

Section 1 (Chapter 2, M&T)

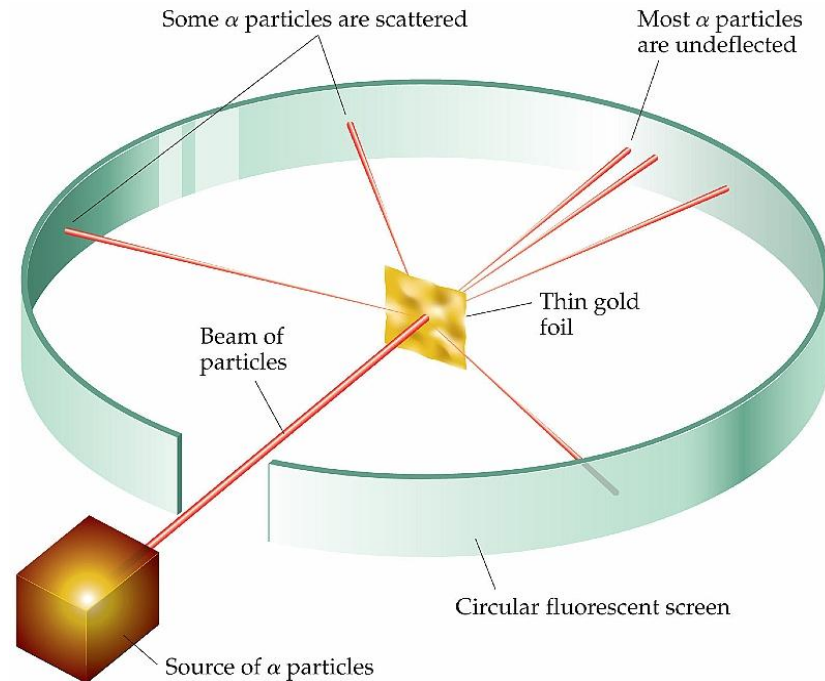
Atomic Structure

Section 1 Outline

- 1. The Bohr model of the atom (Classical Mechanics)**
- 2. Evolution of the Quantum Mechanical (QM) model**
- 3. Features of the QM model (wave functions, orbitals, nodes, probability, quantum numbers)**
- 4. How are electrons arranged in the QM model? (filling/emptying orbitals, electron configurations)**
- 5. Atomic properties/trends in the Periodic Table**

Evolution of the Early Atom

- **Nuclear model of the atom (electrons arranged around a compact core, containing the protons and neutrons) first proposed by Rutherford (gold foil experiment)**



- **Model needed to describe the behaviour (movement/location) of electrons in atoms, supported by scientific evidence**

Evolution of the Early Atom

- Light exhibits wave-particle duality

- Planck: blackbody radiation; $E = h\nu$

h = Planck's constant ($6.626 \times 10^{-34} \text{ J}\cdot\text{s}$)

ν = frequency (s^{-1})

- Einstein: photoelectric effect

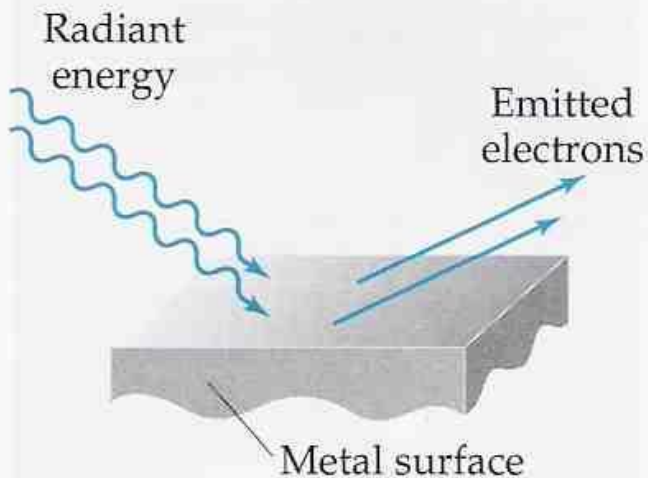
Planck's constant



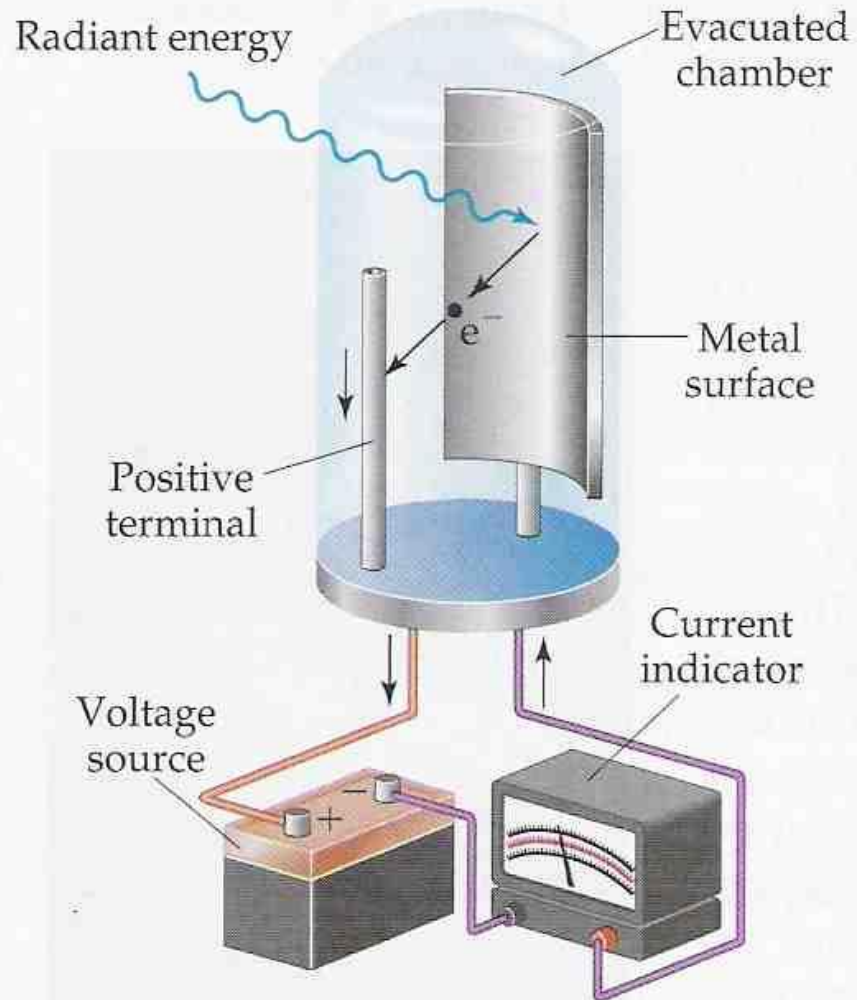
frequency

$$E = h\nu$$

energy



(a)



(b)

The Photoelectric Effect

Proposed:

**Light (EM radiation) consists of discrete particles
“photons”**

$$E = h\nu = hc/\lambda$$

h = Planck's Constant = 6.626×10^{-34} J s

Photon energy = work function + kinetic energy

Einstein, 1905

Atomic Spectra



(a)



(b)



(c)

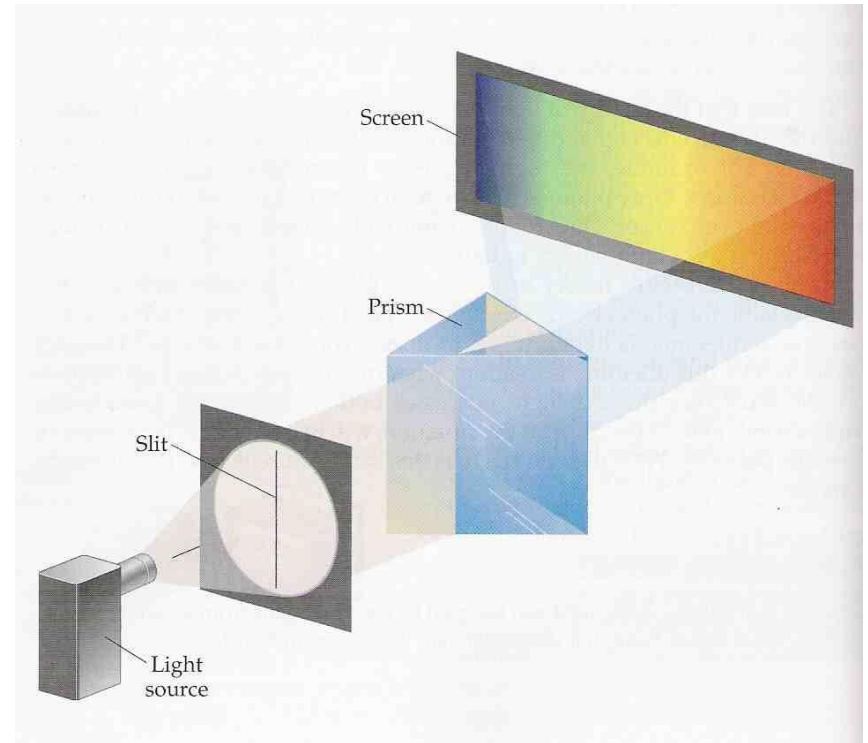


(d)

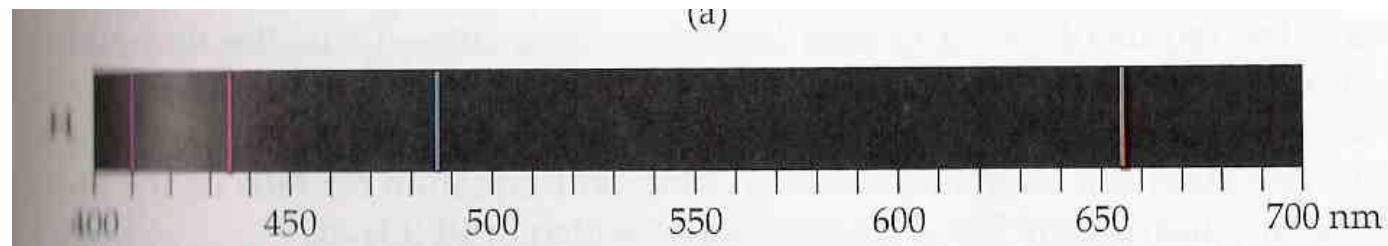


(e)

Continuous spectrum is obtained when white light is separated into its component wavelengths using a prism

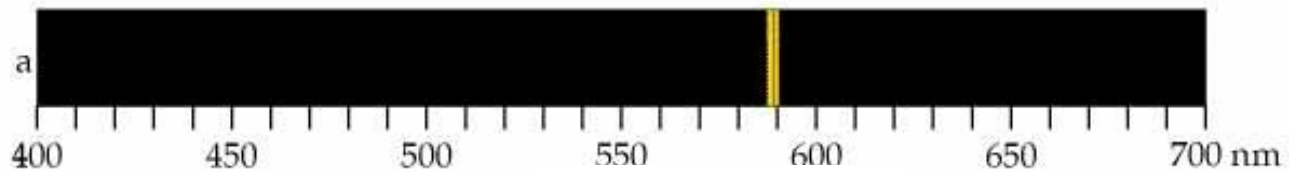


● **Atomic line emission spectrum for hydrogen**

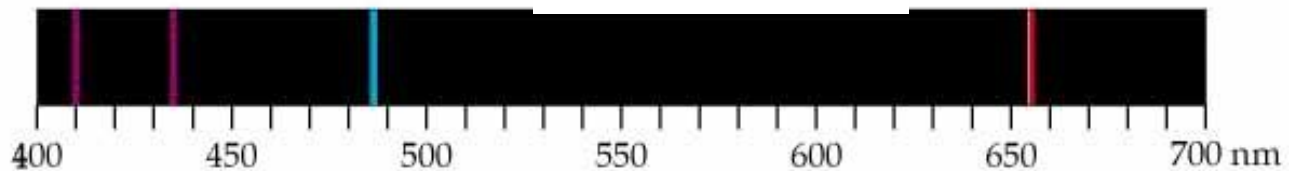


Line spectrum (Balmer Series) for hydrogen

Atomic Spectra



Na atoms



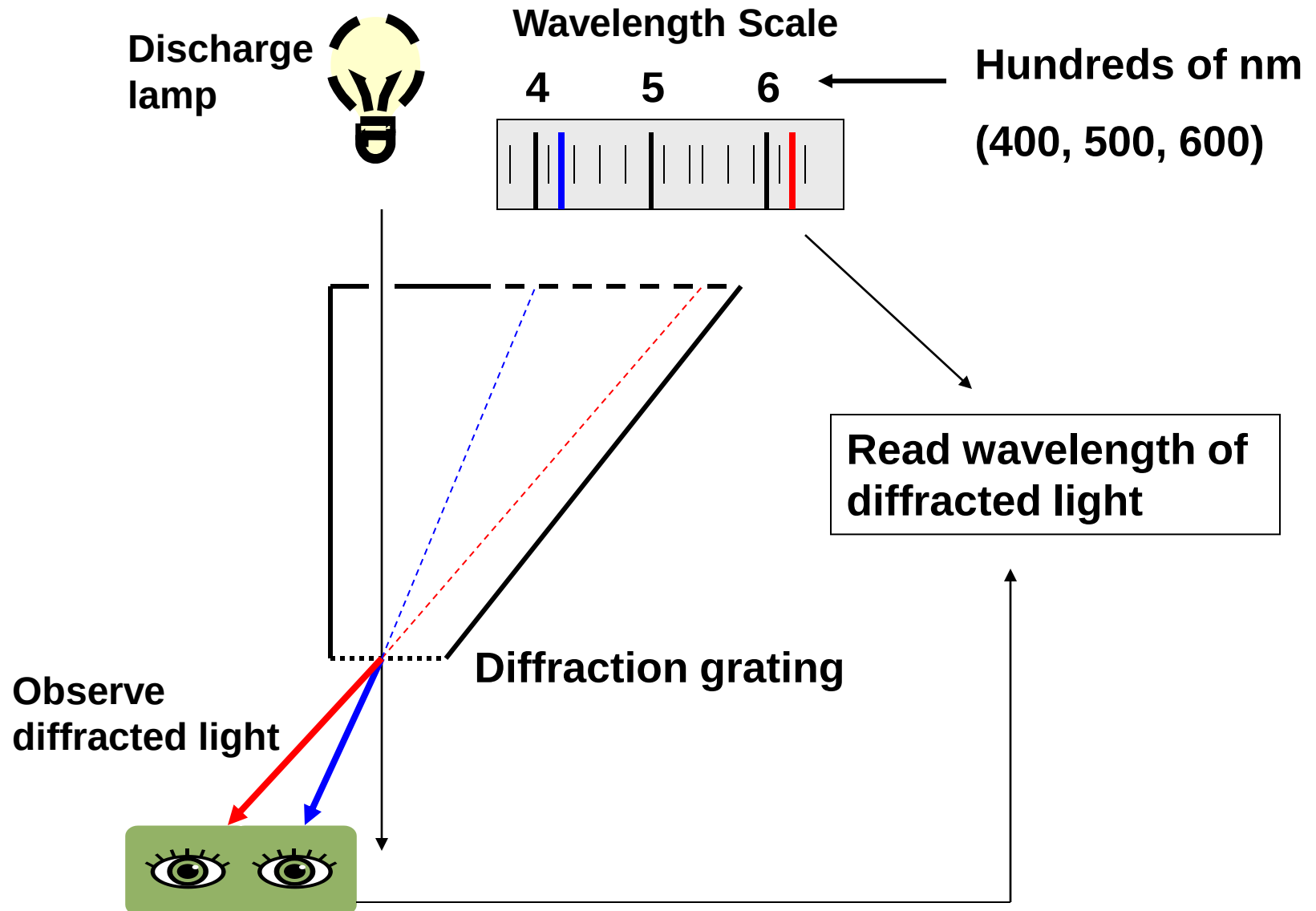
H atoms

Internal electronic energy of atoms can have only certain values or quantities

Atomic Spectra

- Shows that atoms do not have a continuous range of energies but only discrete values (quantization).
- Can use the spectra of simple elements to show this effect.
- Can use a spectroscope to study and characterize these energy lines.

