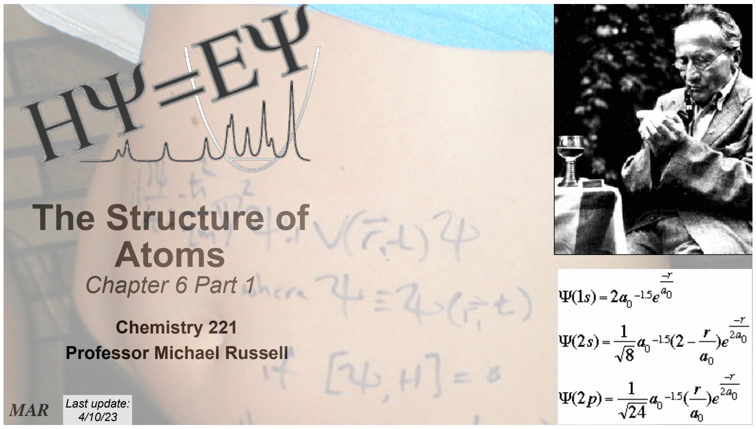
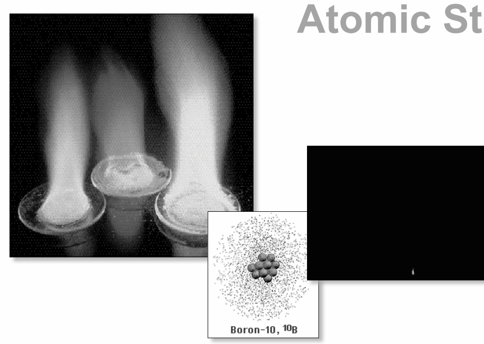


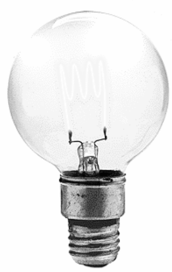
Atomic Structure



Exploring color.... on the atomic level

MAR

ELECTROMAGNETIC RADIATION



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ELECTROMAGNETIC RADIATION

EM theory developed by Maxwell

Most subatomic particles behave as PARTICLES and yet often obey the physics of waves.

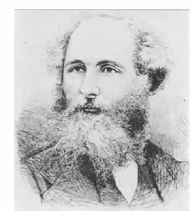
Define properties of WAVES:

Wavelength, λ

Frequency, ν

Node

Amplitude



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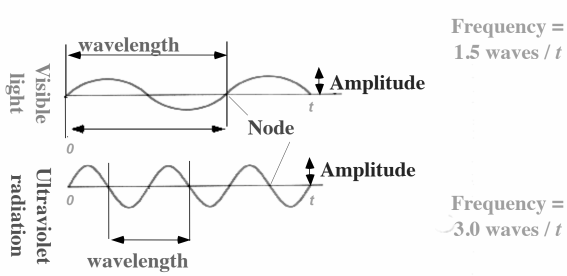
ELECTROMAGNETIC RADIATION



Note:
Wavelength ↑, frequency ↓, *and*
Wavelength ↓, frequency ↑

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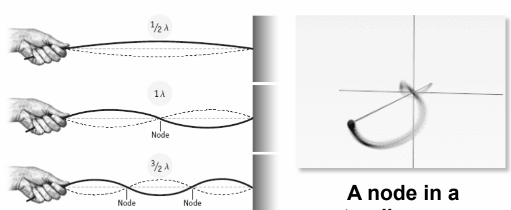
ELECTROMAGNETIC RADIATION



A node in a standing wave

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ELECTROMAGNETIC RADIATION

Waves have a frequency

Use the Greek letter "nu", ν, for frequency, and units are "cycles per sec"

All radiation: $\nu \cdot \lambda = c$

where c = velocity of light = 2.998 x 10^8 m/sec

Note: **long wavelength --> small frequency**
short wavelength --> high frequency

Memorize 2.998 x 10^8 m/sec!

