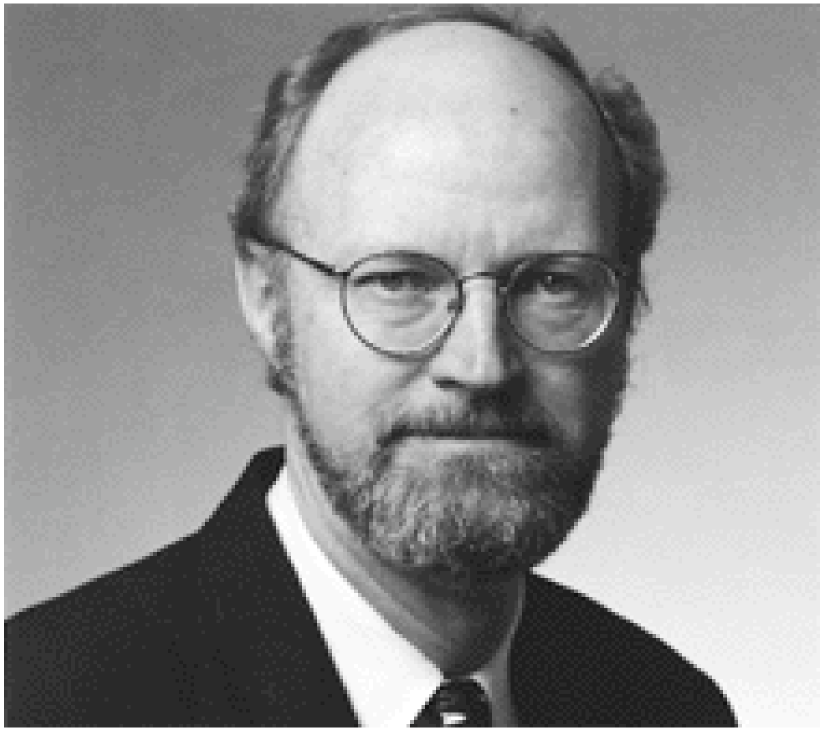
Chem C1403 Lecture 9 Wednesday, October 5, 2005

Today we'll revisit the discharge lamp experiments with an atomic and electronic interpretation based on the Bohr atom.

We'll also review some of the key equations of Einstein, Bohr and deBroglie that provide insight to the paradigm shifts that lead to modern quantum mechanics.

We'll then begin an examination of the modern quantum mechanical interpretation of the H atom.



Robert Grubbs: Nobel Prize in Chemistry: 2005
New methods of forming polymers.

Former graduate student at Columbia and former football and basketball (he's 6' 5" tall) opponent!

James Clerk Maxwell
1831-1879

Maxwell: Light consists of waves (energy is propagated by waves): Energy is spread over space like an oscillating liquid.

Maxwell's theory is called the ***classical*** theory of light.

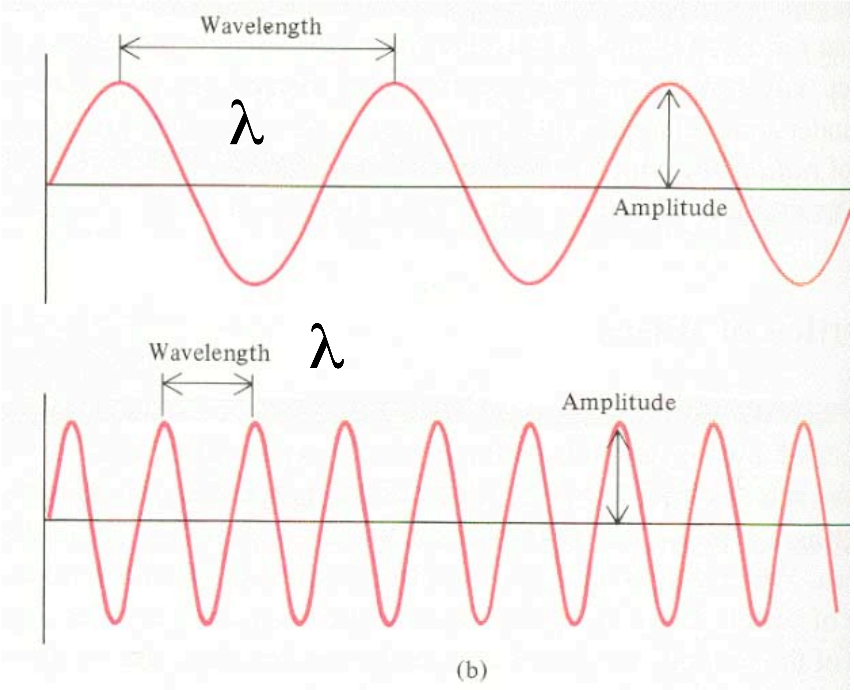
Key equations:

$c = \lambda \nu$ λ (Gk lambda), ν(Gk nu)

c = speed of light wave wave propagation

λ = wavelength, ν = frequency

Classical Paradigm: Energy carried by a light wave is proportional to the *Amplitude* of wave. Big wave, small wave.



Low Frequency

High Frequency

Waves and light

$c = \nu\lambda = 3.0 \times 10^8$ m-s^{-1} $= 3.0 \times 10^{17}$ nm-s^{-1}

$\nu = c/\lambda$, $\lambda = c/\nu$

c = speed of light

ν = frequency of light

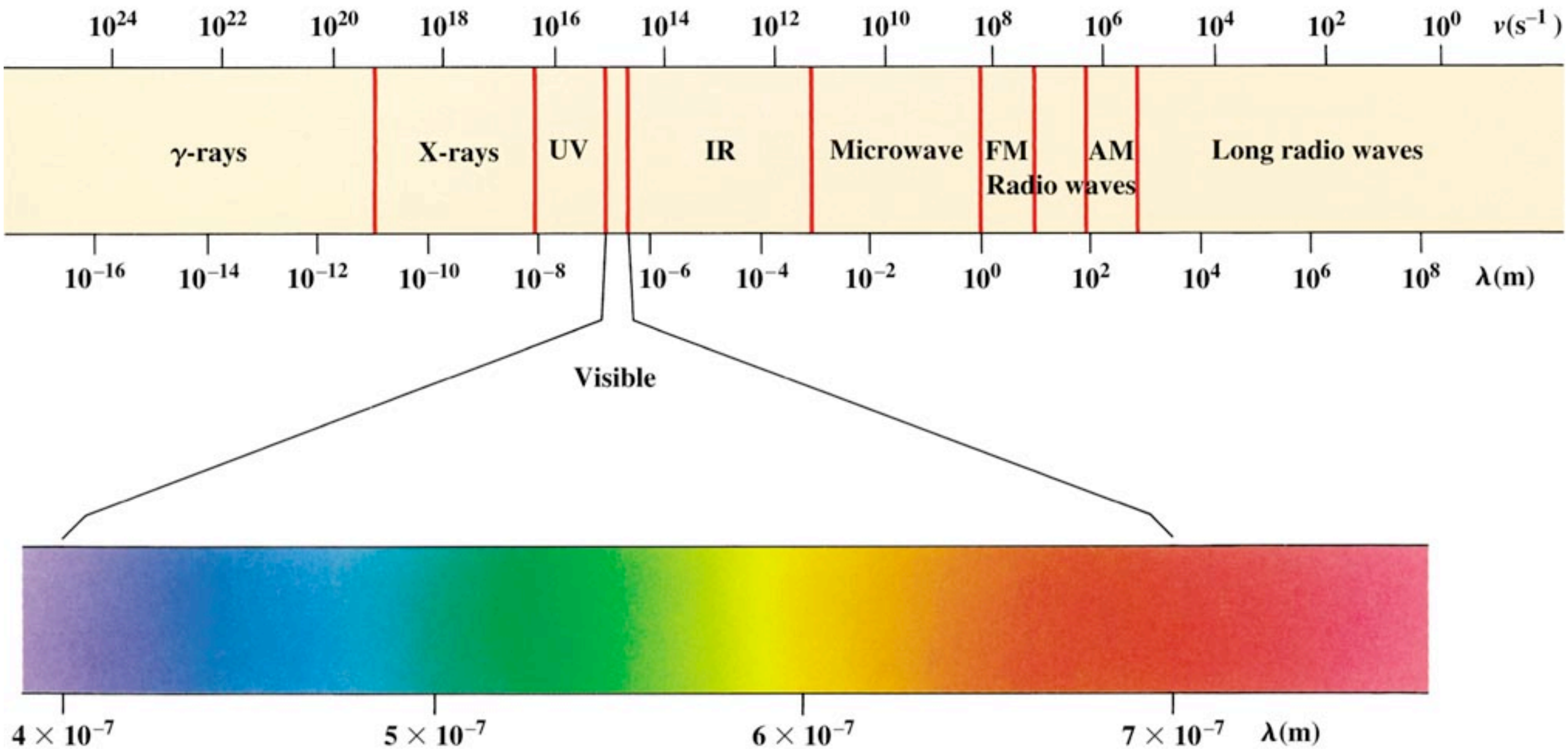
λ = speed of light

A computation:

What is the frequency of 500 nm light?

Answer: $\nu = c/\lambda$; ν = **(3.0 x 10^{17} nm-s^{-1})/500 nm**

ν = **6 x 10^{14} s^{-1}**

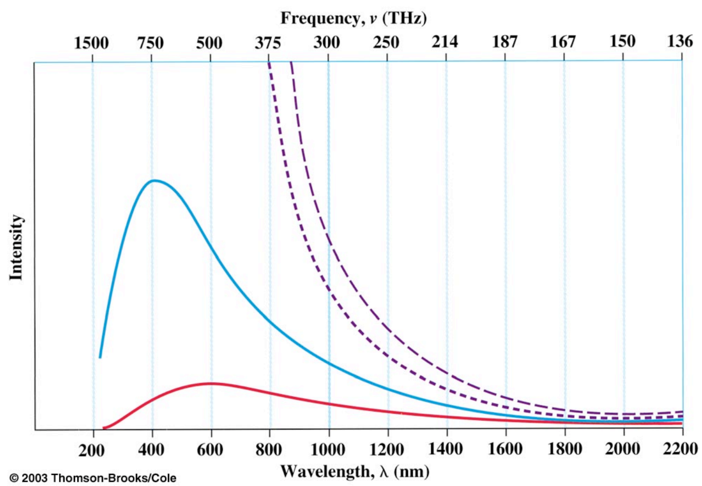


10^{24} 10^{22} 10^{20} 10^{18} 10^{16} 10^{14} 10^{12} 10^{10} 10^{8} 10^{6} 10^{4} 10^{2} 10^{0} $\nu(s^{-1})$
γ-rays
X-rays
UV
IR
Microwave
FM
AM
Radio waves
Long radio waves
10^{-16} 10^{-14} 10^{-12} 10^{-10} 10^{-8} 10^{-6} 10^{-4} 10^{-2} 10^{0} 10^{2} 10^{4} 10^{6} 10^{8} $\lambda(m)$
Visible
4×10^{-7} 5×10^{-7} 6×10^{-7} 7×10^{-7} $\lambda(m)$

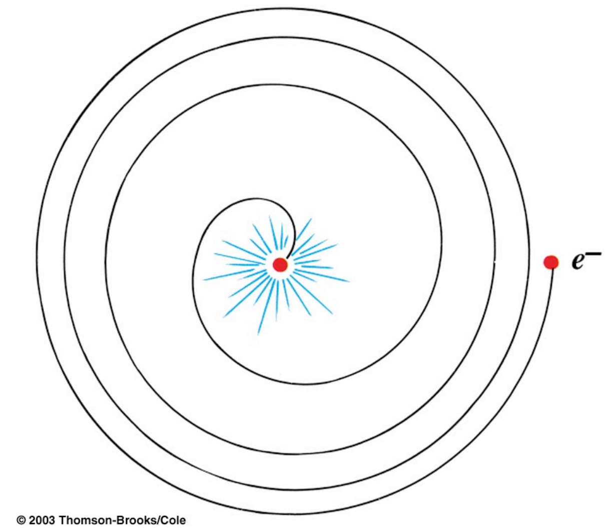
Fig 16-5

4 paradoxes that doomed the classical paradigm of light (and matter)

