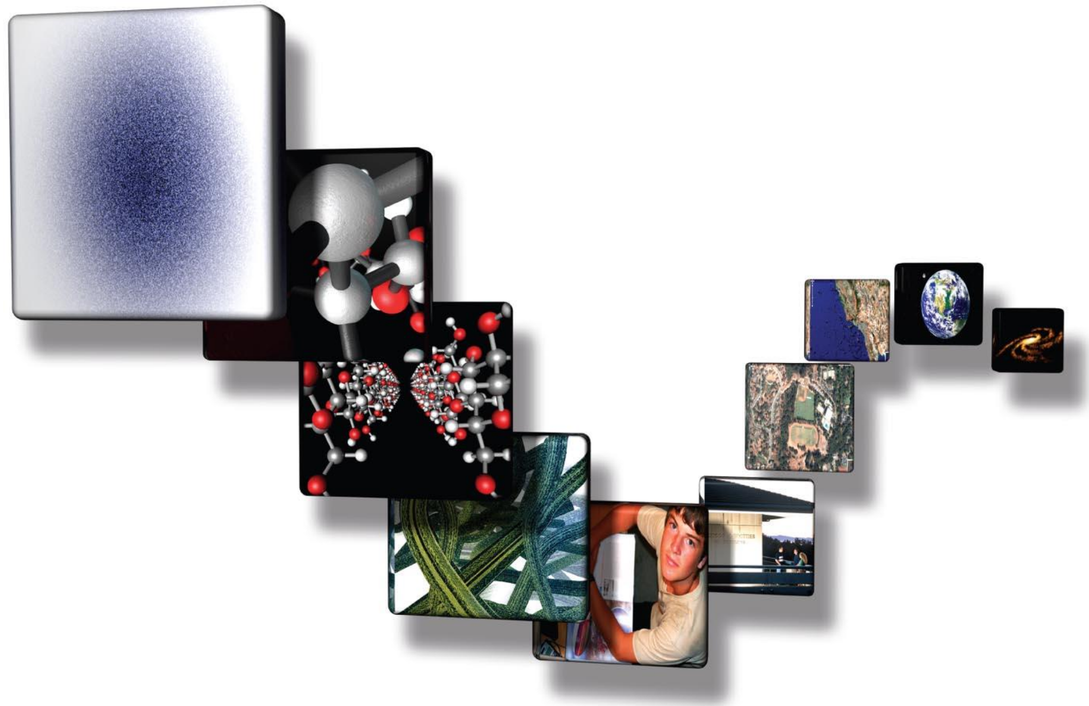
Chemistry: A Molecular Approach, 2nd Ed.
Nivaldo Tro



Chapter 7
The Quantum–Mechanical Model of the Atom

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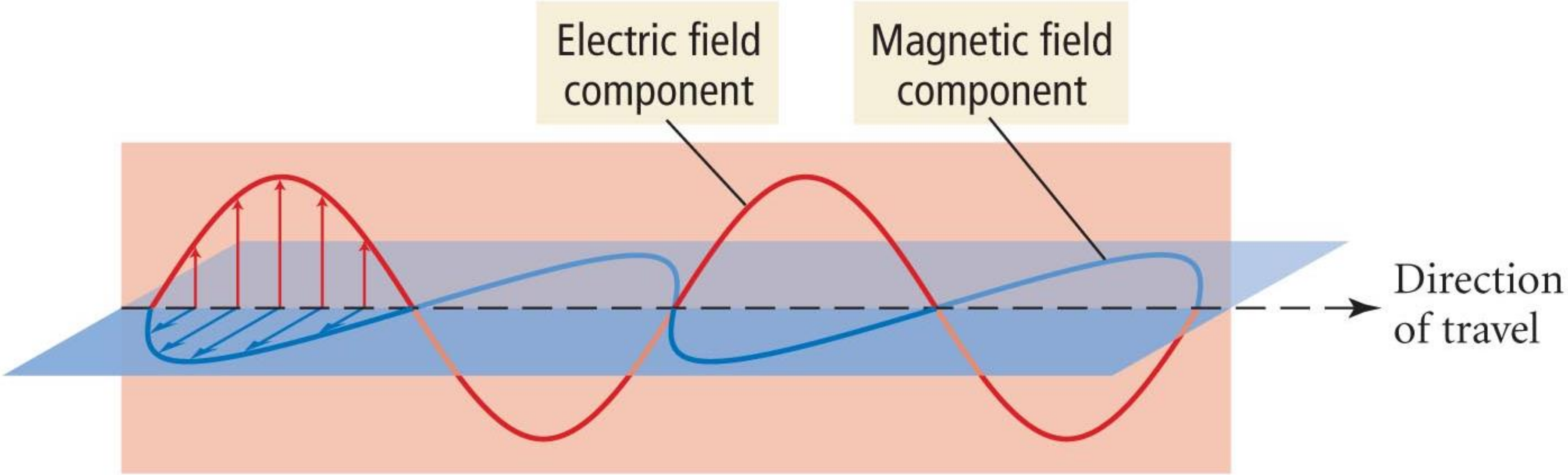
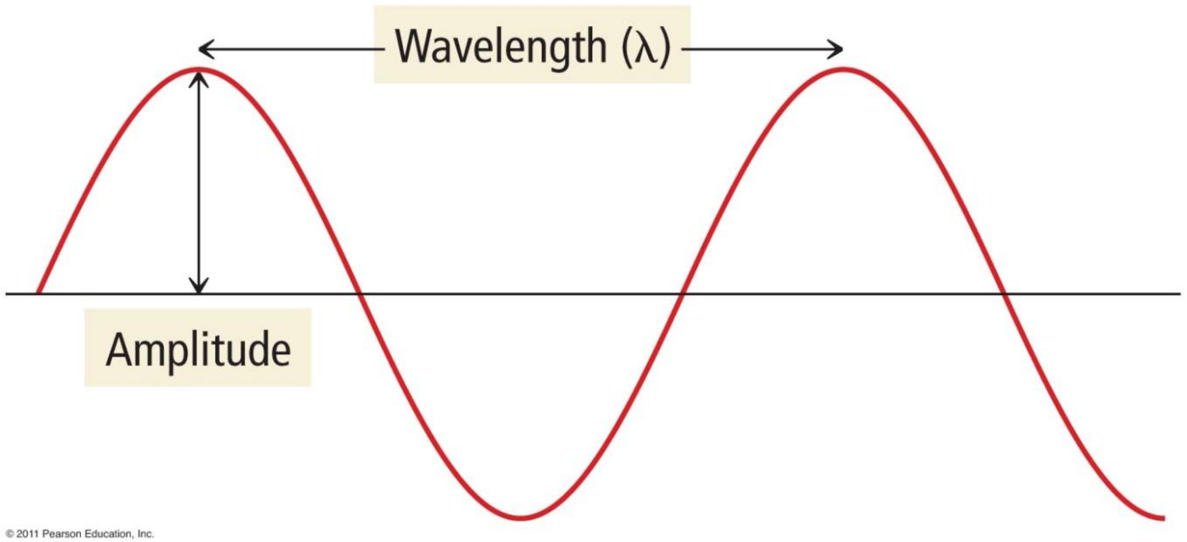
The Nature of Light: Its Wave Nature

- Light is a form of **electromagnetic radiation**
  - ✓ composed of perpendicular oscillating waves, one for the electric field and one for the magnetic field
    - ➢ an electric field is a region where an electrically charged particle experiences a force
    - ➢ a magnetic field is a region where a magnetized particle experiences a force
- All electromagnetic waves move through space at the same, constant speed
  - ✓ 3.00 x 10^8 m/s in a vacuum = **the speed of light, c**

Electromagnetic Radiation



Wave Characteristics



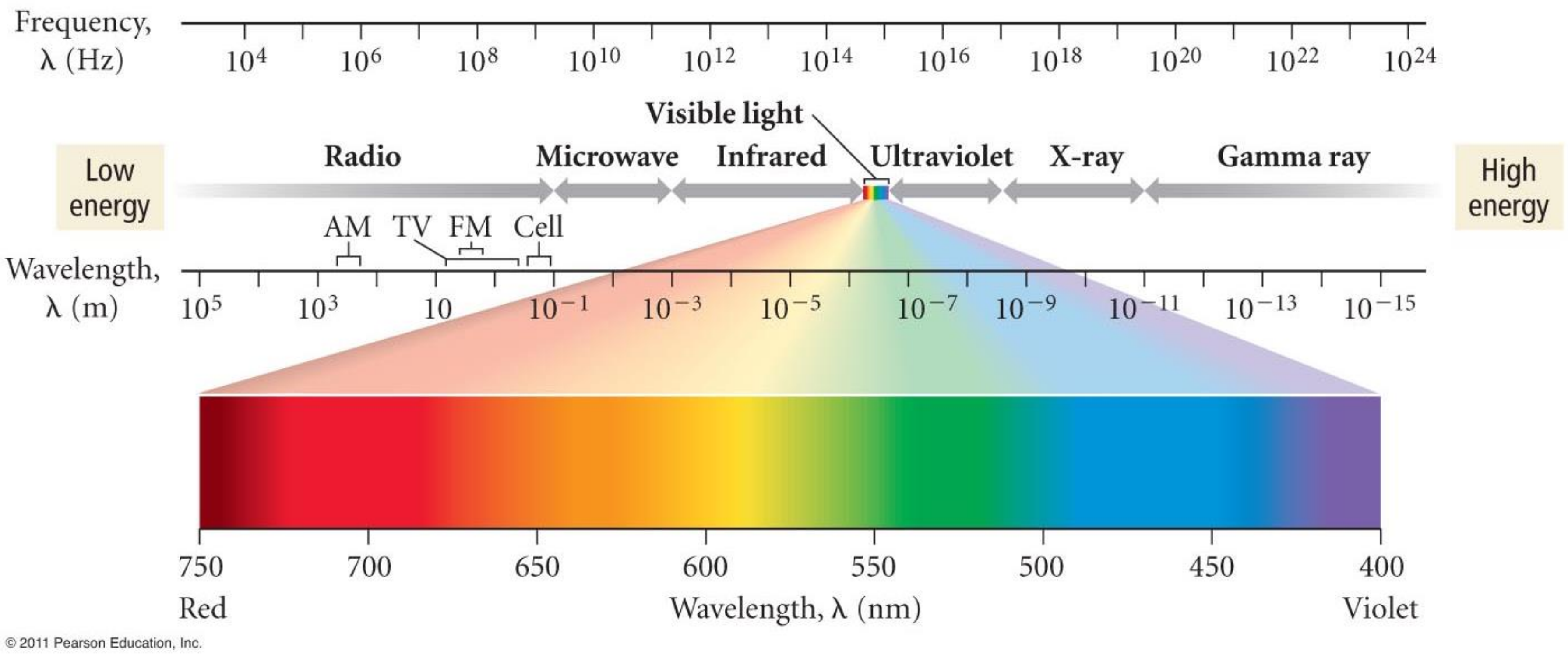
- The **amplitude** is the height of the wave
  - ✓ the amplitude is a measure of how intense the light is – the larger the amplitude, the brighter the light
- The **wavelength (λ)** is a measure of the distance covered by the wave
- The **frequency (ν)** is the number of waves that pass a point in a given period of time

  units are hertz (Hz) or cycles/s = s^{-1}
  - ➢ 1 Hz = 1 s^{-1}

Color

- The color of light is determined by its wavelength
  - ✓ or frequency
- White light is a mixture of all the colors of visible light
  - ✓ **a spectrum**
  - ✓ **R**ed**O**range**Y**ellow**G**reen**B**lue**V**iolet
- When an object absorbs some of the wavelengths of white light and reflects others, it appears colored
  - ✓ the observed color is predominantly the colors reflected

Electromagnetic Spectrum



Continuous Spectrum

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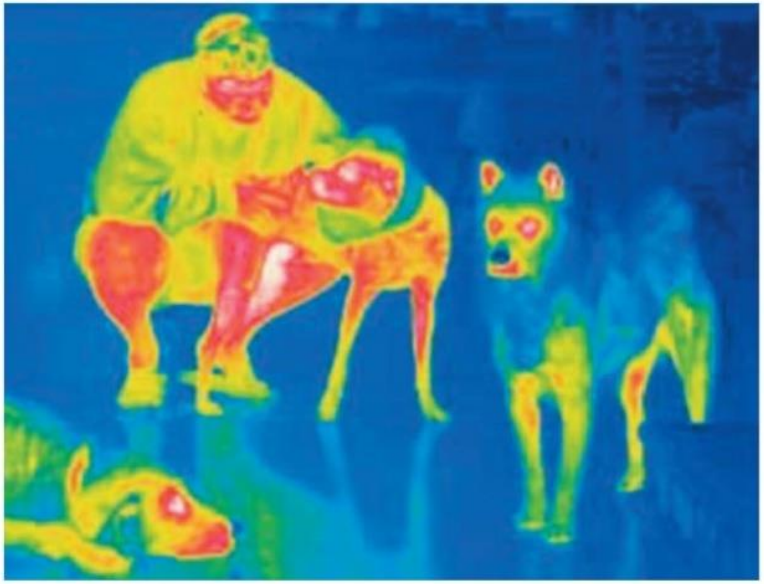
White light spectrum

Thermal Imaging using Infrared Light



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Sunburns Caused by High-Energy UV Radiation