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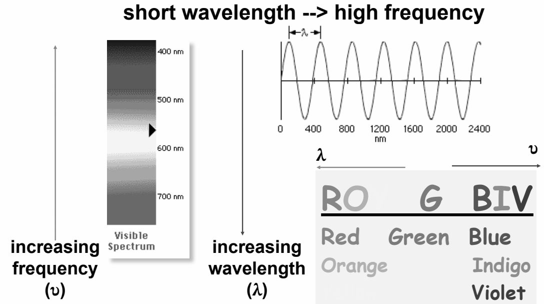
Visible Light / EM Radiation

Note: **long wavelength --> small frequency**
short wavelength --> high frequency



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ELECTROMAGNETIC RADIATION

Red light has λ = 700. nm. Calculate the frequency.

$$700.\ \text{nm} \bullet \frac{1 \times 10^{-9}\ \text{m}}{1\ \text{nm}} = 7.00 \times 10^{-7}\ \text{m}$$

Recall: $\nu = c / \lambda$

$$\text{Freq} = \frac{2.998 \times 10^{8}\ \text{m/s}}{7.00 \times 10^{-7}\ \text{m}} = 4.28 \times 10^{14}\ \text{sec}^{-1}$$

Frequency = 4.28 * 10^{14} s^{-1} *or*
4.28 * 10^{14} Hz

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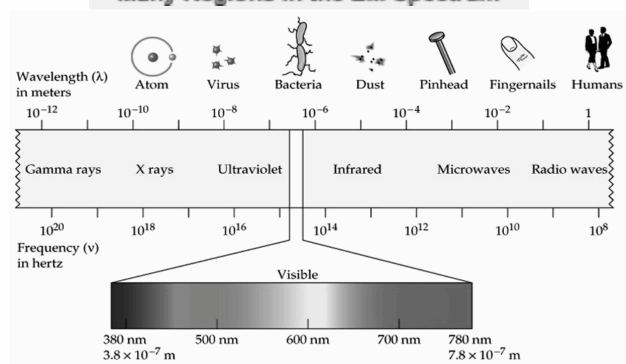
Many Regions in the EM Spectrum



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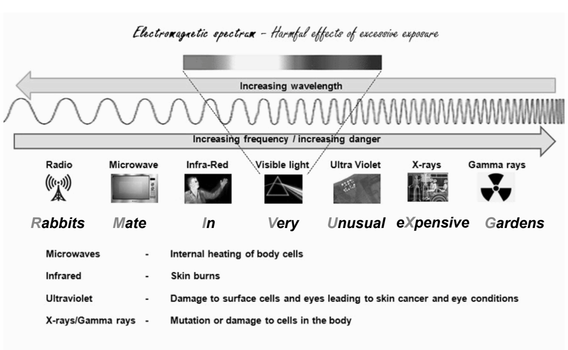

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Lord Kelvin's 1900 "Clouds" Speech

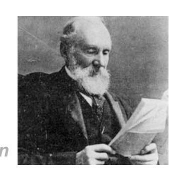
In **1900**, **Lord Kelvin** stated that current thermodynamic understanding explained all energy phenomenon except for two not yet understood "clouds":

- **the failure of the Michelson-Morley experiment** *(which led to special relativity)*

- **the inability to understand black body radiation** *(which led to quantum theory)*

"Pride goeth before a fall"

Great scientists make mistakes as well



Lord Kelvin

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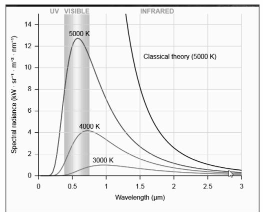
Ultraviolet Catastrophe

At high temperatures, solids emit **red**, **blue**, even white light when heated. Energy of light emitted relative to temperature.

At very high temperature, intensity of light reaches maximum in ultraviolet region, then decreases.