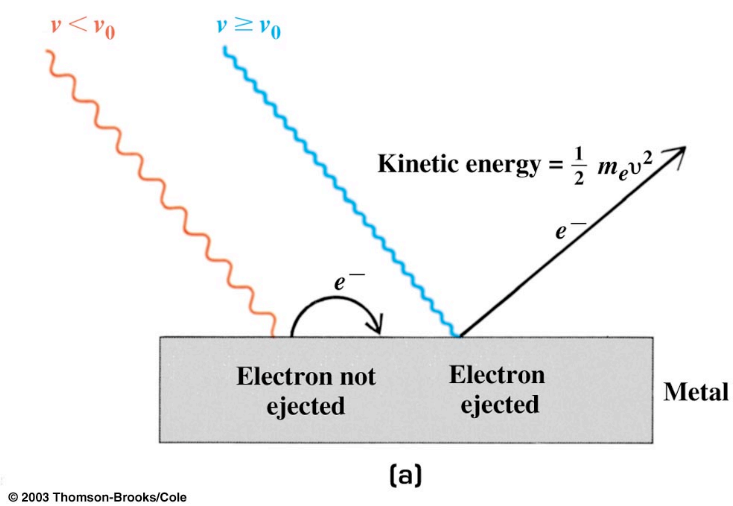
Ultraviolet catastrophe



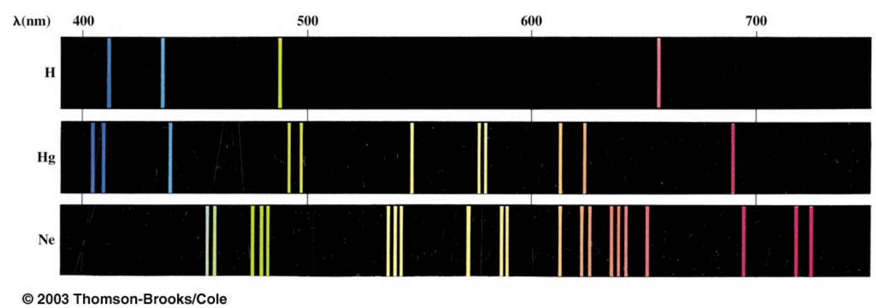
Death spiral of the electron

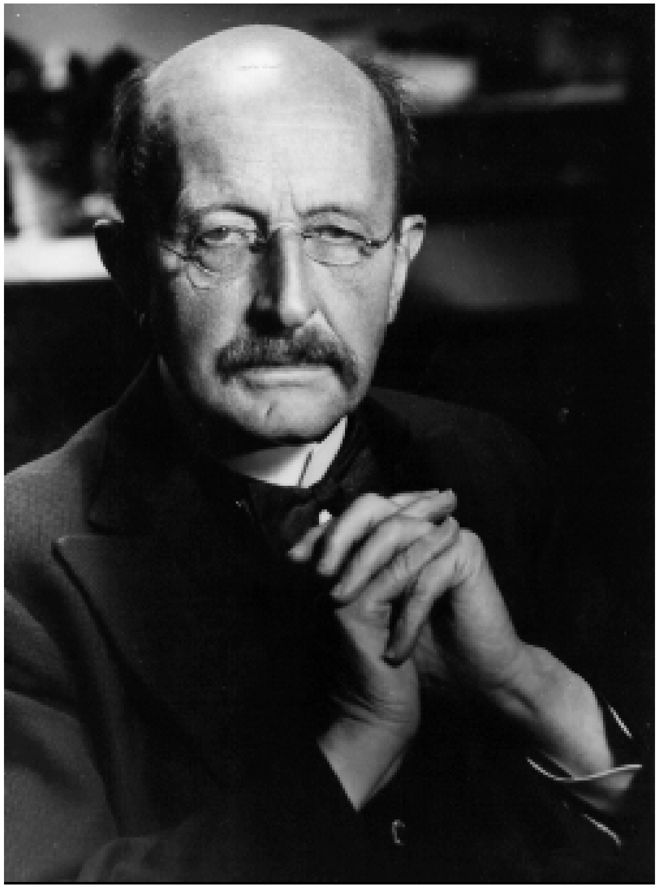


Photoelectric effect

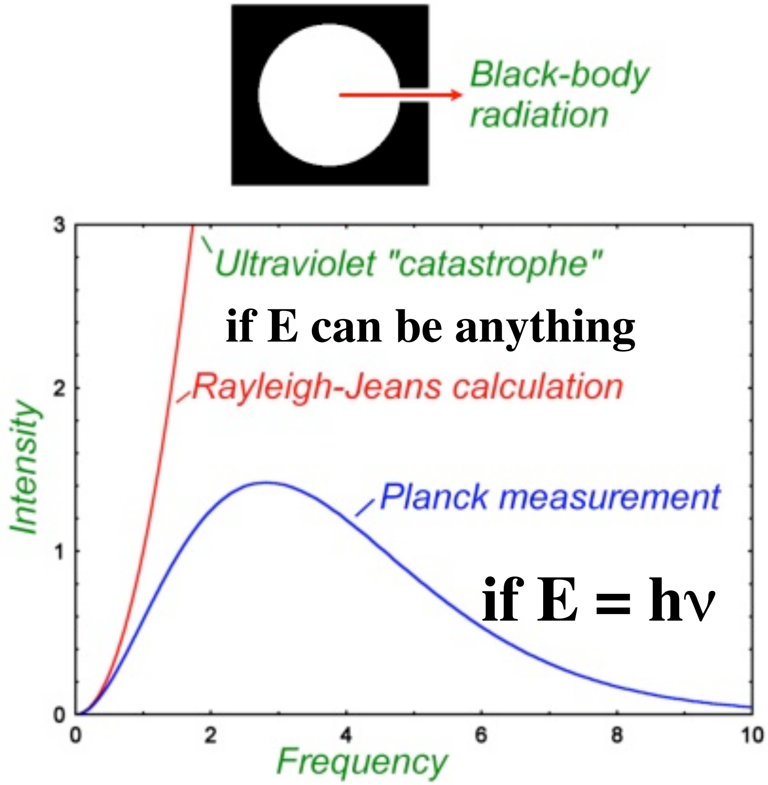


Line spectra of atom





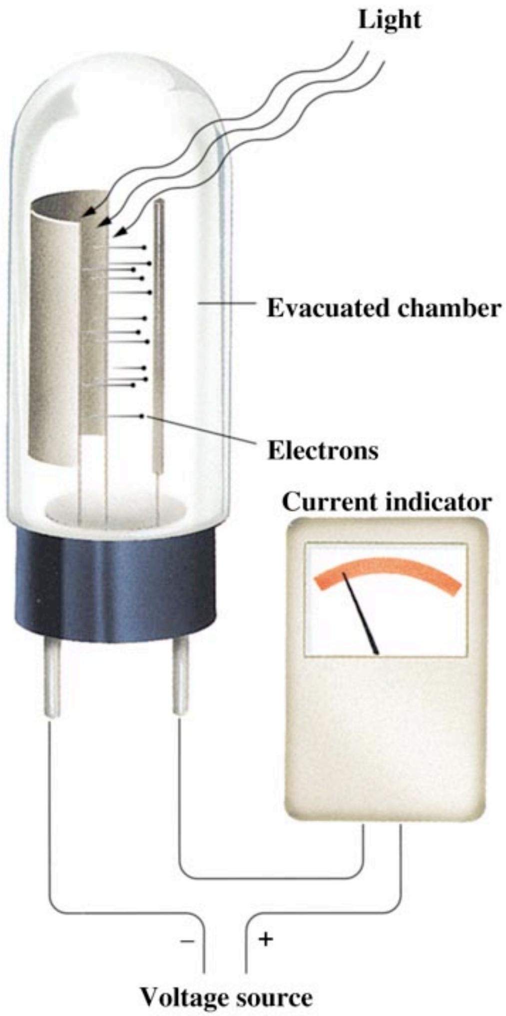
Planck explains the ultraviolet catastrophe by quantizing the energy of light. Light can only have energies given by E = hν. The value of h = 6.6 x 10^{-34} Js fits experiment!

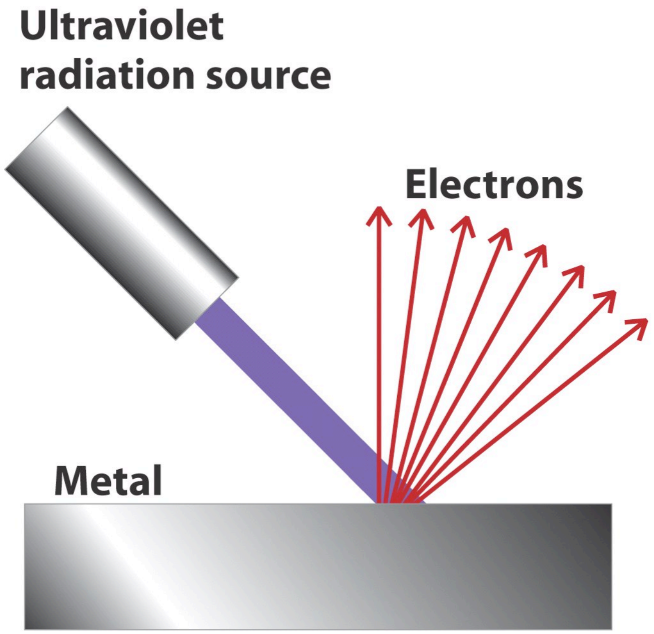


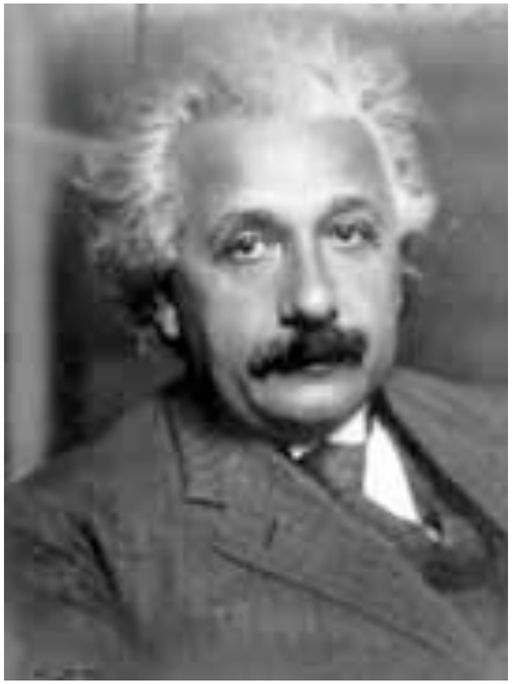
Max Planck
Nobel Prize 1918
"for his explanation of the ultraviolet catastrophe", namely E = hν, the energy of light is bundled and comes in quanta.

$$I(\nu) = \frac{2h\nu^3}{c^2}\frac{1}{\exp(h\nu/kT) - 1}$$

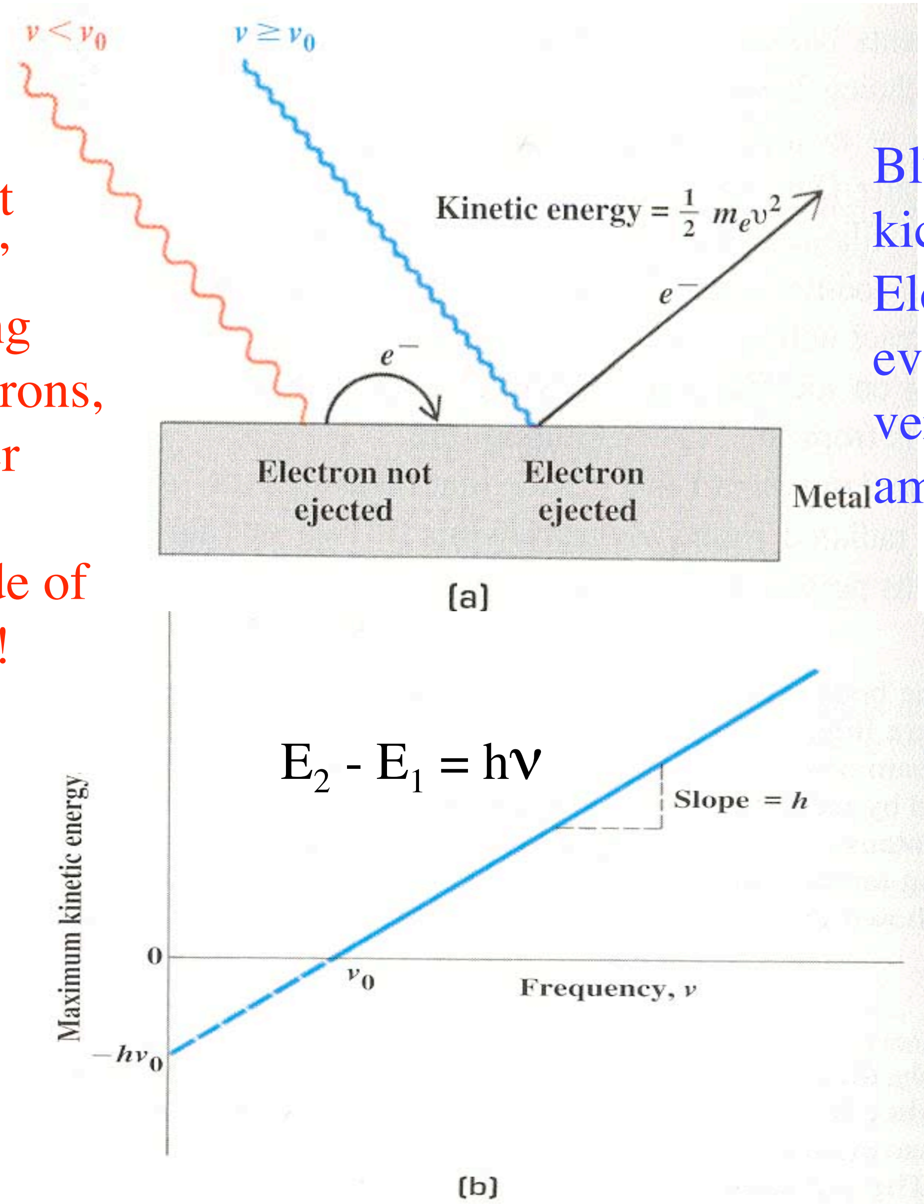
Einstein's explanation of the photoelectric effect"
Light consists of photons which carry quanta of energy.







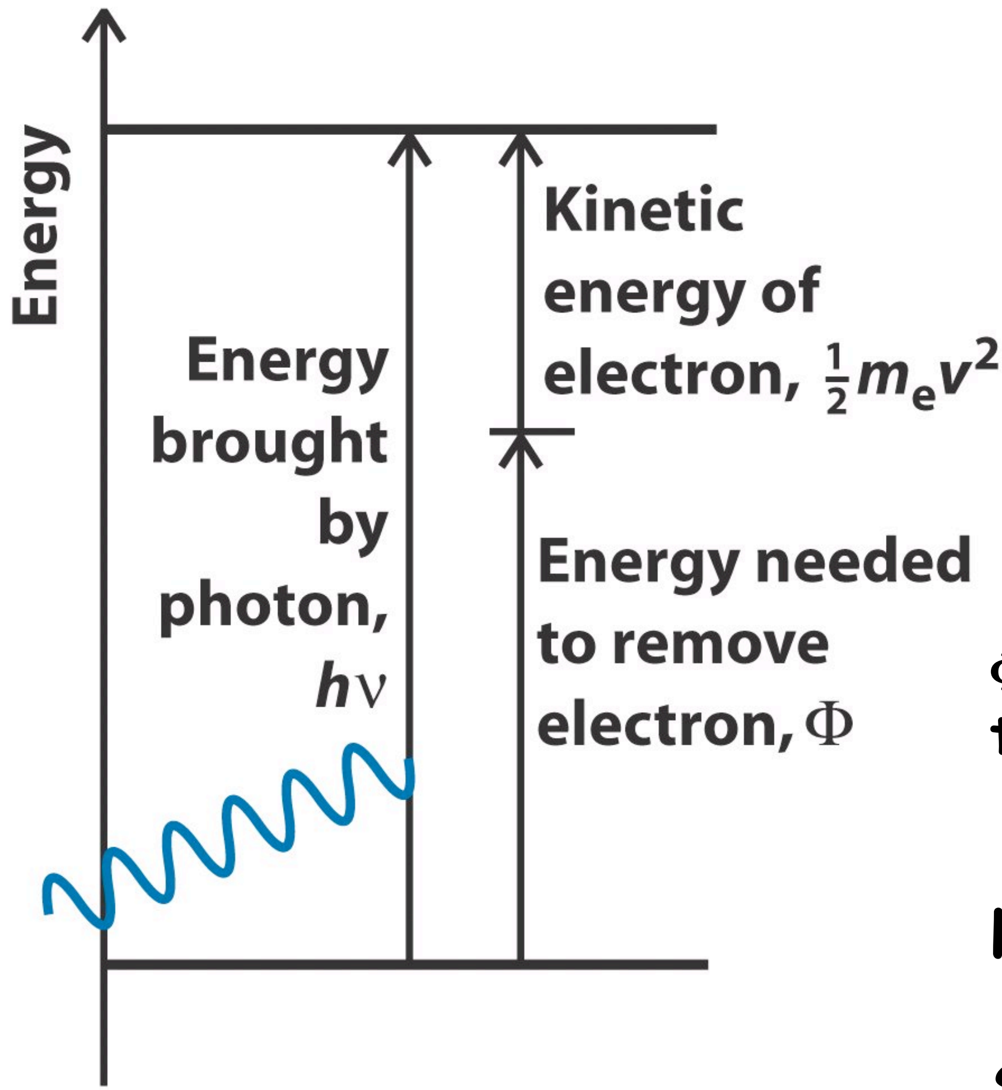
Red light is “inert” to kicking out electrons, no matter what the amplitude of the light!