Using the Spectroscope



Atomic Spectra

- Each element has its own characteristic spectrum (set of lines)
- These characteristic spectra can be used to identify these elements in various environments.

Atomic Spectra

- Electrons in an element can possess only discrete energy values (*quantized*)
- Every element has a characteristic set of values.
- These energy levels are characterized by some whole integer (n)
- This is the “*Principle Quantum Number*”

H Atom Emission Spectrum

For emissions observable in the visible spectrum, Balmer noted that wavelengths of the light emitted fit the following equation:

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

“ n ” must be a positive integer greater than 2

where λ = wavelength of light (m);

R = Rydberg constant ($1.097 \times 10^5 \text{ cm}^{-1}$)

Recall $E = h\nu$ and $c = \lambda\nu$ (ν = frequency (s^{-1});

c = speed of light = $2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1}$)

Also, could represent as wavenumber, $\bar{\nu}$ ($1/\lambda$) units of cm^{-1}

H Atom Emission Spectrum

- Later shown that other transitions occurred (data fit for numbers other than $1/2^2$), corresponding to emissions *outside the visible spectrum*, and in general,

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

Early Atom

- ***Classical mechanics*** (used to develop the Bohr model) was successful in explaining
 - emission spectra
 - the assignment of electron configurations

Bohr Atom

- Neils Bohr: model of atomic structure like solar system
- Electrons existed in “states” (i.e. constant energy) with circular paths called orbits.
- Energy is absorbed when an electron jumps to a higher orbit and lost upon a drop to a lower energy orbit.
- These transitions (jumps) will occur when an energy change occurs which exactly matches the difference in energies between two orbits
- The change in energy is always given by:

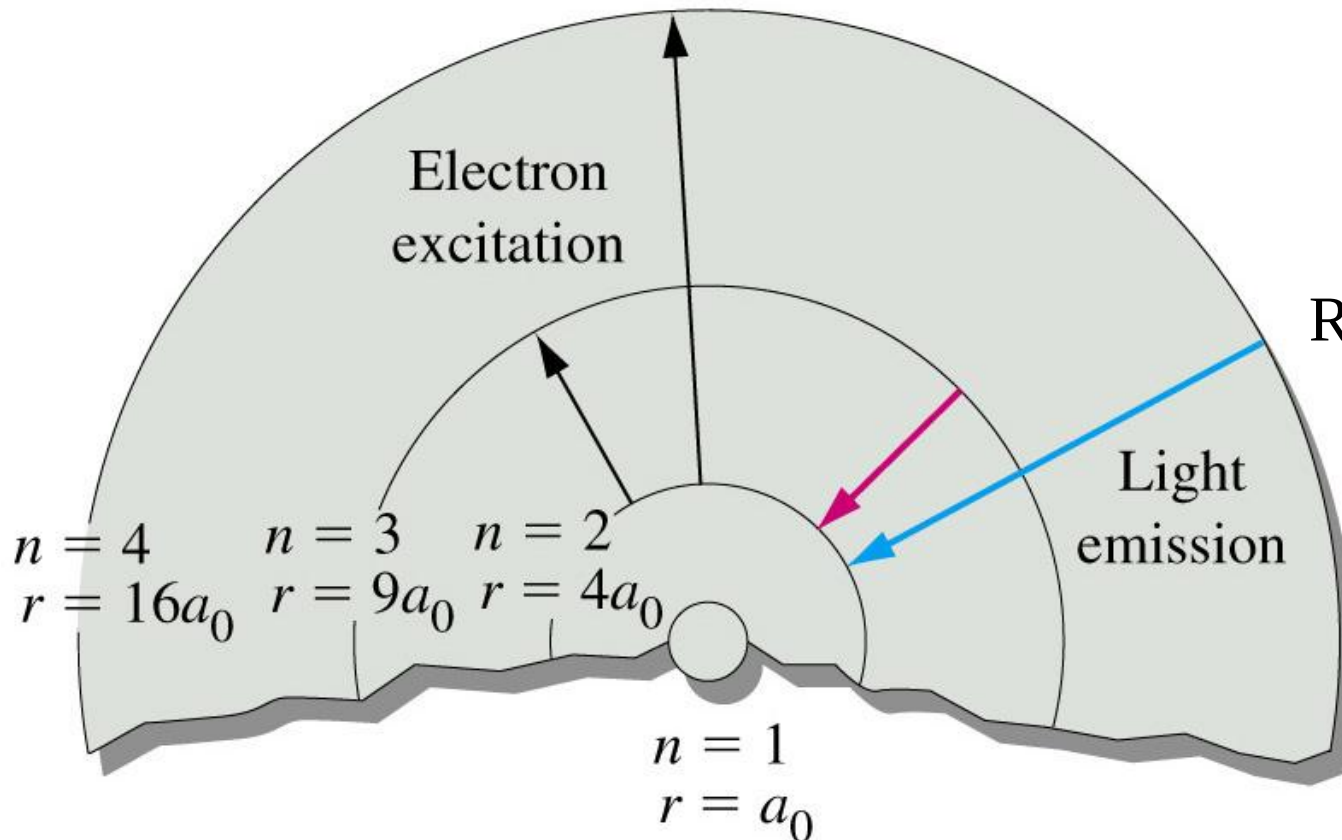
$$\Delta E = E_f - E_i$$

Energy of final “state”

Energy of initial “state”

The Bohr Model of the H atom

The electron in a hydrogen atom moves around the nucleus only in certain allowed circular orbits.



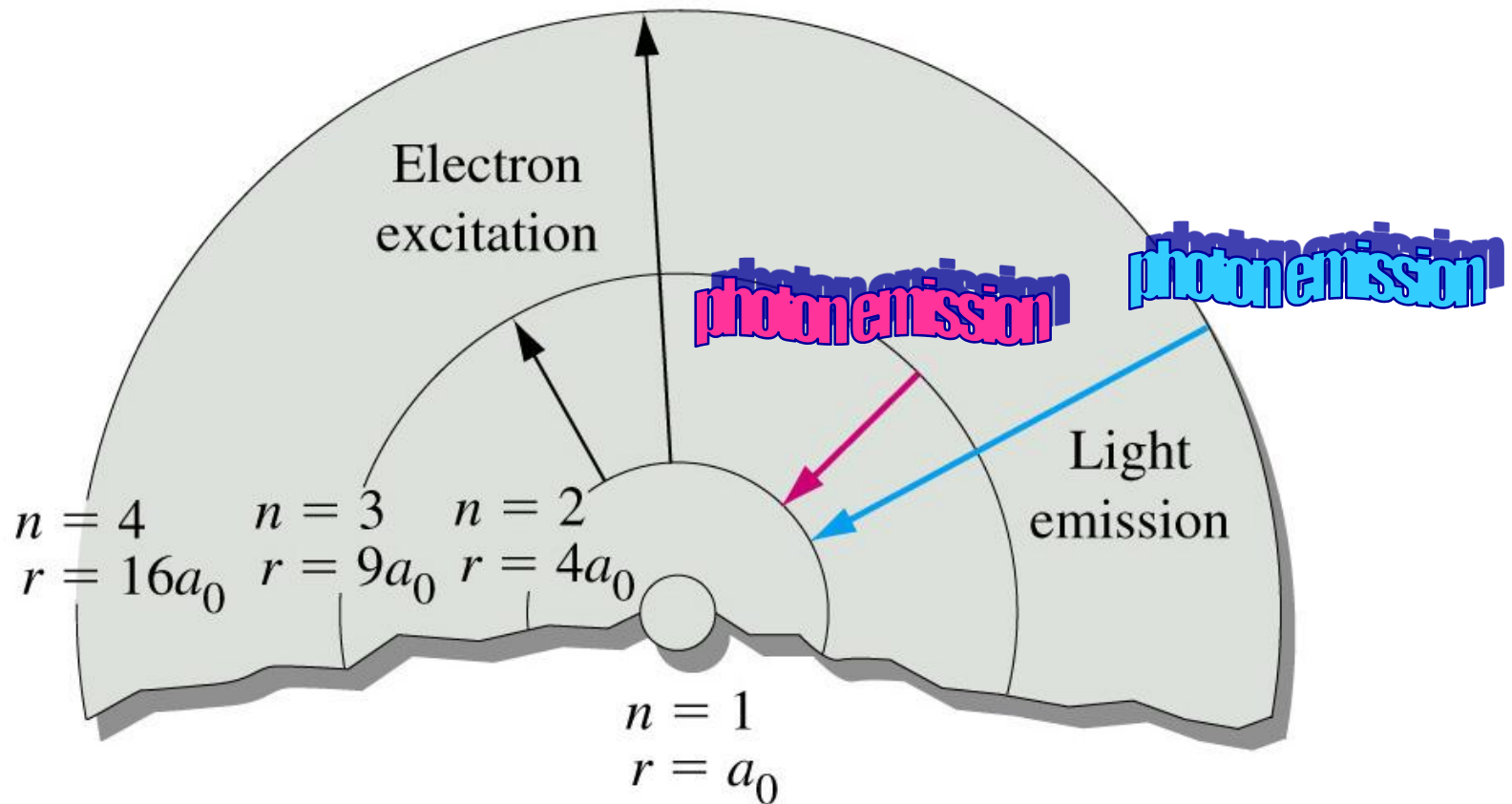
Rydberg constant

$$E = \frac{-R_H}{n^2}$$

$$R_H = 2.179 \times 10^{-18} \text{ J}$$

$$n = 1, 2, 3, \dots$$

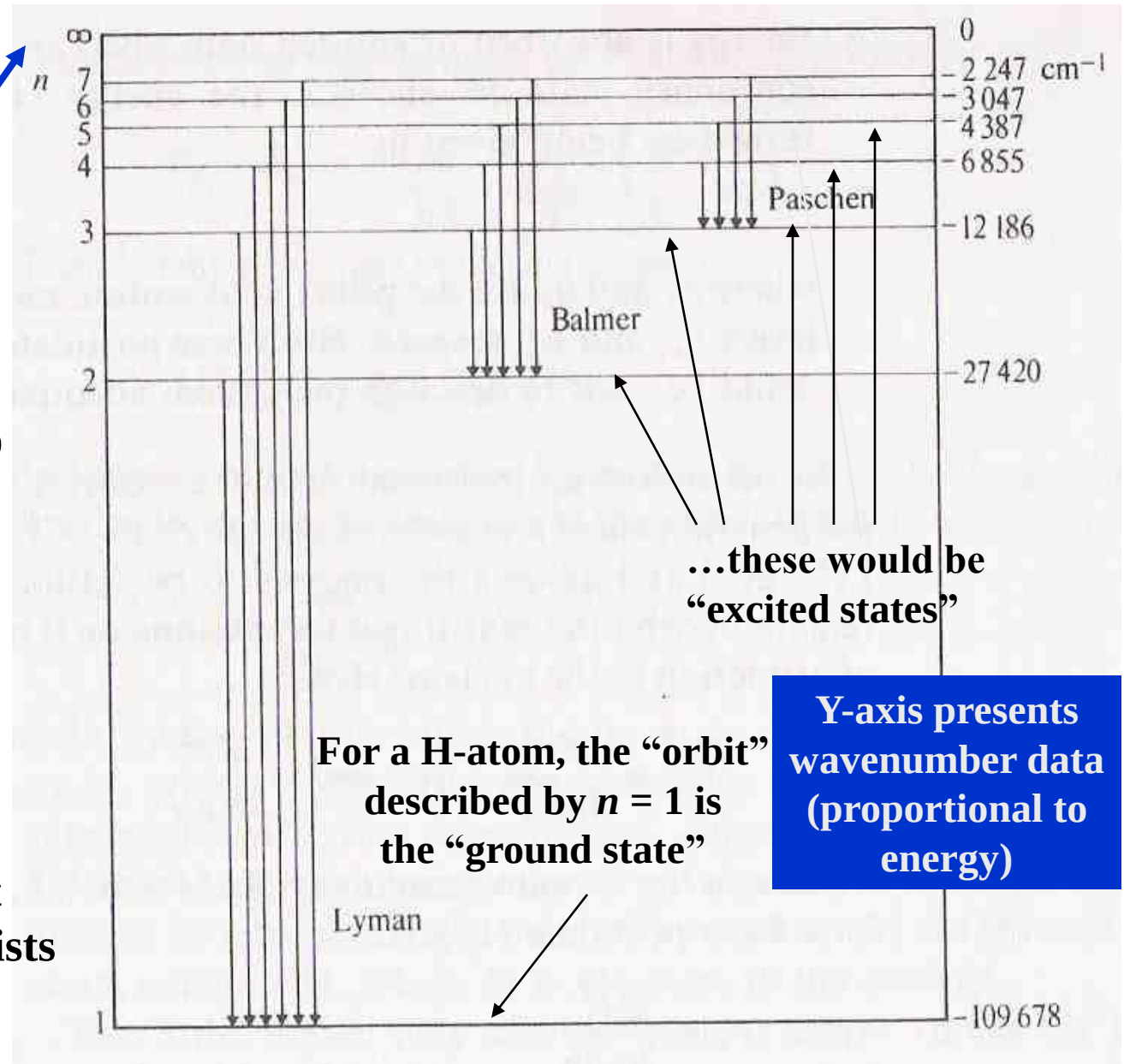
The Bohr Model of the H atom



$$E = hc\bar{\nu}$$

Notice that the energy for $n = \infty$ is defined as zero (no attraction between electron and nucleus)

The lowest (most negative) energy exists at lowest n



The Bohr Model

- The equation describing the energy of emission then becomes

$$\Delta E = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

“***n***” is a number which indicates energy (orbit number)

(using the following)

$$E = h\nu \quad E = \frac{hc}{\lambda}$$

$$\lambda\nu = c$$

- Where n_i describes the initial state (orbit), and n_f the final state ($R = 2.18 \times 10^{-18} \text{ J}$)
 moves closer to the nucleus
- When an electron drops from a higher energy orbit to a lower one, light is given off, and ΔE is negative (emission); when the jump is from low energy to high, ΔE is positive (absorption)
 moves farther away from the nucleus

Bohr Model of the Atom

- **Bohr model: angular momentum (mvr) exists due to the circular trajectory of the electron:**

$$mvr = n \left(\frac{h}{2\pi} \right)$$

- **m = mass of electron; v = velocity of electron;
 r = orbit radius; h = Planck's constant;
 n = positive integer**

The Bohr Model

- The radius of the n^{th} ($n = 1, 2, 3$, etc) orbit in the Bohr model is then given by (balance of electrostatic and centrifugal forces):

$$r_n = \frac{\epsilon_o h^2 n^2}{\pi m_e Z e^2}$$

- ϵ_o = permittivity of free space ($8.854 \times 10^{-12} \text{ F}\cdot\text{m}^{-1}$); m_e = mass of an electron ($9.109 \times 10^{-31} \text{ kg}$); Z = charge on nucleus; e = elementary charge ($1.602 \times 10^{-19} \text{ C}$)

The Bohr Model

- For $n = 1$ (H-atom), have electron in lowest energy orbit. As n increases, electron is farther from nucleus (higher energy). Applying $\Delta E = E_f - E_i$ and

$$\Delta E = \frac{hc}{\lambda}$$

to the hydrogen atom, for $n_f = \infty$, we will get the *ionization energy* for a hydrogen atom:

$$\Delta E = R \left(\frac{1}{\infty^2} - \frac{1}{1^2} \right) = 2.18 \times 10^{-18} J$$

or 1312 kJ *per mole of H-atoms*.

$n = \infty$ means the electron is moved far enough away from the nucleus that no attraction exists between them

The Bohr Model of the H Atom

Applicable ONLY to species with ONE electron:

H, He⁺, Li²⁺, Be³⁺, etc.