Classical physics predicted no maximum intensity - *catastrophe!*



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Quantization of Energy

Max Planck proposed that an object can gain or lose energy by absorbing or emitting radiant energy in QUANTA

Proposed that the energy of radiation proportional to the frequency:

$$E = h \bullet v$$

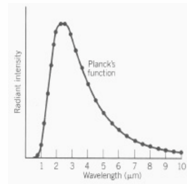

FIGURE 3.13 Planck's function fits the observed data perfectly.

where h = Planck's constant = 6.626×10^{-34} J•s ***memorize***

MAR

Quantization of Energy

$$E = h \bullet v = hc / \lambda$$

Light with large λ (small ν) has a small E.

Light with a short λ (large ν) has a large E.

$h = 6.626 \times 10^{-34}$ J•s

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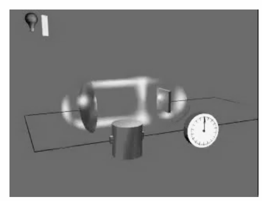
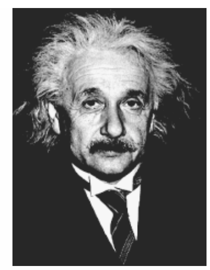
Photoelectric Effect

Light applied to metal; electrons emitted as long as threshold frequency maintained.

Elimination of light halts the process





Albert Einstein (1879-1955) explained phenomenon Received Nobel Prize

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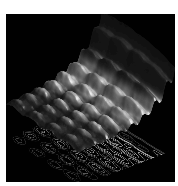
Photoelectric Effect

Photoelectric effect experiment shows *particle* nature of light.

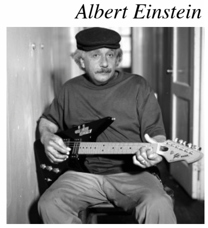
Classical physics said E of ejected e^- should *increase* as light intensity increases - not observed!

No e^- observed until light of a minimum E (or ν) is used.

Light said to display "wave-particle duality" - it behaves like a wave in some experiments *(diffraction, interference)* but as a particle in others *(photoelectric effect)!!!*



Albert Einstein



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Photoelectric Effect

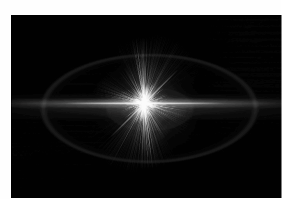
Experimental observations understood if light consists of particles called PHOTONS with discrete energy.

PROBLEM: **Calculate the energy of 1.00 mol of photons of red light (λ = 700. nm)**

From earlier:

λ = 700. nm

$\nu = 4.28 \times 10^{14}$ sec^{-1}



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Energy of Radiation

PROBLEM: Calculate the energy of 1.00 mol of photons of red light.

λ = 700. nm

$\nu = 4.28 \times 10^{14}\ \text{sec}^{-1}$

$E = h \bullet \nu$

$= (6.626 \times 10^{-34}\ \text{J}\bullet\text{s})(4.28 \times 10^{14}\ \text{sec}^{-1})$

$= 2.84 \times 10^{-19}$ J per *photon*

MAR

Energy of Radiation

Energy of 1.00 mol of photons of red light.

$E = h \bullet \nu$

$= (6.626 \times 10^{-34}\ \text{J}\bullet\text{s})(4.28 \times 10^{14}\ \text{sec}^{-1})$

$= 2.84 \times 10^{-19}$ J per photon

E per mol =

$(2.84 \times 10^{-19}\ \text{J/ph})(6.022 \times 10^{23}\ \text{ph/mol})$

= 171,000 J/mol * (kJ / 1000 J)

= 171 kJ/mol

This is within the range of energies that can break bonds.

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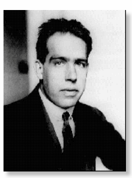
Atomic Line Spectra and Niels Bohr



Niels Bohr

(1885-1962)

Bohr's greatest contribution to science was in building a simple model of the atom. His model was based on an understanding of the SHARP LINE SPECTRA of excited atoms.