Blue light kicks out Electrons even at very low amplitude!

Albert Einstein
Nobel Prize 1921
“For his explanation of the photoelectric effect”, namely, $E_2 - E_1 = h\nu$, light is quantized as photons.

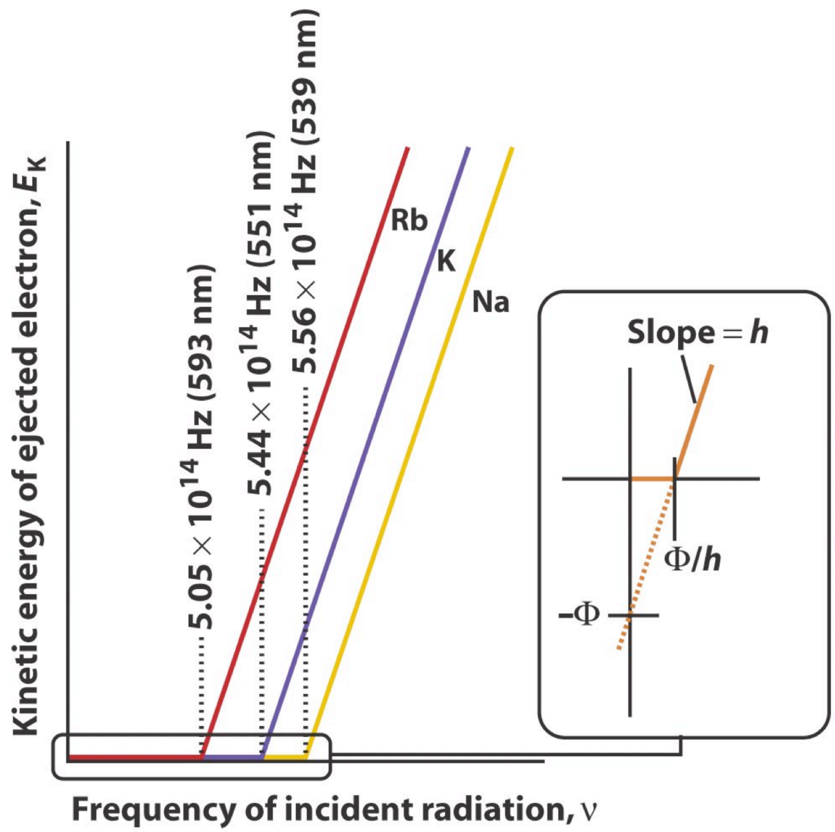
The slope of KE_{Max} vs ν is h!!!!!



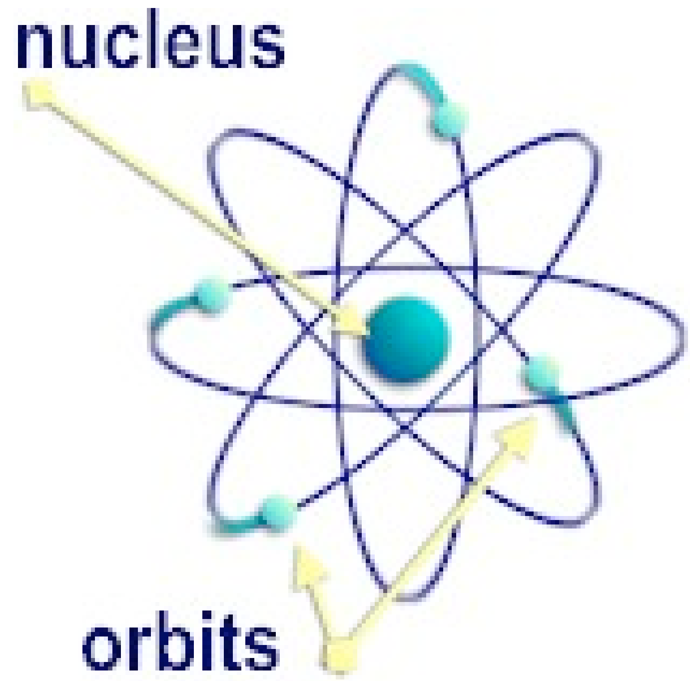
= KE_{MAX} = $h\nu - h\nu_0$
(Excess kinetic energy of the electron)

$\Phi = h\nu_0$ (work function to remove the electron from metal)

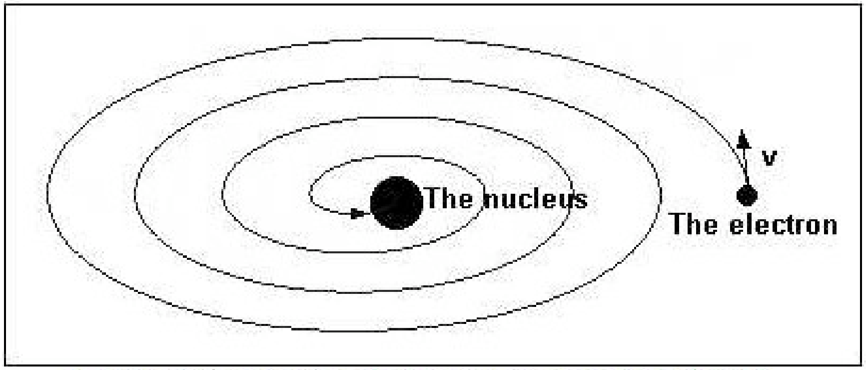
Key equation:
$KE_{MAX} = h(\nu - \nu_0)$
Slope = h!!!!



Interpreting data: Which metal takes least energy to eject an electron?



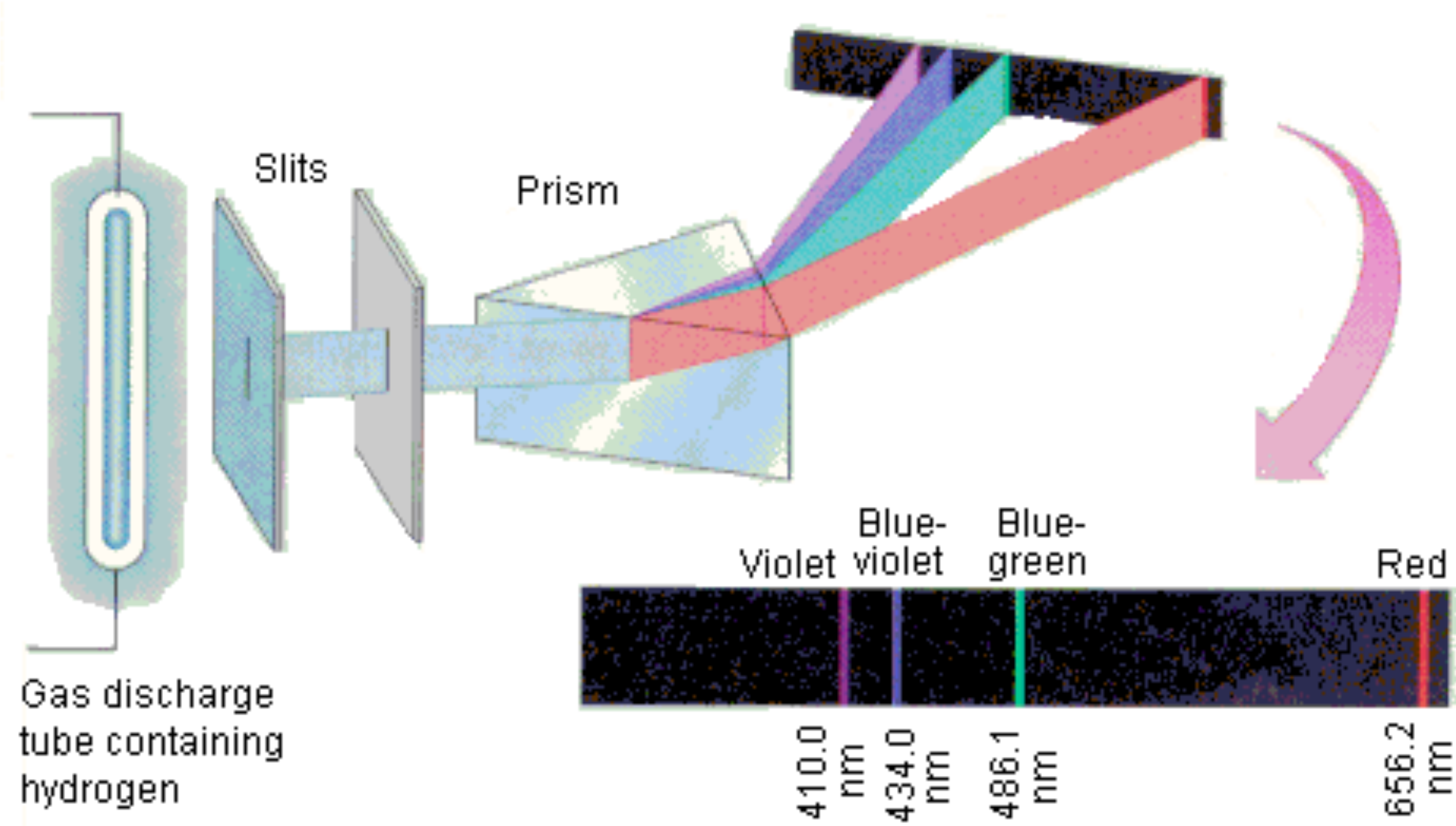
The Rutherford atom.



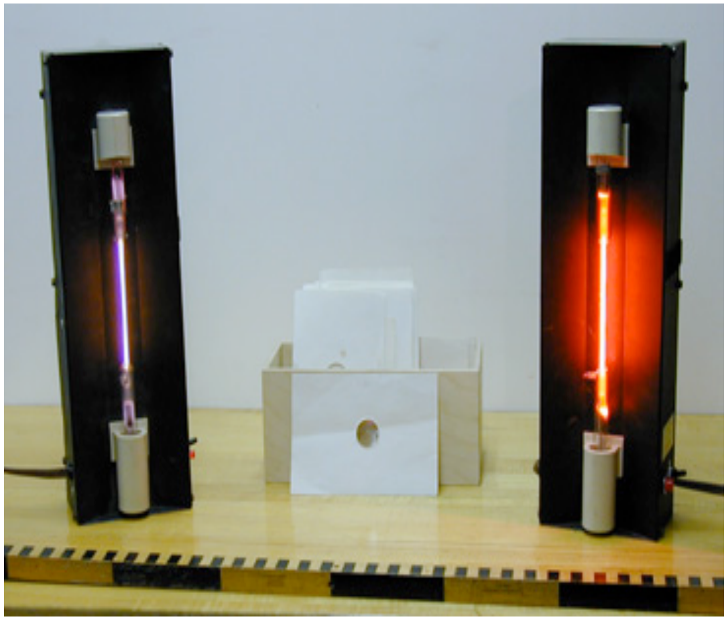
In the planetary model of atom, the electron should emit energy and spirally fall on the nucleus.

The predicted death spiral of the Rutherford atom.

Bohr solved this paradox and the paradox of the line spectra of atoms with an assumption and some algebra http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch6/bohr.html



Wavelength (λ)	Color
656.2	red
486.1	blue-green
434.0	blue-violet
410.1	violet



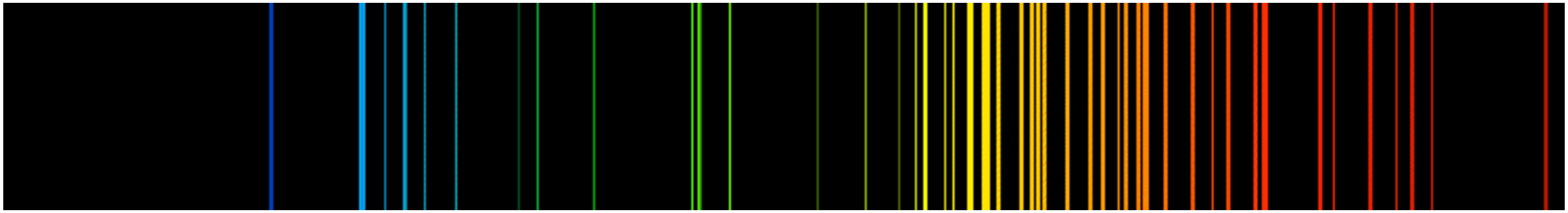
Lamp left

Lamp right

You'll see something like this on the front podium.

You'll see something like this through your diffraction glasses!