However, the model provides some concepts applicable to all atoms:

- **Electrons confined to specific orbits with specific energies (“quantized”), determined by n (“quantum number”).**
- **GROUND state: electrons in orbits closest to nucleus.**
- **Electron promotion: EXCITED states, requires energy input.**
- **Spontaneous decay back to ground state: energy produced.**

Wave Mechanics

- Louis De Broglie argued a wavelike nature of the electron, since any object should have an associated wavelength

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

where m = object mass

$$E = h\nu$$

$$E = mc^2$$

$$m = \frac{h\nu}{c^2} \rightarrow \frac{h}{c\lambda}$$

- Experiments showed that electrons indeed exhibited wavelike properties;
electrons are now thought of as having a “wave-particle duality”

Schrödinger Wave Equation

- Heisenberg Uncertainty Principle: can never know the exact position and momentum of an electron.

$$(\Delta mv)(\Delta x) \geq \frac{h}{4\pi}$$

- Instead, use three-dimensional regions of space (orbitals) to describe probable locations. These probabilities are derived from wavefunctions (Ψ), mathematical functions that contain detailed information about the behaviour of electrons.

Schrödinger Wave Equation

- The Schrödinger equation may be solved exactly only for simple, hydrogen-like systems (i.e. 1-electron: H, He⁺, Li²⁺, etc.).

$$H\Psi = E\Psi$$

E: Eigenvalue
H: Hamiltonian operator **Ψ: Wavefunction**

- The Schrödinger equation for a particle moving along a path confined to 1-D (a line) is given by:

$$\left(-\frac{h^2}{8\pi^2 m} \right) \left(\frac{\partial^2 \Psi}{\partial x^2} \right) + V\Psi = E\Psi$$

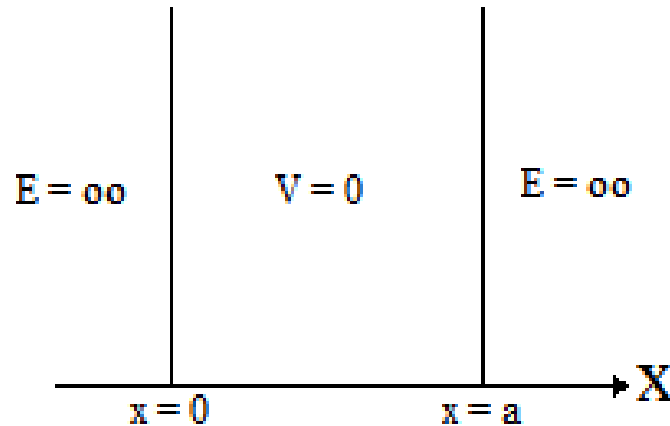
Kinetic energy → Potential energy (V) → Total energy (E) ←

Particle-in-a-Box Problem

- Describe the motion of a particle, which is confined to move within an energy well, using a wave description
- Consider the equation below, for movement of a particle of mass m , confined to one dimension (x -axis) between two impenetrable barriers (at $x = 0$ and $x = a$)
- In order to reach meaningful solutions, a number of constraints have to be applied:
 - Ψ must be finite for all values of x (must have a value)
 - Ψ (and $d\Psi/dx$) must be single-valued (only one solution)
 - Ψ must be continuous (value can't change abruptly)
 - Energy of particle must be positive; can't be infinite

$$\left(-\frac{h^2}{8\pi^2 m} \right) \left(\frac{\partial^2 \Psi}{\partial x^2} \right) + V\Psi = E\Psi$$

Particle-in-a-Box



For $x < 0$ and $x > a$, V is $-\infty$ (so $E = \infty$).

Since Ψ must be finite, the particle cannot exist here ($\Psi = 0$)

Inside the boundary, $V = 0$, and $\left(-\frac{h^2}{8\pi^2 m}\right)\left(\frac{\partial^2 \Psi}{\partial x^2}\right) + V\Psi = E\Psi$

rearranges to $\frac{\partial^2 \Psi}{\partial x^2} = -\frac{8\pi^2 m E}{h^2} \Psi$ for $x = 0 \rightarrow x = a$

Particle-in-a-Box

● We can simplify this expression as follows:

$$\frac{\partial^2 \Psi}{\partial x^2} = -\frac{8\pi^2 mE}{h^2} \Psi = -k^2 \Psi$$

$$k^2 = \frac{8\pi^2 mE}{h^2}$$

An equation describing the particle's motion in wave-like terms would be

$$\Psi = A \sin rx + B \cos sx$$

An expression for
 Ψ inside the $x = 0$
 $\rightarrow x = a$ boundary

Particle-in-a-Box

- Applying a few more steps allows further simplification: $\Psi = A \sin rx + B \cos sx$

- At $x = 0$, Ψ must be zero (infinite energy)

$$A \sin(rx) + B \cos(sx) = 0$$

- $A \sin(r \cdot 0) = 0$ and $B \cos(s \cdot 0) = B$, thus $B = 0$

- At $x = a$, $A \sin(ra) = 0$, but A cannot be 0 (otherwise Ψ would always equal 0) $\int_{x=0}^{x=a} \Psi^2 dx = 1$

- $A \sin(ra) = 0$ when $ra = \pm n\pi$, so $r = \frac{n\pi}{a}$

Valid for all $x = 0 \rightarrow a$

$$\Psi = A \sin \frac{n\pi x}{a}$$

Particle-in-a-Box

- So, an equation that describes the particle's motion in terms of wave behavior between (and including) $x = 0$ and $x = a$ is

$$\Psi = A \sin \frac{n\pi x}{a}$$

and also,

$$k^2 = \frac{8\pi^2 m E}{h^2} \Rightarrow E = \frac{k^2 h^2}{8\pi^2 m}$$

and since

$$k = \frac{n\pi}{a}$$

then

$$E = \frac{n^2 h^2}{8ma^2}$$

“ m ” is the mass of the particle
“ a ” is the length of the box

Particle-in-a-Box

- The value n is called the principal quantum number, and relates the energy of the particle (electron)

$$E = \frac{n^2 h^2}{8ma^2}$$

- Setting $n = 1, 2, 3$, etc. permits calculation of the particle's energy in different states (like different orbits in the Bohr model)
- The constraints applied to Ψ lead to quantized energy levels
- Also: E is inversely proportional to m and inversely proportional to a^2

Particle-in-a-Box

● Meanings:

- Ψ is the wavefunction, which has little physical meaning, but its square indicates probability
- “ a ” corresponds to the length of the box, the distance over which the electron may move (corresponds to the size of a molecule in which the electron is located)
- “ m ” is the mass of the particle, yields a similar effect as that for a^2
 - The effect of larger “ m ” and “ a ” is to reduce the spacing between energy levels

Particle-in-a-Box

- Solving these two equations for $n = 1, 2, 3, \dots$ we get the following behavior

$$\Psi = A \sin \frac{n\pi x}{a}$$

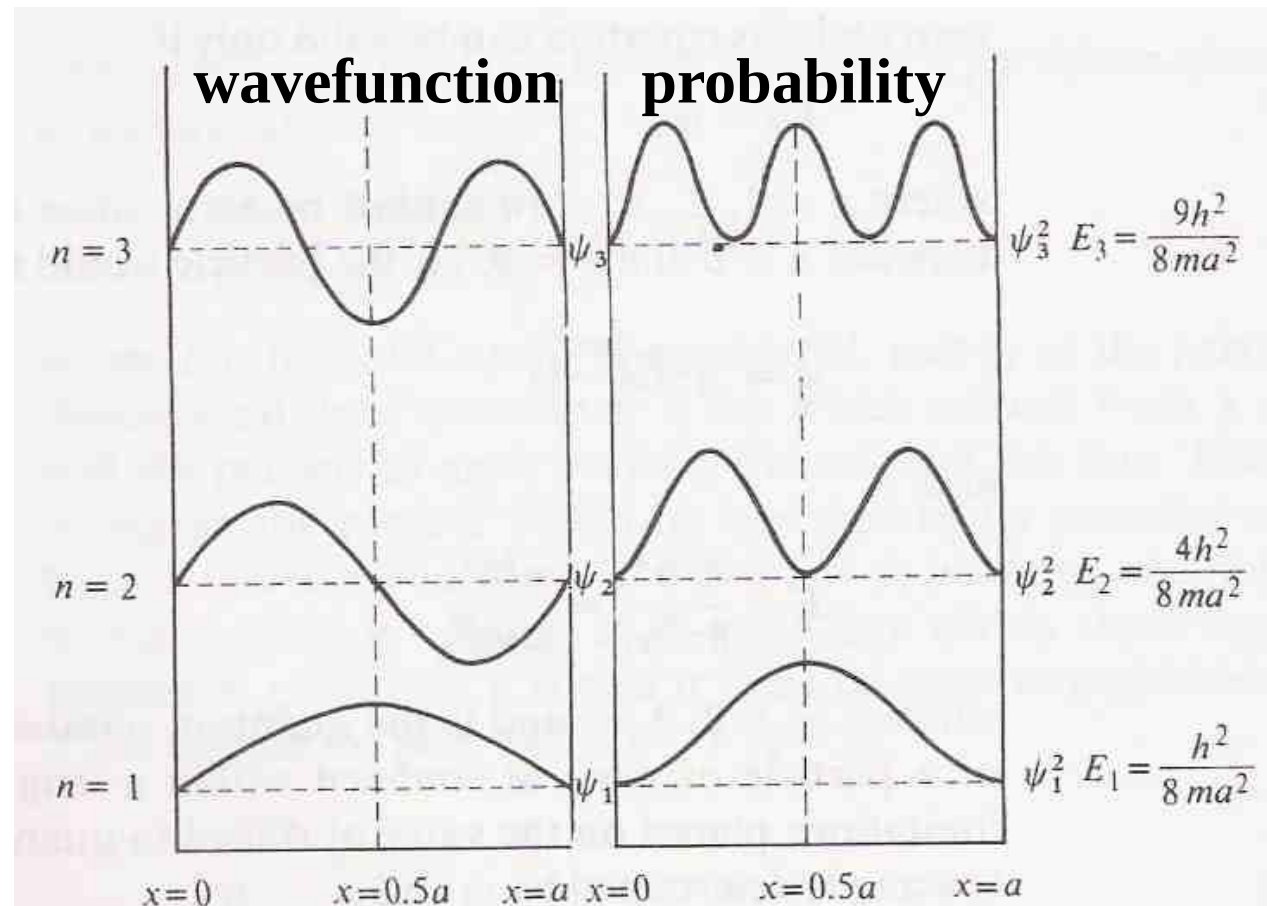
$$\int_{x=0}^{x=a} \Psi^2 dx = 1$$

$$A^2 \int_{x=0}^{x=a} \sin^2 \left(\frac{n\pi x}{a} \right) dx = 1$$

the value of this integral is $a/2$, and so

$$A = \left(\frac{2}{a} \right)^{1/2}$$

$$\Psi = \sqrt{\frac{2}{a}} \sin \left(\frac{n\pi x}{a} \right)$$



Schrödinger Wave Equation: 3-D

- The last solution was for a 1-D problem. A 3-D solution is more useful:

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} E \Psi = 0$$

- Rather than use a Cartesian system to describe atomic orbitals, polar coordinates are often used:

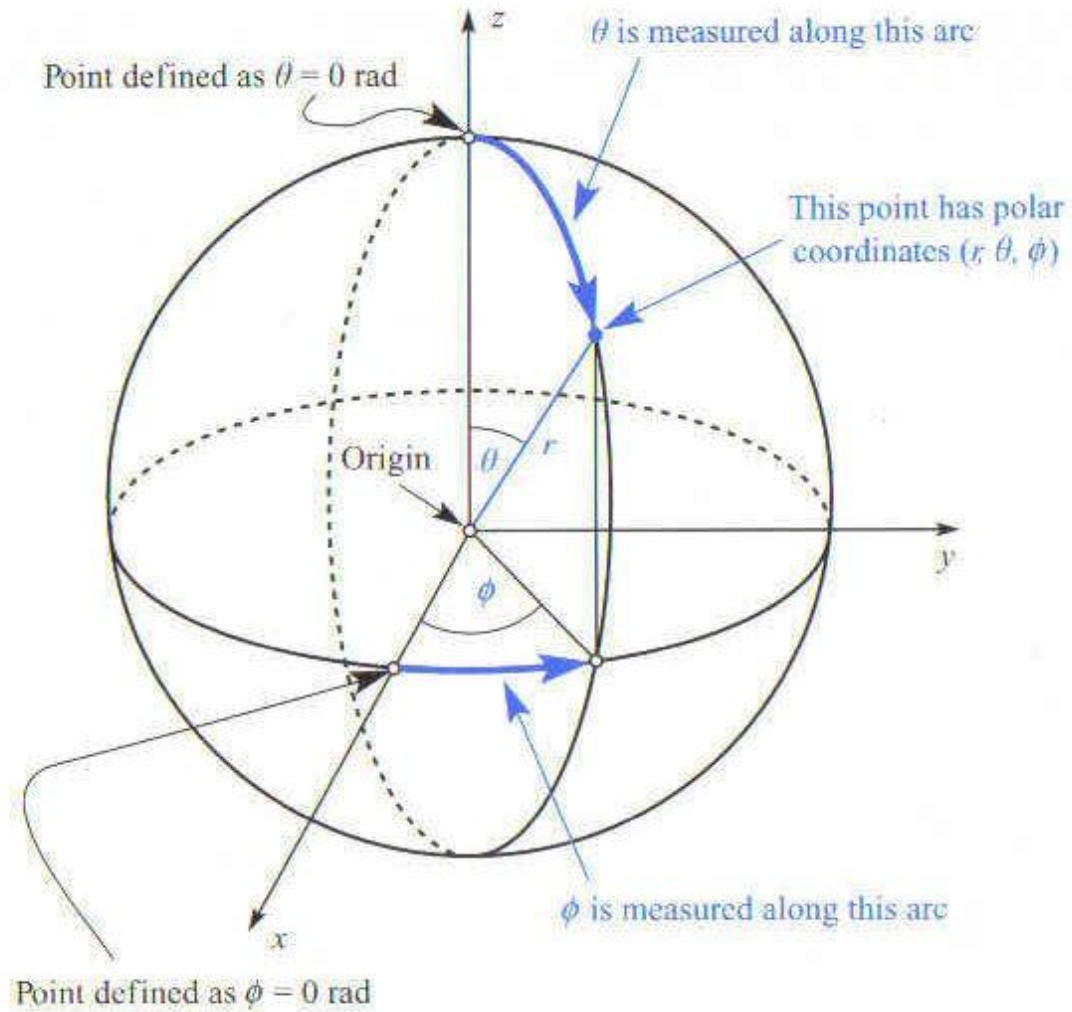
$$\varphi_{\text{cartesian}}(x, y, z) = \varphi_{\text{radial}}(r) \varphi_{\text{angular}}(\theta, \phi) = R(r) A(\theta, \phi)$$

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

$$r^2 = x^2 + y^2 + z^2$$



Wave Functions of H-Atom

- The particle-in-a-box problem is useful in helping us to think of how particle behavior can be described with wave functions
- Electrons are not confined between two impenetrable barriers in an atom, but are still confined between the region close to the nucleus and to the limits of the atom's diameter
- Some of the functions that describe this picture, for the possible transitions involved in atomic line spectrum of hydrogen, are shown on the next slide (in both Cartesian and radial terms)

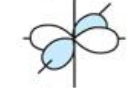
Give the value of the wavefunction
at a given distance from the nucleus

Gives the value of the wavefunction along a
vector as a function of distance from the nucleus

$$Y_{cartesian}(x, y, z) = Y_{radial}(r) Y_{angular}(q, j) = R(r) A(q, j)$$

Ψ^2 will indicate probability of locating an electron. The higher the value of Ψ^2 , the more probable it is that an electron can be found in that space. The various solutions we will look at next correspond to solutions of Schrödinger's equation for the H-atom