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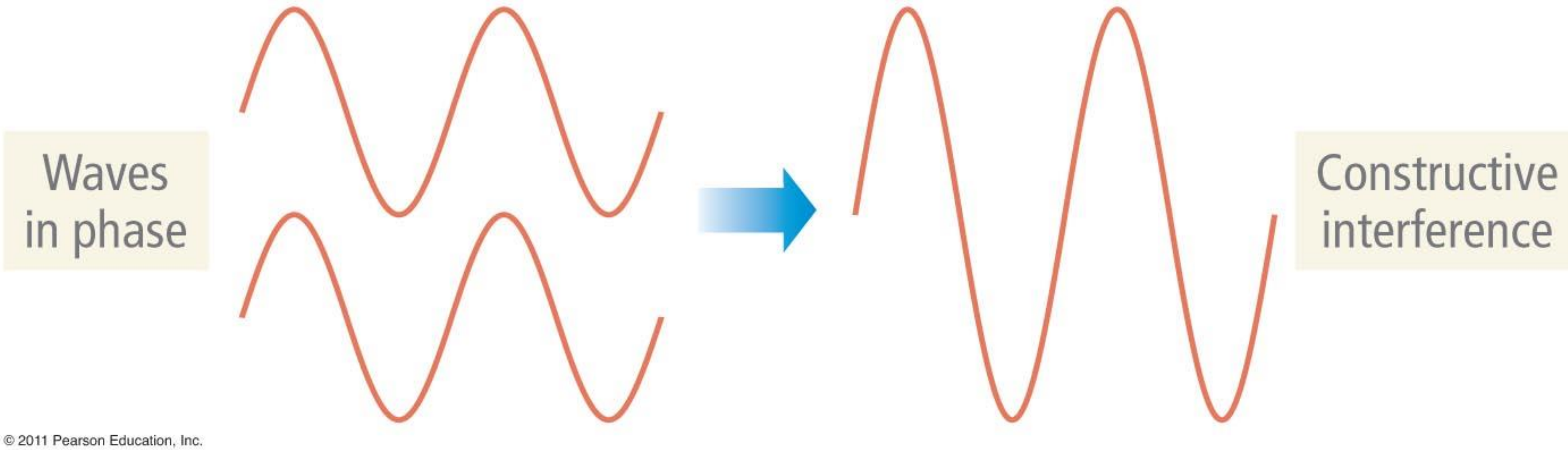
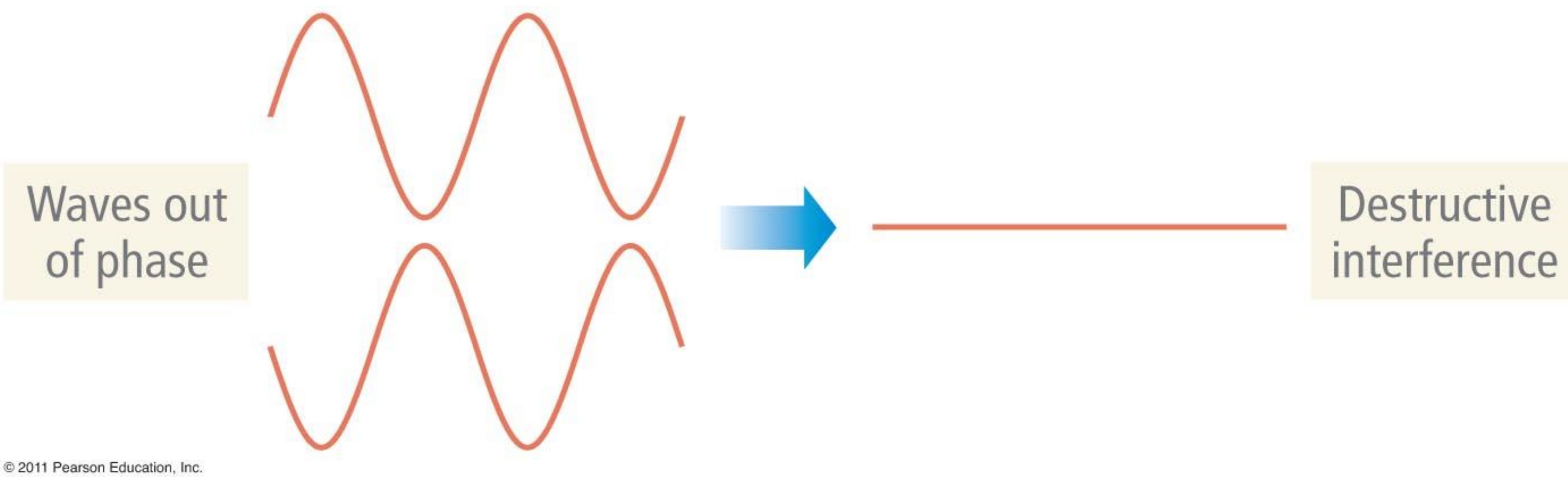
Interference

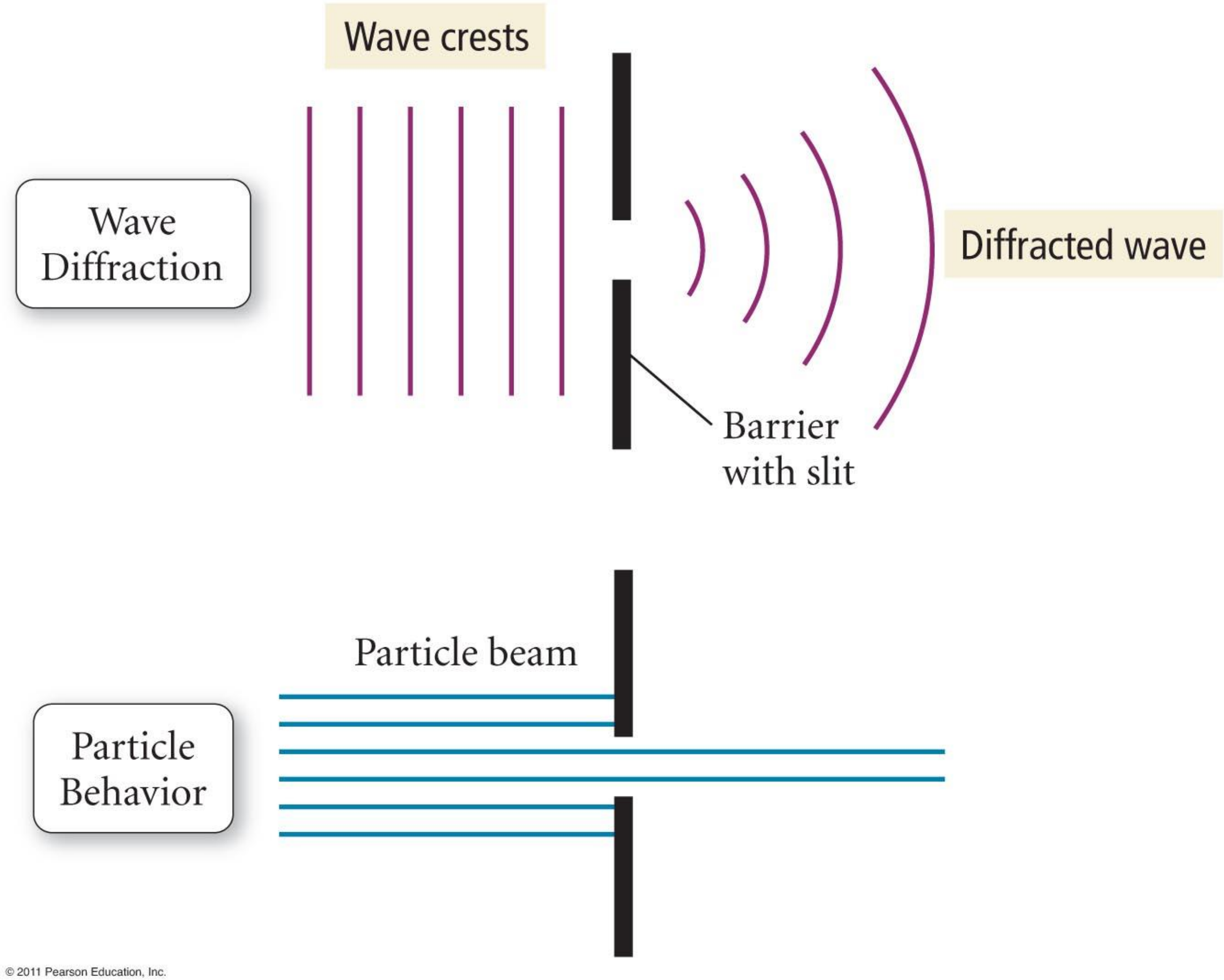
- The interaction between waves is called **interference**
- When waves interact so that they add to make a larger wave it is called **constructive interference**
  - ✓ waves are **in-phase**
- When waves interact so they cancel each other it is called **destructive interference**
  - ✓ waves are **out-of-phase**