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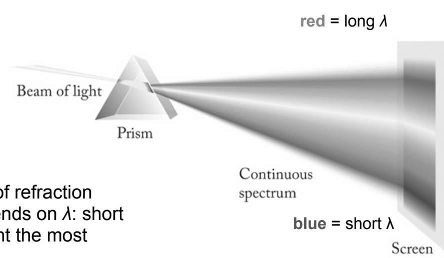
Refractive Spectrum of White Light



Angle of refraction depends on λ: short λ bent the most

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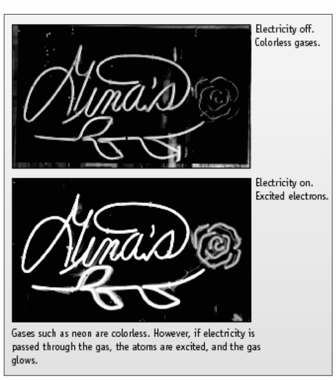
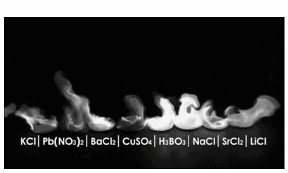


Excited Gases & Atomic Structure



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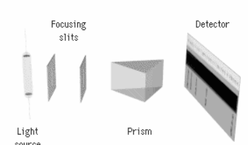
Line Spectra of Excited Atoms

Excited atoms emit light of only certain wavelengths

The wavelengths of emitted light depend on the element.



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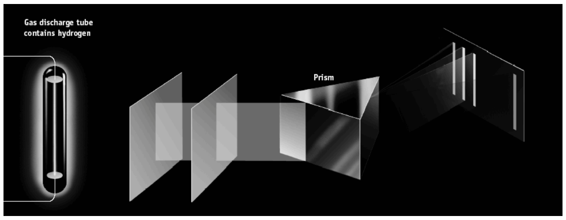
Spectrum of Excited Hydrogen Gas



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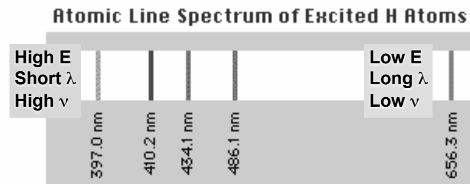
Line Emission Spectra of Excited Atoms



Visible lines in H atom spectrum are called the BALMER series.

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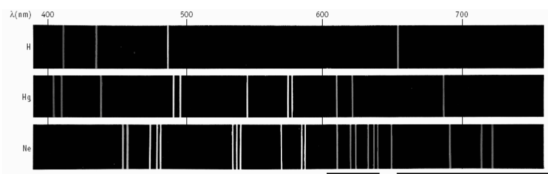
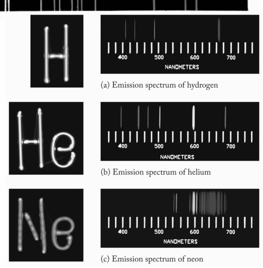


Line Spectra of Other Elements



(a) Emission spectrum of hydrogen

(b) Emission spectrum of helium

(c) Emission spectrum of neon

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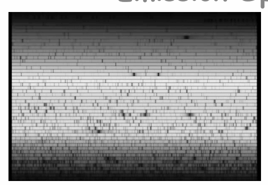
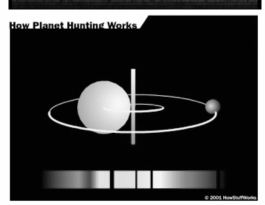
Emission Spectra in Astronomy





Composition of stars and stellar objects determined through emission spectrographs

Astronomers must account for red and blue shifts (the "Doppler effect") of moving objects in emission spectra

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The Electric Pickle

Excited atoms can emit light.