Let's do an experiment: Look at the discharge lamps through the diffraction glasses. They work just like a prism and break up light into its components. Notice the dark spots between the "lines" of the different colors. The number and positions of the lines are the unique signature of the elements. A lab experiment. Note the number and color of the lines. See if you can identify the element.



Unknown

Certain orbits have special values of angular momentum and do not radiate:

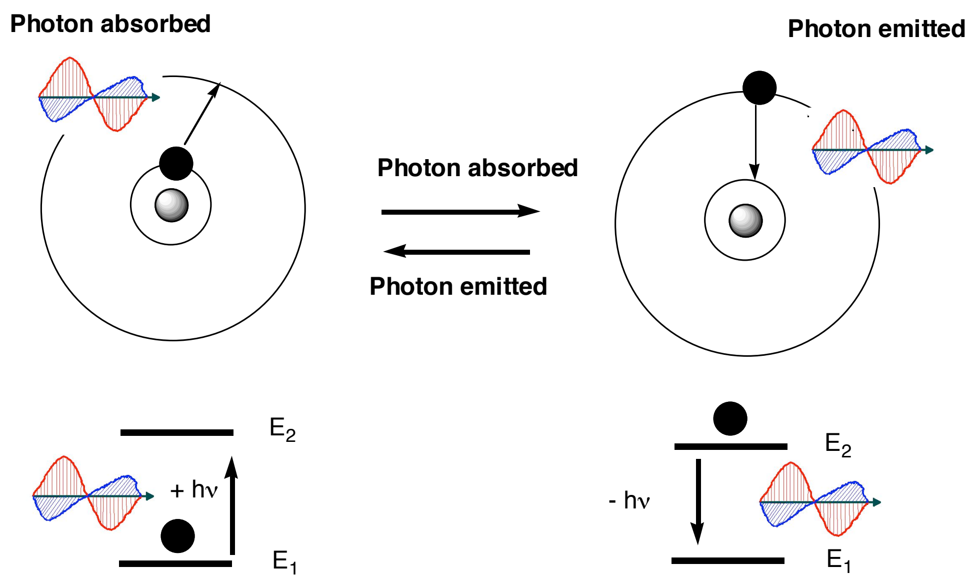
$$m_e v_e r = n(h/2\pi) \quad n = 1, 2, 3, \ldots \text{infinity}$$

(This solves the death spiral problem)

The energy and frequency of light emitted or absorbed is given by the difference between the two orbit energies, e.g., E(photon) = E_2 - E_1 (Energy difference) = hν

(This solves the line spectrum paradox)

Niels Bohr
Nobel Prize 1922
"the structure of atoms and the radiation emanating from them"



The basis of all photochemistry and spectroscopy!

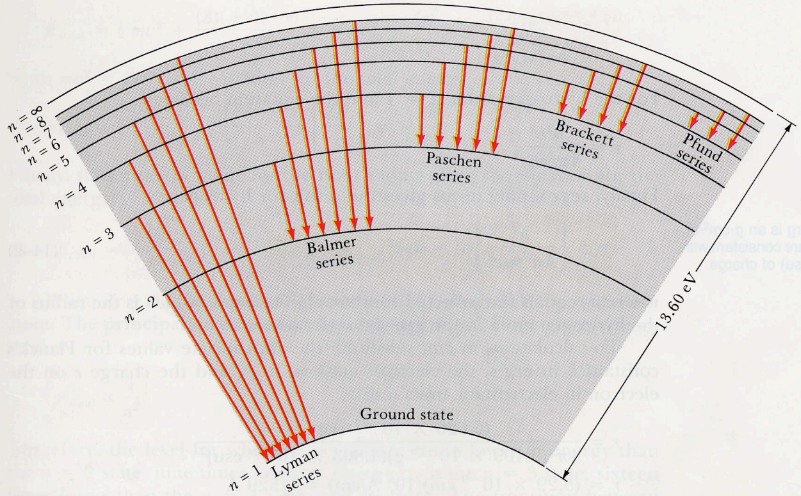


FIGURE 14–8 Energy level diagram for the hydrogen atom, with some of the predicted transitions between energy states. There are five principal sets of lines, beginning with the Lyman series in the ultraviolet and moving out to the Pfund series in the very far infrared.

the nucleus to be stable, the coulombic force (of attraction) between the nucleus (Ze^+) and electron (e^-) must be exactly the force required to cause circular motion of the orbiting electron:

coulomb force = force for circular motion

$$\frac{(Ze^+)(e^-)}{r^2} = \frac{Ze^2}{r^2} = \frac{m_e v^2}{r}$$

Solving for the radial distance r separating the electron charge and the nuclear charge:

$$r = \frac{Ze^2}{m_e v^2} \qquad (14\text{–}1)$$

Bohr quantized the angular momentum for the orbiting electron, dividing it into n integral packets of $h/2\pi$ units:

$$m_e v r = n\left(\frac{h}{2\pi}\right)$$

Solving for the velocity v of the orbiting electron:

$$v = \frac{nh}{2\pi m_e r}$$

Substituting the value for v into Eq. (14–1) for r:

$$r = \frac{Ze^2}{m_e(nh/2\pi m_e r)^2}$$

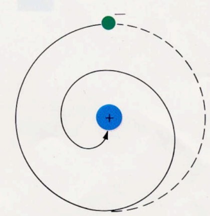


FIGURE 14–9 The hydrogen atom would presumably collapse if the circular motion of the electron about the oppositely charged nucleus was not balanced by the coulombic interaction between the two.

This simple equation is based upon Coulomb's Law, $F = q_1 q_2/r^2$, where F is in dynes or g·cm/s², r is in cm, and q is in electrostatic units (esu). Since an esu is very small, a much larger unit of charge known as the coulomb, equal to approximately 3×10^9 esu, is usually used.

But there was more, much more that Bohr did than qualitatively take care of the two remaining paradoxes. He then applies some quantitative thinking to figure out what the size of the H atom was based on his hypothesis and then to compute the energies of the jumps between orbits!

$$r = \frac{n^2h^2}{4\pi^2 m_e e^2 Z}$$

For the hydrogen atom, $Z = 1$ and the equation becomes

$$r = \frac{n^2h^2}{4\pi^2 m_e e^2}$$

Finally, regrouping terms gives the result for hydrogen:

Keep in mind that an erg is an g·cm²/s², and therefore the units are consistent with the electrostatic unit (esu) of charge.

$$r = \left[\frac{h^2}{4\pi^2 m_e e^2}\right] n^2 = a_0 n^2 \qquad (14\text{–}2)$$

where a_0 equals the collected constants $[h^2/4\pi^2 m_e e^2]$, which is the radius of the hydrogen atom in the **ground state**, where $n = 1$.

To calculate a_0 in cm, substitute the appropriate values for Planck's constant h in erg·s, the electron mass m_e in g, and the charge e on the electron in electrostatic units (esu):

$$r = \frac{(6.626 \times 10^{-27}\ \text{erg·s})^2}{4\pi^2(9.109 \times 10^{-28}\ \text{g})(4.803 \times 10^{-10}\ \text{esu})^2}$$

$$r = (5.29 \times 10^{-9}\ \text{cm})(10^8\ \text{Å/cm}) = 0.529\ \text{Å}$$

Expressing the electron charge in esu is consistent with energy units in ergs and results in units of length in cm. On the atomic scale, it has been traditional to convert units of length to angstroms (or nanometers).

EXAMPLE 14–5

Calculate the speed of an electron in the first Bohr orbit for atomic hydrogen.

Solution According to the Bohr theory, $mvr = nh/2\pi$, or

$$v = \frac{nh}{2\pi mr} = \frac{(1)(6.626 \times 10^{-27}\ \text{erg·s})}{2\pi(9.109 \times 10^{-28}\ \text{g})(5.29 \times 10^{-9}\ \text{cm})}$$

$$v = 2.19 \times 10^8\ \text{cm/s}$$ ■

EXERCISE 14–5

By what factor is the speed of an electron in the second Bohr orbit different from that in the first?

Answer: 0.500. ■

Having defined the basic unit of length on the atomic scale as the radius for the ground state hydrogen atom, Bohr turned his attention to the energy states themselves. How did this model explain the empirical Rydberg equation and the discrete lines in the emission spectrum of atomic hydrogen? The electron in its orbit has a total energy equal to the sum of the kinetic energy and the potential energy:

$$E_{\text{total}} = \text{K.E.} + \text{P.E.}$$

But the kinetic energy is $\frac{1}{2}mv^2$. The potential energy, due to the electrostatic attraction between oppositely charged nuclei and electrons, is $(Ze^+)(e^-)/r$. Therefore,

$$E_{\text{total}} = \tfrac{1}{2}mv^2 + \frac{(Z)(+e)(-e)}{r} = \tfrac{1}{2}mv^2 - \frac{Ze^2}{r}$$

Since $mv^2 = Ze^2/r$, the equation for the total energy can be rewritten:

$$E_{\text{total}} = \tfrac{1}{2}\left[\frac{Ze^2}{r}\right] - \frac{Ze^2}{r} = -\tfrac{1}{2}\left[\frac{Ze^2}{r}\right] = -\frac{Ze^2}{2r}$$

Finally, substitute the value for the Bohr radius r into the equation for the total energy:

$$E_{\text{total}} = -\frac{2\pi^2 m_e e^4 Z^2}{n^2h^2}$$

When $Z = 1$, the equation gives the total energy for the hydrogen atom. The **principal quantum number** n is an integer. For a given energy level

$$E_{\text{total}} \propto \frac{1}{n^2}$$

Therefore, the level for which $n = 1$ is four times lower in energy than the $n = 2$ state, nine times lower in energy than the $n = 3$ state, sixteen times lower than the $n = 4$ state, and so forth. The transition between states is discrete and abrupt.

The discrete nature of the emission lines in the optical spectrum for atomic hydrogen and the Rydberg relationship follow directly from the equation for E_{total}. Consider an electron in a higher energy n_2 state changing to a lower energy n_1 state:

$$E(n_2) = -\frac{2\pi^2 m_e e^4 Z^2}{n_2^{\,2}h^2}$$

$$E(n_1) = -\frac{2\pi^2 m_e e^4 Z^2}{n_1^{\,2}h^2}$$

The photon energy for the emission line is given by the Planck equation:

$$\Delta E = h\nu = E(n_1) - E(n_2)$$

$$\Delta E = -\frac{2\pi^2 m_e e^4 Z^2}{n_1^{\,2}h^2} - \left[-\frac{2\pi^2 m_e e^4 Z^2}{n_2^{\,2}h^2}\right]$$

$$\Delta E = \frac{2\pi^2 m_e e^4 Z^2}{h^2}\left[\frac{1}{n_2^{\,2}} - \frac{1}{n_1^{\,2}}\right]$$

Solving for the frequency term in the equation $\Delta E = h\nu$ and substituting for ΔE,

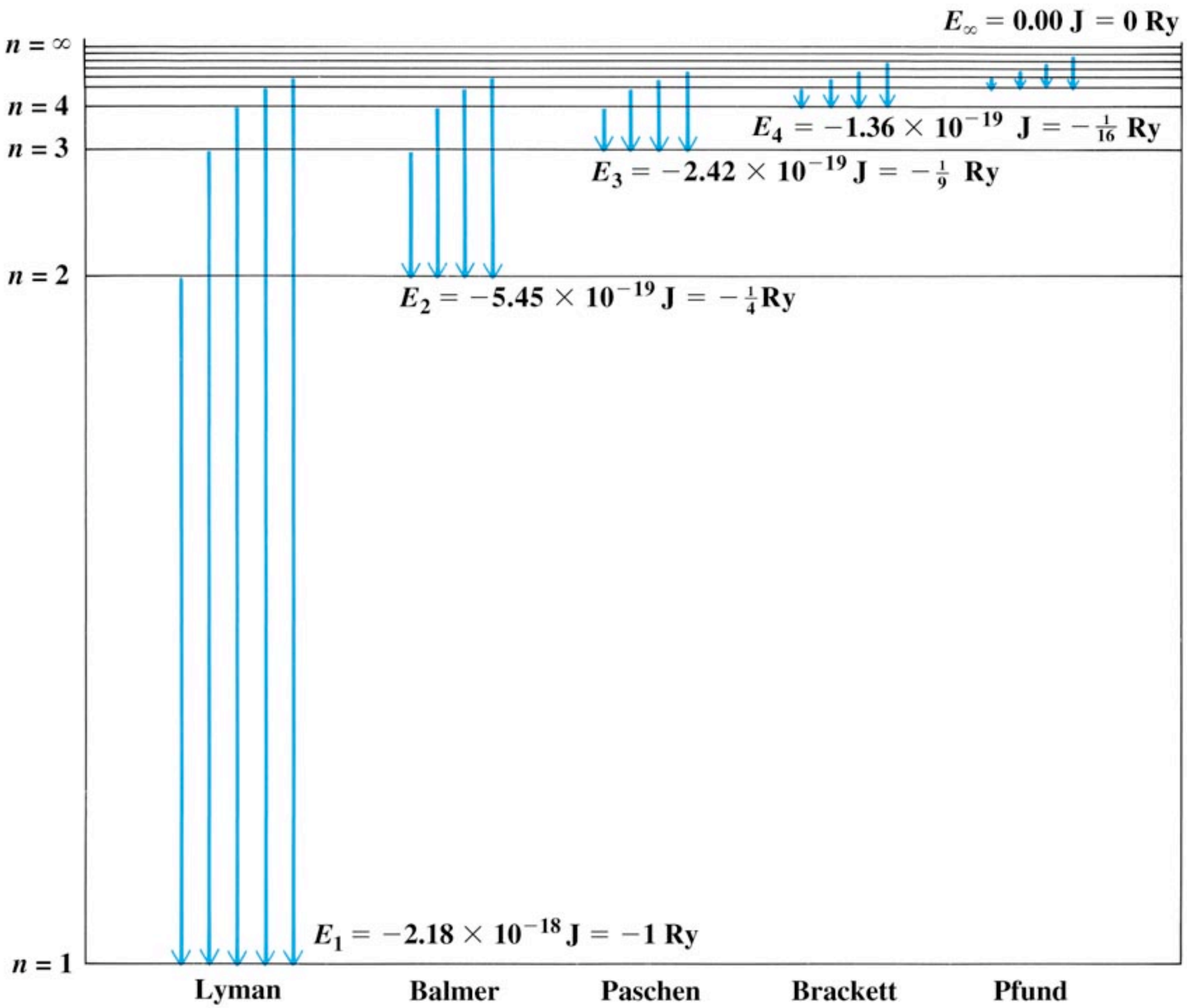
$$\nu = \frac{2\pi^2 m_e e^4 Z^2}{h^3}\left[\frac{1}{n_2^{\,2}} - \frac{1}{n_1^{\,2}}\right]$$

Since $\nu = c/\lambda$ and $Z = 1$ for H, we can rewrite the equation in its more familiar form:

$$\frac{1}{\lambda} = \frac{2\pi^2 m_e e^4}{h^3 c}\left[\frac{1}{n_2^{\,2}} - \frac{1}{n_1^{\,2}}\right] = \bar{\nu} = \frac{\nu}{c}$$

$$\nu = R_{\text{H}}\left[\frac{1}{n_2^{\,2}} - \frac{1}{n_1^{\,2}}\right] \qquad (14\text{–}3)$$

By solving the line spectrum paradox, the Bohr model allowed the computation of the energy of an electron in a one electron atom: $E_n = -Ry(Z_2/n^2)$ $Ry = 2.18 \times 10^{-18}$ J



The results of his computations compared very favorably with experimental data for one electron atoms, but failed completely for atoms with more than one electron! Something was still missing!