TABLE 2.3 Hydrogen Atom Wave Functions: Angular Functions

Angular Factors				Real Wave Functions			
Related to Angular Momentum				Functions of θ	In Polar Coordinates	In Cartesian Coordinates	Shapes Label
l	m_l	Φ	Θ		$\Theta\Phi(\theta, \phi)$	$\Theta\Phi(x, y, z)$	
0(s)	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$		$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{2\sqrt{\pi}}$	 s
1(p)	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos \theta$		$\frac{1}{2\sqrt{\pi}} \cos \theta$	$\frac{1}{2\sqrt{\pi}} \frac{z}{r}$	 p_z
	+1	$\frac{1}{\sqrt{2\pi}} e^{i\phi}$	$\frac{\sqrt{3}}{2} \sin \theta$		$\frac{1}{2\sqrt{\pi}} \sin \theta \cos \phi$	$\frac{1}{2\sqrt{\pi}} \frac{x}{r}$	 p_x
	-1	$\frac{1}{\sqrt{2\pi}} e^{-i\phi}$	$\frac{\sqrt{3}}{2} \sin \theta$		$\frac{1}{2\sqrt{\pi}} \sin \theta \sin \phi$	$\frac{1}{2\sqrt{\pi}} \frac{y}{r}$	 p_y
2(d)	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{2\sqrt{2}} (3 \cos^2 \theta - 1)$		$\frac{1}{4\sqrt{\pi}} (3 \cos^2 \theta - 1)$	$\frac{1}{4\sqrt{\pi}} \frac{(2z^2 - x^2 - y^2)}{r^2}$	 d_{z^2}
	+1	$\frac{1}{\sqrt{2\pi}} e^{i\phi}$	$\frac{\sqrt{15}}{2} \cos \theta \sin \theta$		$\frac{1}{2\sqrt{\pi}} \cos \theta \sin \theta \cos \phi$	$\frac{1}{2\sqrt{\pi}} \frac{xz}{r^2}$	 d_{xz}
			$\frac{\sqrt{15}}{2} \cos \theta \sin \theta$		$\frac{1}{2\sqrt{\pi}} \cos \theta \sin \theta \sin \phi$	$\frac{1}{2\sqrt{\pi}} \frac{yz}{r^2}$	 d_{yz}
	-2	$\frac{1}{\sqrt{2\pi}} e^{-2i\phi}$	$\frac{\sqrt{15}}{4} \sin^2 \theta$		$\frac{1}{4\sqrt{\pi}} \sin^2 \theta \cos 2\phi$	$\frac{1}{4\sqrt{\pi}} \frac{(x^2 - y^2)}{r^2}$	 $d_{x^2-y^2}$
			$\frac{\sqrt{15}}{4} \sin^2 \theta$		$\frac{1}{4\sqrt{\pi}} \sin^2 \theta \sin 2\phi$	$\frac{1}{4\sqrt{\pi}} \frac{xy}{r^2}$	 d_{xy}

Orbital shape determined by l, m_l

$$Y_{cartesian}(x, y, z) = Y_{radial}(r) Y_{angular}(q, j) = R(r)A(q, j)$$

TABLE 2-4

Hydrogen Atom Wave Functions: Radial Functions

Radial Functions $R(r)$, with $\sigma = Zr/a_0$

<i>Orbital</i>	<i>n</i>	<i>l</i>	<i>R(r)</i>
1s	1	0	$R_{1s} = 2 \left[\frac{Z}{a_0} \right]^{3/2} e^{-\sigma}$
2s	2	0	$R_{2s} = \left[\frac{Z}{2a_0} \right]^{3/2} (2 - \sigma) e^{-\sigma/2}$
2p		1	$R_{2p} = \frac{1}{\sqrt{3}} \left[\frac{Z}{2a_0} \right]^{3/2} \sigma e^{-\sigma/2}$
3s	3	0	$R_{3s} = \frac{2}{27} \left[\frac{Z}{3a_0} \right]^{3/2} (27 - 18\sigma + 2\sigma^2) e^{-\sigma/3}$
3p		1	$R_{3p} = \frac{1}{81\sqrt{3}} \left[\frac{2Z}{a_0} \right]^{3/2} (6 - \sigma) \sigma e^{-\sigma/3}$
3d		2	$R_{3d} = \frac{1}{81\sqrt{15}} \left[\frac{2Z}{a_0} \right]^{3/2} \sigma^2 e^{-\sigma/3}$

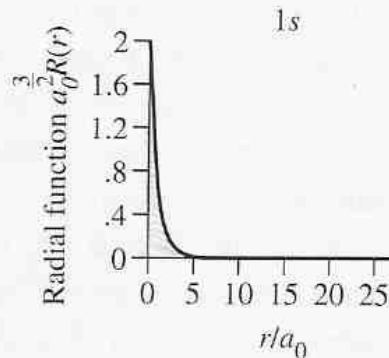
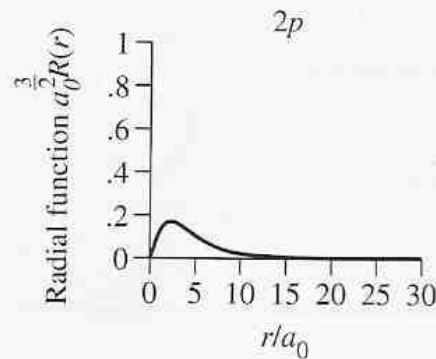
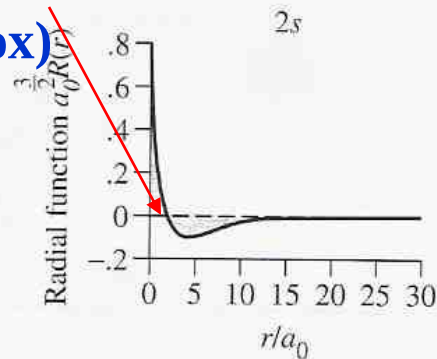
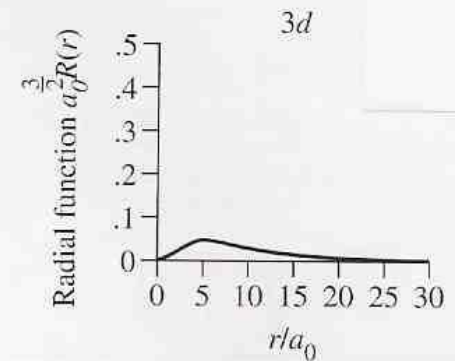
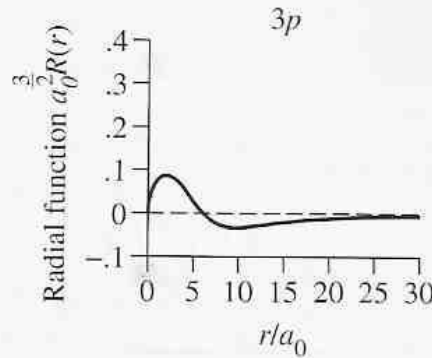
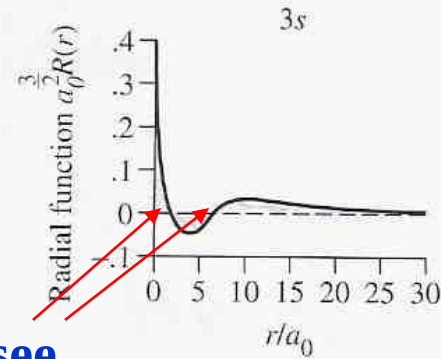
**a_0 = Bohr radius
(corresponds
to maximum radial
probability
for 1s electron in H-atom)**

$$y_{cartesian}(x, y, z) = y_{radial}(r) y_{angular}(q, j) = R(r) A(q, j)$$

Radial wavefunctions for hydrogen atom

Wavefunction
crosses x-axis (see
particle-in-a-box)

Radial Wave Functions

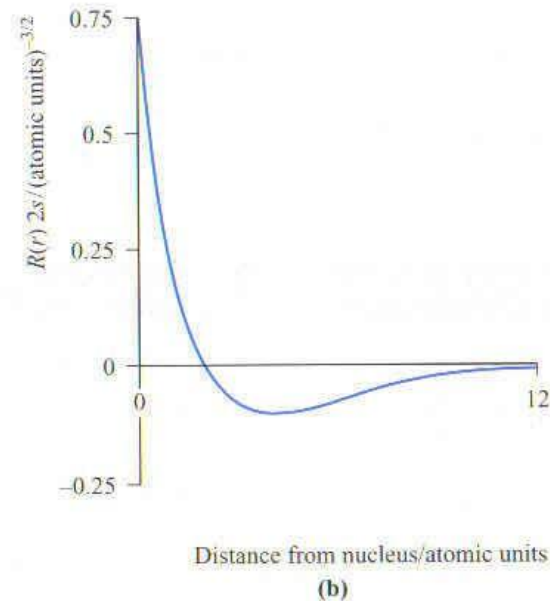
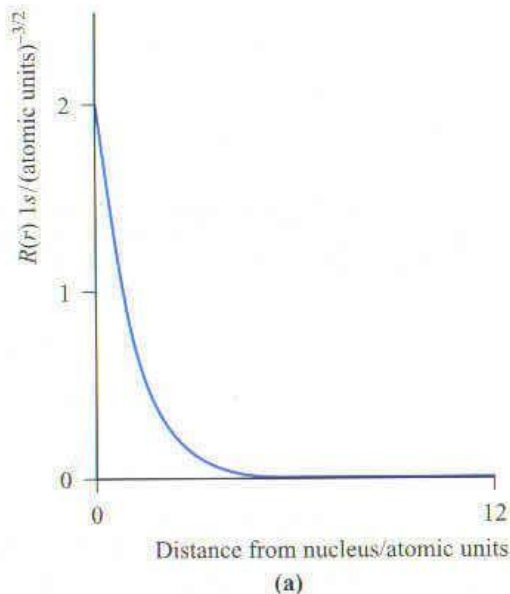


Features:

- 1) Functions all drop off to zero as $r \rightarrow \infty$
- 2) Some cross x-axis – yield “radial nodes”
- 3) Sometimes function is max near $r = 0$ (s-type) and sometimes not

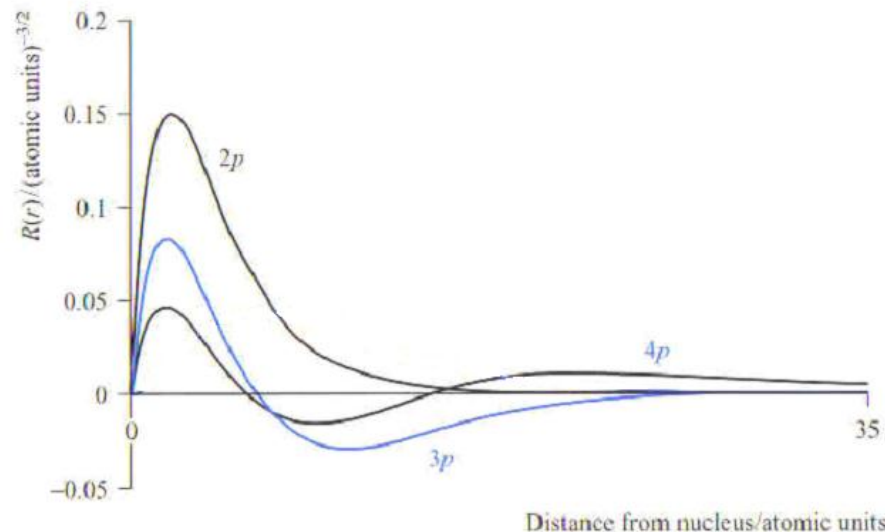
Atomic Orbitals (Radial Distributions)

- Just looking at the radial part of the wavefunction for the 1s electron of a hydrogen atom, it is seen that the value of the function is maximum close to the nucleus, decaying rapidly as the distance from the nucleus increases.
- For “s” orbitals, wavefunction is always large near the nucleus



Radial Wavefunctions of Other Orbitals

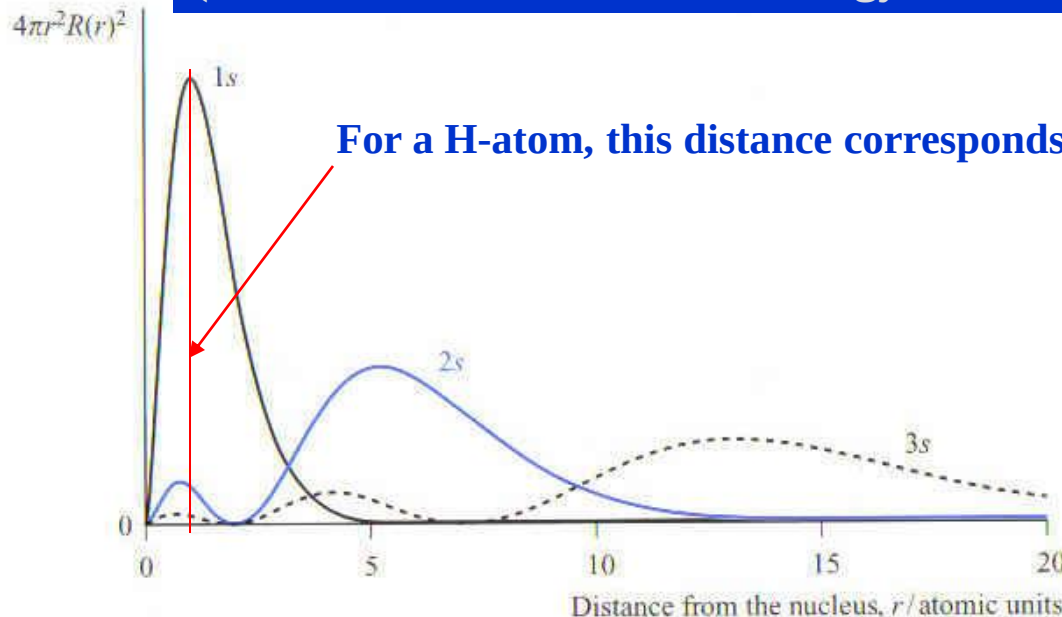
- Notice that other orbitals do not have maxima near the nucleus
- First occurrence of each subshell (1s, 2p, 3d) have wavefunctions that are always positive
- The second orbital of each type (e.g. 2s, 3p, 4d) have one point where the radial wavefunction changes sign (corresponds to “radial node”)
- The third orbital of each type (3s, 4p, 5d) has two of these sign changes (two radial nodes)



Radial Probability

- The wavefunction (Ψ) *squared* yields the probability of finding an electron in a three-dimensional space
- The square of the radial wavefunction, $\Psi_{\text{radial}}(r)$, will tell us the probability of finding an electron a given distance from the nucleus
- Radial probabilities are shown in the figure below
- See that the regions where probability falls to zero coincide with sign changes for radial wavefunctions – no chance of finding electrons here (radial node)

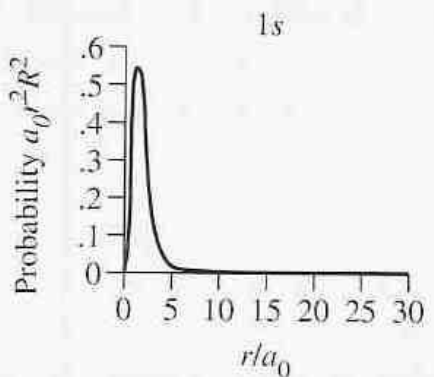
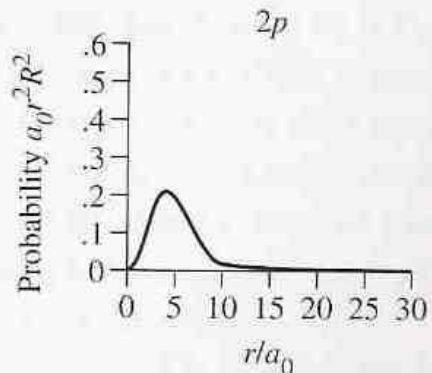
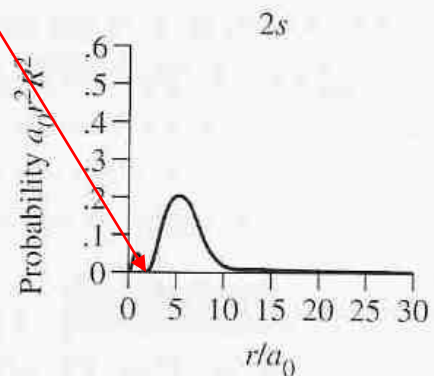
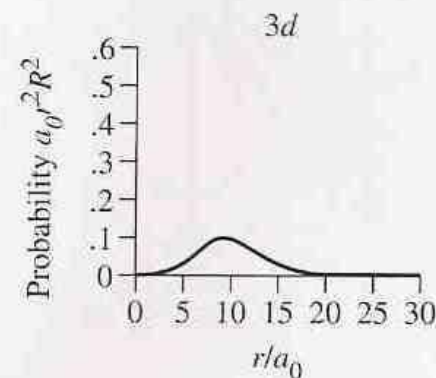
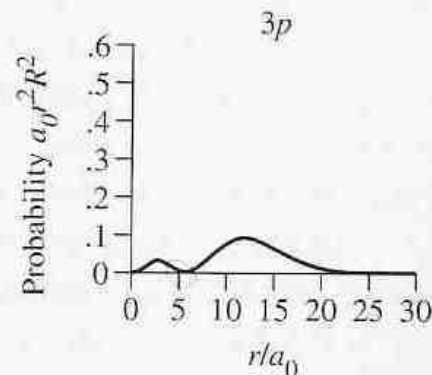
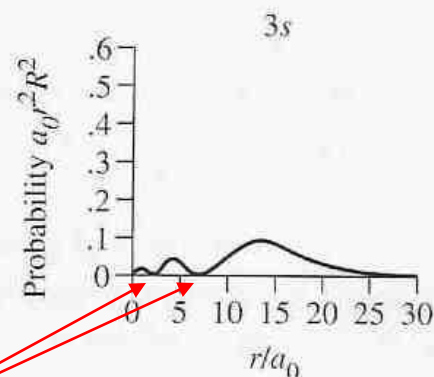
As “ n ” increases, so does the size of the radial wavefunction (how did “ n ” relate to size / energy in Bohr model?)



