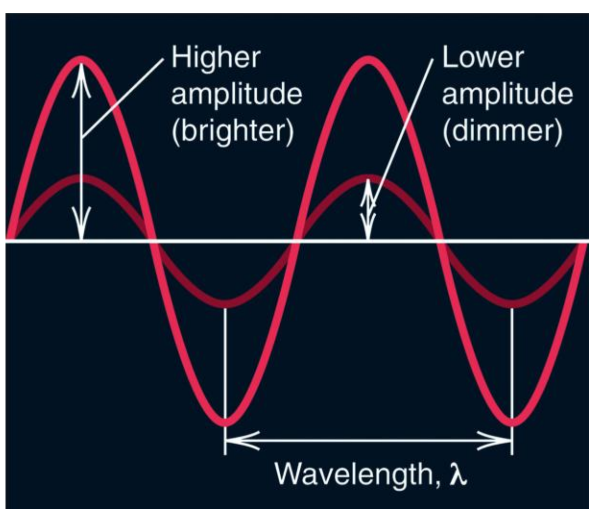
7-4

Figure 7.1 The reciprocal relationship of frequency and wavelength.



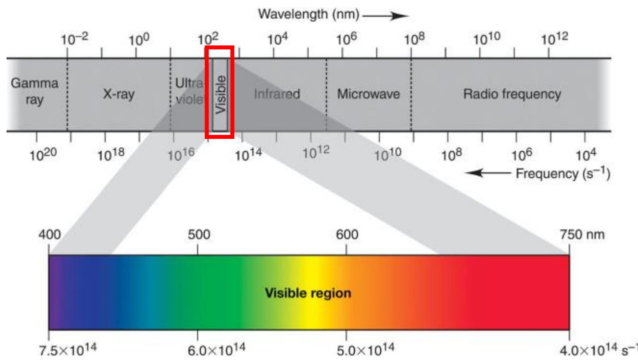
7-5

Figure 7.2 Differing amplitude (brightness, or intensity) of a wave.



7-6

Figure 7.3 **Regions of the electromagnetic spectrum.**

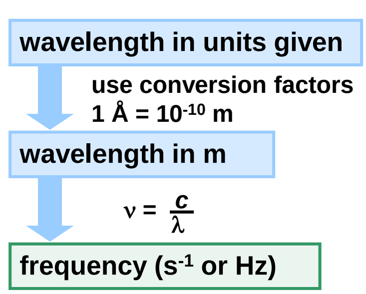


7-7

Sample Problem 7.1 **Interconverting Wavelength and Frequency**

PROBLEM: A dental hygienist uses x-rays (λ= 1.00Å) to take a series of dental radiographs while the patient listens to a radio station (λ = 325 cm) and looks out the window at the blue sky (λ= 473 nm). What is the frequency (in s^{-1}) of the electromagnetic radiation from each source? (Assume that the radiation travels at the speed of light, 3.00×10^{8} m/s.)

PLAN: Use the equation $c = \nu\lambda$ to convert wavelength to frequency. Wavelengths need to be in meters because c has units of m/s.



7-8

Sample Problem 7.1

SOLUTION:

For the x-rays: $\lambda = 1.00\ \text{Å} \times \dfrac{10^{-10}\ \text{m}}{1\ \text{Å}} = 1.00 \times 10^{-10}\ \text{m}$

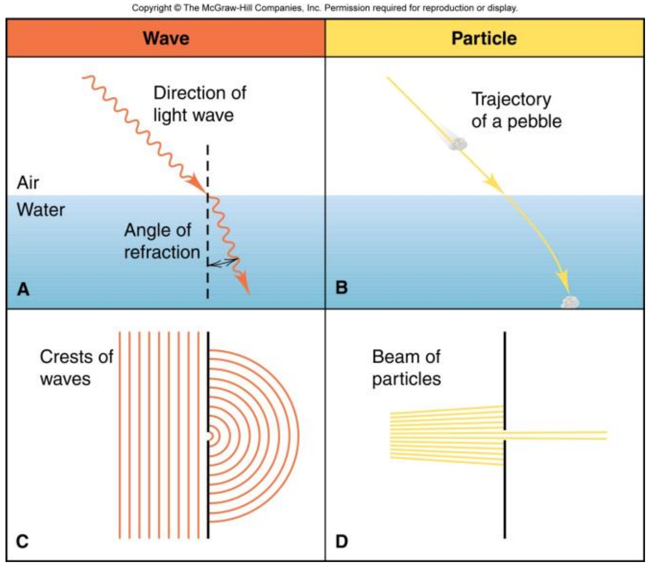
$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{8}\ \text{m/s}}{1.00 \times 10^{-10}\ \text{m}} \quad \boxed{= 3.00 \times 10^{18}\ \text{s}^{-1}}$$