What was missing? The electron was being treated as a particle. If waves can mimic particles, then perhaps particles can mimic waves.

Louis de Broglie 1892-1987
Nobel Prize 1929
"for his discovery of the wave nature of electrons"

Light: $E = h\nu$ (Planck)

Mass: $E = mc^2$ (Einstein)

then

$h\nu = h(c/\lambda) = mc^2$ (de Broglie)

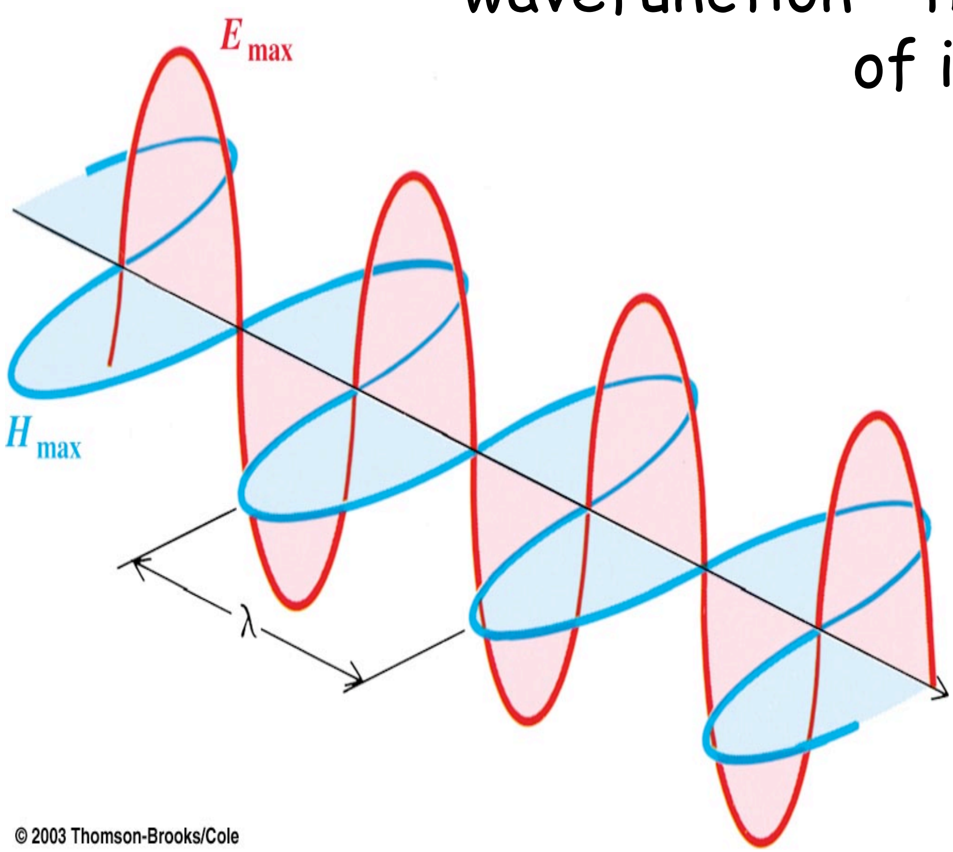
Light = Matter

$\lambda = h/mv$

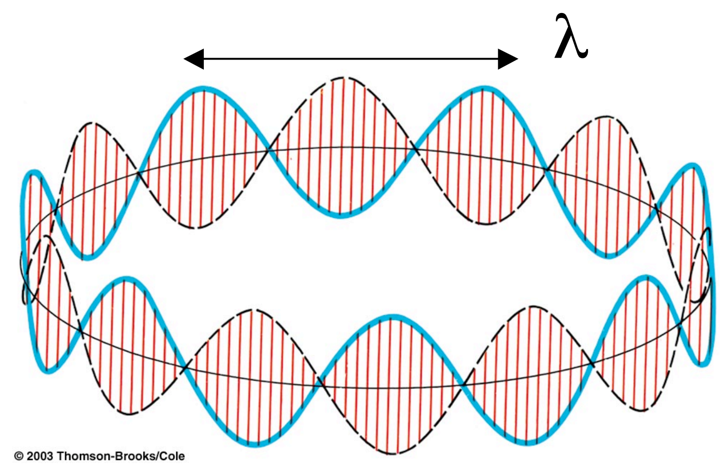
Two seemingly incompatible conceptions can each represent an aspect of the truth ... They may serve in turn to represent the facts without ever entering into direct conflict. ***de Broglie, Dialectica***

Traveling waves and standing waves

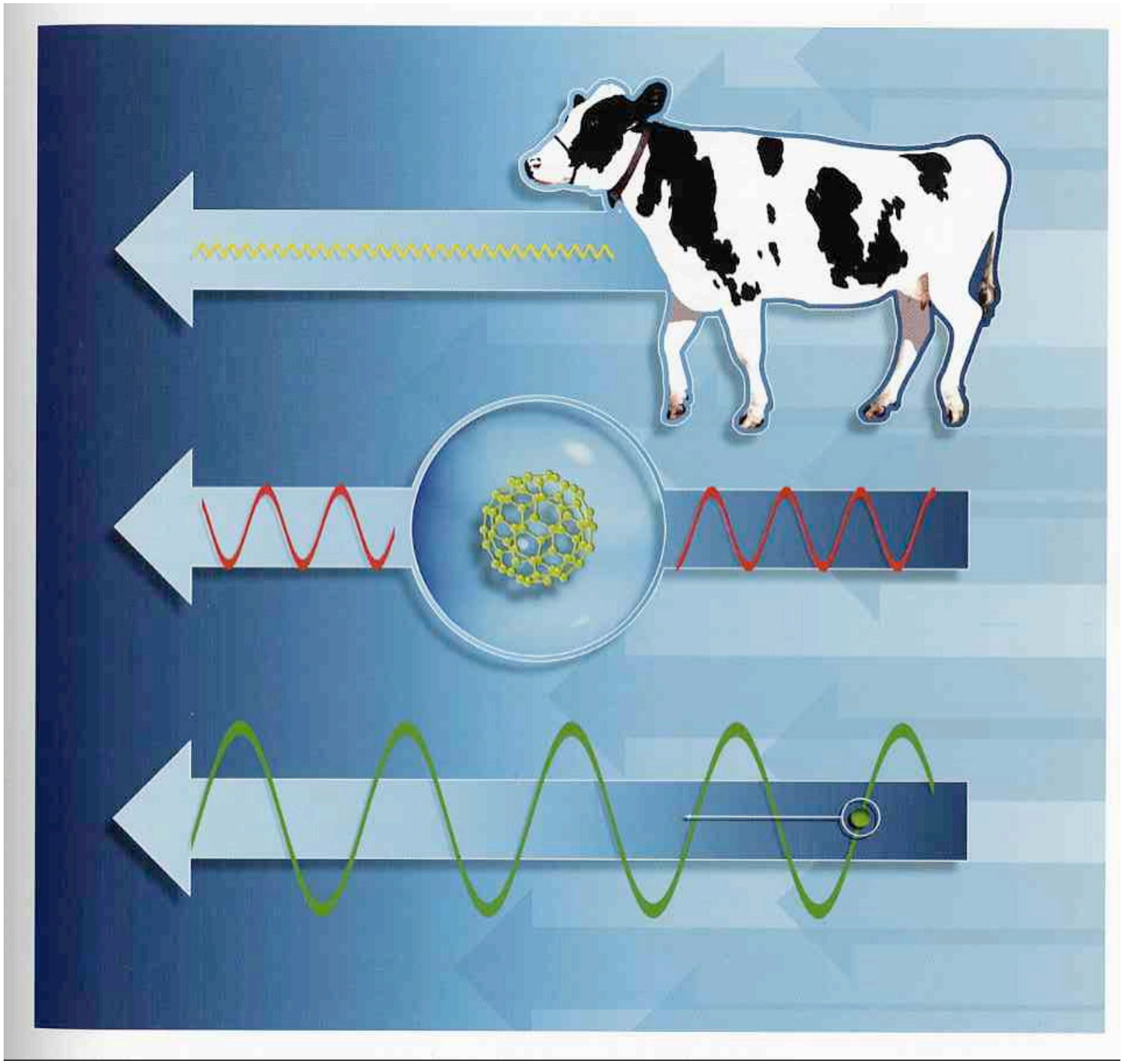
Every wave has a corresponding "wavefunction" that completely describes all of its properties.



Light as a traveling wave.
No beginning and no end



A circular standing wave
With 7 wavelengths around the circle. Localized in space (on an atom!)



Wavy cows?

$\lambda = h/mv$

The value of
h = 6.6×10^{-34} Js

Electrons show wave properties, cows do not.

The wave properties of matter are only apparent for very small masses of matter.

A computations of the wavelength of a macroscopic object (smaller than a cow): A baseball of 0.145 kg of mass, traveling at 30 $m\text{-}s^{-1}$

DeBrolie equation: $\lambda = h/mv$

$h = 6.63 \times 10^{-34}$ J-s

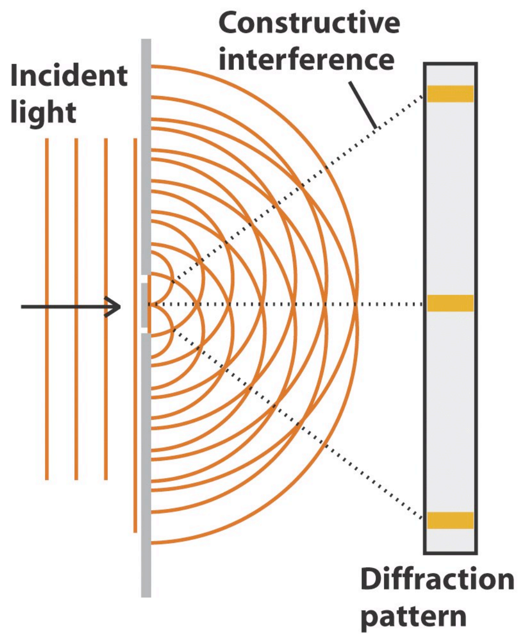
$m = 0.145$ kg, $v = 30\ m\text{-}s^{-1}$

$\lambda = h/mv = 6.63 \times 10^{-34}$ J-s/(0.145 kg, $v = 30\ m\text{-}s^{-1}$)

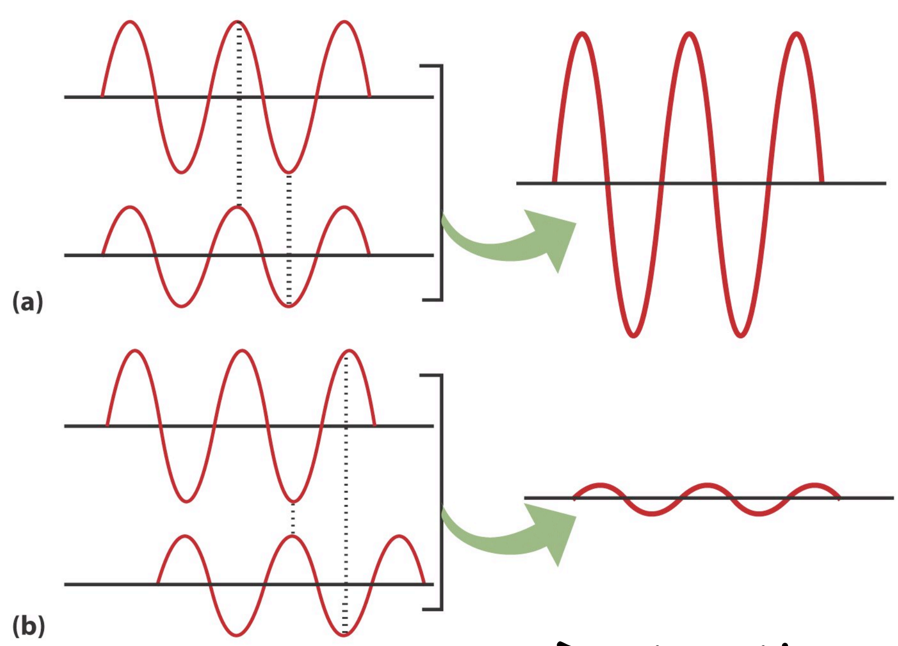
$\lambda = 1.5 \times 10^{-34}\ m = 1.5 \times 10^{-24}$ Å

This is such a small number that it cannot be measured and completely masks the wave behavior of macroscopic objects.