Radial probabilities, expressed as $\Psi_r^2 r^2$

Radial nodes

Radial Probability Functions



These are radial wavefunctions squared

The higher Ψ^2 is, the more likely the electron will be found at this distance from the nucleus

Atomic Orbitals

- Thus, in the QM model of the atom, solutions to Schrödinger's equation yield mathematical functions (“orbitals”) that describe an electron's position, mass, total energy potential energy (describe an electron wave in space)
- There are three quantum numbers used to describe an orbital
- Recall quantum numbers from first year chemistry course:
 - $n = \text{principal quantum number (energy)}$ ($n = 1, 2, \dots \text{infinity}$)
 - $l = \text{orbital angular momentum quantum number (orbital shape)}$ ($l = 0, 1, 2, \dots n-1$)
 - $m_l = \text{magnetic quantum number (directionality)}$ ($m_l = -l, \dots 0 \dots +l$)

A Brief Review of Terminology

- Orbitals having the same *principal quantum number* belong to the same *energy shell* (example, the 3s, 3p and 3d orbitals and the electrons in them all belong to the third energy shell)
- Orbitals (and electrons) of a given “n” and having the same “l” (for example, the three 2p orbitals, $2p_x$, $2p_y$, and $2p_z$) belong to the same “subshell”

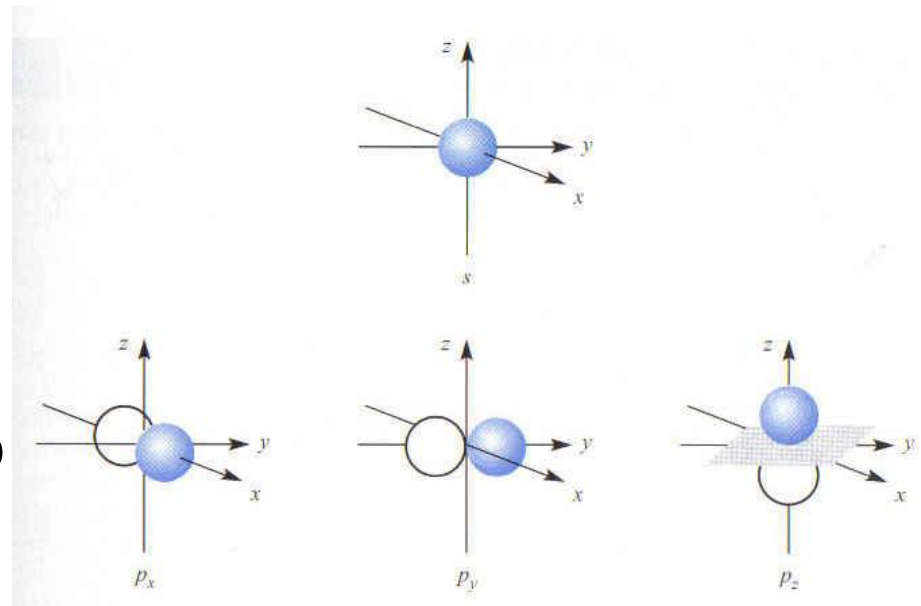
Radial Probability

- **Easy to remember how many radial nodes are present for a given orbital:**
 - ns orbitals have $(n - 1)$ radial nodes
 - np orbitals have $(n - 2)$ radial nodes
 - nd orbitals have $(n - 3)$ radial nodes
 - nf orbitals have $(n - 4)$ radial nodes

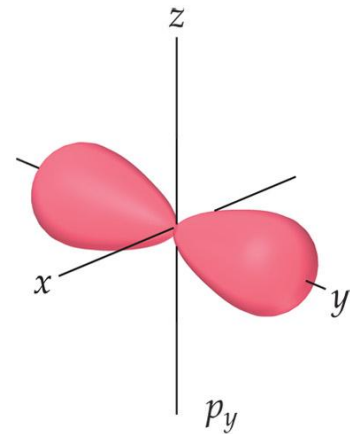
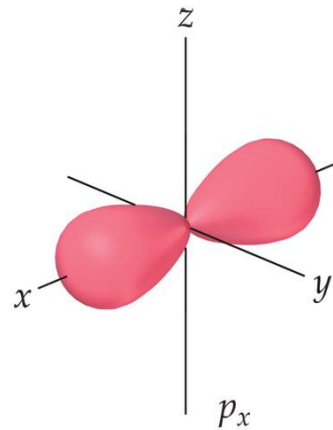
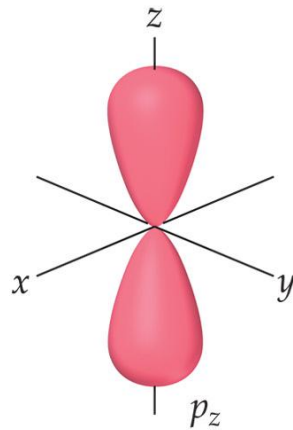
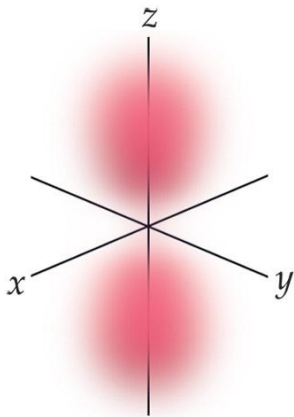
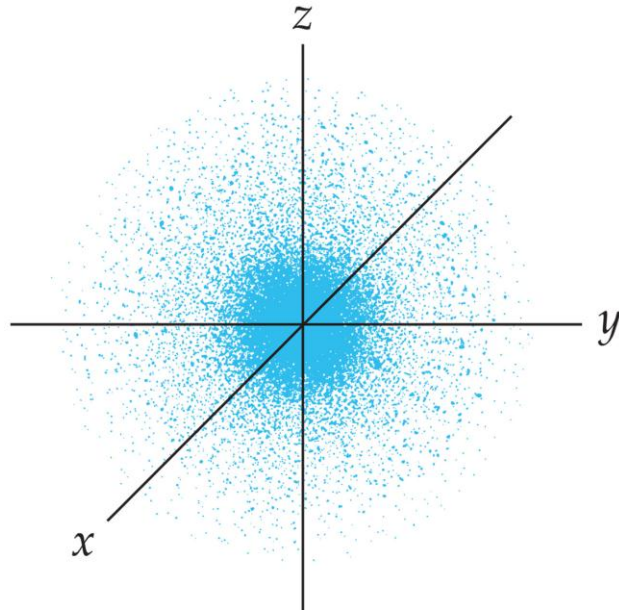
In general, # radial nodes = $n - l - 1$

Boundary Surfaces

- Representations of atomic orbitals are often given as boundary surfaces – pictorial representations of the probable locations of electrons in a given orbital
- A boundary surface describes a volume which is (usually) 95% certain to contain an electron
- Some boundary surfaces for various orbitals are given in the figure



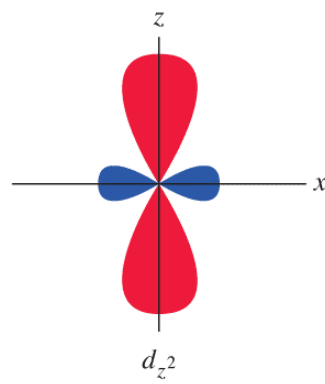
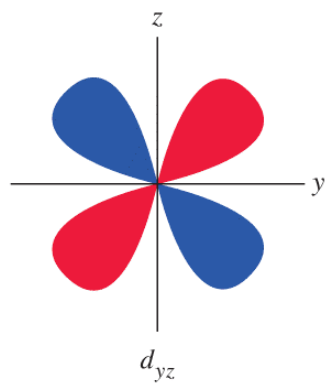
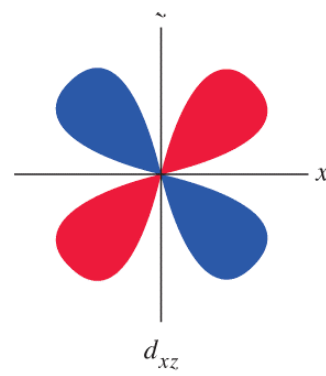
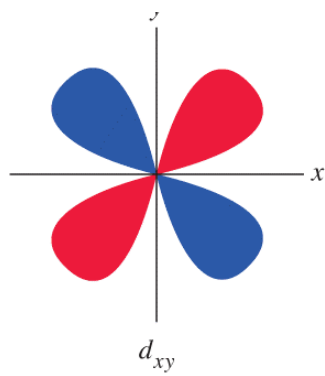
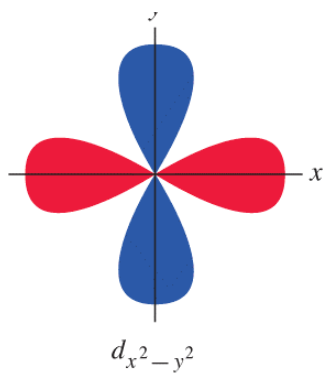
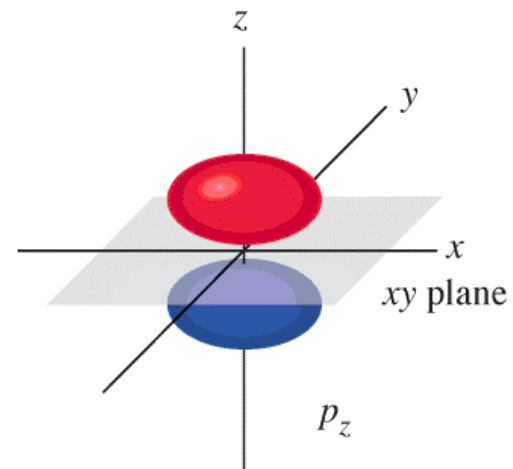
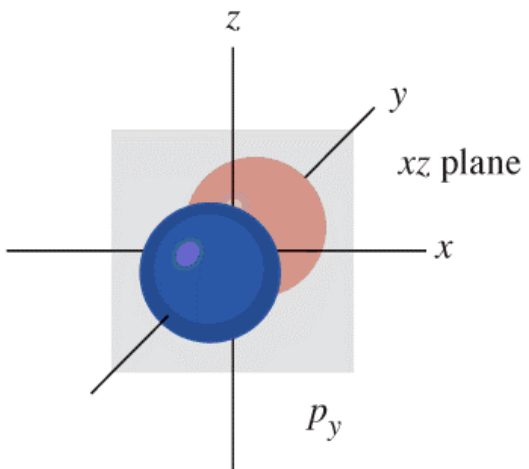
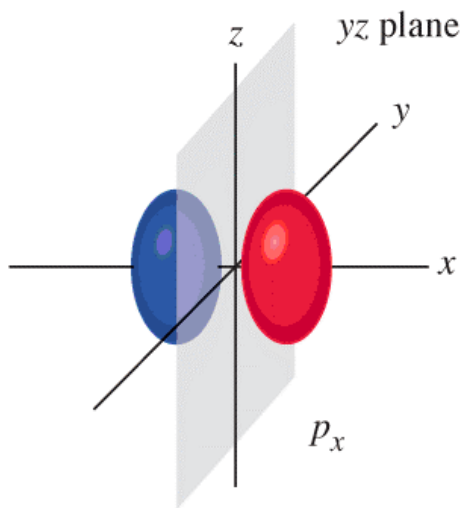
Boundary Surfaces

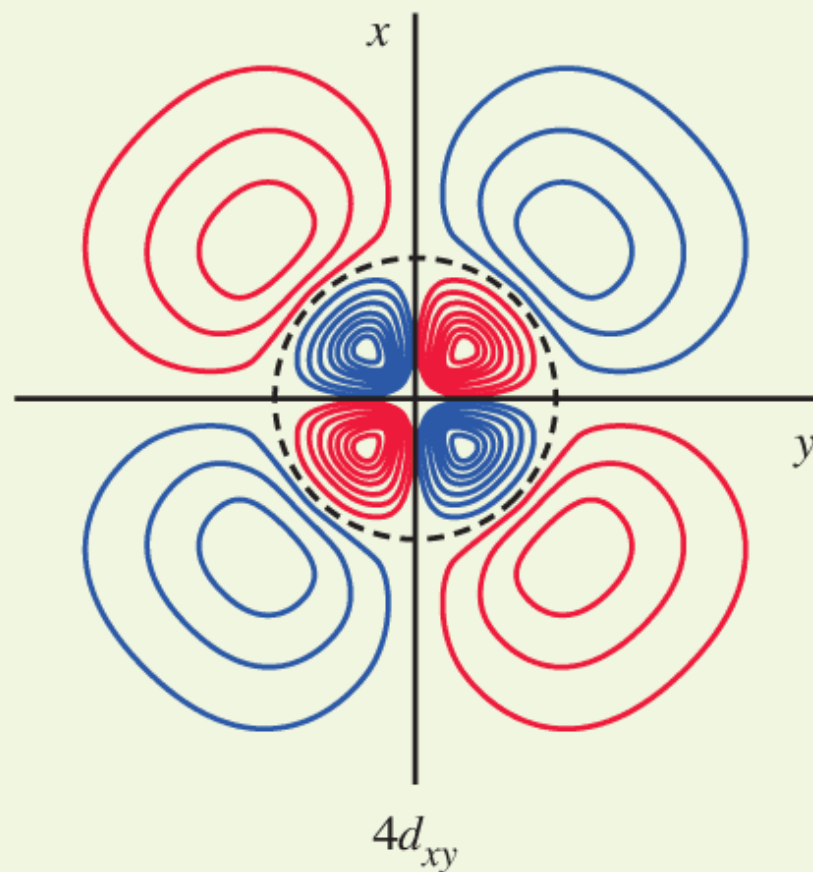
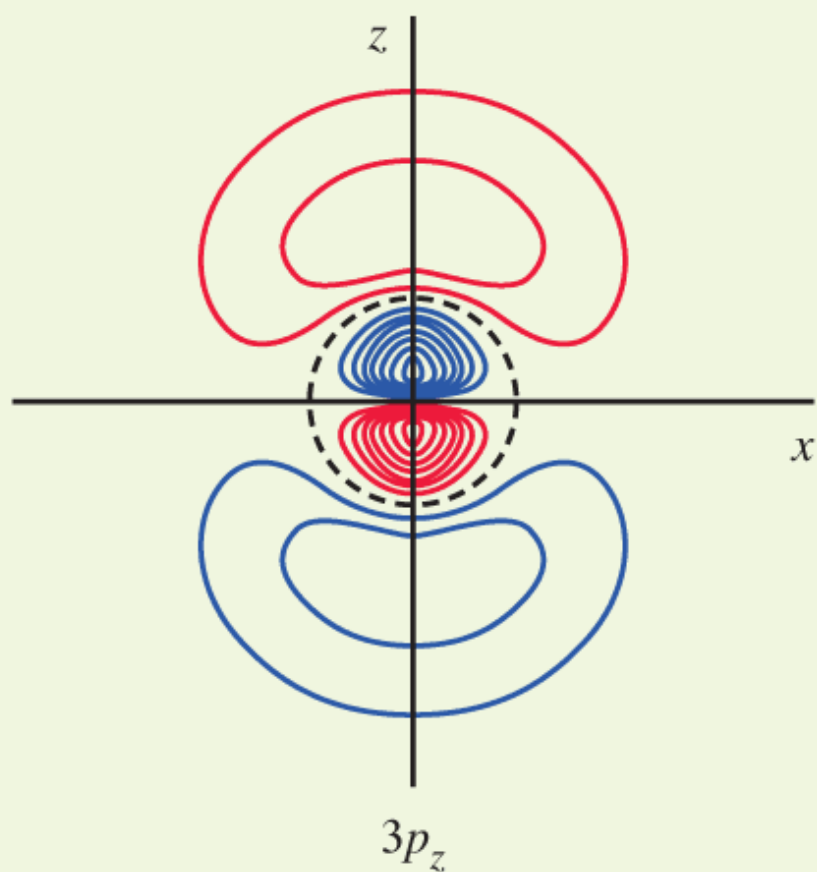