Interference

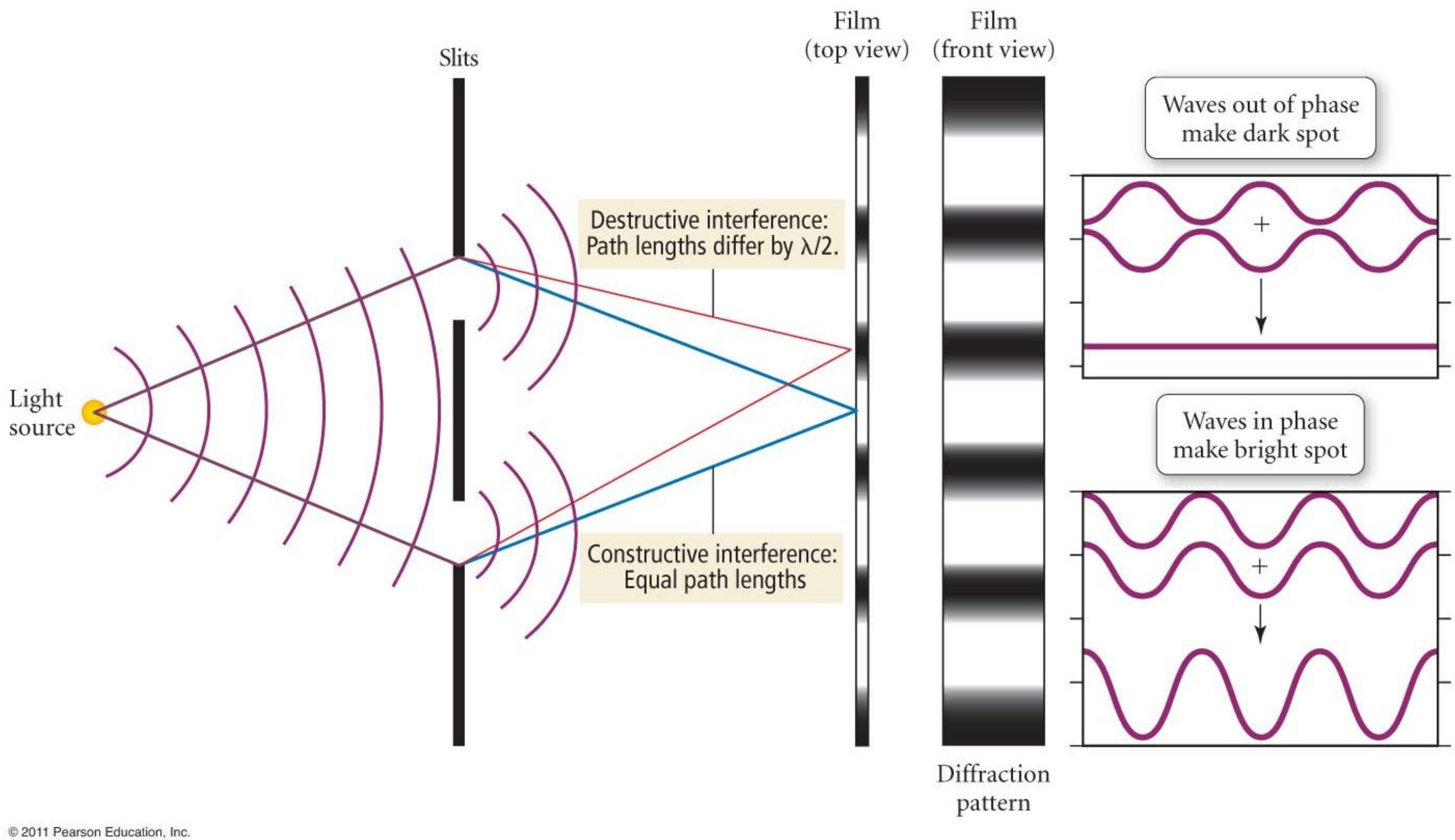




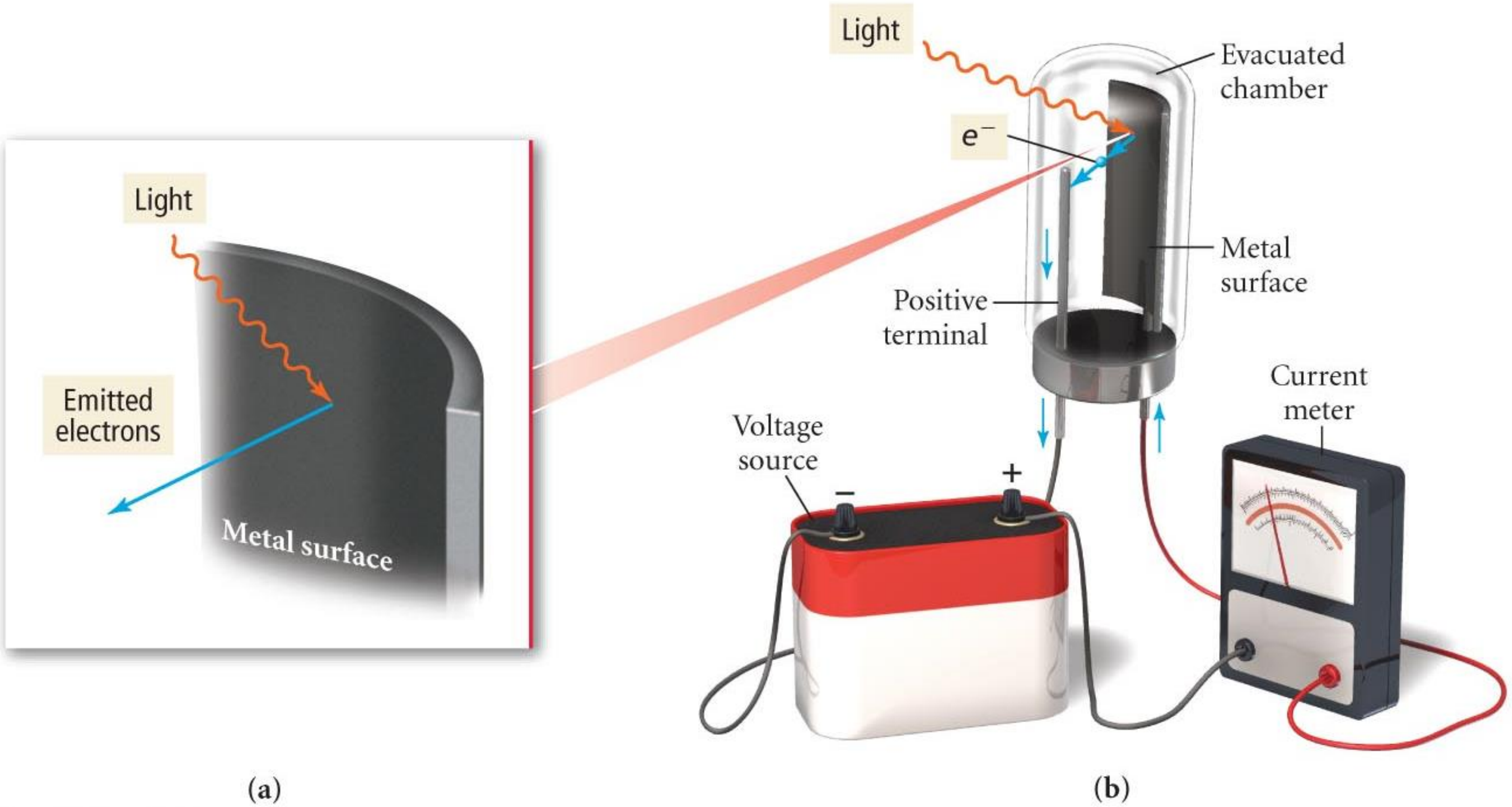
Diffraction



2-Slit Interference



The Photoelectric Effect



Einstein's Explanation

- Einstein proposed that the light energy was delivered to the atoms in packets, called **quanta** or **photons**
- ***The energy of a photon of light is directly proportional to its frequency***
  - ✓ inversely proportional to its wavelength
  - ✓ the proportionality constant is called **Planck's Constant, (h)** and has the value 6.626×10^{-34} J·s

$$E = h\nu = \frac{h \cdot c}{\lambda}$$

Ejected Electrons

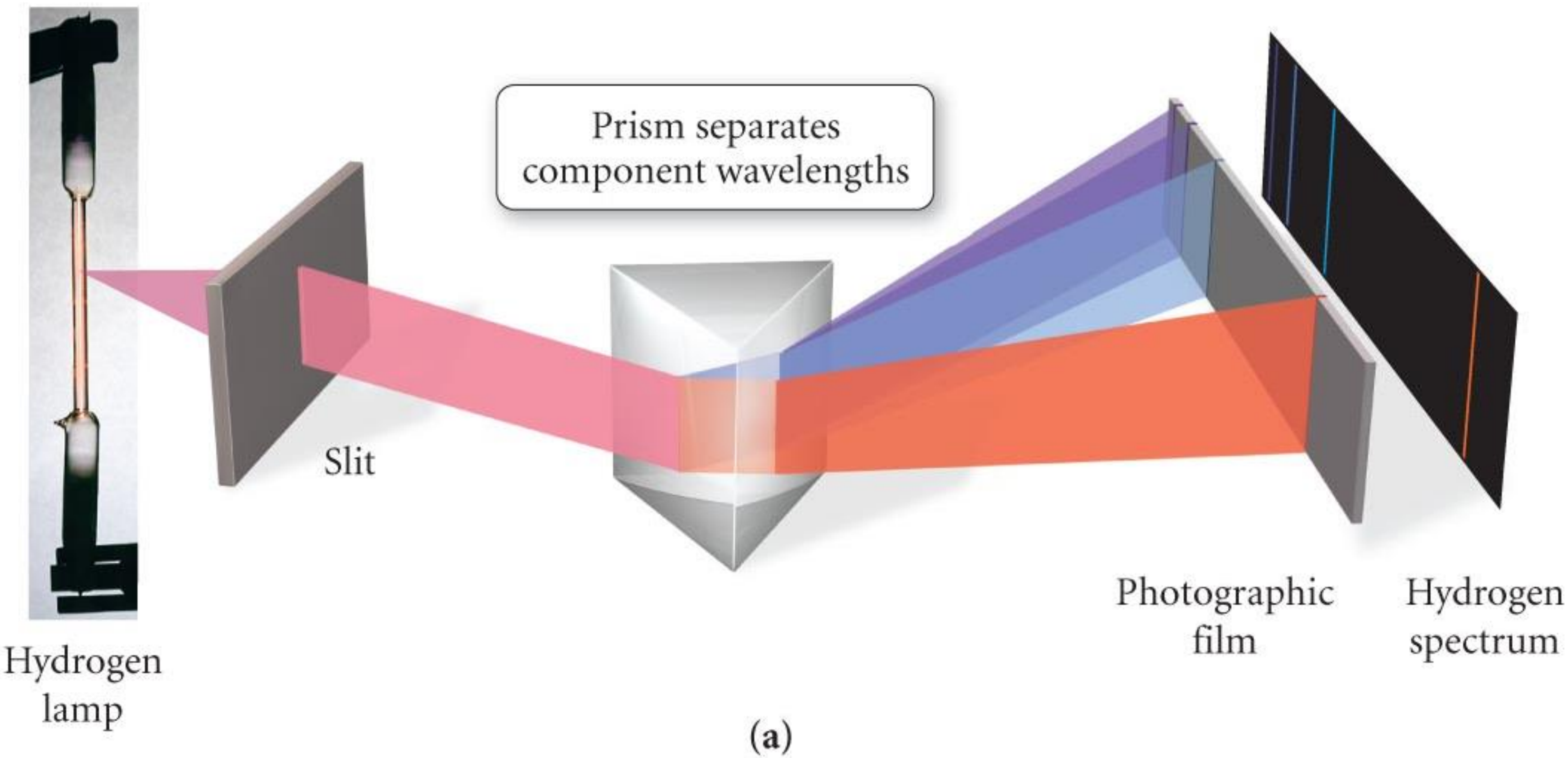
- One photon at the threshold frequency gives the electron just enough energy for it to escape the atom
  - ✓ **binding energy, ϕ**
- When irradiated with a shorter wavelength photon, the electron absorbs more energy than is necessary to escape
- This excess energy becomes kinetic energy of the ejected electron

$$\text{Kinetic Energy} = E_{\text{photon}} - E_{\text{binding}}$$

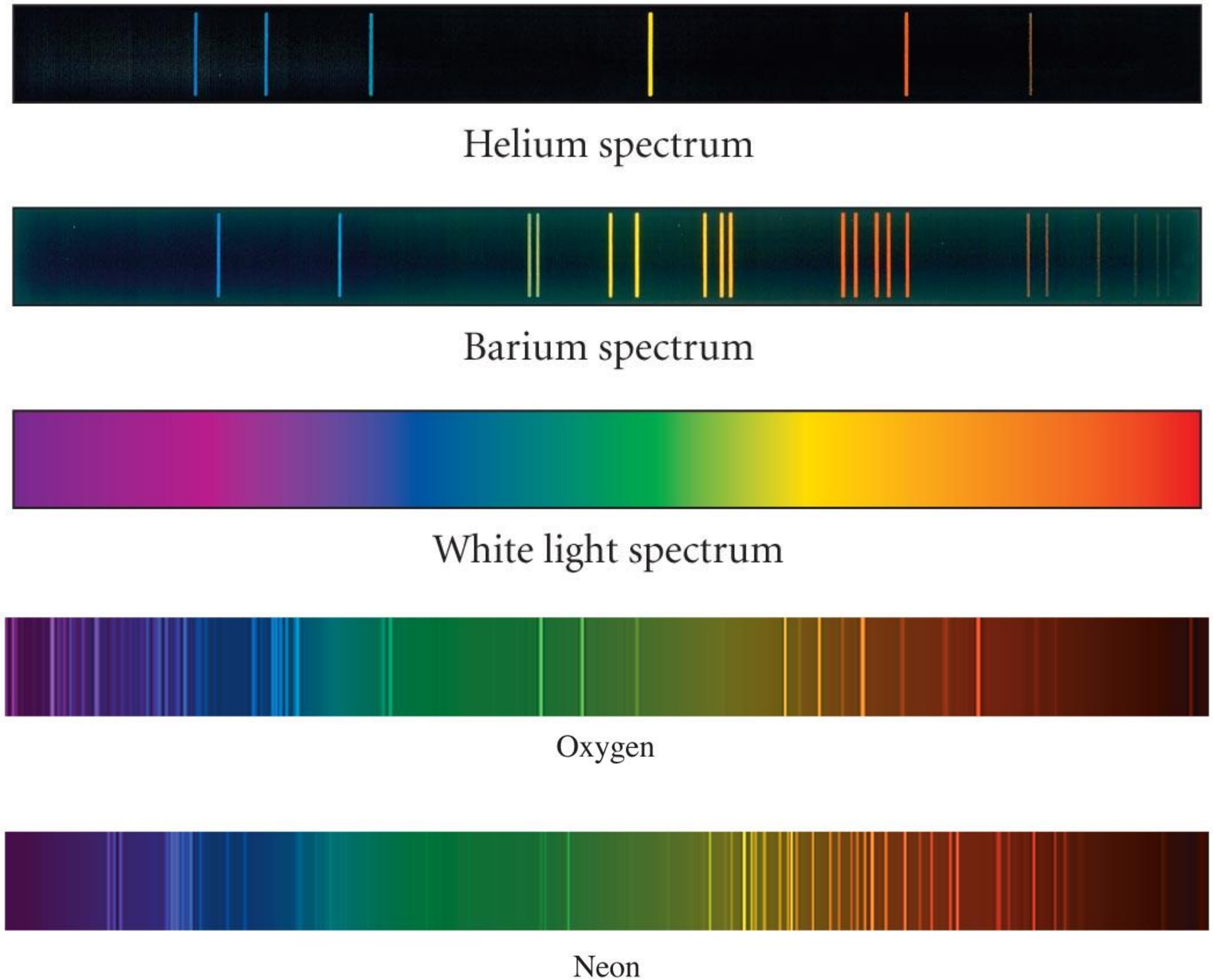
$$KE = h\nu - \phi$$

Exciting Gas Atoms to Emit Light with Electrical Energy

Emission Spectra



Examples of Spectra



Rydberg's Spectrum Analysis

Johannes Rydberg (1854–1919)

- Rydberg analyzed the spectrum of hydrogen and found that it could be described with an equation that involved an inverse square of integers

$$\frac{1}{\lambda} = 1.097 \times 10^{7}\ \mathrm{m}^{-1}\left(\frac{1}{n_1^{\,2}} - \frac{1}{n_2^{\,2}}\right)$$

Rutherford’s Nuclear Model

- The atom contains a tiny dense center called the **nucleus**
  - ✓ the volume is about 1/10 trillionth the volume of the atom
- The nucleus is essentially the entire mass of the atom
- The nucleus is positively charged
  - ✓ the amount of positive charge balances the negative charge of the electrons
- The electrons move around in the empty space of the atom surrounding the nucleus

Problems with Rutherford's Nuclear Model of the Atom

- Electrons are moving charged particles
- According to classical physics, moving charged particles give off energy
- Therefore electrons should constantly be giving off energy
  - ✓ should cause the atom to glow!
- The electrons should lose energy, crash into the nucleus, and the atom should collapse!!
  - ✓ but it doesn't!