Wave, particles and the Schroedinger equation



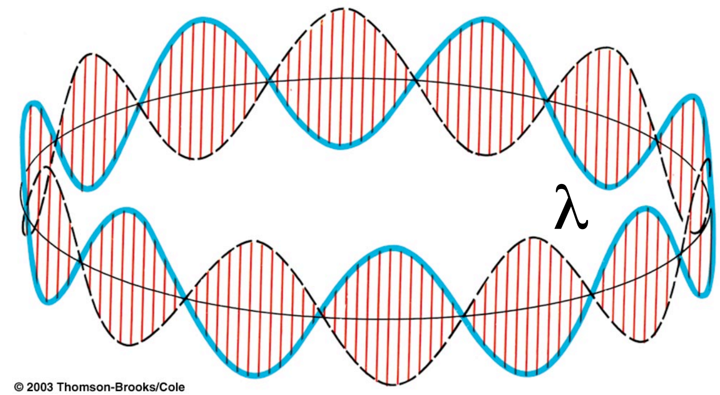
Constructive interference



Destructive interference

Diffraction patterns: Constructive and destructive interference, the signature characteristic of waves.

Schroedinger:
wave equation and
wavefunctions



The electron as a bound wave: what is its wavefunction?

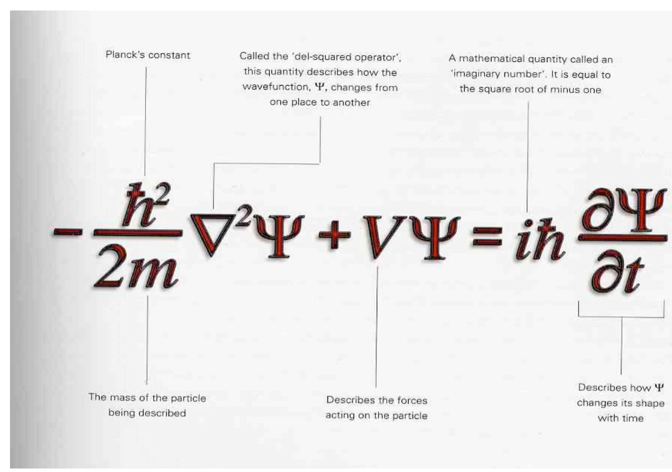


TABLE 1.2 Hydrogen Wavefunctions (Atomic Orbitals), $\psi = RY$

(a) Radial wavefunctions, $R_{nl}(r)$

n	l	$R_{nl}(r)$
1	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$
2	0	$\frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2 - \frac{Zr}{a_0}\right)e^{-Zr/2a_0}$
	1	$\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$
3	0	$\frac{1}{9\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}\left(3 - \frac{2Zr}{a_0} + \frac{2Z^2r^2}{9a_0^2}\right)e^{-Zr/3a_0}$
	1	$\frac{2}{27\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2 - \frac{Zr}{3a_0}\right)e^{-Zr/3a_0}$
	2	$\frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$

(b) Angular wavefunctions, $Y_{lm_l}(\theta,\phi)$

l	"m_l"*	$Y_{lm_l}(\theta,\phi)$
0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
1	x	$\left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\cos\phi$
	y	$\left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\sin\phi$
	z	$\left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$
2	xy	$\left(\frac{15}{16\pi}\right)^{1/2} \sin^2\theta\cos 2\phi$
	yz	$\left(\frac{15}{4\pi}\right)^{1/2} \cos\theta\sin\theta\sin\phi$
	zx	$\left(\frac{15}{4\pi}\right)^{1/2} \cos\theta\sin\theta\cos\phi$
	$x^2 - y^2$	$\left(\frac{15}{16\pi}\right)^{1/2} \sin^2\theta\sin 2\phi$
	z^2	$\left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$

Note: In each case, $a_0 = 4\pi\varepsilon_0{}^2/m_e e^2$, or close to 52.9 pm; for hydrogen itself, $Z = 1$.
*In all cases except $m_l = 0$, the orbitals are sums and differences of orbitals with specific values of m_l.

Wavefunctions and orbitals

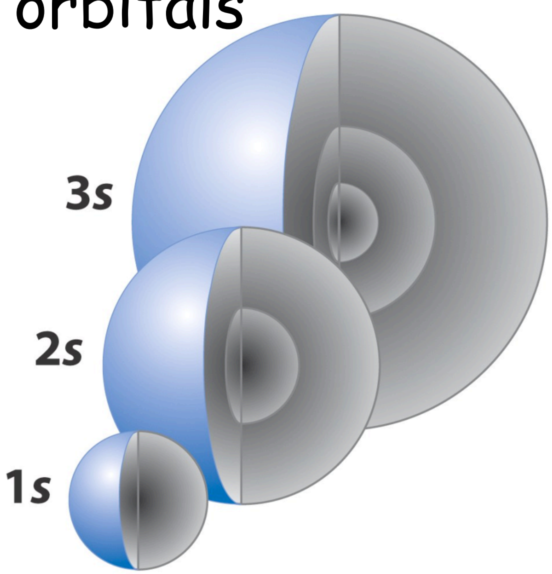
An orrbital is a wavefunction

Obital: defined by the quantum numbers n, l and m_l (which are solutions of the wave equation)

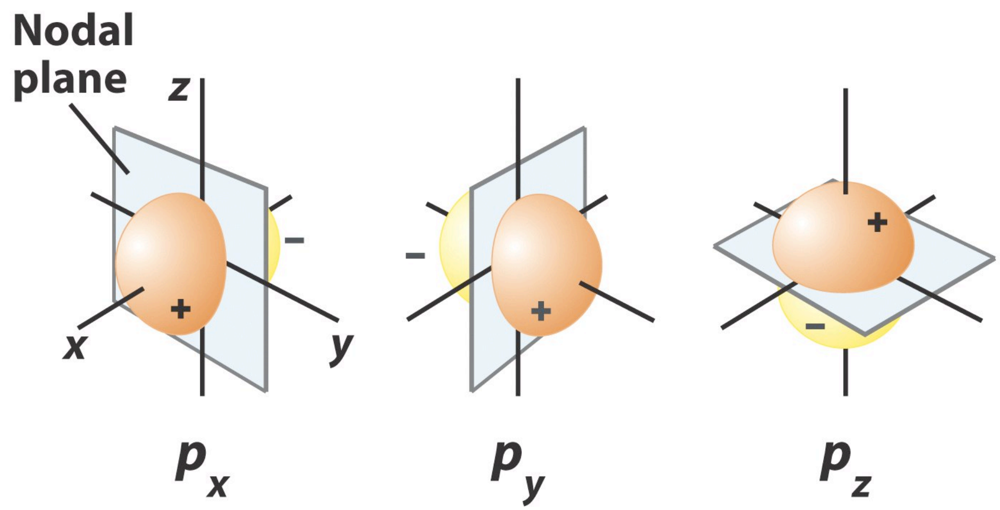
Orbital is a region of space occupied by an electron

Orbitals has energies, shapes and orientation in space

s orbitals

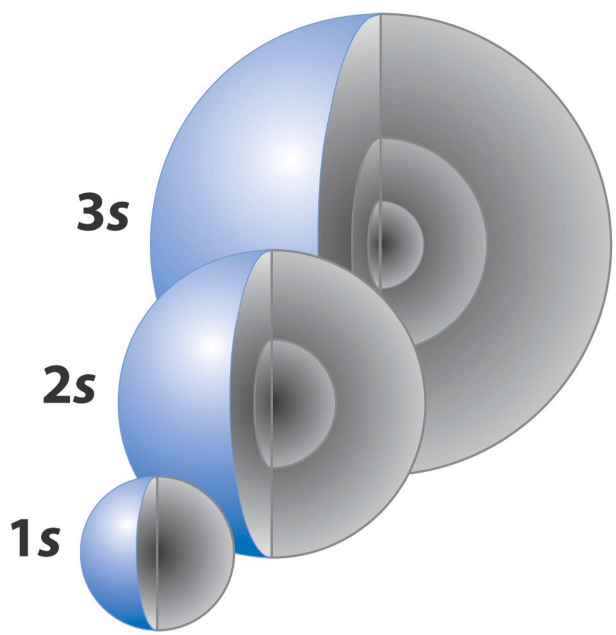


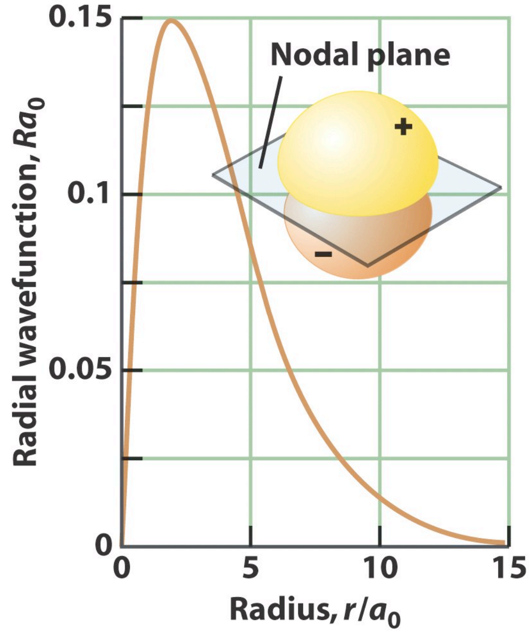
p orbitals



Sizes, Shapes, and orientations of orbitals

n determines size; *l* determines shape
m_l determines orientation





The hydrogen s orbitals (solutions to the Schroedinger equation.

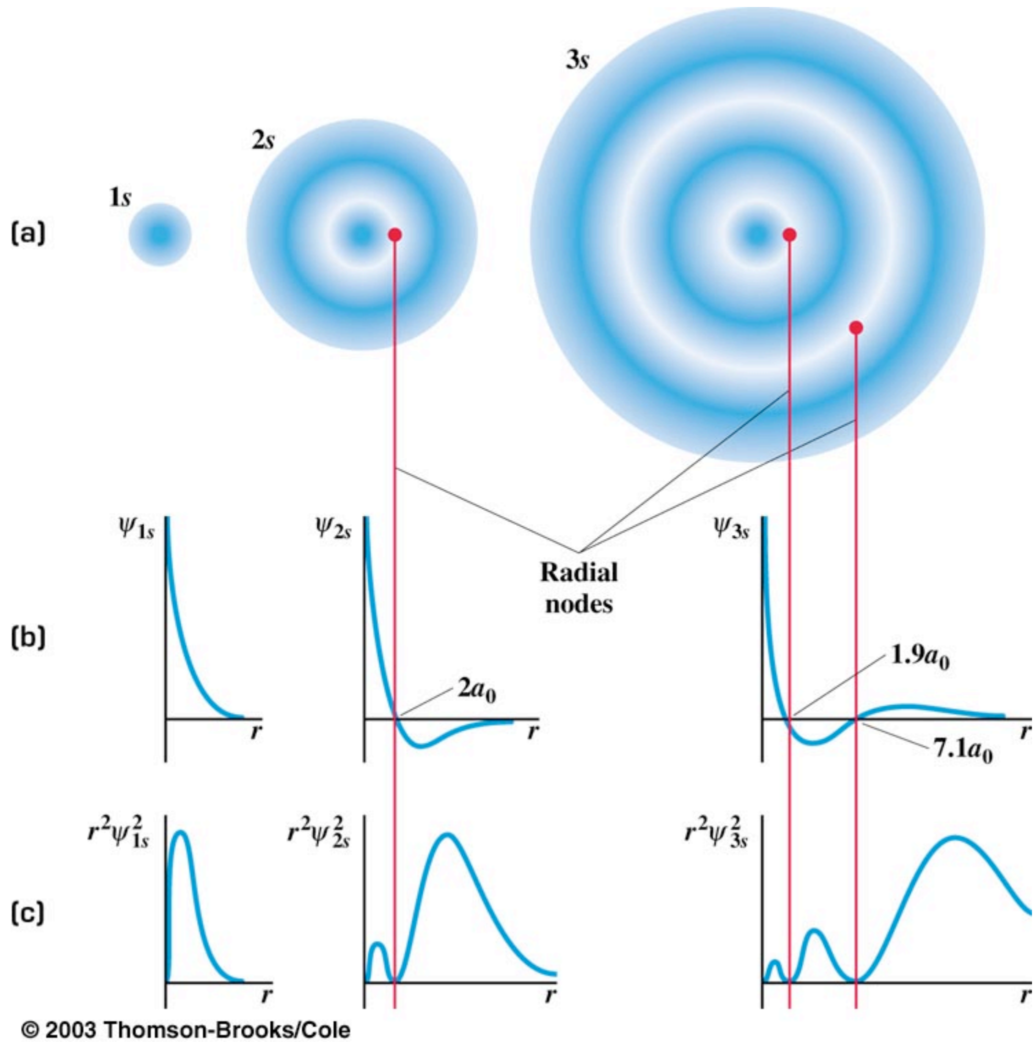
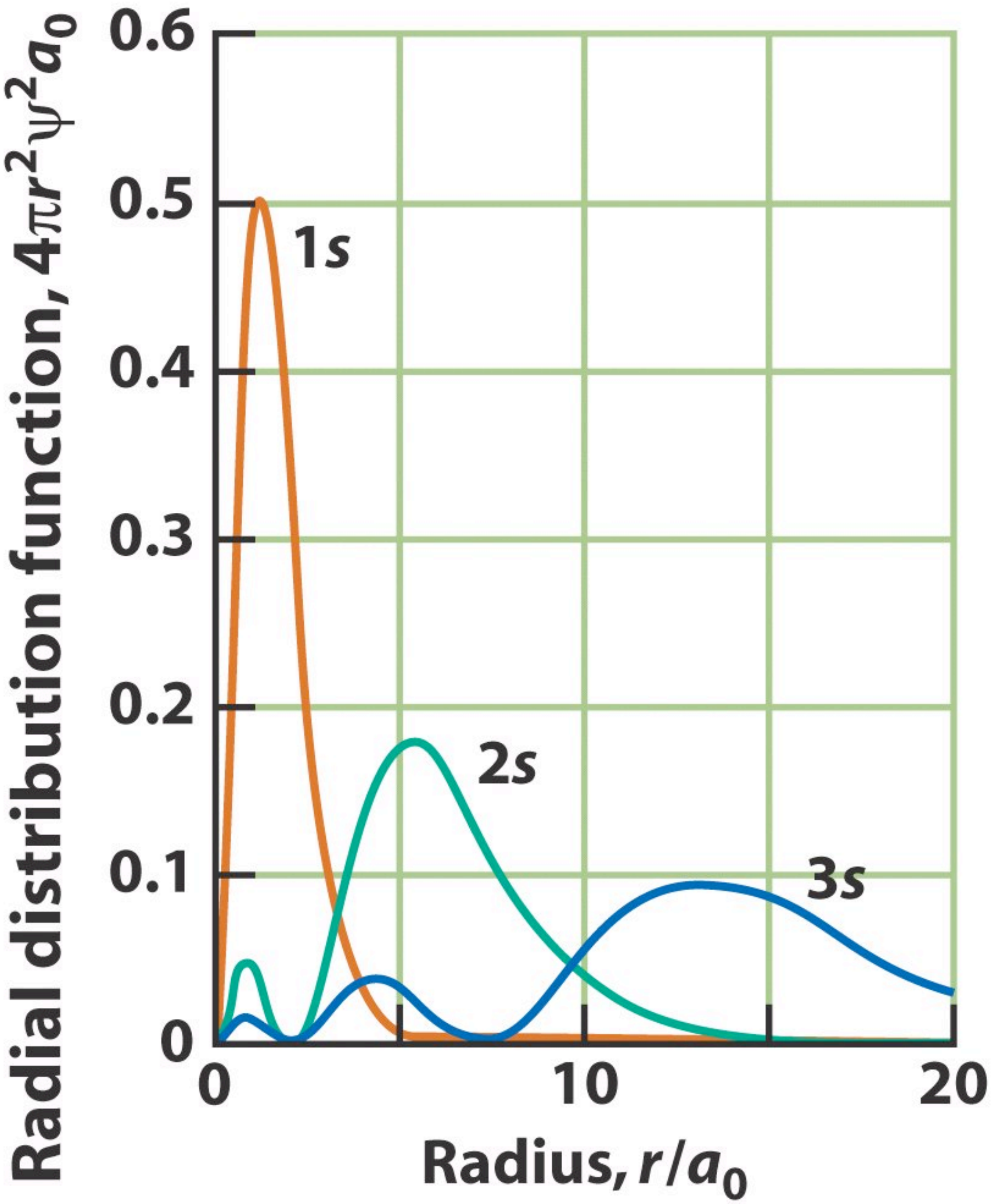