Boundary Surfaces

- For p , d , and f -orbitals, sometimes see that there are different-colored lobes in the picture
- Can fit a plane between these lobes which describes a region where electron probability is zero (*angular node: planar or conical*)
- The sign of the wavefunction changes at nodal plane (have a positive signed lobe and a negative signed lobe)
- Lobe *signs* (+ or -) are important in bonding models – see later

of angular nodes for an orbital = l (orbital quantum number)





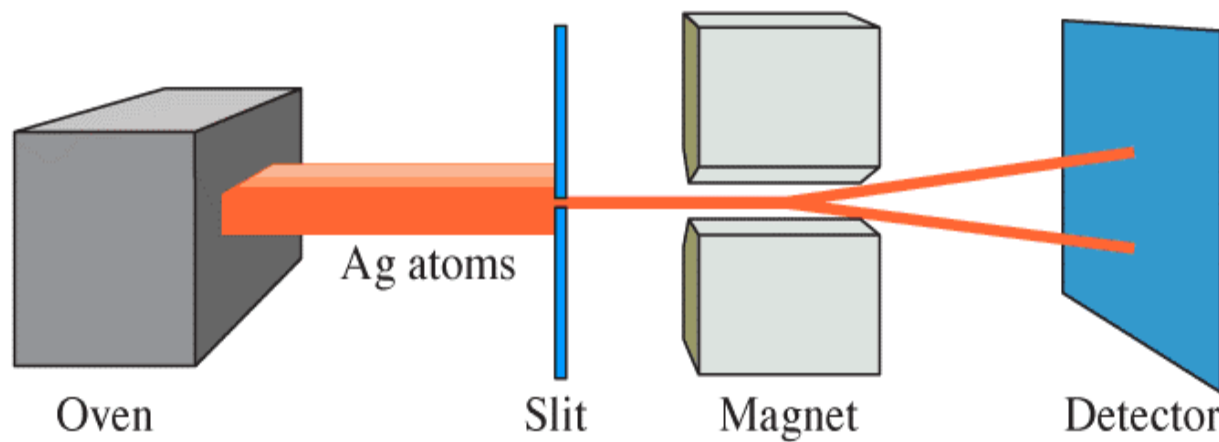
▲ FIGURE 8-31

Contour plots for $3p_z$ and the $4d_{xy}$ orbital

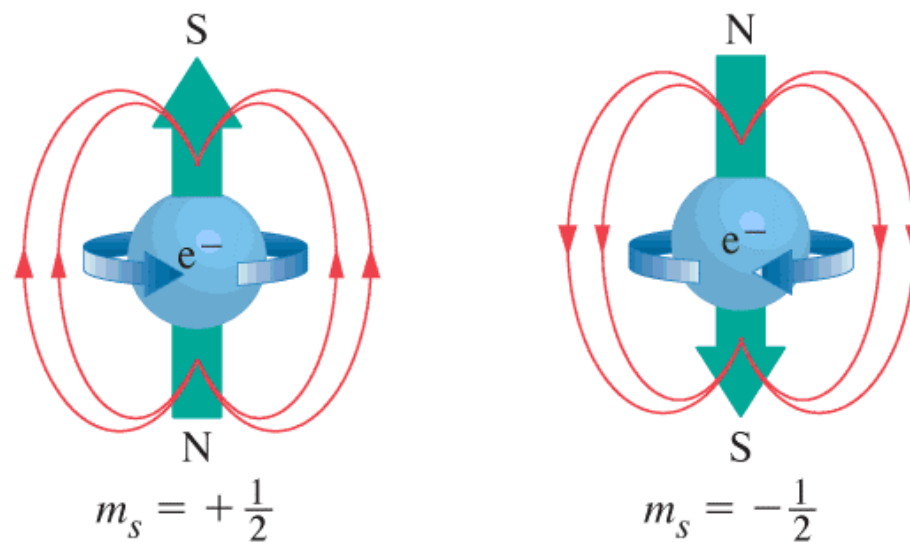
The relative phases in these orbitals are shown by the colors red and blue. The radial nodes are represented by the dashed circles.

The Fourth Quantum Number

- ***Orbitals* are characterized by three quantum numbers: n , l , m_l**
- **A fully occupied orbital contains two electrons. These electrons are not identical (Pauli Exclusion principle)**



▲ FIGURE 8-33
The Stern–Gerlach experiment



▲ FIGURE 8-32
Electron spin visualized

The Fourth Quantum Number

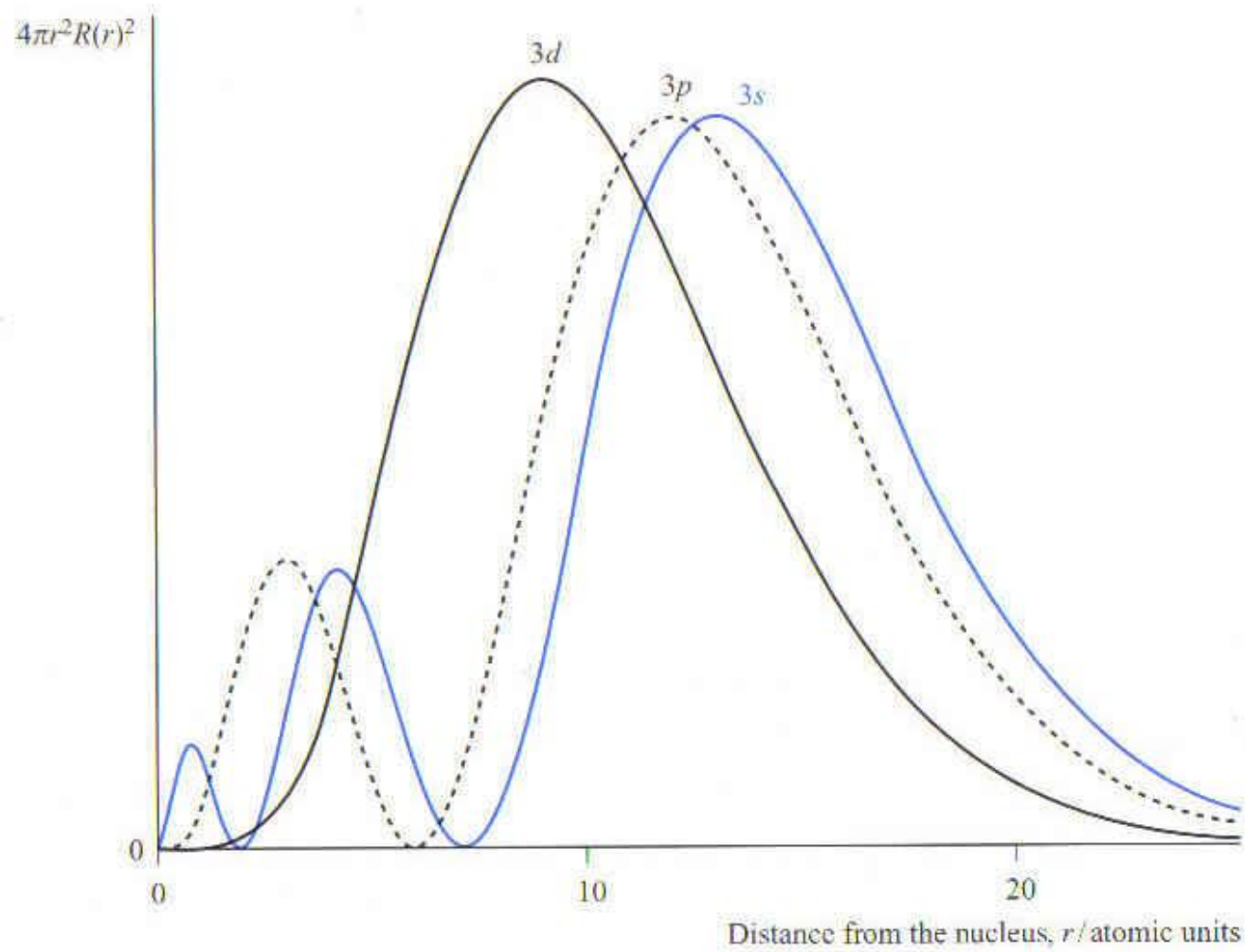
- The two electrons assume different spin directions (arbitrarily, the *spin quantum number*, m_s , has a value of $\pm \frac{1}{2}$)
- One electron in an orbital has $m_s = + \frac{1}{2}$, the other has $m_s = - \frac{1}{2}$
- Thus four quantum numbers are required to fully describe an electron in the Q.M. model of the atom

Orbital Degeneracy/Non-degeneracy

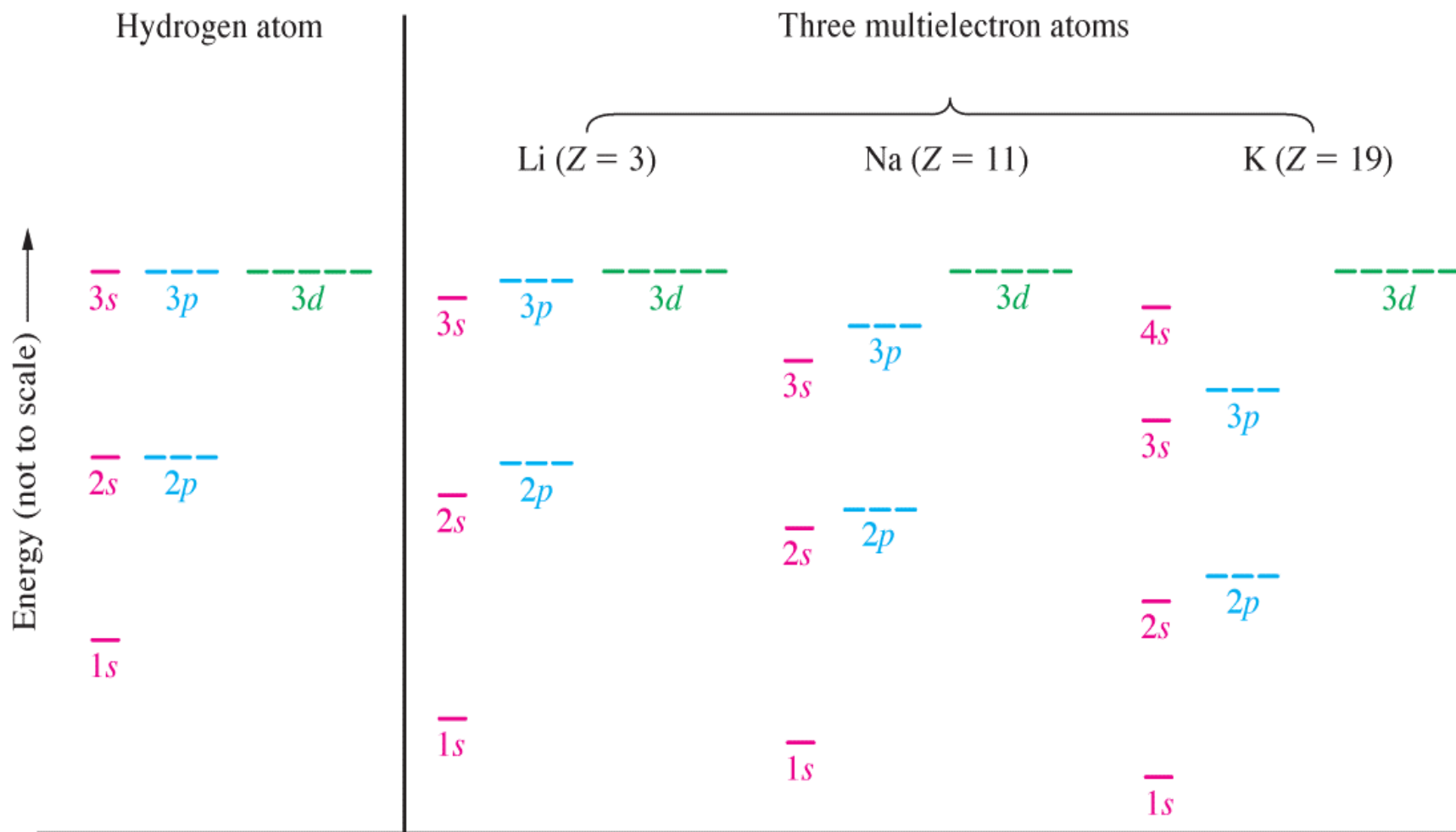
- In a *hydrogen-like species*, all orbitals of a given energy shell have the same energy (they are “degenerate”), as the only electrostatic force that exists is electron-nucleus. Thus, excitation of the electron from the ground to the first excited state ($n = 2$) will result in the electron occupying either the 2s or a 2p orbital
- In a multi-electron species (e.g. He), this is not true. There are three electrostatic interactions that need to be considered. What are they?
- Excitation to the $n = 2$ level will result in the electron occupying the 2s orbital.