The Bohr Model of the Atom

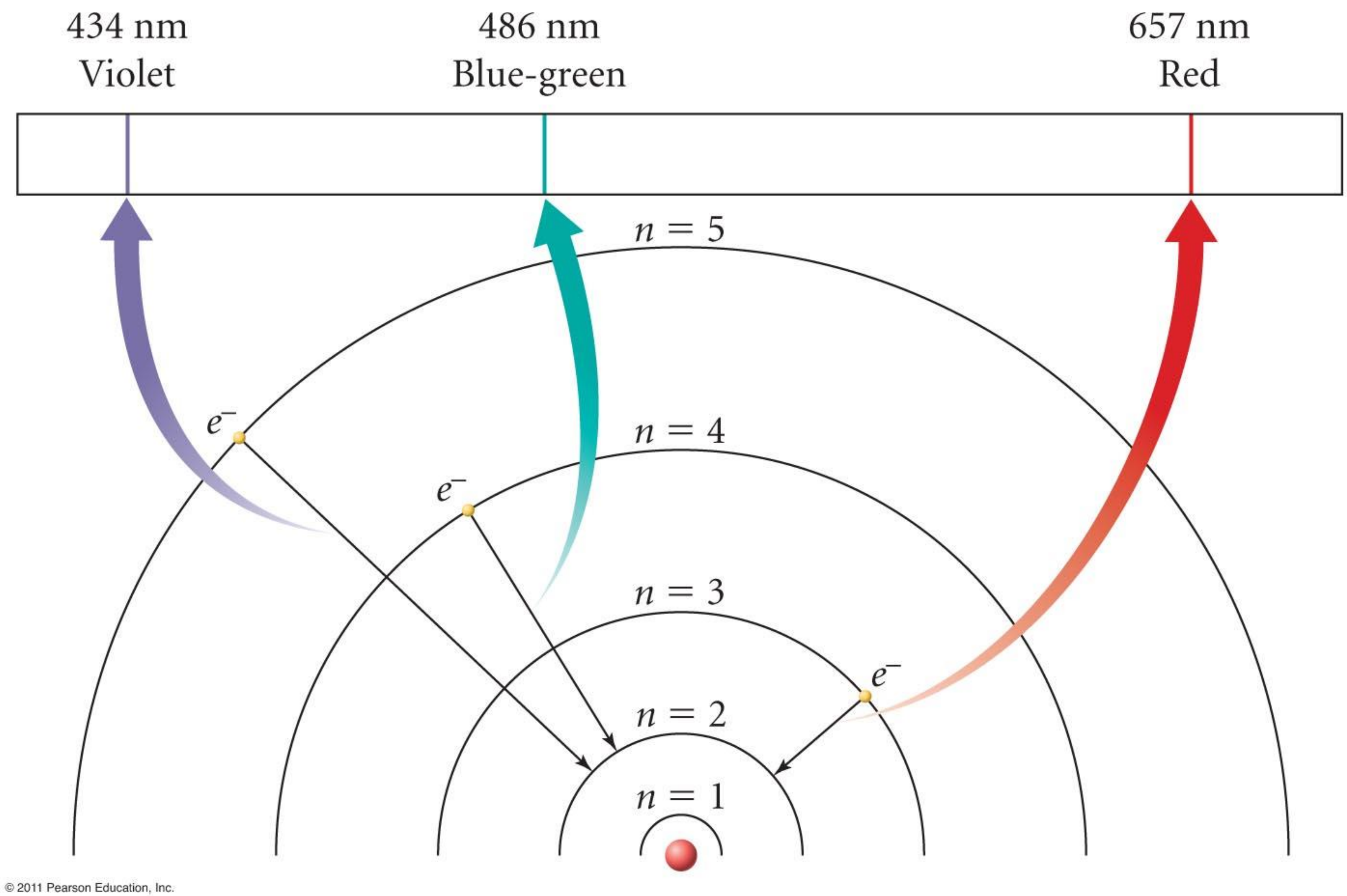
Neils Bohr (1885–1962)

- The nuclear model of the atom does not explain what structural changes occur when the atom gains or loses energy
- Bohr developed a model of the atom to explain how the structure of the atom changes when it undergoes energy transitions
- Bohr's major idea was that the energy of the atom was **quantized**, and that the amount of energy in the atom was related to the electron's position in the atom
  - ✓ **quantized** means that the atom could only have very specific amounts of energy

Bohr's Model

- The electrons travel in orbits that are at a fixed distance from the nucleus
  - ✓ **stationary states**
  - ✓ therefore the energy of the electron was proportional to the distance the orbit was from the nucleus
- Electrons emit radiation when they "jump" from an orbit with higher energy down to an orbit with lower energy
  - ✓ the emitted radiation was a photon of light
  - ✓ the distance between the orbits determined the energy of the photon of light produced

Bohr Model of H Atoms



Wave Behavior of Electrons

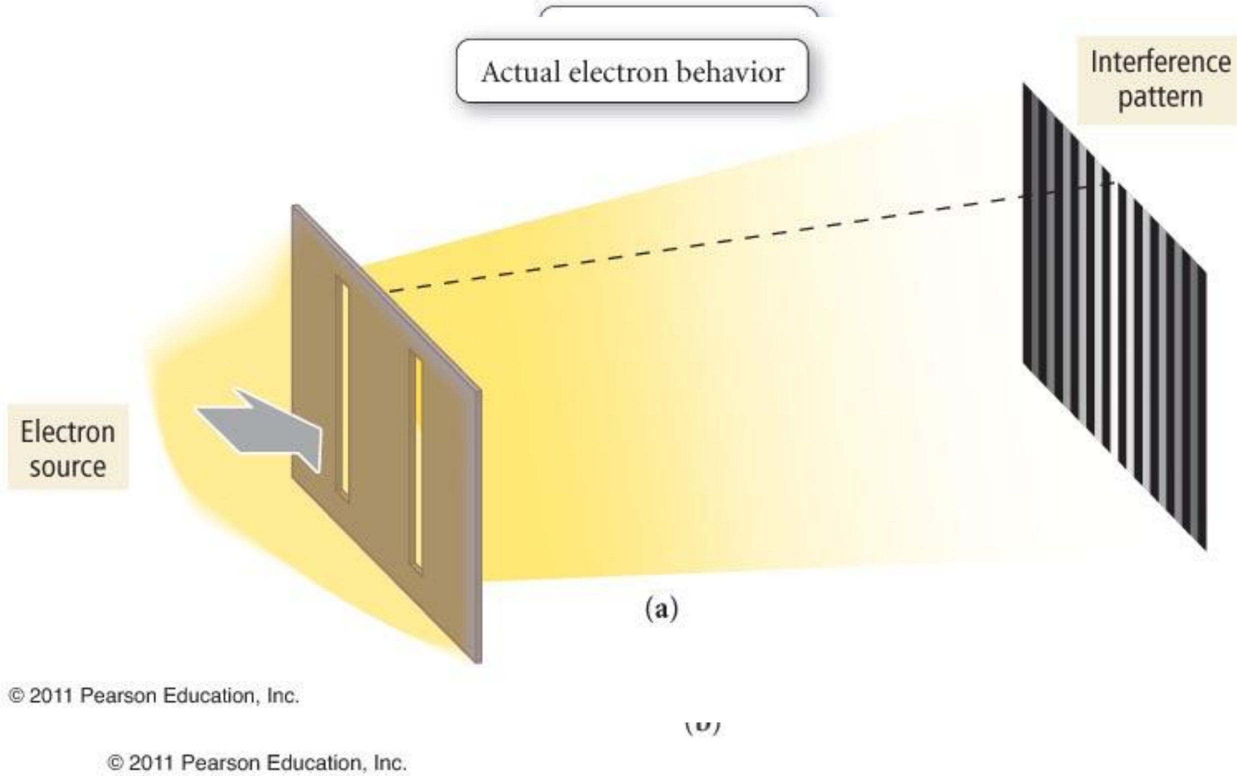
Louis de Broglie (1892–1987)

- de Broglie proposed that particles could have wave-like character
- de Broglie predicted that the wavelength of a particle was inversely proportional to its momentum
- Because it is so small, the wave character of electrons is significant

$$\lambda(\mathrm{m}) = \frac{h\left(\frac{\mathrm{kg} \bullet \mathrm{m}^2}{\mathrm{s}^2} \bullet \mathrm{s}\right)}{\mathrm{mass}_{(\mathrm{kg})} \bullet \mathrm{velocity}_{(\mathrm{m} \bullet \mathrm{s}^{-1})}}$$

Electron Diffraction

- Proof that the electron had wave nature came a few years later with the demonstration that a beam of electrons would produce an interference pattern as waves do



If electrons behave only like particles, there should only be two bright spots on the target

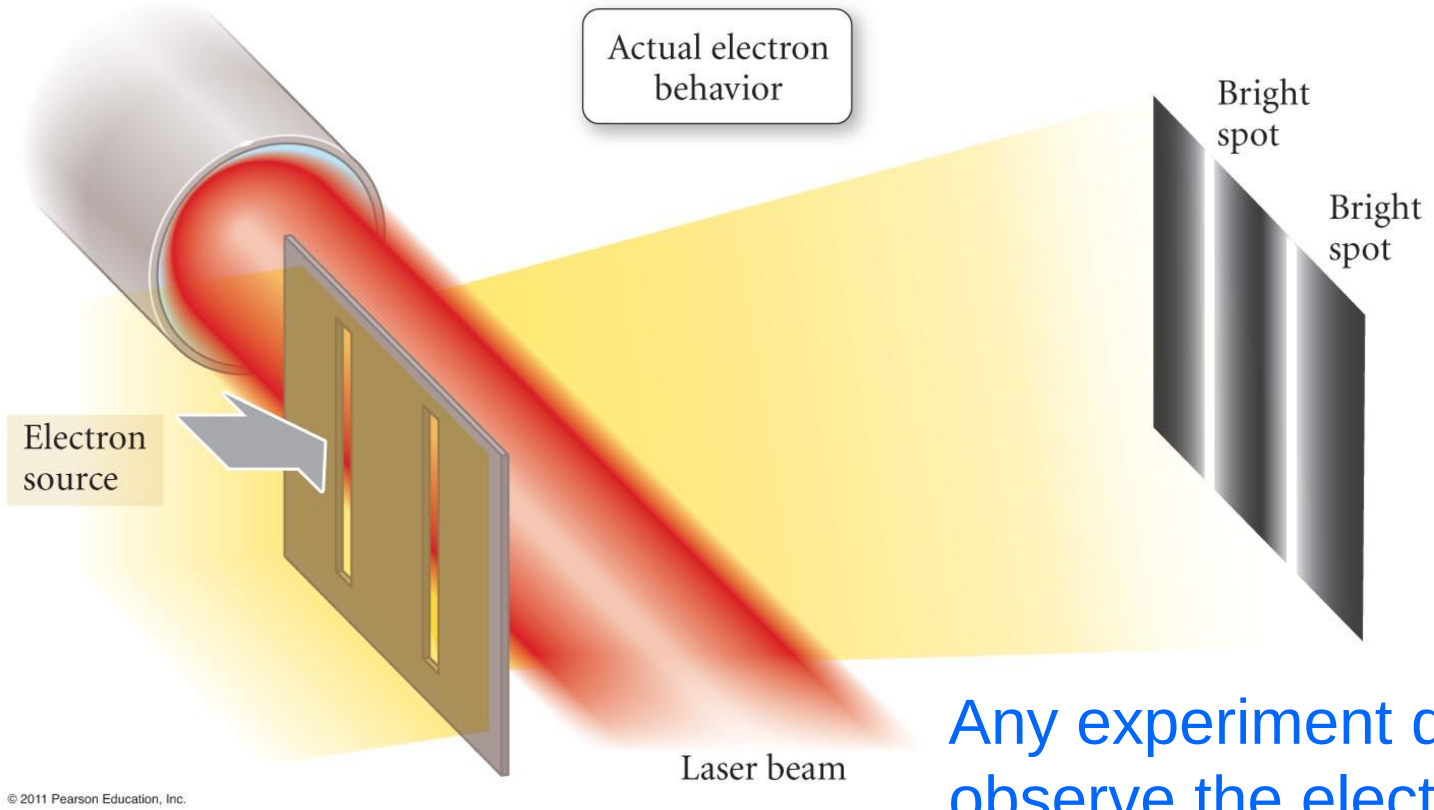
However, electrons actually present an interference pattern, demonstrating they behave like waves

Uncertainty Principle

$$\Delta x \times \Delta v \geq \frac{h}{4\pi}\left(\frac{1}{m}\right)$$

- Heisenberg stated that the product of the uncertainties in both the position and speed of a particle was inversely proportional to its mass
  - ✓ x = position, Δx = uncertainty in position
  - ✓ v = velocity, Δv = uncertainty in velocity
  - ✓ m = mass
- This means that the more accurately you know the position of a small particle, such as an electron, the less you know about its speed
  - ✓ and vice-versa

Uncertainty Principle Demonstration



Any experiment designed to observe the electron results in detection of a single electron particle and no interference pattern

Electron Energy

- Electron energy and position are complementary
  - ✓ because $KE = \frac{1}{2}mv^2$
- For an electron with a given energy, the best we can do is describe a region in the atom of high probability of finding it
- Many of the properties of atoms are related to the energies of the electrons

Schrödinger's Equation $\mathcal{H}\psi = E\psi$

- Schödinger's Equation allows us to calculate the probability of finding an electron with a particular amount of energy at a particular location in the atom
- Solutions to Schödinger's Equation produce many wave functions, Ψ
- A plot of distance vs. Ψ^2 represents an **orbital**, a probability distribution map of a region where the electron is likely to be found