Fig 16-19



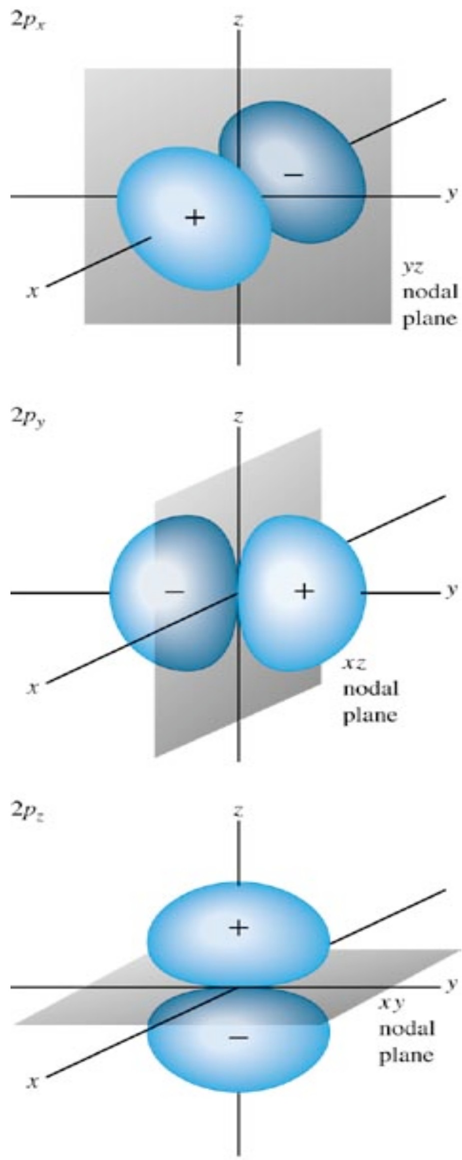
Electron probability x space occupied as a function of distance from the nucleus

The p orbitals of a one electron atom

p_x

p_y

p_z



The d orbitals of a one electron atom

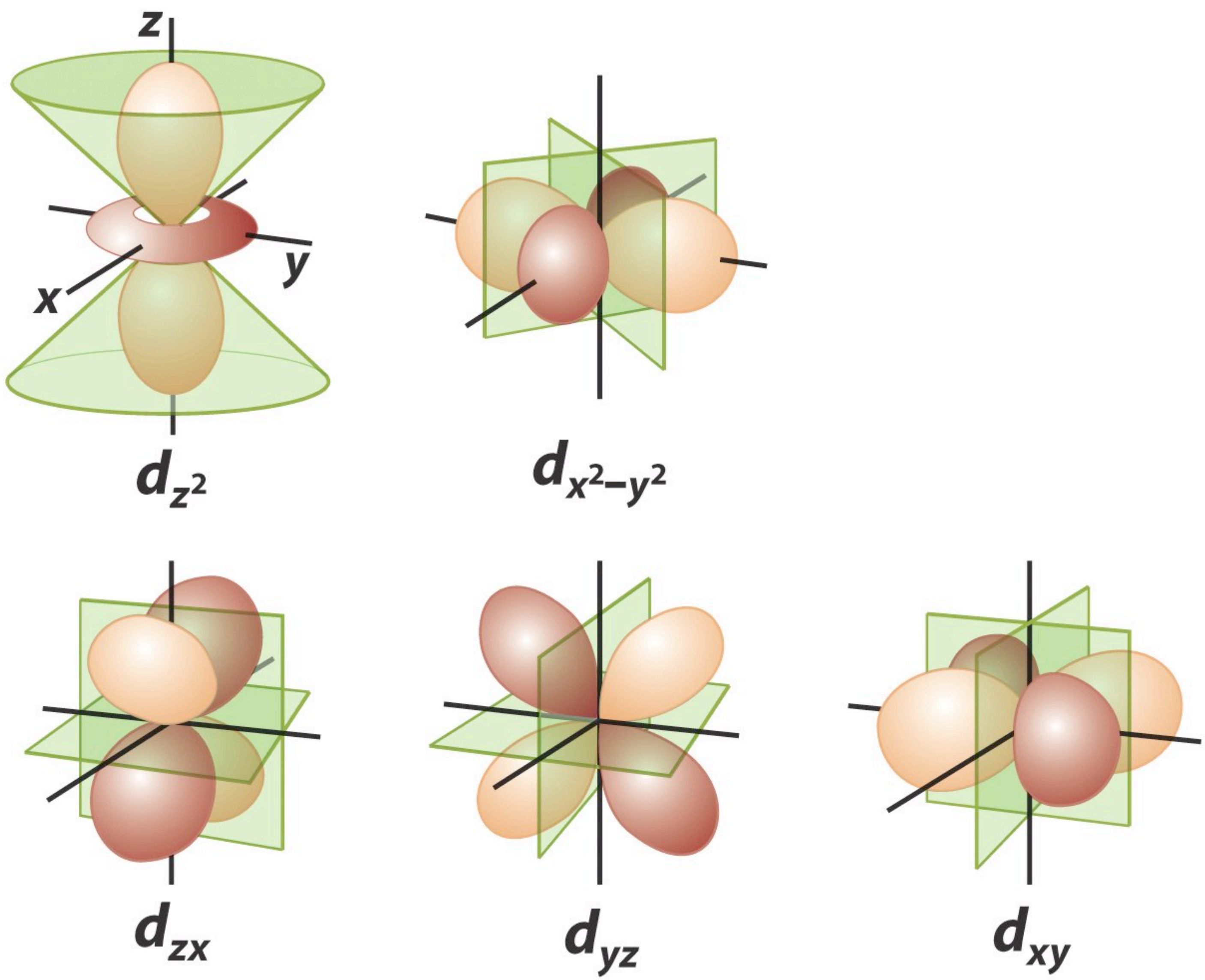
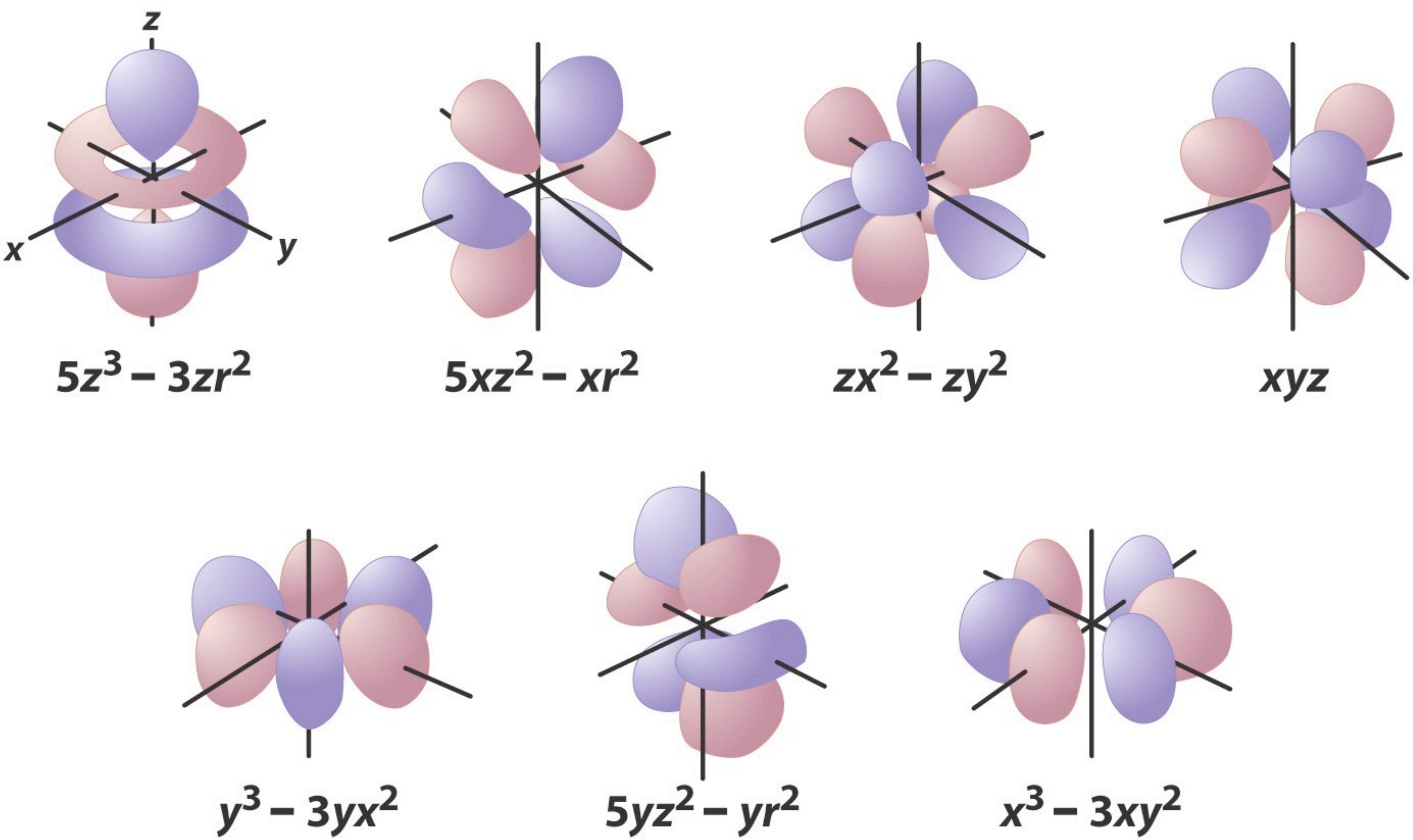


Fig 16-2

The f orbitals of a one electron atom



Quantum Numbers (QN)

Principal QN:

$n = 1, 2, 3, 4......$

Angular momentum QN:

$l = 0, 1, 2, 3.... (n-1)$

Rule: $l = (n - 1)$

Magnetic QN:

$m_l = ...-2, -1, 0, 1, 2, ..$

Rule: $-l....0....+l$

Shorthand notation for orbitals

Rule: $l = 0$, s orbital;

$l = 1$, p orbital;

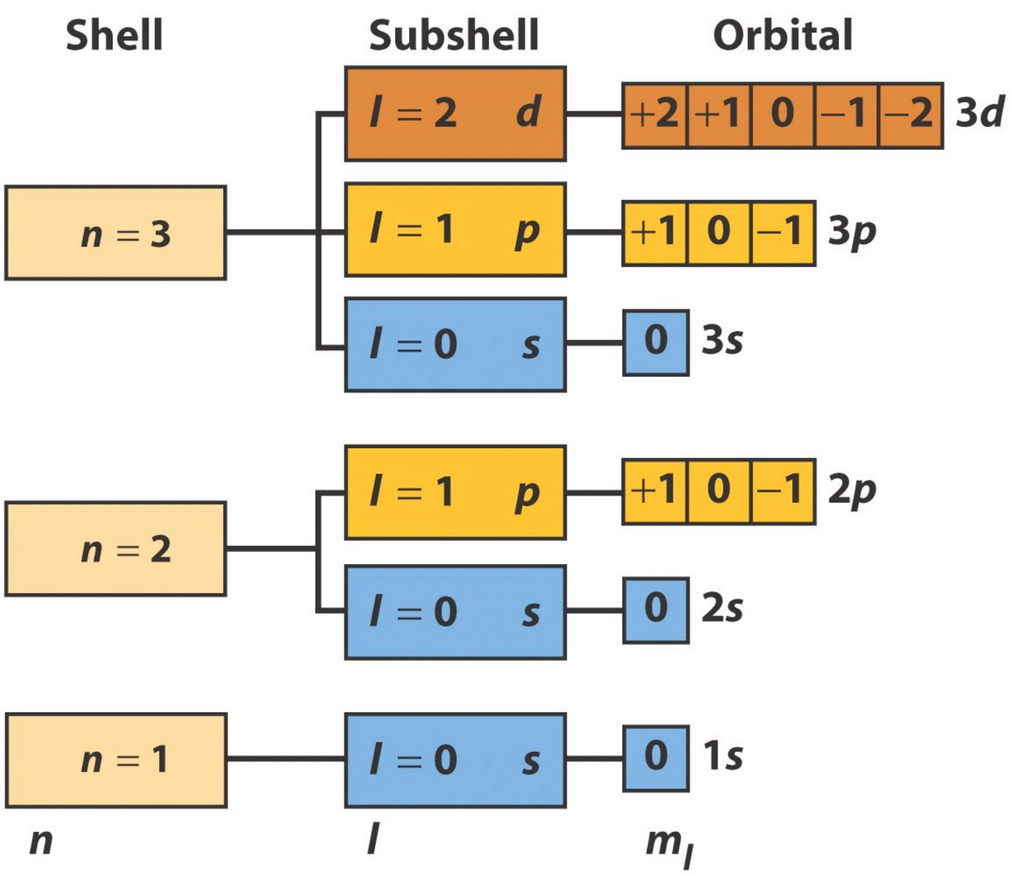
$l = 2$, d orbital

$l = 3$, f orbital

1s, 2s, 2p, 3s, 3p, 4s, 4p, 4d, etc.