For the radio signal:
$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{8}\ \text{m/s}}{325\ \text{cm} \times \dfrac{10^{-2}\ \text{m}}{1\ \text{cm}}} \quad \boxed{= 9.23 \times 10^{7}\ \text{s}^{-1}}$$

For the blue sky:
$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{8}\ \text{m/s}}{473\ \text{nm} \times \dfrac{10^{-9}\ \text{m}}{1\ \text{cm}}} \quad \boxed{= 6.34 \times 10^{14}\ \text{s}^{-1}}$$

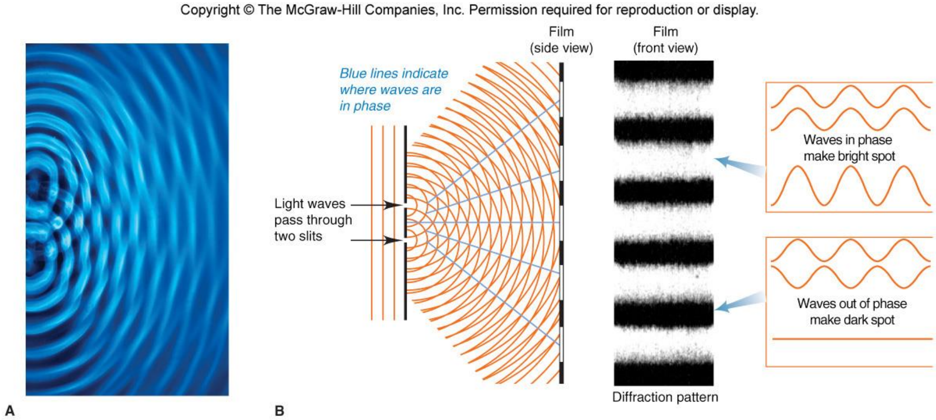
7-9

Figure 7.4 Different behaviors of waves and particles.



7-10

Figure 7.5 Formation of a diffraction pattern.



7-11

Energy and frequency

A solid object emits visible light when it is heated to about 1000 K. This is called ***blackbody radiation***.

The *color* (and the intensity) of the light changes as the temperature changes. Color is related to ***wavelength*** and ***frequency***, while temperature is related to ***energy***.

Energy is therefore related to frequency and wavelength:

$$E = nh\nu$$

E = energy
n is a positive integer
h is Planck's constant

7-12

The Quantum Theory of Energy

Any object (including atoms) can emit or absorb only ***certain quantities*** of energy.

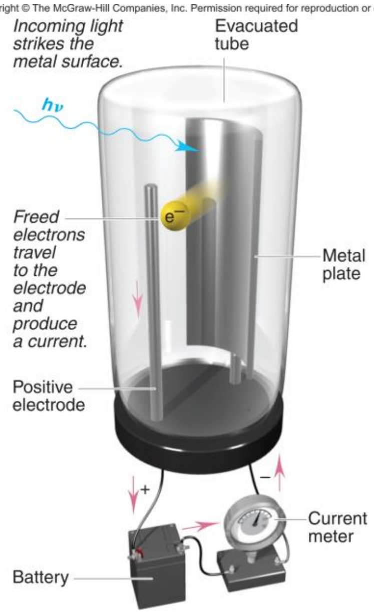
Energy is ***quantized***; it occurs in fixed quantities, rather than being continuous. Each fixed quantity of energy is called a ***quantum***.

An atom changes its energy state by emitting or absorbing one or more ***quanta*** of energy.

$\Delta E = nh\nu$ where *n* can only be a whole number.

7-13

Figure 7.6 The photoelectric effect.



7-14

Sample Problem 7.2 **Calculating the Energy of Radiation from Its Wavelength**

PROBLEM: A cook uses a microwave oven to heat a meal. The wavelength of the radiation is 1.20 cm. What is the energy of one photon of this microwave radiation?

PLAN: We know λ in cm, so we convert to m and find the frequency using the speed of light. We then find the energy of one photon using $E = h\nu$.

SOLUTION:

$$E = h\nu = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}\ \text{J·s})(3.00 \times 10^{8}\ \text{m/s})}{(1.20\ \text{cm})\left(\frac{10^{-2}\ \text{m}}{1\ \text{cm}}\right)} = 1.66 \times 10^{-23}\ \text{J}$$