Solutions to the Wave Function, Ψ

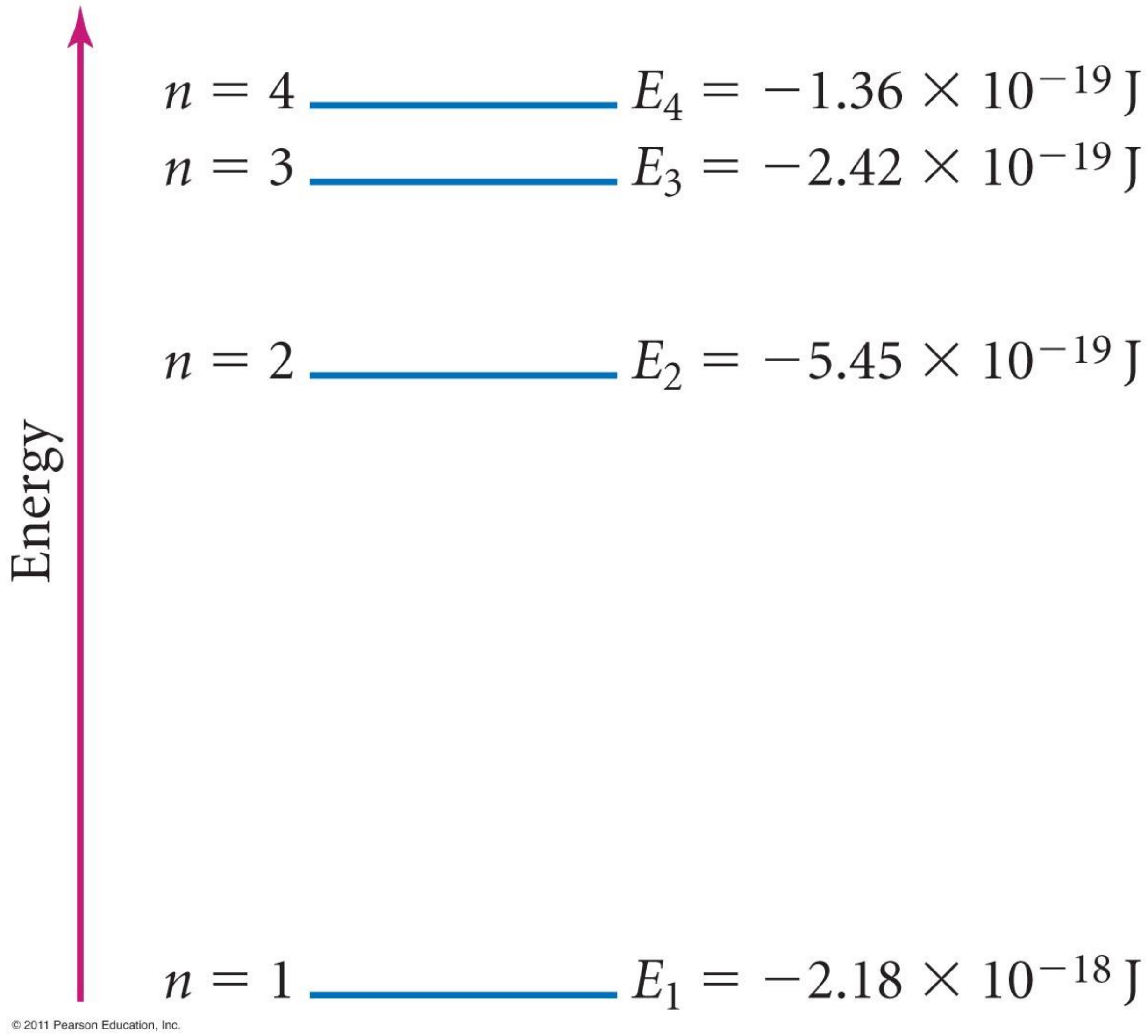
- Calculations show that the size, shape, and orientation in space of an orbital are determined to be three integer terms in the wave function
  - ✓ added to quantize the energy of the electron
- These integers are called **quantum numbers**
  - ✓ principal quantum number, ***n***
  - ✓ angular momentum quantum number, ***l***
  - ✓ magnetic quantum number, $\boldsymbol{m_l}$

Principal Quantum Number, *n*

- Characterizes the energy of the electron in a particular orbital
  - ✓ corresponds to Bohr's energy level
- *n* can be any integer ≥ 1
- The larger the value of *n*, the more energy the orbital has
- Energies are defined as being negative
  - ✓ an electron would have E = 0 when it just escapes the atom
- The larger the value of *n*, the larger the orbital
- As *n* gets larger, the amount of energy between orbitals gets smaller

$$E_n = -2.18 \times 10^{-18}\ \mathrm{J}\left(\frac{1}{n^2}\right)$$ for an electron in H

Principal Energy Levels in Hydrogen



Angular Momentum Quantum Number, *l*

- The angular momentum quantum number determines the shape of the orbital
- ***l*** can have integer values from 0 to (n – 1)
- Each value of *l* is called by a particular letter that designates the shape of the orbital
  - ✓ ***s*** orbitals are spherical
  - ✓ ***p*** orbitals are like two balloons tied at the knots
  - ✓ ***d*** orbitals are mainly like four balloons tied at the knot
  - ✓ ***f*** orbitals are mainly like eight balloons tied at the knot

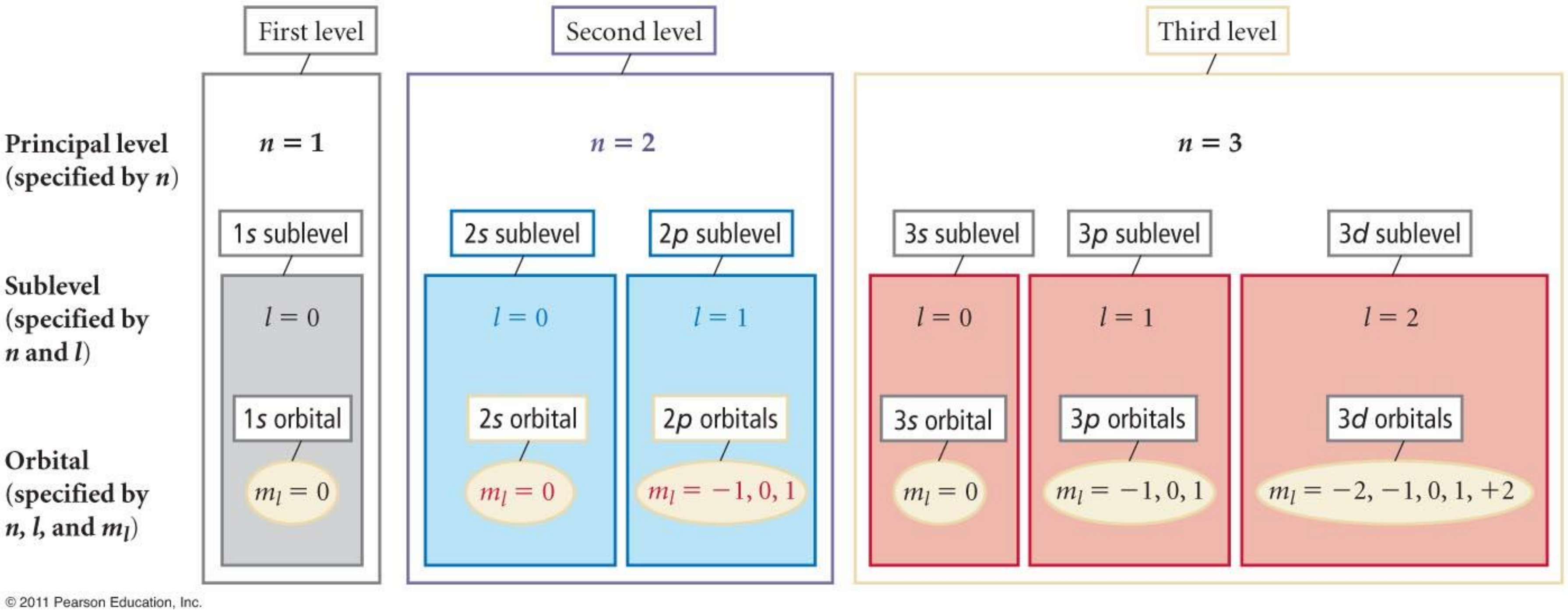
Magnetic Quantum Number, m_l

- The magnetic quantum number is an integer that specifies the orientation of the orbital
  - ✓ the direction in space the orbital is aligned relative to the other orbitals
- Values are integers from −*l* to +*l*
  - ✓ including zero
  - ✓ gives the number of orbitals of a particular shape
    - ➢ when $l = 2$, the values of m_l are −2, −1, 0, +1, +2; which means there are five orbitals with $l = 2$

Describing an Orbital

- Each set of n, l, and m_l describes one orbital
- Orbitals with the same value of n are in the same **principal energy level**
  - ✓aka principal shell
- Orbitals with the same values of n and l are said to be in the same **sublevel**
  - ✓aka subshell

Energy Shells and Subshells



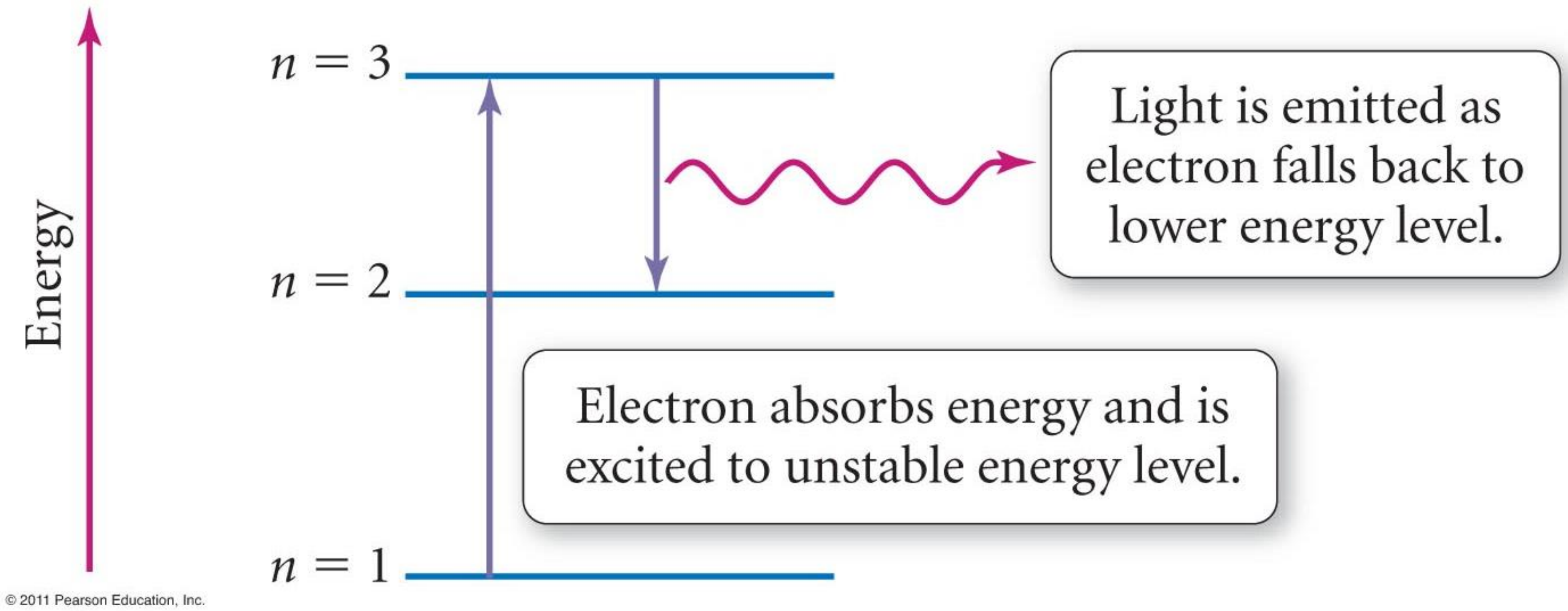
Quantum Mechanical Explanation of Atomic Spectra

- Each wavelength in the spectrum of an atom corresponds to an electron transition between orbitals
- When an electron is **excited**, it transitions from an orbital in a lower energy level to an orbital in a higher energy level
- When an electron **relaxes**, it transitions from an orbital in a higher energy level to an orbital in a lower energy level
- When an electron relaxes, a photon of light is released whose energy equals the energy difference between the orbitals

Electron Transitions

- To transition to a higher energy state, the electron must gain the correct amount of energy corresponding to the difference in energy between the final and initial states
- Electrons in high energy states are unstable and tend to lose energy and transition to lower energy states
- Each line in the emission spectrum corresponds to the difference in energy between two energy states

Quantum Leaps



Predicting the Spectrum of Hydrogen

- The wavelengths of lines in the emission spectrum of hydrogen can be predicted by calculating the difference in energy between any two states
- For an electron in energy state *n*, there are (n – 1) energy states it can transition to, therefore (n – 1) lines it can generate
- Both the Bohr and Quantum Mechanical Models can predict these lines very accurately for a 1-electron system