The energy of an orbital of a hydrogen atom or any one electron atom only depends on the value of n

shell = all orbitals with the same value of n
subshell = all orbitals with the same value of n and *l*
an orbital is fully defined by three quantum numbers, n, *l*, and m_l



Each shell of QN = n contains n subshells

n = 1, one subshell
n= 2, two subshells, etc

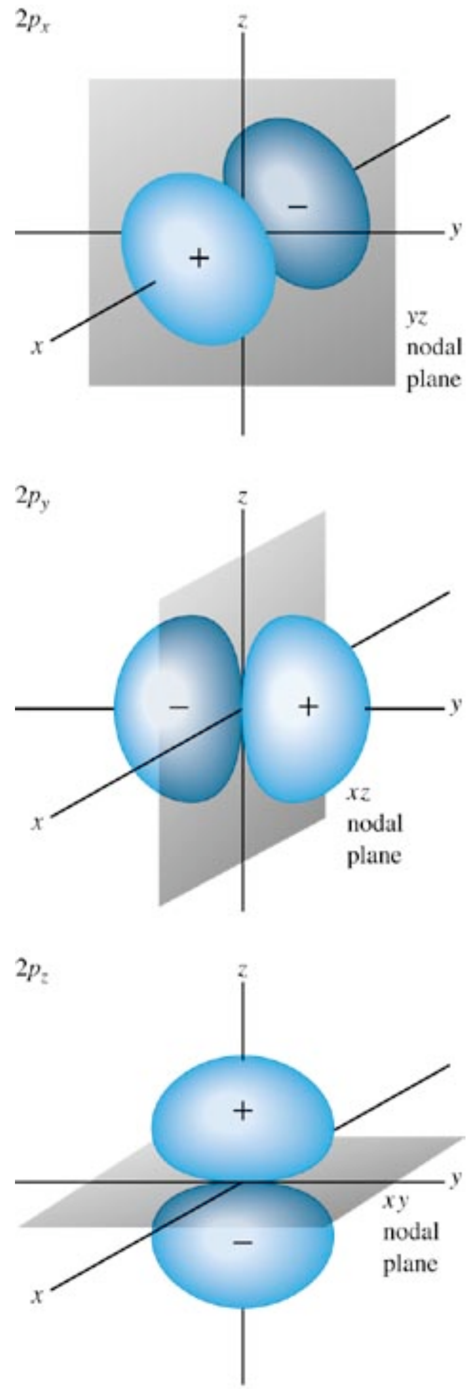
Each subshell of QN = *l*, contains 2*l* + 1 orbitals

l = 0, 2(0) + 1 = 1
l = 1, 2(1) + 1 = 3

Nodes in orbitals: 2p orbitals:
angular node that passes through the nucleus

Orbital is "dumb bell" shaped

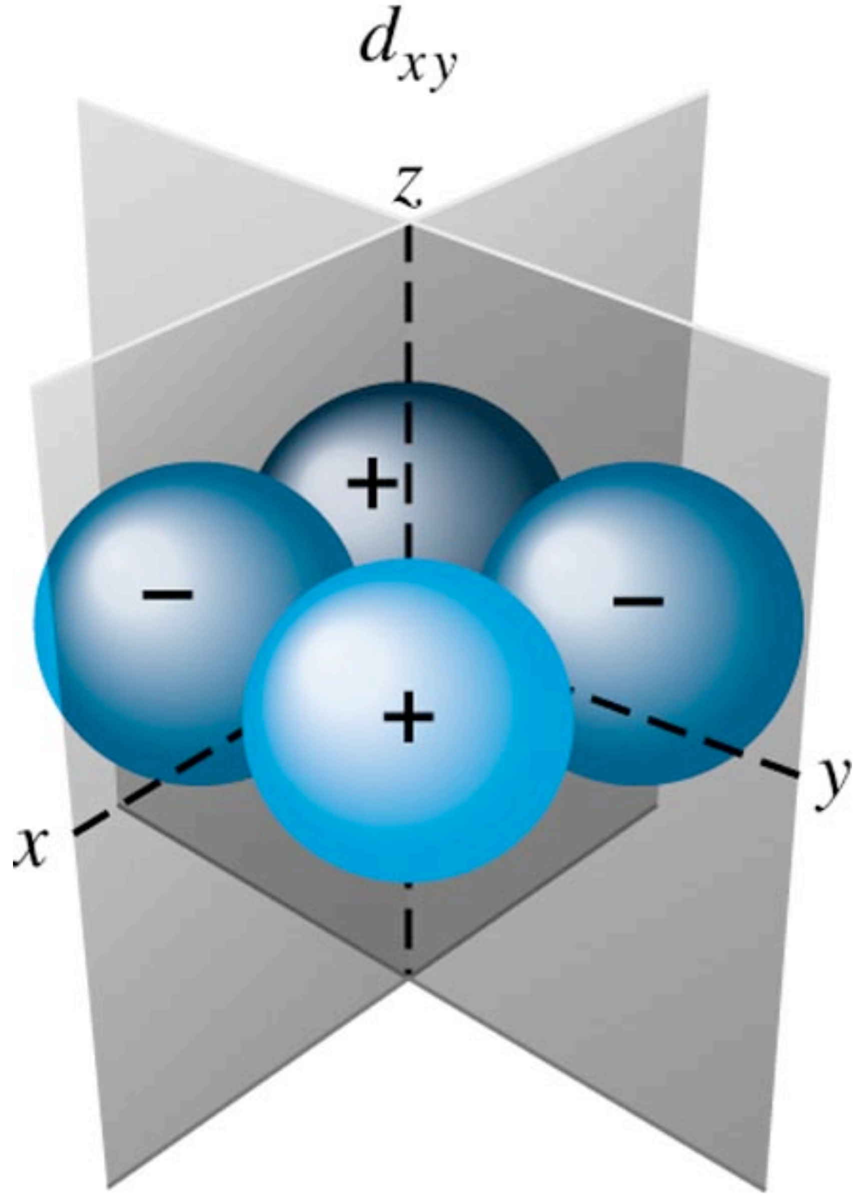
Important: the + and - that is shown for a p orbital refers to the mathematical sign of the wavefunction, not electric charge!



Nodes in orbitals: 3d orbitals:
two angular nodes that passes through the nucleus

Orbital is "four leaf clover" shaped

d orbitals are important for metals

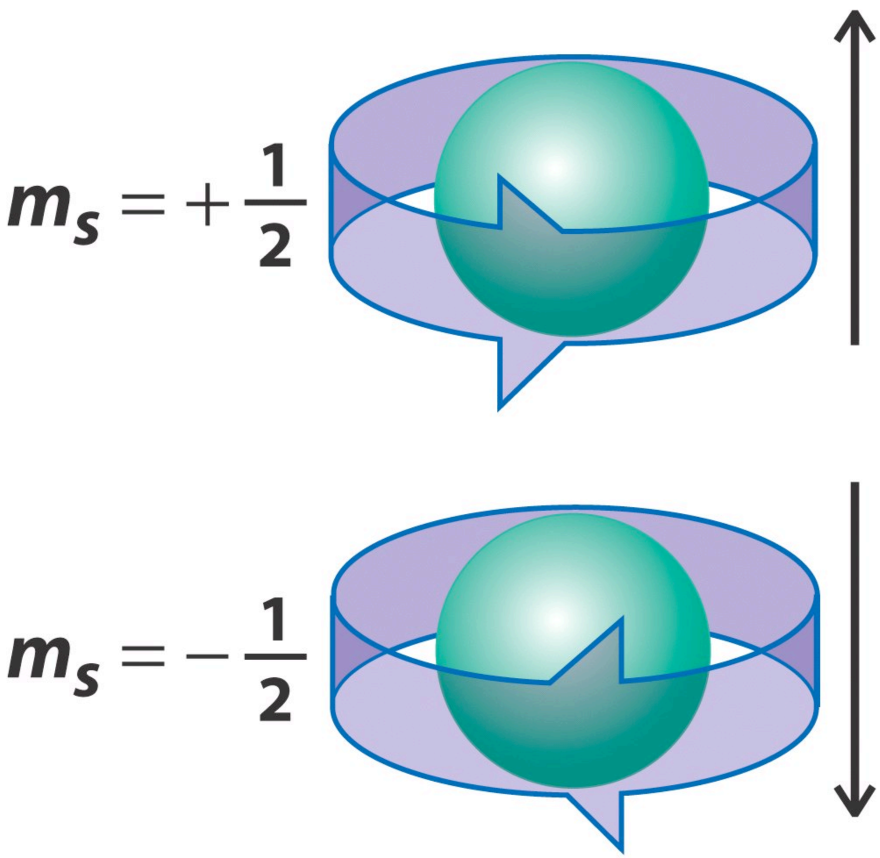


(a)

The fourth quantum number: Electron Spin

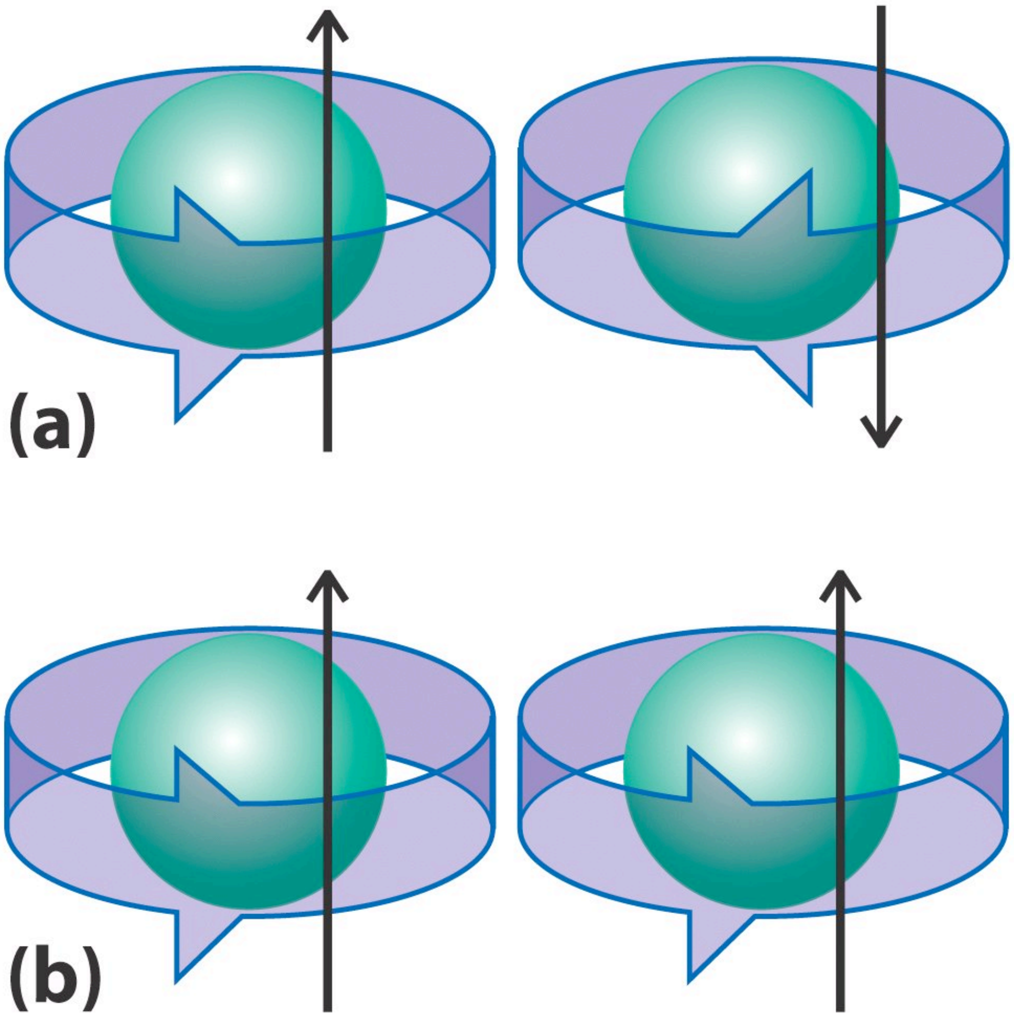
m_s = +1/2 (spin up) or -1/2 (spin down)

Spin is a fundamental property of electrons, like its charge and mass.



(spin up)

(spin down)



A singlet state

A triplet state

Electrons in an orbital must have different values of m_s

This statement demands that if there are two electrons in an orbital one must have $m_s = +1/2$ (spin up) and the other must have $m_s = -1/2$ (spin down)
This is the Pauli Exclusion Principle

An *empty orbital* is fully described by the three quantum numbers: n, l and m_l

An electron in an orbital is fully described by the four quantum numbers: n, l, m_l and m_s

Summary of quantum numbers and their interpretation

TABLE 1.3 Quantum Numbers for Electrons in Atoms

Name	Symbol	Values	Specifies	Indicates
principal	n	$1, 2, \ldots$	shell	size
orbital angular momentum*	l	$0, 1, \ldots, n-1$	subshell: $l = 0, 1, 2, 3, 4, \ldots$ $s, p, d, f, g, \ldots$	shape
magnetic	m_l	$l, l-1, \ldots, -l$	orbitals of subshell	orientation
spin magnetic	m_s	$+\frac{1}{2}, -\frac{1}{2}$	spin state	spin direction

*Also called the *azimuthal quantum number.*