7-15

Figure 7.7A **The line spectrum of hydrogen.**

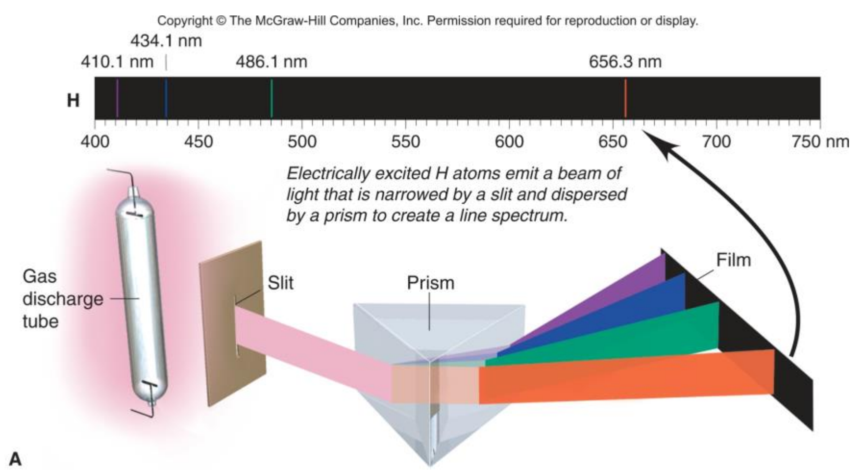


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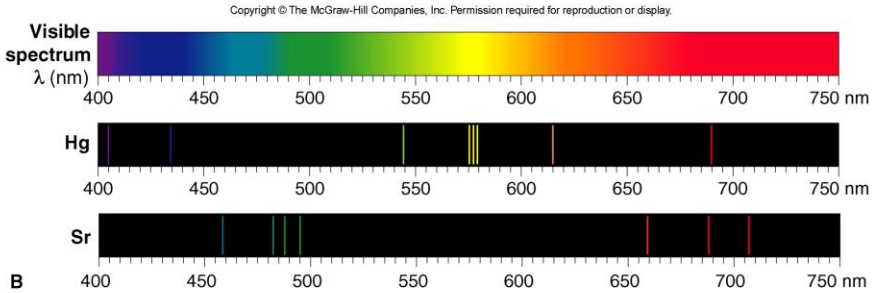
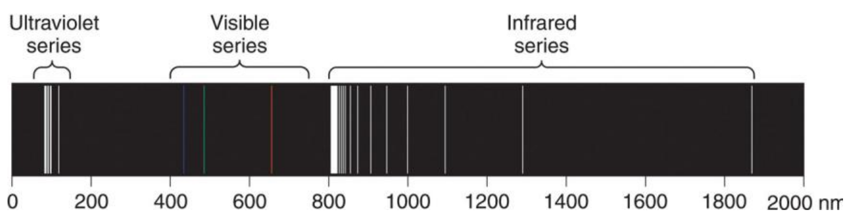
Figure 7.7B **The line spectra of Hg and Sr.**



7-17

Figure 7.8 Three series of spectral lines of atomic hydrogen.



Rydberg equation

$$\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

R is the Rydberg constant = 1.096776x10^{7} m^{-1}

for the visible series, n_1 = 2 and n_2 = 3, 4, 5, ...

7-18

The Bohr Model of the Hydrogen Atom

Bohr's atomic model postulated the following:

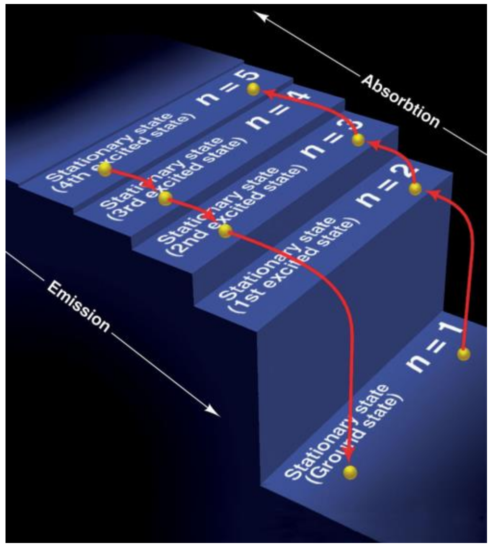
- The H atom has only certain energy levels, which Bohr called ***stationary states***.
  - Each state is associated with a fixed circular orbit of the electron around the nucleus.
  - The higher the energy level, the farther the orbit is from the nucleus.
  - When the H electron is in the first orbit, the atom is in its lowest energy state, called the ***ground state***.

7-19

- The atom does not radiate energy while in one of its stationary states.
- The atom changes to another stationary state only by absorbing or emitting a photon.
  - The energy of the photon ($h\nu$) equals the difference between the energies of the two energy states.
  - When the E electron is in any orbit higher than $n = 1$, the atom is in an ***excited state***.