Energy Transitions in Hydrogen

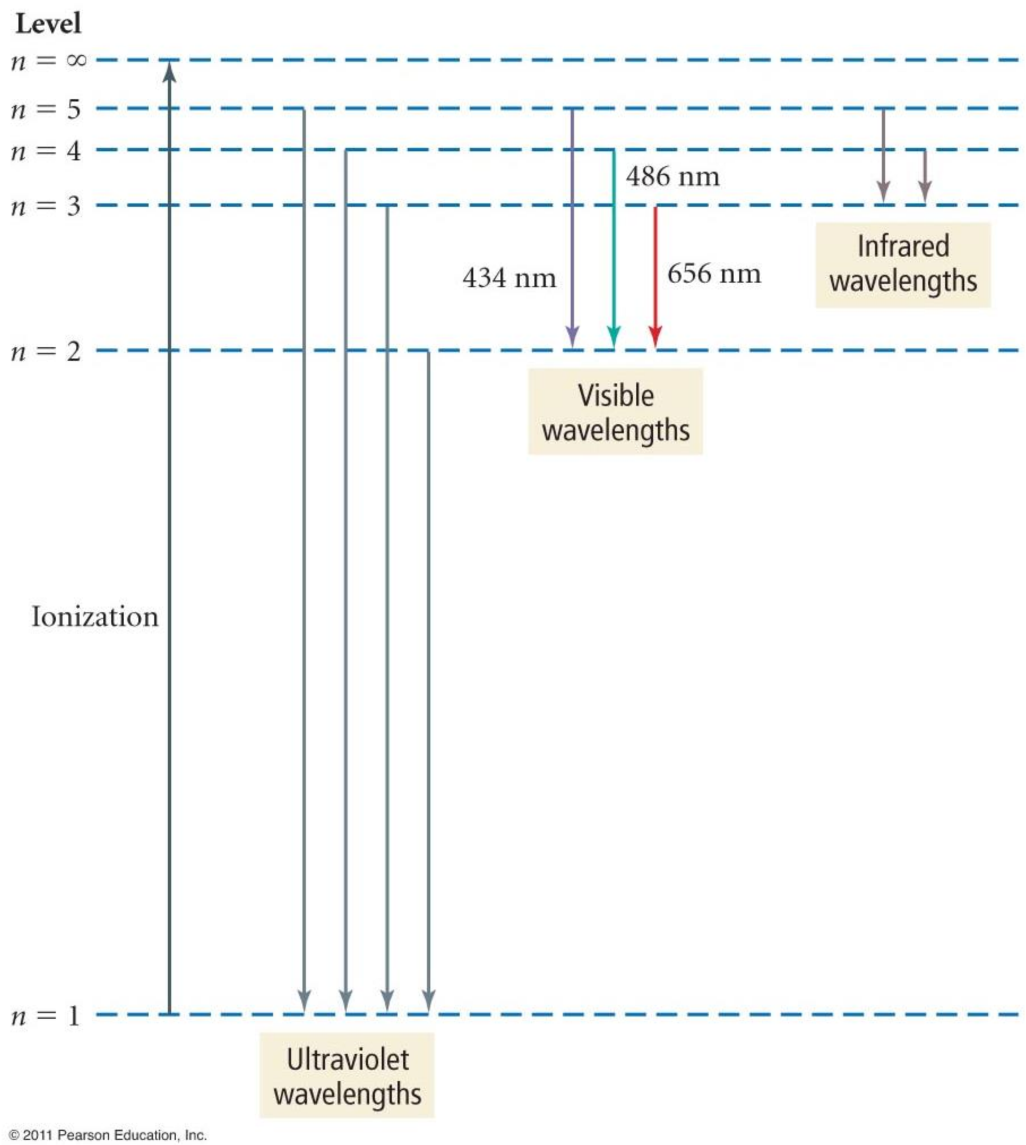
- The energy of a photon released is equal to the difference in energy between the two levels the electron is jumping between
- It can be calculated by subtracting the energy of the initial state from the energy of the final state

$$\Delta E_{electron} = E_{final\ state} - E_{initial\ state} \qquad E_{emitted\ photon} = -\Delta E_{electron}$$

$$E_{photon} = -\left[\left(-2.18\times10^{-18}\ \mathrm{J}\left(\frac{1}{n_{final}^{\ 2}}\right)\right) - \left(-2.18\times10^{-18}\ \mathrm{J}\left(\frac{1}{n_{initial}^{\ 2}}\right)\right)\right]$$

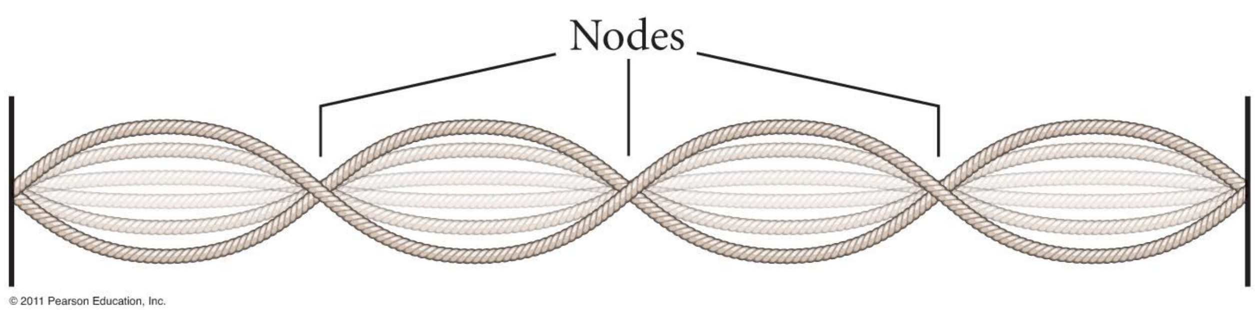
$$\frac{hc}{\lambda} = E_{photon} = 2.18\times10^{-18}\ \mathrm{J}\left[\left(\frac{1}{n_{final}^{\ 2}}\right) - \left(\frac{1}{n_{initial}^{\ 2}}\right)\right]$$

Hydrogen Energy Transitions



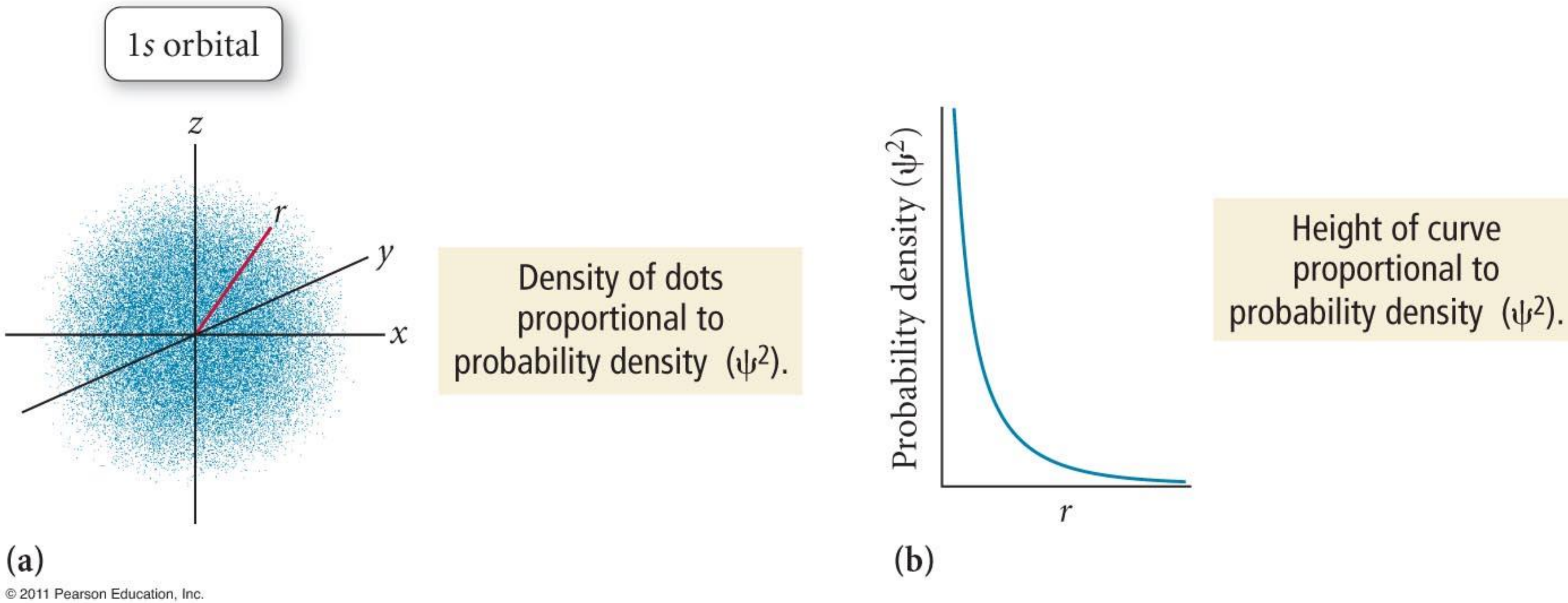
Probability & Radial Distribution Functions

- ψ^2 is the probability density
  - ✓ the probability of finding an electron at a particular point in space
  - ✓ for ***s*** orbital maximum at the nucleus?
  - ✓ decreases as you move away from the nucleus
- The Radial Distribution function represents the total probability at a certain distance from the nucleus
  - ✓ maximum at most probable radius
- **Nodes** in the functions are where the probability drops to 0



Probability Density Function

The probability density function represents the total probability of finding an electron at a particular point in space

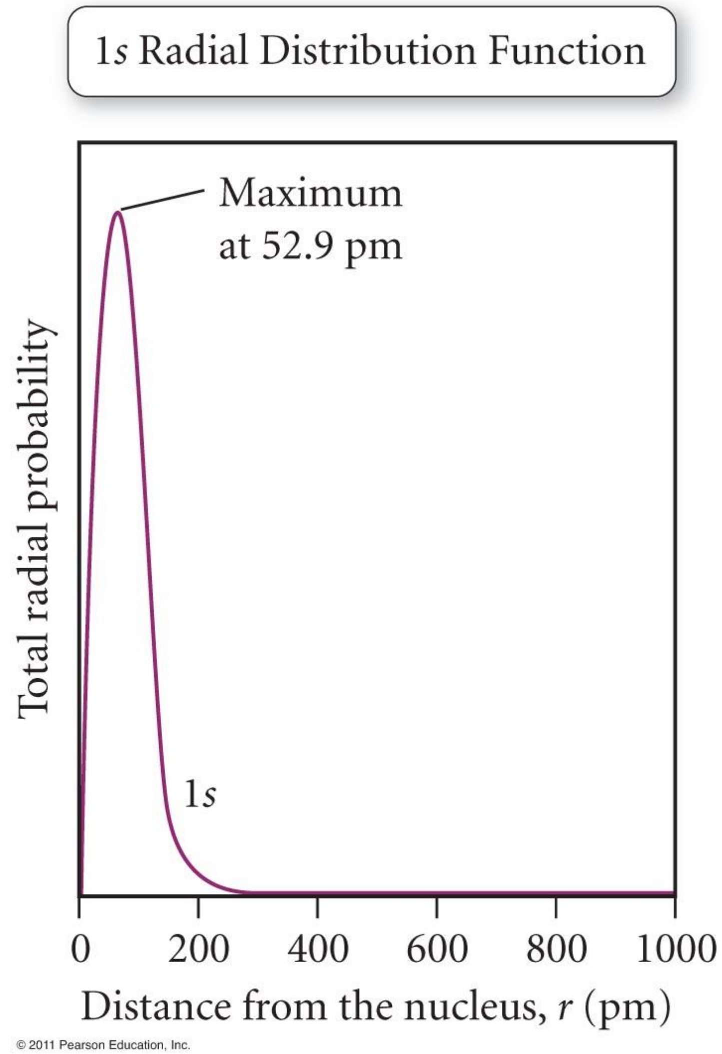


Radial Distribution Function

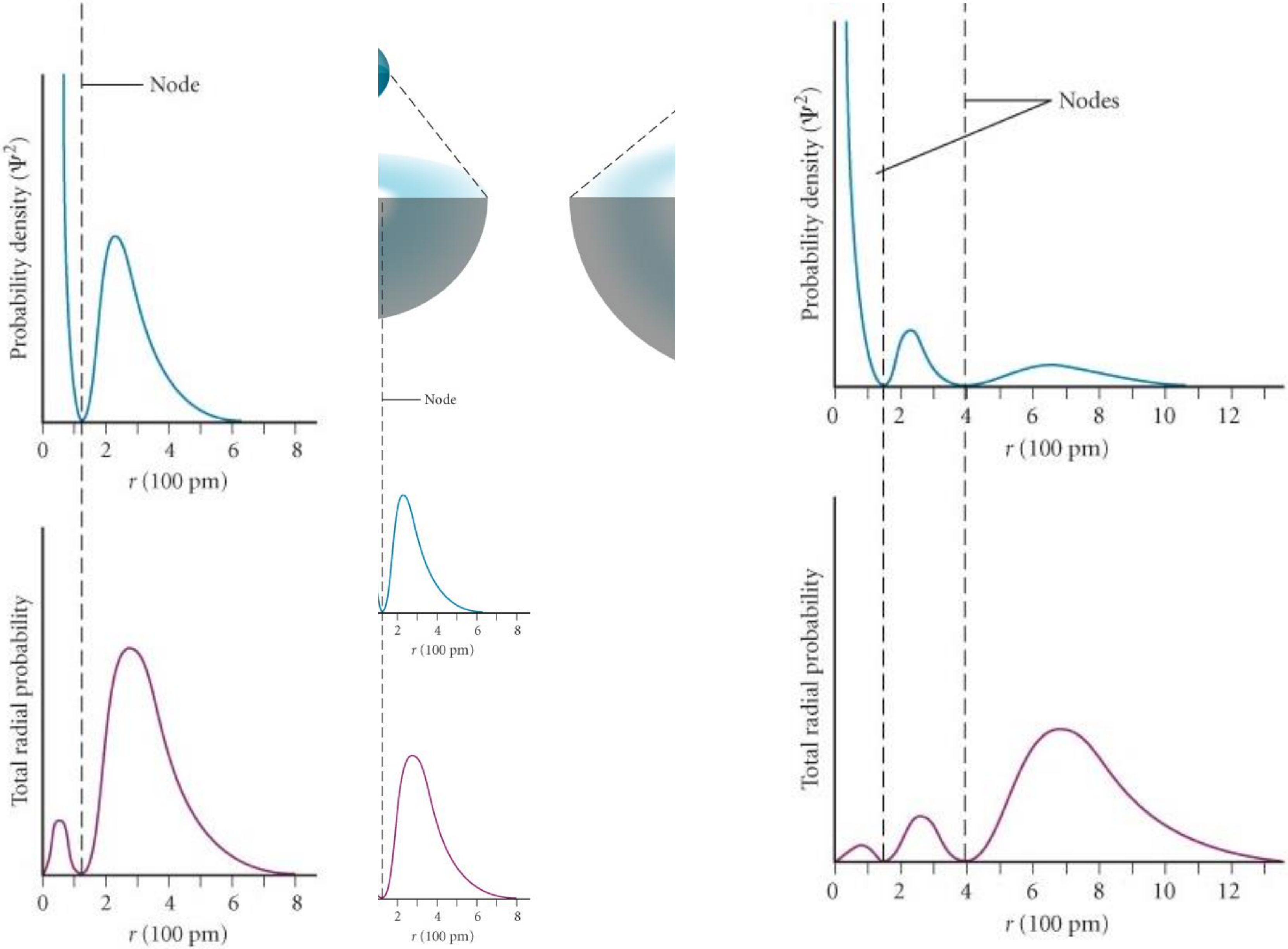
The radial distribution function represents the **total probability** of finding an electron within a thin spherical shell at a **distance** *r* from the nucleus