Here the solution in a pickle is excited electrically. The Na^+ ions in the pickle juice give off light characteristic of that element.

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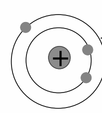
Atomic Spectra and Bohr

One view of atomic structure in early 20th century was that an electron (e-) traveled about the nucleus in an orbit.



Electron orbit

1. **Any orbit should be possible and so is any energy.**
2. **But a charged particle moving in an electric field should emit energy.**

End result should be destruction - according to classical physics!

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Atomic Spectra and Bohr

Bohr said classical view is wrong.

Need a new theory - now called QUANTUM or WAVE MECHANICS.

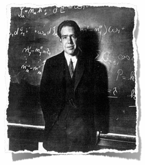
e- can only exist in certain discrete orbits - called stationary states.

e- is restricted to QUANTIZED energy states.

Energy of state = - Rhc/n^2

n = quantum no. = 1, 2, 3, 4, ….

(R = Rydberg constant, $1.097*10^7$ m^{-1})



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Atomic Spectra and Bohr

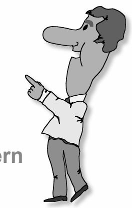
Energy of quantized state = - Rhc/n^2

n = quantum no. = 1, 2, 3, 4, ….

R = Rydberg constant = $1.097*10^7$ m^{-1}

h = Planck's constant = $6.626*10^{-34}$ J s

c = speed of light = $2.998*10^8$ m s^{-1}



But note - same eqns. come from modern wave mechanics approach.

Results can be used to explain atomic spectra.

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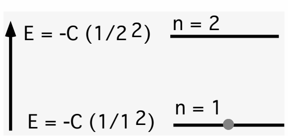
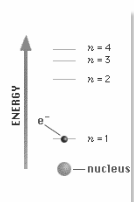
Atomic Spectra and Bohr

If e-'s are in quantized energy states, then ΔE of states can have only certain values. This explain sharp line spectra.



Note that C = Rhc



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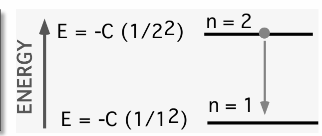
Energy of quantized state = - Rhc/n^2

Atomic Spectra and Bohr



Calculate ΔE for 1 mol of e- "falling" from high energy level (n = 2) to low energy level (n = 1). ***(L = Avogadro's number)***

$\Delta E = E_{final} - E_{initial} = -RhcL[(1/n_f^2) - (1/n_i^2)]$

$= -RhcL[(1/1^2) - (1/2^2)] = -RhcL[(1) - (1/4)]$

ΔE = -(3/4)RhcL = - 984 kJ/mol

Note that the process is exothermic!

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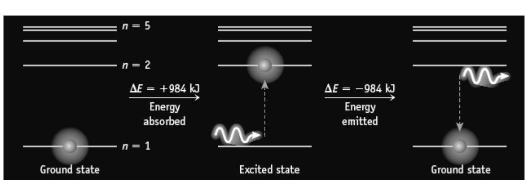
R = 1.097 x 10^7 m^{-1}



ΔE = -(3/4)Rhc = -984 kJ/mol

What is the ν and λ of the emitted light photon?

$\nu = -984*10^3$ J/mol / (h * $6.022*10^{23}$ mol^{-1})

$\nu = 2.47*10^{15}$ s^{-1} *(always positive!)*

and λ = c/ν = 122 nm

This is exactly in agreement with experiment!