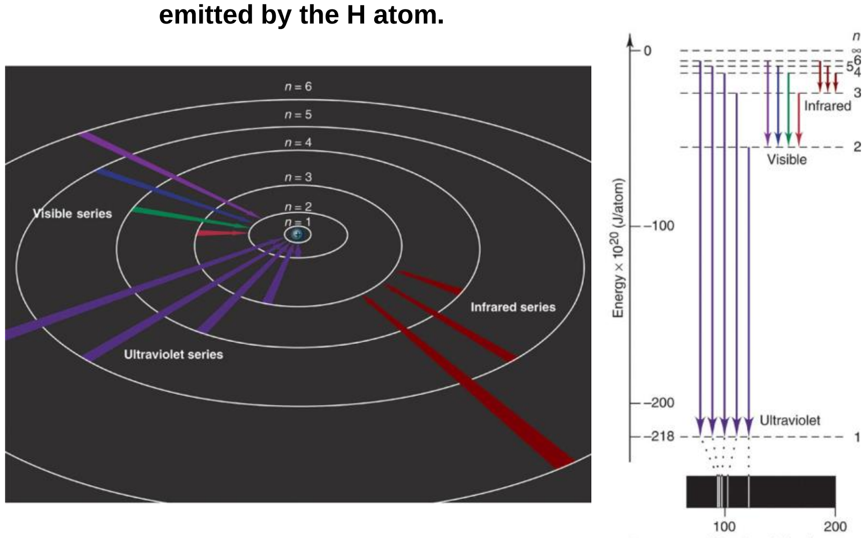
7-20

Figure 7.9 **A quantum "staircase" as an analogy for atomic energy levels.**



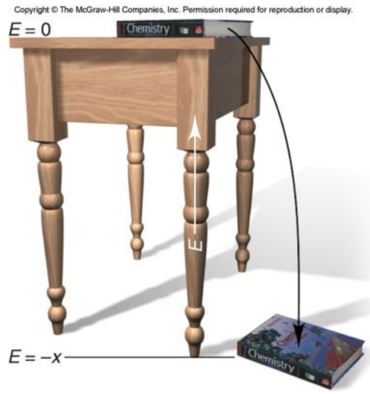
7-21

Figure 7.10 **The Bohr explanation of three series of spectral lines emitted by the H atom.**



7-22

A tabletop analogy for the H atom's energy.



$$\Delta E = E_{final} - E_{initial} = -2.18\text{x}10^{-18}\ \text{J} \left(\frac{1}{n^2_{final}} - \frac{1}{n^2_{initial}} \right)$$

7-23

Sample Problem 7.3

Determining ΔE and λ of an Electron Transition

PROBLEM: A hydrogen atom absorbs a photon of UV light (see Figure 7.10) and its electron enters the $n = 4$ energy level. Calculate **(a)** the change in energy of the atom and **(b)** the wavelength (in nm) of the photon.

PLAN: **(a)** The H atom absorbs energy, so $E_{final} > E_{initial}$. We are given $n_{final} = 4$, and Figure 7.10 shows that $n_{initial} = 1$ because a UV photon is absorbed. We apply Equation 7.4 to find ΔE.

(b) Once we know ΔE, we find frequency and wavelength.

7-24

Sample Problem 7.3

SOLUTION:

(a) $\Delta E = -2.18\text{x}10^{-18}\ \text{J} \left(\frac{1}{n^2_{\text{final}}} - \frac{1}{n^2_{\text{initial}}}\right) = -2.18\text{x}10^{-18}\ \text{J} \left(\frac{1}{4^2} - \frac{1}{1^2}\right)$

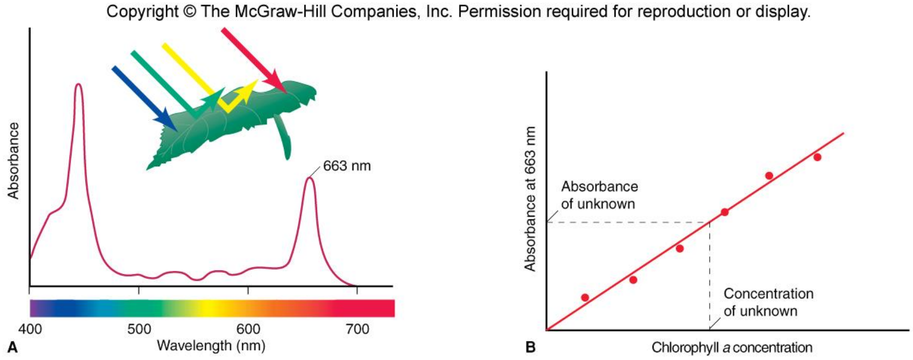
$= -2.18\text{x}10^{-18}\ \text{J} \left(\frac{1}{16} - \frac{1}{4}\right)$ **$= 2.04\text{x}10^{-18}\ \text{J}$**

(b) $\lambda = \frac{hc}{\Delta E} = \frac{(6.626\text{x}10^{-34}\ \text{J·s})(3.00\text{x}10^{8}\ \text{m/s})}{2.04\text{x}10^{-18}\ \text{J}}$ **$= 9.74\text{x}10^{-8}\ \text{m}$**

$9.74\text{x}10^{-8}\ \text{m x} \frac{1\ \text{nm}}{10^{-9}\ \text{m}}$ **$= 97.4\ \text{nm}$**

7-25

Figure 7.11 Measuring chlorophyll *a* concentration in leaf extract.