The probability at a point decreases with increasing distance from the nucleus, but the volume of the spherical shell increases

The net result is a plot that indicates the most probable distance of the electron in a 1*s* orbital of H is 52.9 pm



2*s* and 3*s*



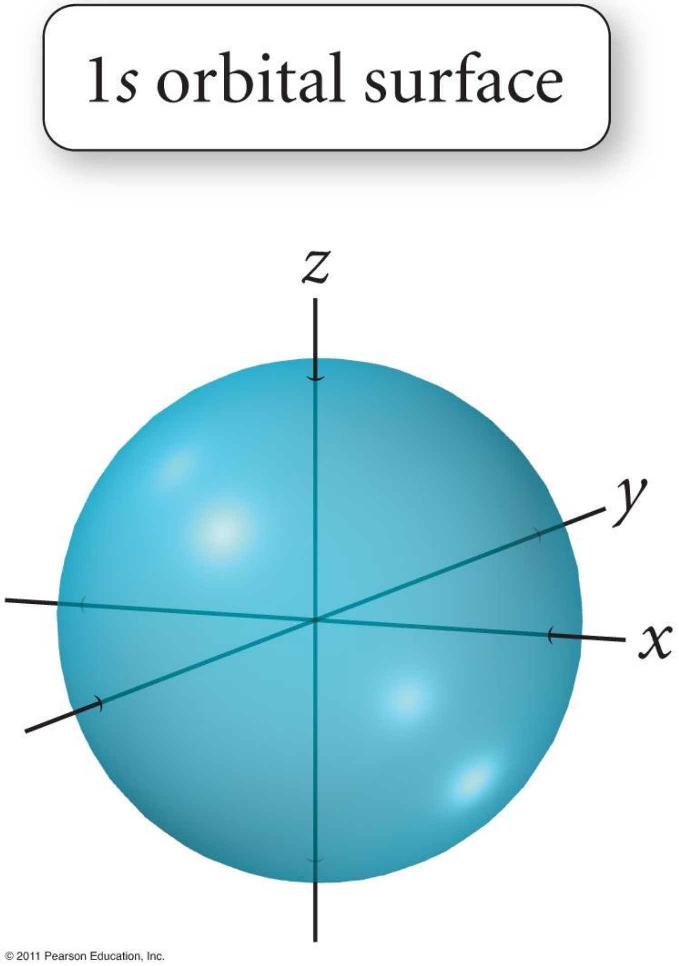
Node
Probability density (Ψ^2)
0 2 4 6 8
r (100 pm)
Total radial probability
0 2 4 6 8
r (100 pm)
Node
2 4 6 8
r (100 pm)
2 4 6 8
r (100 pm)
Nodes
Probability density (Ψ^2)
0 2 4 6 8 10 12
r (100 pm)
Total radial probability
0 2 4 6 8 10 12
r (100 pm)

The Shapes of Atomic Orbitals

- The ***l*** quantum number primarily determines the shape of the orbital
- ***l*** can have integer values from 0 to (n – 1)
- Each value of *l* is called by a particular letter that designates the shape of the orbital
  - ✓ ***s*** orbitals are spherical
  - ✓ ***p*** orbitals are like two balloons tied at the knots
  - ✓ ***d*** orbitals are mainly like four balloons tied at the knot
  - ✓ ***f*** orbitals are mainly like eight balloons tied at the knot

l = 0, the ***s*** orbital

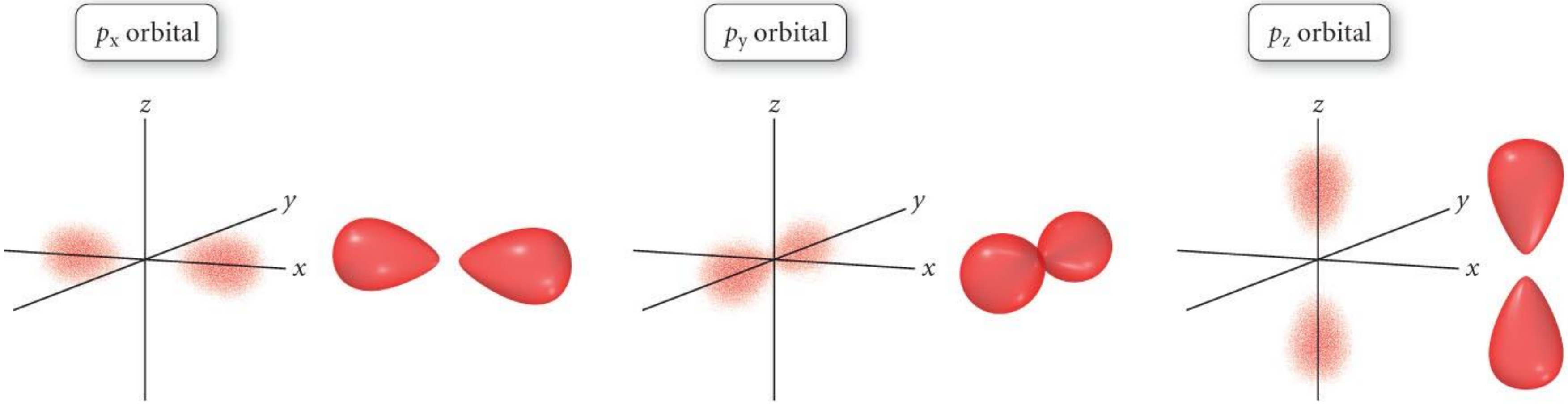
- Each principal energy level has one ***s*** orbital
- Lowest energy orbital in a principal energy state
- Spherical
- Number of nodes = (*n* – 1)

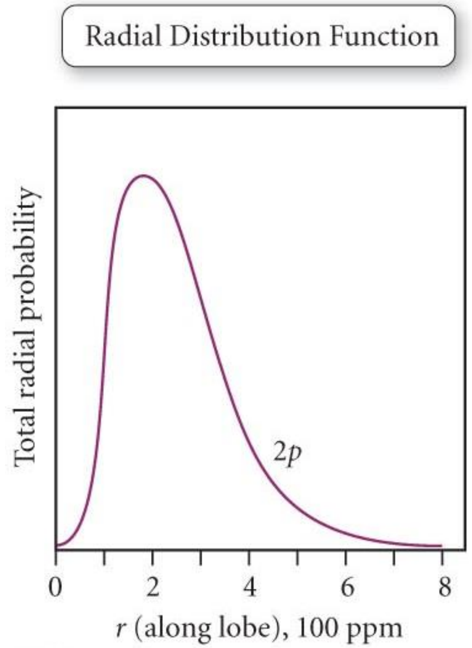


l = 1, ***p*** orbitals

- Each principal energy state above *n* = 1 has three ***p*** orbitals
  - ✓ $m_l = -1, 0, +1$
- Each of the three orbitals points along a different axis
  - ✓ $\boldsymbol{p_x, p_y, p_z}$
- 2nd lowest energy orbitals in a principal energy state
- Two-lobed
- One node at the nucleus, total of *n* nodes

p orbitals

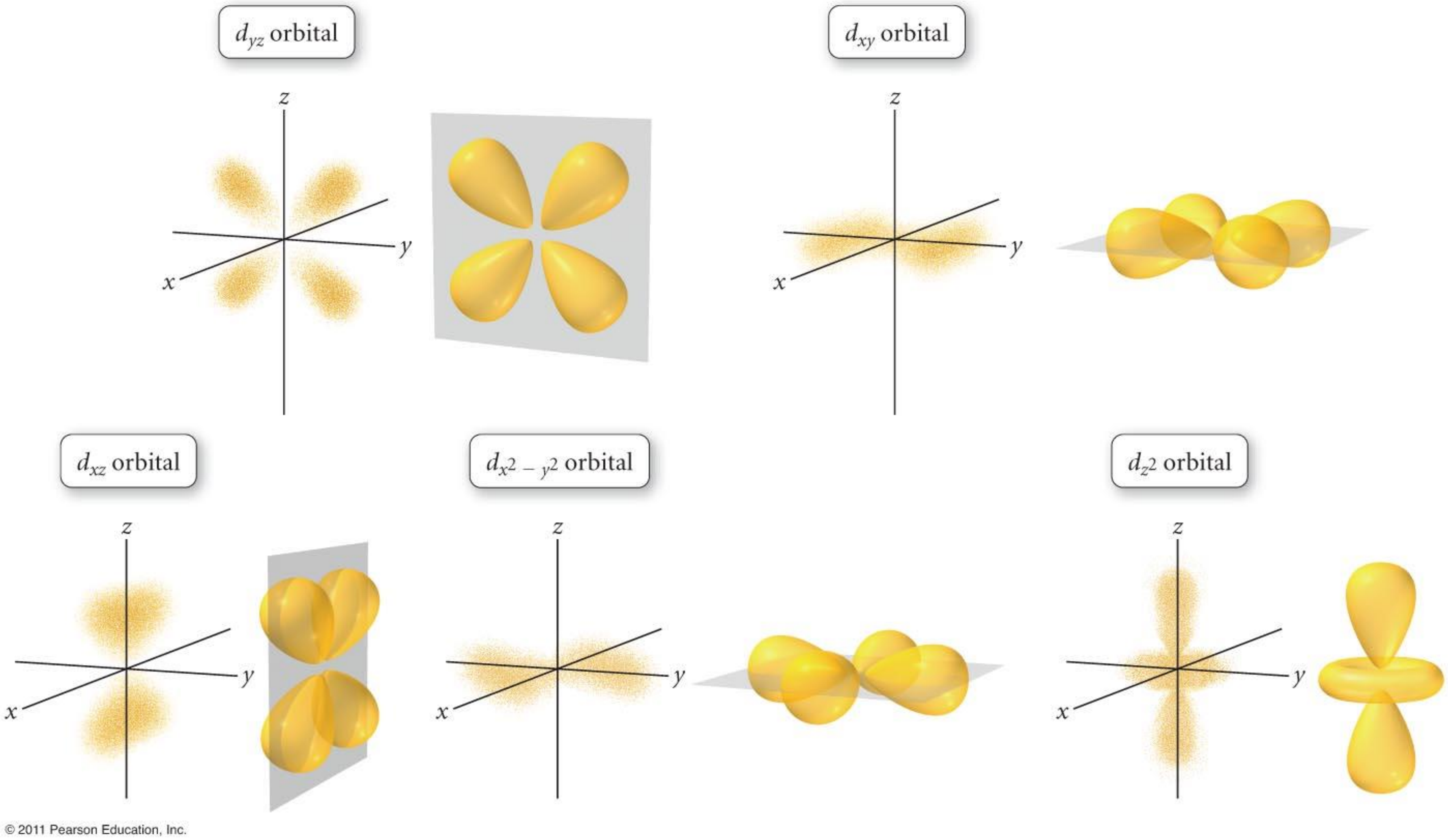

p_x orbital
p_y orbital
p_z orbital
z
y
x


Radial Distribution Function
Total radial probability
2p
0
2
4
6
8
r (along lobe), 100 ppm

l = 2, *d* orbitals

- Each principal energy state above $n = 2$ has five ***d*** orbitals
  - ✓ $m_l = -2, -1, 0, +1, +2$
- Four of the five orbitals are aligned in a different plane
  - ✓ the fifth is aligned with the *z* axis, $\boldsymbol{d_{z\ squared}}$
  - ✓ $\boldsymbol{d_{xy}, d_{yz}, d_{xz}, d_{x\ squared\ -\ y\ squared}}$
- 3rd lowest energy orbitals in a principal energy level
- Mainly four-lobed
  - ✓ one is two-lobed with a toroid
- Planar nodes
  - ✓ higher principal levels also have spherical nodes