Effective Nuclear Charge

- Look at Li: third electron occupies 2s orbital (*Aufbau* Principle – orbitals are filled in order of increasing energy)
- Why does the 2s orbital offer a lower energy than the 2p?
 - Electrons in different subshells experience different percentages of the total nuclear charge (total number of protons) **shielding**
 - Different subshells of a shell penetrate the atom differently (compare 3s, 3p, and 3d radial probabilities)



Orbital Energies



▲ FIGURE 8-36

Orbital energy-level diagram for the first three electronic shells

Rules for Filling Orbitals

- There are three rules applied in filling atomic orbitals in multi-electron atoms:
 - Aufbau Principle: orbitals are filled in order of increasing energy
 - Pauli Exclusion Principle: no two electrons may have the same *four* quantum numbers
 - Hund's Rule of Maximum Multiplicity: degenerate orbitals are each singly occupied before electron-pairing can occur, and spins are “parallel”

Hund's Rule

TABLE 2-6
Hund's Rule and Multiplicity

<i>Number of Electrons</i>	<i>Arrangement</i>	<i>Unpaired e^-</i>	<i>Multiplicity</i>
1	$\uparrow$ — —	1	2
2	$\uparrow$ $\uparrow$ —	2	3
3	$\uparrow$ $\uparrow$ $\uparrow$	3	4
4	$\uparrow\downarrow$ $\uparrow$ $\uparrow$	2	3
5	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow$	1	2
6	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	0	1

$m_s = +1/2$

Multiplicity = $n + 1$; n = # of unpaired electrons

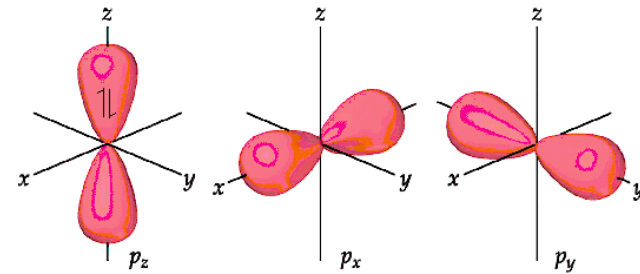
Hund's Rule

- The 2p electrons of carbon could be arranged in three ways

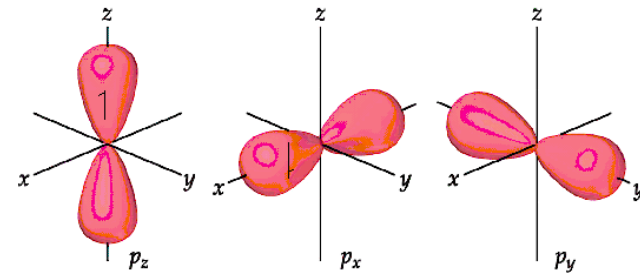


- These arrangements have different energies

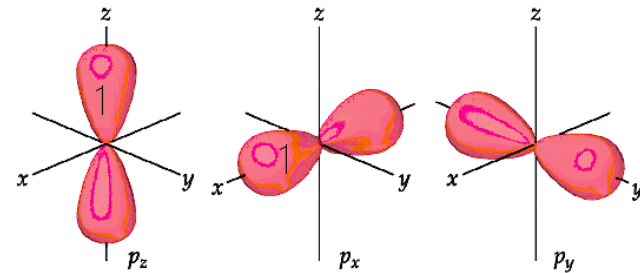
1



2

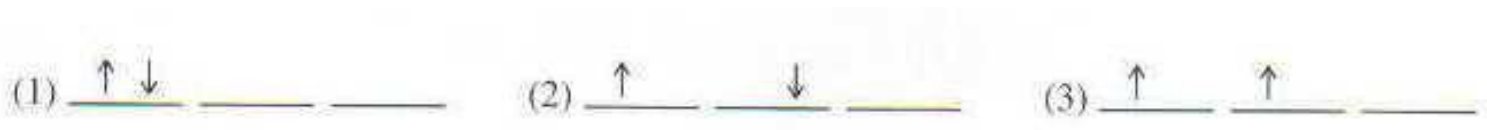


3



Hund's Rule

- Placing two electrons in the same orbital requires overcoming electrostatic repulsion
- This energy is known as coulombic energy, Π_c , and is positive (unfavorable)



Pairing energy required

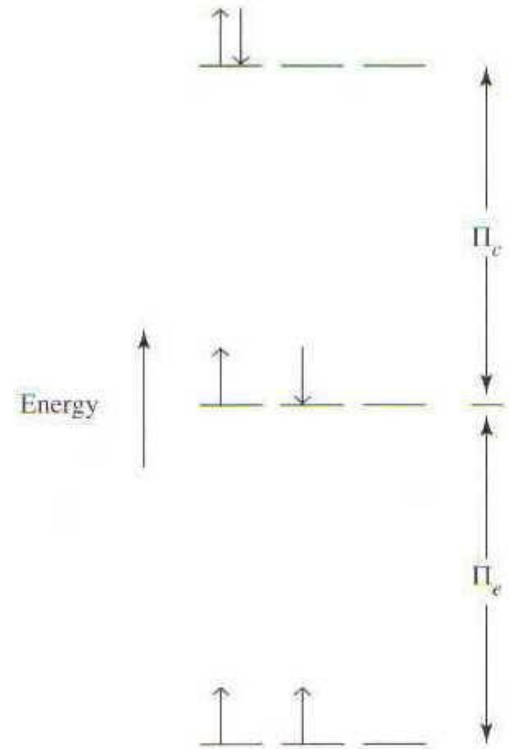
Hund's Rule

- It is possible to describe the last arrangement of electrons in more than one way
- If electrons are numbered 1 and 2 and are exchanged, the same picture is obtained (an equivalent description)
- This equates to a situation where the energy of this state can be distributed over a larger number of states, lowering its energy
- The last arrangement is more stable than the second by the exchange energy, Π_e (negative, and so favorable)



Pairing Energy, Π

- The pairing energy is the energy required to transform the bottom arrangement (see fig.) to the top one
- It requires supplying exchange energy to create “paired spins” and then coulombic energy to place them in the same orbital



These two pairing terms add to produce the total pairing energy, Π :

$$\Pi = \Pi_c + \Pi_e$$

<http://winter.group.shef.ac.uk/orbitron/>



The Orbitron gallery of atomic orbitals



1s



2s



3s



4s



5s



6s

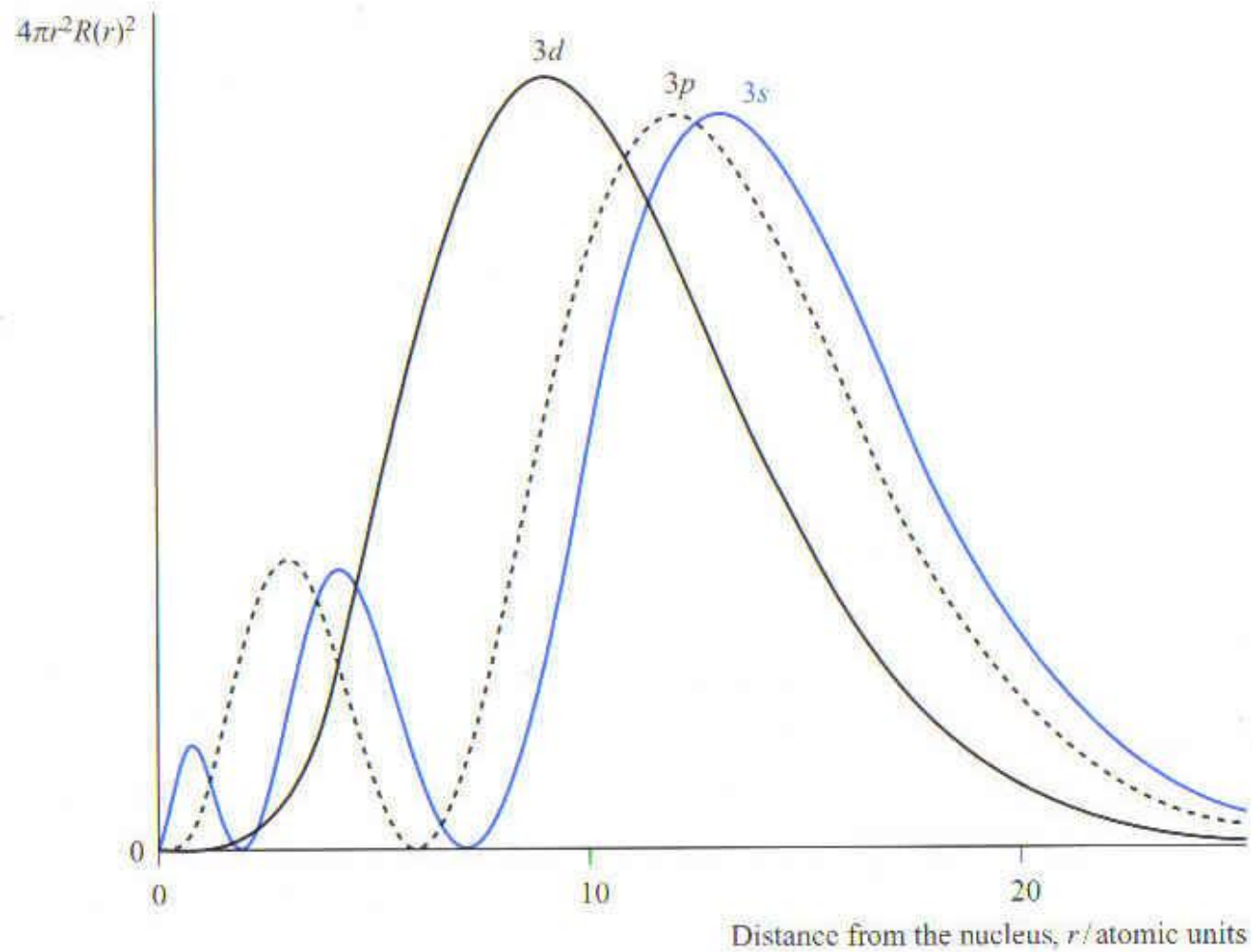


7s



Effective Nuclear Charge

- Not all electrons experience the full magnitude of the nuclear charge. Electrons in higher energy orbits (farther away from the nucleus and in more diffuse orbitals) will experience only a fraction of the full nuclear charge, as inner electrons will shield them from the nucleus
- We can calculate the “effective nuclear charge” experienced by an electron using **Slater's Rules**



Slater's Rules

- Empirical rules for the calculation of effective nuclear charges – the greater this number, the more strongly the electron is held
- $Z_{\text{eff}} = Z - S$
 - Z_{eff} = effective nuclear charge
 - Z = nuclear charge
 - S = shielding constant

What factors would affect Z_{eff} ?

How to Calculate Z_{eff}

1. Write the electronic configuration of the element, grouping subshells or similar shells together (e.g. $(1s^2)(2s^22p^6)(3s^23p^6)(3d^{10})(4s^2)$)
2. Electrons of higher energy than the electron under consideration do not contribute
3. *When looking at an ns or np electron:*
 - Other electrons of the same (ns,np) group contribute $S = 0.35$
 - Each electron in the (n-1) shell contributes $S = 0.85$
 - Each electron in the (n-2) or lower shell contributes $S = 1.00$

← weakness of model

How to Calculate Z_{eff}

4. When looking at a *nd* or *nf* electron
 - Each of the other electrons in the *nd* or *nf* group contributes $S = 0.35$
 - All electrons of lower grouping (energy) contribute $S = 1.00$

Using Slater's Rules

- Why is the electronic configuration of potassium ($Z = 19$) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ and not $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$?
- Use Slater's Rules to calculate the effective nuclear charge for a 4s electron and a 3d electron in each configuration and see which is more stable

Using Slater's Rules

● $(1s^2)(2s^22p^6)(3s^23p^6)(4s^1)$:

- $Z_{\text{eff}} = Z - S = [(19) - (8 \times 0.85) + (10 \times 1.00)] = 2.20$

● $(1s^2)(2s^22p^6)(3s^23p^6)(3d^1)$:

- $Z_{\text{eff}} = Z - S = [(19) - (18 \times 1.00)] = 1.00$

● Can you tell which electrons are valence electrons and which are core?

Electron Configurations and the Periodic Table

- Since the Periodic Table is arranged in groups of s-block, p-block, d-block elements, it can (and should) be used to determine electron configurations for elements
- C: $1s^2 2s^2 2p^2$
- Mg: $1s^2 2s^2 2p^6 3s^2$
- Br: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$

Main-group elements																	
s block																	
1	2															18	
1 H	2 He															2 He	
3 Li	4 Be															10 Ne	
11 Na	12 Mg															18 Ar	
19 K	20 Ca	3 Sc	4 Ti	5 V	6 Cr	7 Mn	8 Fe	9 Co	10 Ni	11 Cu	12 Zn	13 Ga	14 Ge	15 As	16 Se	17 Br	18 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57-71 La-Lu*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89-103 Ac-Lr†	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg							

Elements with Unusual Electron Configurations

- Some elements possess electron configurations that would not be predicted using the Periodic Table:

- Cr: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$ ← instead of $\dots 4s^2 3d^4$
- Cu: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$ ← instead of $\dots 4s^2 3d^9$

Several explanations for this behavior have been proposed

Electron Configurations of Ions

- When electrons are removed from atoms, cations are formed.
- The electron removed from an atom will be the one experiencing the least attraction to the nucleus (highest energy)
- Valence electrons are the highest energy electrons (have the highest value of “n”)
- To form anions, electrons are added to atoms. These electrons are added to the lowest energy, available orbitals

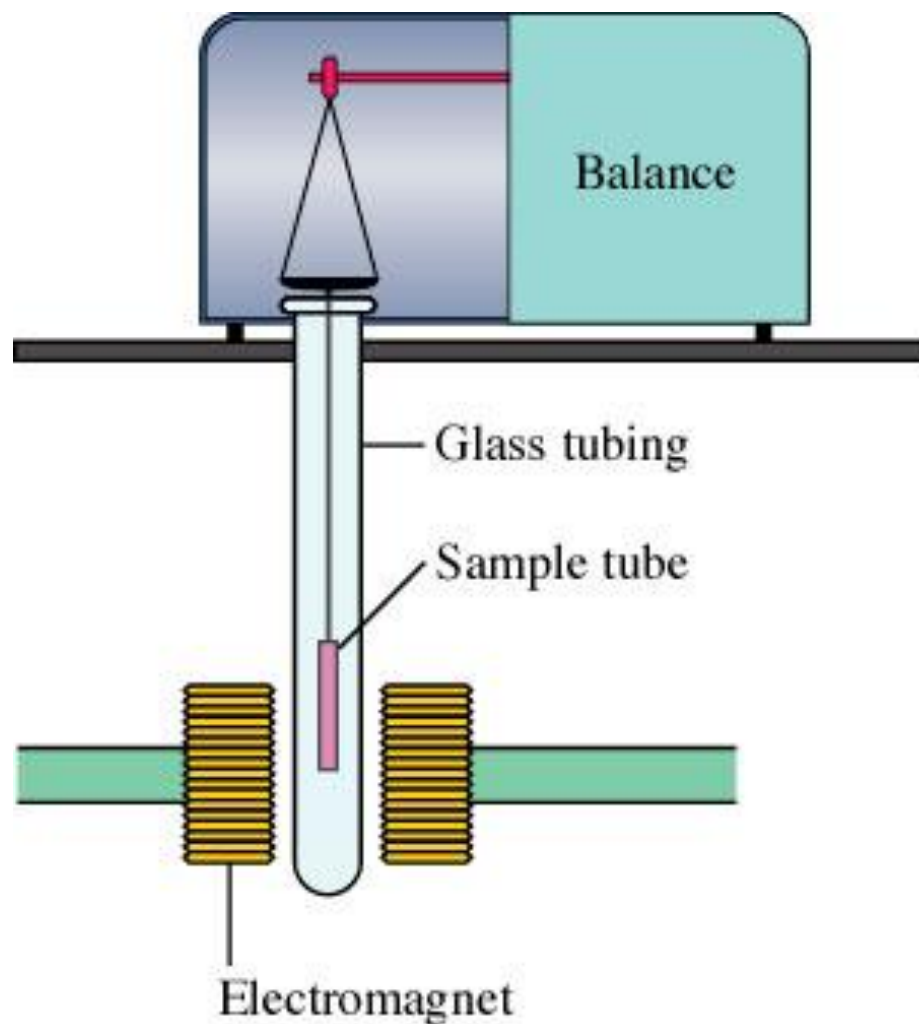
What are the electron configurations for the following ions?



Measurement of Magnetic Moments

- Atoms and ions that possess unpaired electrons are said to be paramagnetic (drawn into a magnetic field)
- Species with no unpaired electrons are said to be diamagnetic (weakly repelled by a magnetic field)
- The measurement of the magnetic properties (magnetic susceptibility) is a powerful method for detecting the presence (and number) of unpaired electrons in elements and compounds

Measuring Paramagnetism

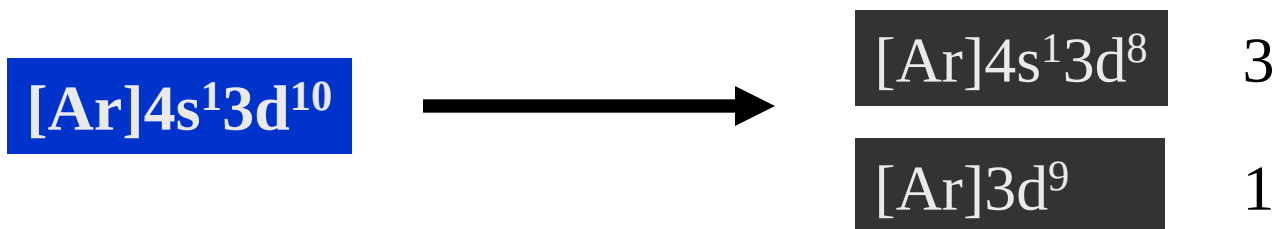


Magnetic Properties of Atoms and Ions

- The magnetic moment, μ (units of Bohr magnetons, BM), is related to the number of unpaired electrons

$$\mu = 2\sqrt{S(S + 1)}$$

- In this equation, S is the sum of the spins of all the unpaired electrons (so for three unpaired e⁻'s, $S = 3/2$)
- So a given number of unpaired electrons will correspond to a certain magnetic susceptibility
- Example, Cu²⁺ ions in CuSO₄·5H₂O yields *magnetic susceptibility* data which indicates $\mu = 1.80$ BM. What is the electron configuration of Cu²⁺ in this complex?