7-26

The Wave-Particle Duality of Matter and Energy

Matter and Energy are alternate forms of the same entity.

$$E = mc^2$$

All matter exhibits properties of ***both particles and waves***. Electrons have wave-like motion and therefore have only certain allowable frequencies and energies.

Matter behaves as though it moves in a wave, and the ***de Broglie wavelength*** for any particle is given by:

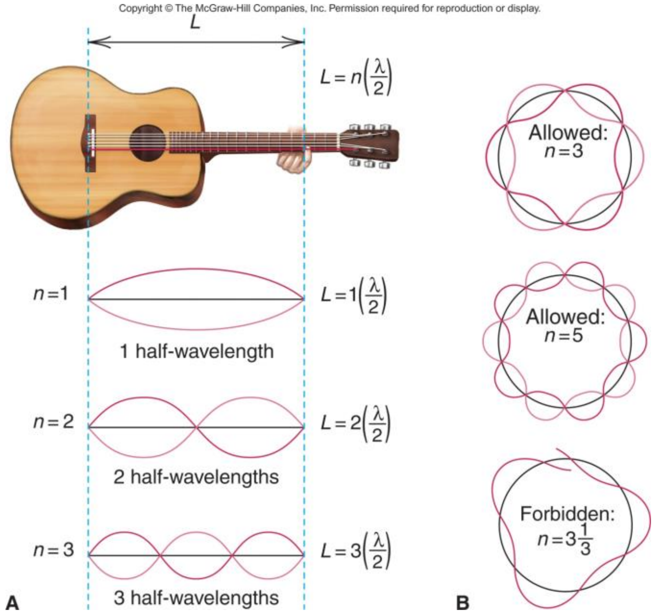
$$\lambda = \frac{h}{mu}$$

m = mass

u = speed in m/s

7-27

Figure 7.12 **Wave motion in restricted systems.**



7-28

Table 7.1 The de Broglie Wavelengths of Several Objects

Substance	Mass (g)	Speed (m/s)	λ (m)
slow electron	$9x10^{-28}$	1.0	$7x10^{-4}$
fast electron	$9x10^{-28}$	$5.9x10^{6}$	$1x10^{-10}$
alpha particle	$6.6x10^{-24}$	$1.5x10^{7}$	$7x10^{-15}$
one-gram mass	1.0	0.01	$7x10^{-29}$
baseball	142	25.0	$2x10^{-34}$
Earth	$6.0x10^{27}$	$3.0x10^{4}$	$4x10^{-63}$

7-29

Sample Problem 7.4 **Calculating the de Broglie Wavelength of an Electron**

PROBLEM: Find the de Broglie wavelength of an electron with a speed of $1.00x10^{6}$ m/s (electron mass = $9.11x10^{-31}$ kg; $h = 6.626x10^{-34}$ kg·m^2/s).

PLAN: We know the speed and mass of the electron, so we substitute these into Equation 7.5 to find λ.

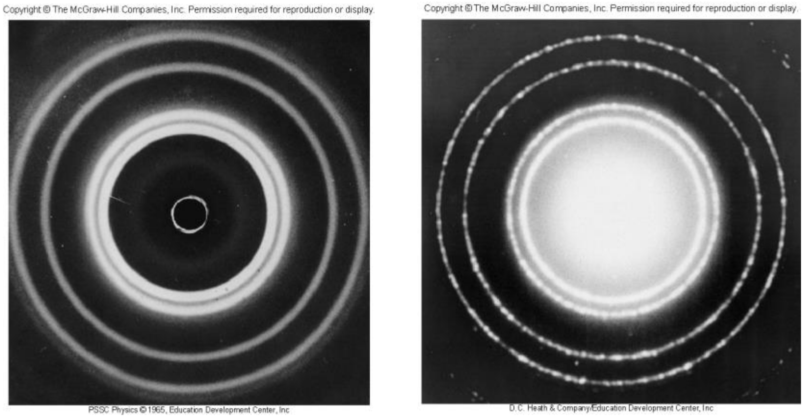
SOLUTION:

$$\lambda = \frac{h}{mu}$$

$$\lambda = \frac{6.626x10^{-34}\ kg \cdot m^2/s}{9.11x10^{-31}\ kg \times 1.00x10^{6}\ m/s} = \mathbf{7.27x10^{-10}\ m}$$

7-30

Figure 7.13 Diffraction patterns of aluminum with x-rays and electrons.



x-ray diffraction of aluminum foil | electron diffraction of aluminum foil

7-31

Figure 7.14

Major observations and theories leading from classical theory to quantum theory

CLASSICAL THEORY

Matter particulate, massive	Energy continuous, wavelike

Since *matter* is discontinuous and particulate, perhaps *energy* is discontinuous and particulate.