d orbitals



d_{yz} orbital
z
y
x
d_{xy} orbital
z
y
x
d_{xz} orbital
z
y
x
$d_{x^2-y^2}$ orbital
z
y
x
d_{z^2} orbital
z
y
x
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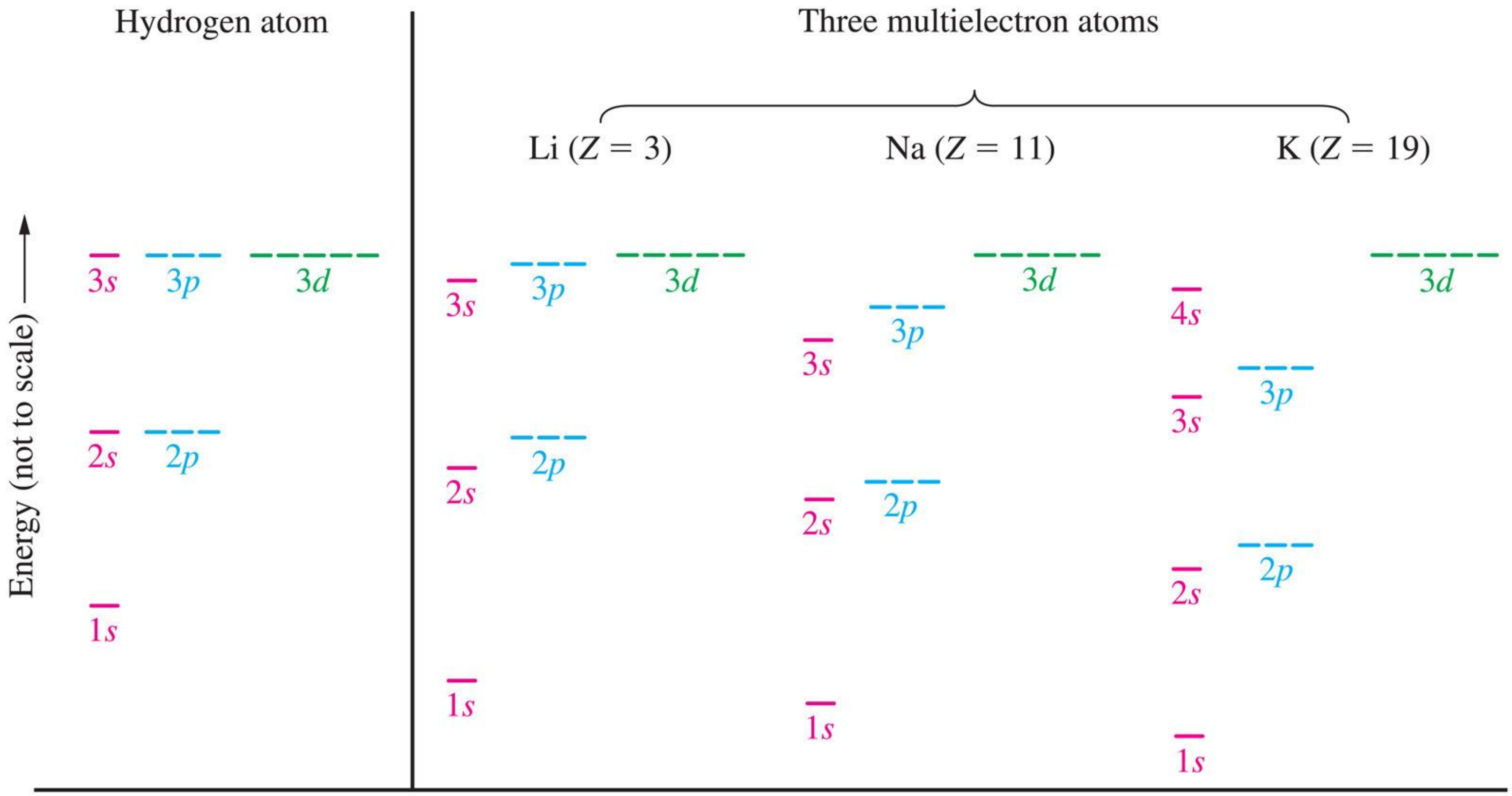
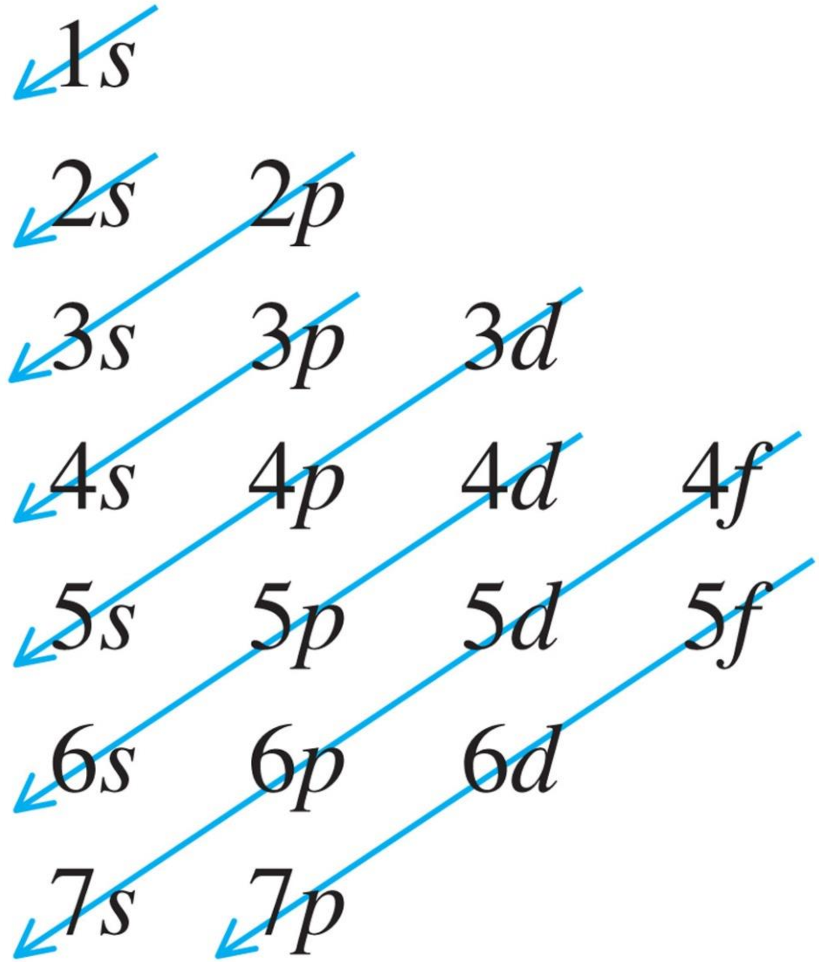
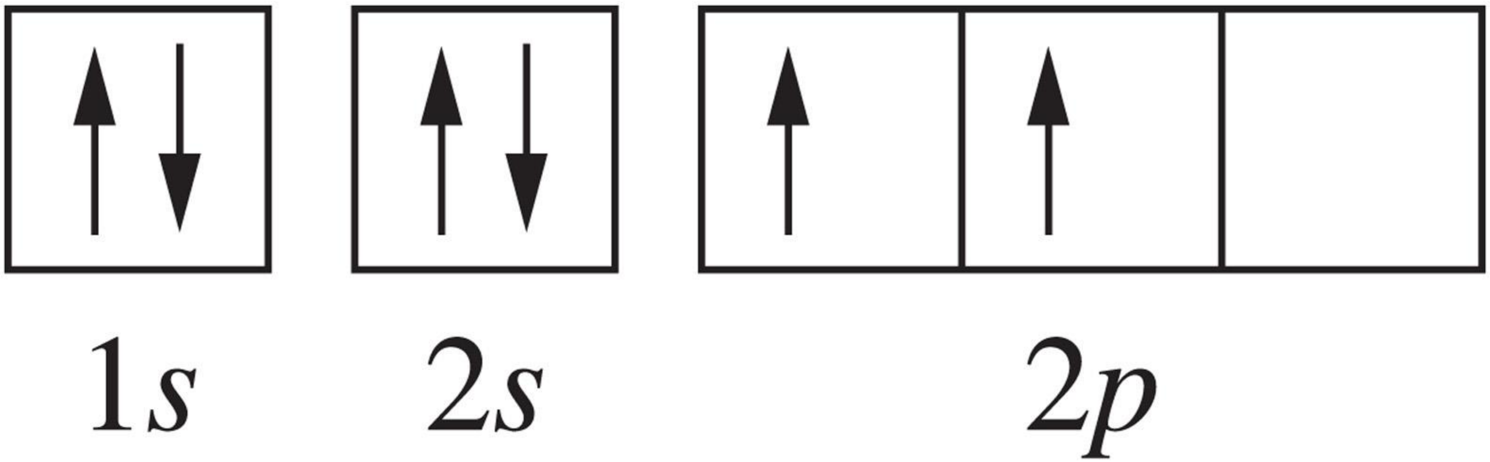
Orbital Energies



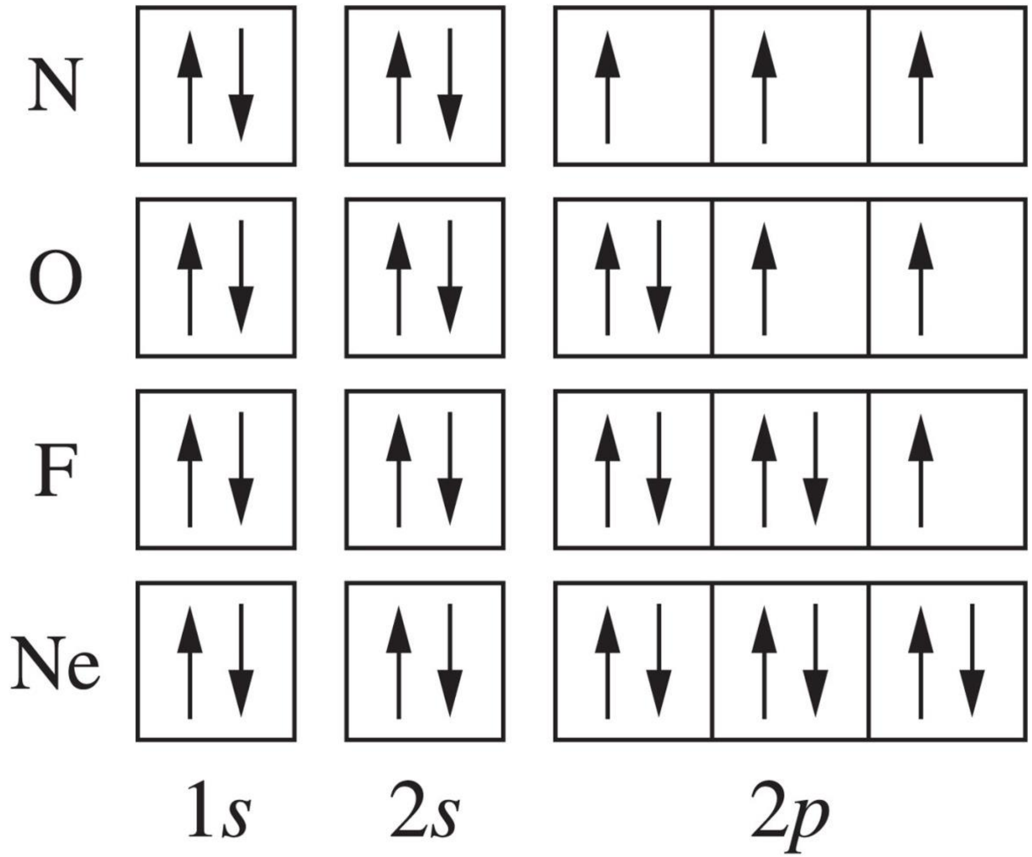
Orbital Filling



Aufbau Process and Hunds Rule



Filling p Orbitals



Filling the d Orbitals

		3d					4s	
Sc:	[Ar]	↑					↑↓	[Ar]$3d^{1}4s^{2}$
Ti:	[Ar]	↑	↑				↑↓	[Ar]$3d^{2}4s^{2}$
V:	[Ar]	↑	↑	↑			↑↓	[Ar]$3d^{3}4s^{2}$
Cr:	[Ar]	↑	↑	↑	↑	↑	↑	[Ar]$3d^{5}4s^{1}$
Mn:	[Ar]	↑	↑	↑	↑	↑	↑↓	[Ar]$3d^{5}4s^{2}$
Fe:	[Ar]	↑↓	↑	↑	↑	↑	↑↓	[Ar]$3d^{6}4s^{2}$
Co:	[Ar]	↑↓	↑↓	↑	↑	↑	↑↓	[Ar]$3d^{7}4s^{2}$
Ni:	[Ar]	↑↓	↑↓	↑↓	↑	↑	↑↓	[Ar]$3d^{8}4s^{2}$
Cu:	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑	[Ar]$3d^{10}4s^{1}$
Zn:	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	[Ar]$3d^{10}4s^{2}$

TABLE 8.2 Electron Configurations of Some Groups of Elements

Group	Element	Configuration
1	H	$1s^1$
	Li	$[He]2s^1$
	Na	$[Ne]3s^1$
	K	$[Ar]4s^1$
	Rb	$[Kr]5s^1$
	Cs	$[Xe]6s^1$
	Fr	$[Rn]7s^1$
17	F	$[He]2s^22p^5$
	Cl	$[Ne]3s^23p^5$
	Br	$[Ar]3d^{10}4s^24p^5$
	I	$[Kr]4d^{10}5s^25p^5$
	At	$[Xe]4f^{14}5d^{10}6s^26p^5$
18	He	$1s^2$
	Ne	$[He]2s^22p^6$
	Ar	$[Ne]3s^23p^6$
	Kr	$[Ar]3d^{10}4s^24p^6$
	Xe	$[Kr]4d^{10}5s^25p^6$
	Rn	$[Xe]4f^{14}5d^{10}6s^26p^6$

8-12 Electron Configurations and the Periodic Table