Trends in Atomic Properties

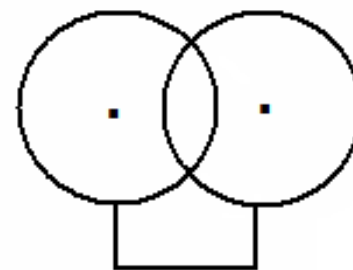
Ionic and Covalent Radii

Homonuclear Diatomic Molecules

The covalent radius is determined from diffraction experiments, which locate nuclei. The distance between the nuclei is the bond length.

The covalent radius of an atom is considered to be half this distance.

Covalent (atomic) radii increase down a group, and decrease across a period



bond length

$$r_{\text{cov}} = 1/2 \text{ bond length}$$

Trends in Covalent Radii

TABLE 2-8
Nonpolar Covalent Radii (pm)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H 32																	He 31
Li 123	Be 89											B 82	C 77	N 75	O 73	F 71	Ne 69
Na 154	Mg 136											Al 118	Si 111	P 106	S 102	Cl 99	Ar 98
K 203	Ca 174	Sc 144	Ti 132	V 122	Cr 118	Mn 117	Fe 117	Co 116	Ni 115	Cu 117	Zn 125	Ga 126	Ge 122	As 120	Se 117	Br 114	Kr 111
Rb 216	Sr 191	Y 162	Zr 145	Nb 134	Mo 130	Tc 127	Ru 125	Rh 125	Pd 128	Ag 134	Cd 148	In 144	Sn 140	Sb 140	Te 136	I 133	Xe 126
Cs 235	Ba 198	La 169	Hf 144	Ta 134	W 130	Re 128	Os 126	Ir 127	Pt 130	Au 134	Hg 149	Tl 148	Pb 147	Bi 146	Po (146)	At (145)	Ra

Source: R. T. Sanderson, *Inorganic Chemistry*, Reinhold, New York, 1967, p. 74; and E. C. M. Chen, J. G. Dojahn, and W. E. Wentworth, *J. Phys. Chem. A*, 1997, 101, 3088.

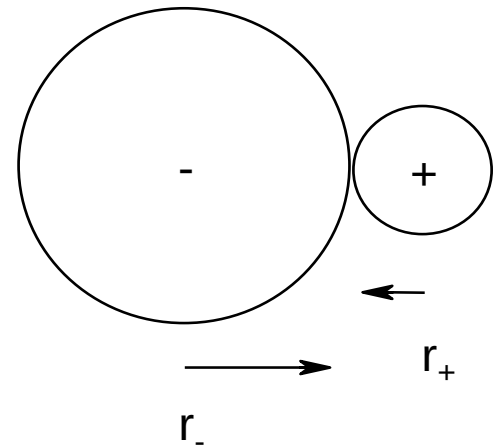
Z_{eff} for valence electrons in each 2nd row element

Li: 1.30 Be: 1.95 B: 2.60 C: 3.25 N: 3.90 O: 4.55 F: 5.20 Ne: 5.85

- Moving L → R, Z_{eff} increases as # of protons increases; radius decreases.
- Moving down a group, electrons are being added to larger orbitals (higher energy shells, bigger orbitals); radius increases.

Ionic Radii

- In making measurements on ionic compounds (crystalline), the structures aren't homonuclear, and so radius is defined differently in these cases
- Ionic radii (like covalent radii) also increase down a group
- Ionic radii of cations *decrease as magnitude of positive charge increases*
- Radii of anions *increase with magnitude of negative charge*



Sizes of Atoms and Ions

Li 152 Li⁺ 59	Be 111 Be²⁺ 27											B 88	C 77	N 75 N³⁻ 171	O 73 O²⁻ 140	F 71 F⁻ 133		
Na 186 Na⁺ 99	Mg 160 Mg²⁺ 72											Al 143 Al³⁺ 53	Si 117	P 110 P³⁻ 212	S 104 S²⁻ 184	Cl 99 Cl⁻ 181		
K 227 K⁺ 138	Ca 197 Ca²⁺ 100	Sc 161 Sc³⁺ 75	Ti 145 Ti²⁺ 86	V 132 V²⁺ 79 V³⁺ 64	Cr 125 Cr²⁺ 82 Cr³⁺ 62	Mn 124 Mn²⁺ 83	Fe 124 Fe²⁺ 77 Fe³⁺ 65	Co 125 Co²⁺ 75 Co³⁺ 61	Ni 125 Ni²⁺ 70	Cu 128 Cu⁺ 96 Cu²⁺ 73	Zn 133 Zn²⁺ 75	Ga 122 Ga³⁺ 62	Ge 122	As 121	Se 117 Se²⁻ 198	Br 114 Br⁻ 196		
Rb 248 Rb⁺ 149	Sr 215 Sr²⁺ 113											Ag 144 Ag⁺ 115	Cd 149 Cd²⁺ 95	In 163 In³⁺ 79	Sn 141 Sn²⁺ 93	Sb 140 Sb³⁺ 76	Te 137 Te²⁻ 221	I 133 I⁻ 220

Ionic Radii

TABLE 2-9
Crystal Radii for Selected Ions

	<i>Z</i>	<i>Element</i>	<i>Radius (pm)</i>
<i>Alkali metal ions</i>	3	Li ⁺	90
	11	Na ⁺	116
	19	K ⁺	152
	37	Rb ⁺	166
	55	Cs ⁺	181
<i>Alkaline earth ions</i>	4	Be ²⁺	59
	12	Mg ²⁺	86
	20	Ca ²⁺	114
	38	Sr ²⁺	132
	56	Ba ²⁺	149
<i>Other cations</i>	13	Al ³⁺	68
	30	Zn ²⁺	88
<i>Halide ions</i>	9	F ⁻	119
	17	Cl ⁻	167
	35	Br ⁻	182
	53	I ⁻	206
<i>Other anions</i>	8	O ²⁻	126
	16	S ²⁻	170

As more electrons are removed, ion becomes smaller

3rd row cations

Na⁺: 116 pm

Mg²⁺: 86 pm

Al³⁺: 68 pm

2nd row anions

F⁻: 119 pm

O²⁻: 126 pm

SOURCE: R. D. Shannon, *Acta Crystallogr.* **1976**, A32, 751. A longer list is given in Appendix B-I. All the values are for 6-coordinate ions.

1 pm (picometer) = 10⁻¹²m

Ionic Radii

TABLE 2-10
Crystal Radius and Nuclear Charge

<i>Ion</i>	<i>Protons</i>	<i>Electrons</i>	<i>Radius (pm)</i>
O^{2-}	8	10	126
F^-	9	10	119
Na^+	11	10	116
Mg^{2+}	12	10	86

These are *isoelectronic* species
(have the same number of
electrons)

TABLE 2-11
Crystal Radius and Total Number of Electrons

<i>Ion</i>	<i>Protons</i>	<i>Electrons</i>	<i>Radius (pm)</i>
O^{2-}	8	10	126
S^{2-}	16	18	170
Se^{2-}	34	36	184
Te^{2-}	52	54	207

Z_{eff} for valence electrons increases
across the series

O^{2-}	F^-	Na^+	Mg^{2+}
3.85	4.85	6.85	7.85

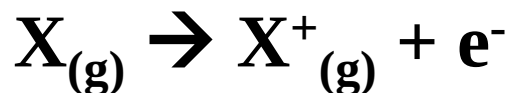
TABLE 2-12
Crystal Radius and Ionic Charge

<i>Ion</i>	<i>Protons</i>	<i>Electrons</i>	<i>Radius (pm)</i>
Ti^{2+}	22	20	100
Ti^{3+}	22	19	81
Ti^{4+}	22	18	75

Data shows the effect of removing
more and more electrons from the
same parent species (Ti)

Ionization Energies and Electron Affinities

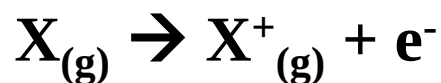
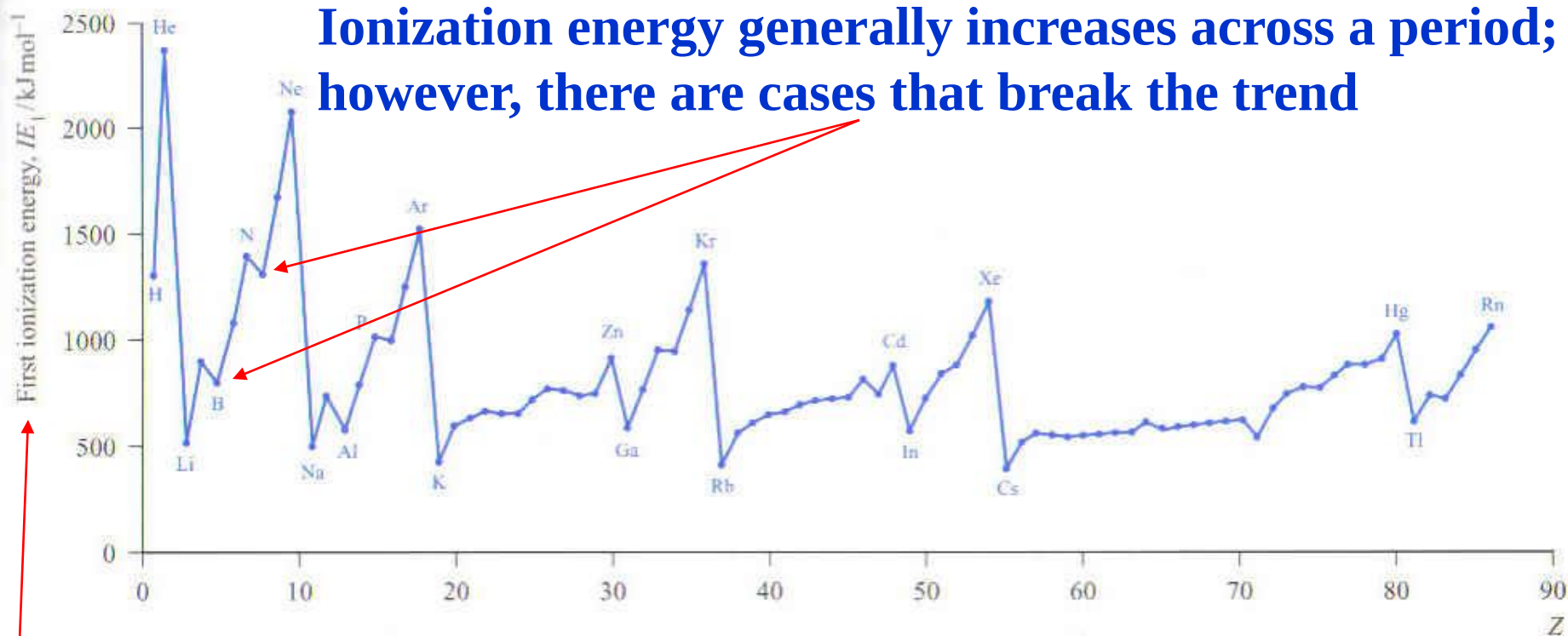
- **First ionization energy for element X, $\Delta U(0K)$: the internal energy change (ΔH) associated with the loss of the first valence electron from an atom (gas phase)**



- **Often, $\Delta U(0K)$ is equated with $\Delta H(298K)$ so that this information can be used in thermochemical calculations**

Ionization Energies

Ionization energy generally increases across a period; however, there are cases that break the trend



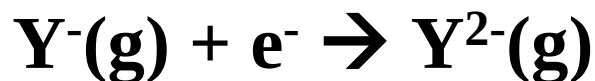
The higher the ionization energy, the more difficult it is to remove the valence electron

Electron Affinity

- Electron affinity for element Y is the internal energy change, $\Delta U(0K)$, that accompanies the gain of an electron by a gas phase atom*



- *Second* electron affinity for element Y:



*Defined in Miessler and Tarr so that ΔH (ΔU) values are positive
In M&T, first EA is defined as $\Delta U(0K)$ for



Process	$\approx \Delta_{\text{EA}}H / \text{kJ mol}^{-1}$
$\text{H(g)} + \text{e}^{-} \rightarrow \text{H}^{-}(\text{g})$	-73
$\text{Li(g)} + \text{e}^{-} \rightarrow \text{Li}^{-}(\text{g})$	-60
$\text{Na(g)} + \text{e}^{-} \rightarrow \text{Na}^{-}(\text{g})$	-53
$\text{K(g)} + \text{e}^{-} \rightarrow \text{K}^{-}(\text{g})$	-48
$\text{N(g)} + \text{e}^{-} \rightarrow \text{N}^{-}(\text{g})$	≈ 0
$\text{P(g)} + \text{e}^{-} \rightarrow \text{P}^{-}(\text{g})$	-72
$\text{O(g)} + \text{e}^{-} \rightarrow \text{O}^{-}(\text{g})$	-141
$\text{O}^{-}(\text{g}) + \text{e}^{-} \rightarrow \text{O}^{2-}(\text{g})$	+798*
$\text{S(g)} + \text{e}^{-} \rightarrow \text{S}^{-}(\text{g})$	-201
$\text{S}^{-}(\text{g}) + \text{e}^{-} \rightarrow \text{S}^{2-}(\text{g})$	+640*
$\text{F(g)} + \text{e}^{-} \rightarrow \text{F}^{-}(\text{g})$	-328
$\text{Cl(g)} + \text{e}^{-} \rightarrow \text{Cl}^{-}(\text{g})$	-349
$\text{Br(g)} + \text{e}^{-} \rightarrow \text{Br}^{-}(\text{g})$	-325
$\text{I(g)} + \text{e}^{-} \rightarrow \text{I}^{-}(\text{g})$	-295

† Tables of data differ in whether they list values of EA or $\Delta_{\text{EA}}H$ and it is essential to take note of the sign convention being used.

- Not multiplied by -1 here (from Housecroft and Sharpe, *Inorganic Chemistry*, 1st ed.)
- 2 trends: EA is generally larger (magnitude) for elements on right side of table
- Second electron affinity (acquisition of second electron) appears unfavorable

Electronegativity, χ

- This is often described as an atom's ability to attract bonding electrons when it is part of a molecule. It is really an atomic property, defined by Mulliken* as

$$\chi = \frac{1}{2}(IE_1 + EA_1)$$

- Electronegativity is highest for elements at the top right (e.g. F, Ne) and lowest for elements at the lower left (e.g. Cs)

*EA as defined in Miessler and Tarr

Hardness and Softness

- Hardness, η , is calculated as follows

$$\eta = \frac{1}{2}(IE_1 - EA_1)$$

“softness”, $\sigma = 1/\eta$

- The “hardest” elements and ions are those at the top right hand side of the periodic table (e.g. F); the softest are those at the lower left (heavy alkali metals, etc.)
- Hardness is related to the *polarizability*, α , of a species (how easily its electron cloud can be distorted)

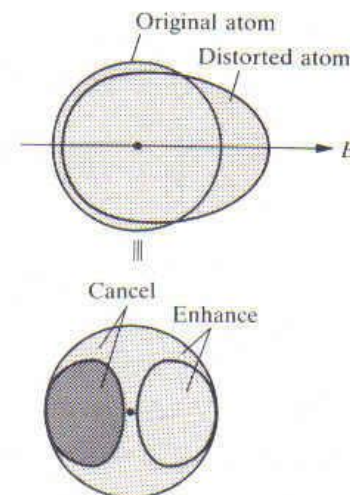


Fig. 1.24 The distortion of a 1s orbital caused by an electric field and its approximation as a superposition of s and p orbitals.

***EA as defined in Miessler and Tarr**