Observation	***Theory***	
Blackbody radiation →	Planck:	Energy is quantized; only certain values allowed
Photoelectric effect →	Einstein:	Light has particulate behavior (photons)
Atomic line spectra →	Bohr:	Energy of atoms is quantized; photon emitted when electron changes orbit.

7-32

Figure 7.14 continued

Since *energy* is wavelike, perhaps *matter* is wavelike.

Observation		***Theory***
Davisson/Germer: Electron beam is diffracted by metal crystal	←	deBroglie: All matter travels in waves; energy of atom is quantized due to wave motion of electrons

Since *matter* has mass, perhaps *energy* has mass

Observation		***Theory***
Compton: Photon's wavelength increases (momentum decreases) after colliding with electron	←	Einstein/deBroglie: Mass and energy are equivalent; particles have wavelength and photons have momentum.

QUANTUM THEORY

Energy *and* **Matter**

particulate, massive, wavelike

7-33

Heisenberg's Uncertainty Principle

Heisenberg's Uncertainty Principle states that it is not possible to know both the position *and* momentum of a moving particle at the same time.

$$\Delta x \cdot m \Delta u \geq \frac{h}{4\pi}$$

x = position

u = speed

The more accurately we know the speed, the less accurately we know the position, and vice versa.

7-34

The Quantum-Mechanical Model of the Atom

The matter-wave of the electron occupies the space near the nucleus and is continuously influenced by it.

The ***Schrödinger wave equation*** allows us to solve for the energy states associated with a particular atomic orbital.

The square of the wave function gives the ***probability density***, a measure of the ***probability*** of finding an electron of a particular energy in a particular region of the atom.

7-35

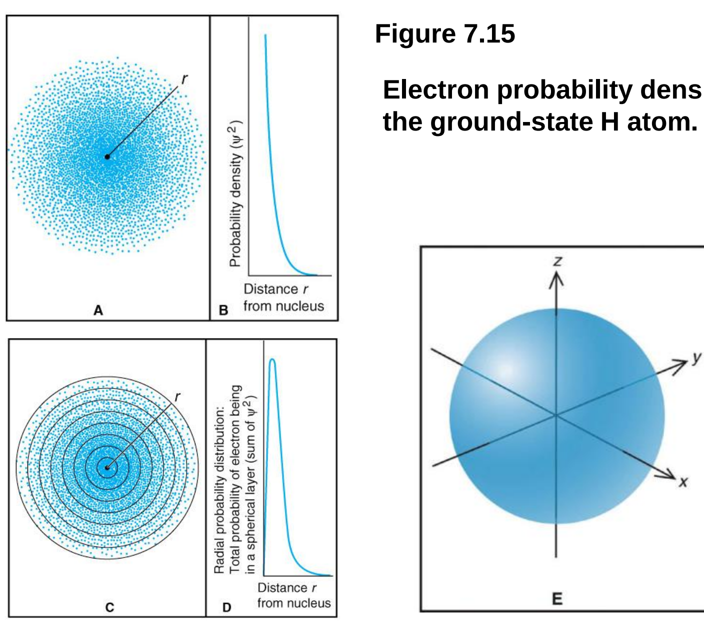


Figure 7.15

Electron probability density in the ground-state H atom.

7-36

Quantum Numbers and Atomic Orbitals

An atomic orbital is specified by three quantum numbers.

The ***principal*** quantum number (***n***) is a positive integer.
The value of *n* indicates the relative ***size*** of the orbital and therefore its relative ***distance*** from the nucleus.

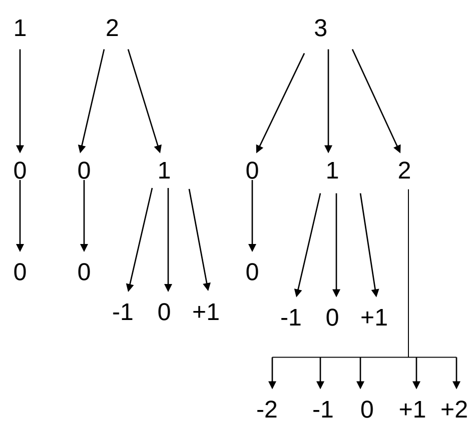
The ***angular momentum*** quantum number ***(l)*** is an integer from 0 to (*n* -1).
The value of *l* indicates the ***shape*** of the orbital.

The ***magnetic*** quantum number **(m_l)** is an integer with values from –*l* to +*l*
The value of m_l indicates the spatial ***orientation*** of the orbital.

Table 7.2 The Hierarchy of Quantum Numbers for Atomic Orbitals

Name, Symbol (Property)	Allowed Values
Principal, *n* (size, energy)	Positive integer (1, 2, 3, ...)
Angular momentum, ***l*** (shape)	0 to *n* – 1
Magnetic, m_l (orientation)	***-l***,…,0,…,***+l***

Quantum Numbers



Sample Problem 7.5 **Determining Quantum Numbers for an Energy Level**

PROBLEM: What values of the angular momentum (***l***) and magnetic (m_l) quantum numbers are allowed for a principal quantum number (*n*) of 3? How many orbitals are allowed for *n* = 3?

PLAN: Values of *l* are determined from the value for *n*, since *l* can take values from 0 to (*n*-1). The values of m_l then follow from the values of *l*.

SOLUTION: For *n* = 3, allowed values of *l* are = 0, 1, and 2

For *l* = 0 m_l = 0

For *l* = 1 m_l = -1, 0, or +1

For *l* = 2 m_l = -2, -1, 0, +1, or +2

There are 9 m_l values and therefore 9 orbitals with *n* = 3.

Sample Problem 7.6 **Determining Sublevel Names and Orbital Quantum Numbers**

PROBLEM: Give the name, magnetic quantum numbers, and number of orbitals for each sublevel with the following quantum numbers:

(a) *n* = 3, *l* = 2 **(b)** *n* = 2, *l* = 0 **(c)** *n* = 5, *l* = 1 **(d)** *n* = 4, *l* = 3

PLAN: Combine the *n* value and *l* designation to name the sublevel. Knowing *l*, we can find m_l and the number of orbitals.

SOLUTION:

	n	*l*	sublevel name	possible m_l values	# of orbitals
(a)	3	2	3*d*	-2, -1, 0, 1, 2	5
(b)	2	0	2*s*	0	1
(c)	5	1	5*p*	-1, 0, 1	3
(d)	4	3	4*f*	-3, -2, -1, 0, 1, 2, 3	7

Sample Problem 7.7 **Identifying Incorrect Quantum Numbers**

PROBLEM: What is wrong with each of the following quantum numbers designations and/or sublevel names?

	n	*l*	m_l	Name
(a)	1	1	0	1*p*
(b)	4	3	+1	4*d*
(c)	3	1	-2	3*p*

SOLUTION:

(a) A sublevel with *n* = 1 can only have *l* = 0, not *l* = 1. The only possible sublevel name is 1*s*.

(b) A sublevel with *l* = 3 is an *f* sublevel, to a *d* sublevel. The name should be 4*f*.

(c) A sublevel with *l* = 1 can only have m_l values of -1, 0, or +1, not -2.

7-41

Figure 7.16 **The 1*s*, 2*s*, and 3*s* orbitals.**

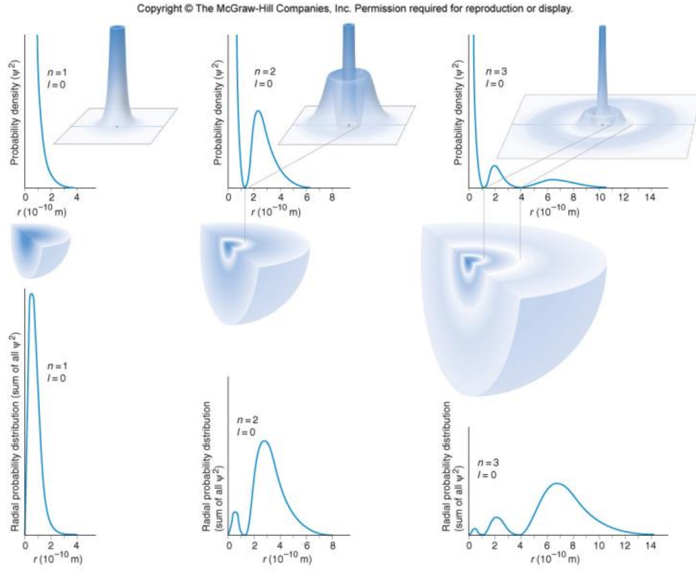


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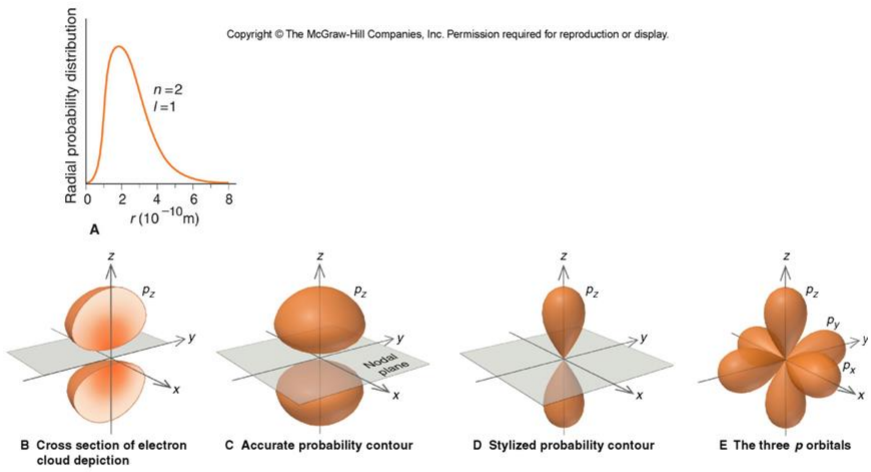
Figure 7.17 The 2*p* orbitals.



7-43

Figure 7.18 The 3*d* orbitals.

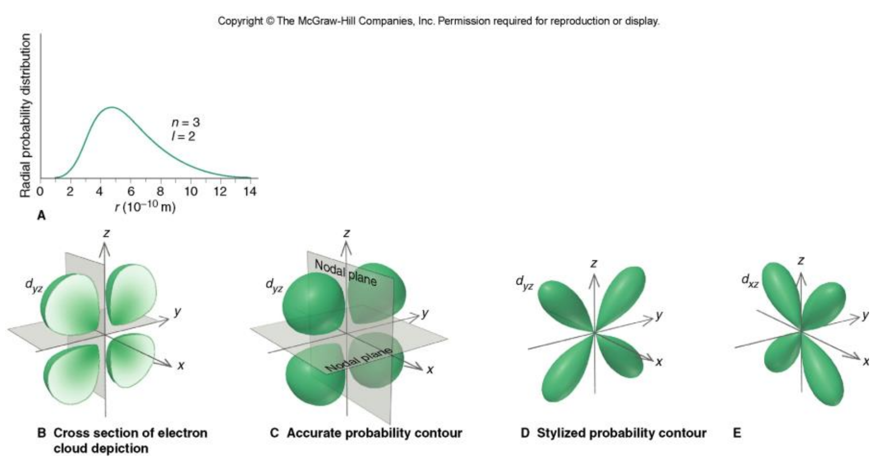


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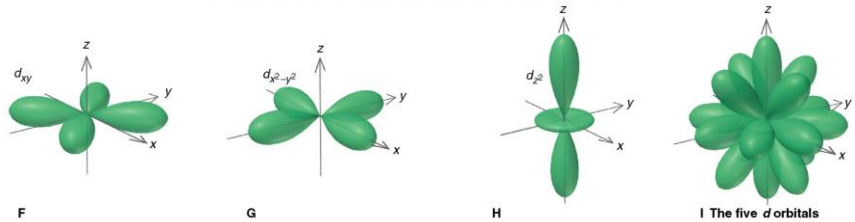
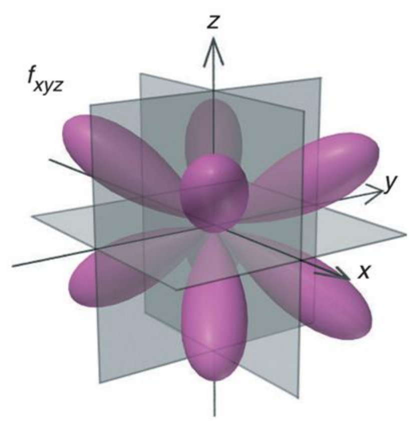
Figure 7.18



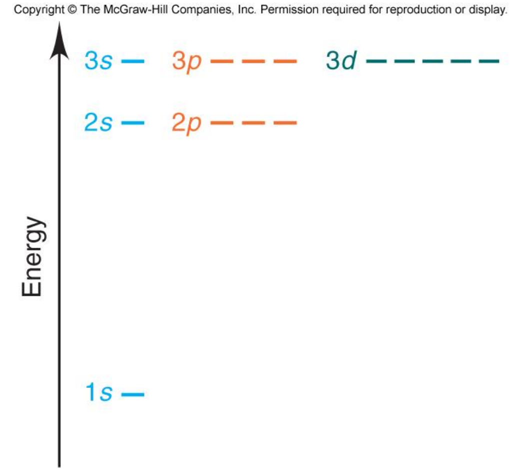
7-45

Figure 7.19 **The 4f_{xyz} orbital, one of the seven 4*f* orbitals.**



7-46

Figure 7.20 **Energy levels of the H atom.**



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