Remember: absorption = endothermic, emission = exothermic

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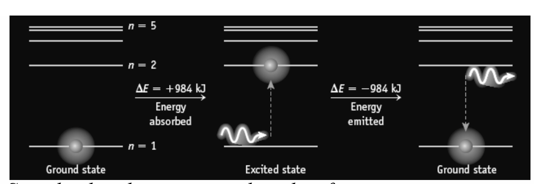
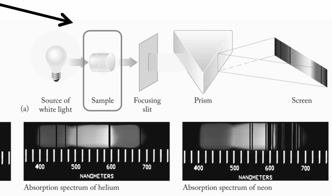


Sample absorbs some wavelengths of light, causing dark lines in the continuous spectra

Absorption Spectra



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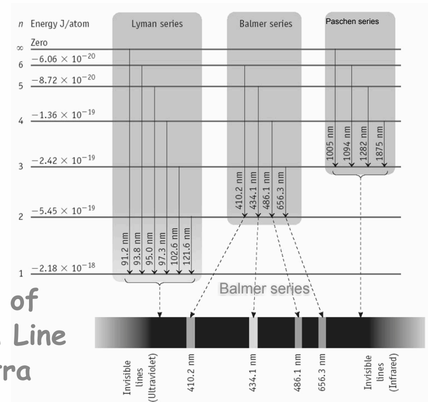

Origin of Emission Line Spectra

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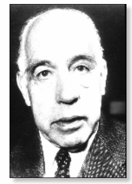
Atomic Line Spectra and Niels Bohr



Niels Bohr
(1885-1962)

Bohr's theory was a great accomplishment.

Received Nobel Prize, 1922

Problems with theory -

- **theory only successful for H & He^{+1}**
- **introduced quantum idea artificially.**

So, we go on to QUANTUM or WAVE MECHANICS

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Quantum or Wave Mechanics

L. de Broglie
(1892-1987)

de Broglie (1924) proposed that *all* moving objects have wave properties.

For light: E = mc²

E = hν = hc / λ

Therefore, mc = h / λ

and for particles

λ = h / mv

(for particles traveling less than speed of light)

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The de Broglie Wave Equation

Louis de Broglie

***Example:* Calculate the wavelength of an electron traveling at 75.0% the speed of light:**

λ = h / mv

$$\lambda = \frac{6.626 \times 10^{-34}\ \text{J}\bullet\text{s}}{9.11 \times 10^{-31}\ \text{kg} * 2.998 \times 10^{8}\ \frac{m}{s} * 0.750}$$

λ = 3.23 x 10⁻¹² m

***Note:* 1 J = 1 kg m² s⁻²** *(derived SI unit)*
Must use kg for mass in these problems

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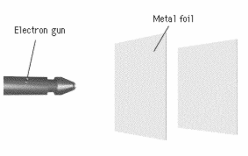
The de Broglie Wave Equation: λ = h / mv



Experimental proof of wave properties of electrons

electron with velocity = 1.90 x 10⁸ cm/sec
λ = 0.388 nm
measurable!

Baseball (115 g) at 1000 mph
λ = 1.3 x 10⁻³³ cm
unmeasurable, but deadly!

Electrons and light both exhibit wave-particle duality!

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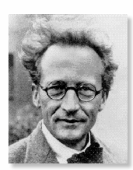
Quantum or Wave Mechanics



E. Schrödinger
1887-1961

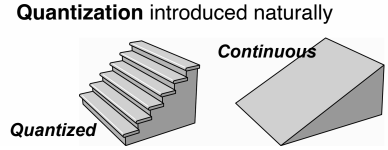
Schrödinger applied idea of e- behaving as a wave to the problem of electrons in atoms.

He developed the WAVE EQUATION

Solution to wave equation gives set of mathematical expressions called WAVE FUNCTIONS, Ψ

Ψ describes the *motion* of electron waves with location and time

Quantization introduced naturally



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WAVE FUNCTIONS, Ψ

Ψ is a function of distance and two angles.

Each Ψ corresponds to an ORBITAL, the region of space within which an electron is found.

Ψ does NOT describe the exact location of the electron.

Ψ^2 is proportional to the probability of finding an e- at a given point.

$$\hat{H}\Psi = i\hbar\frac{\partial}{\partial t}\Psi \qquad \hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})$$

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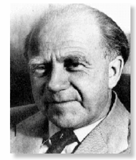
Uncertainty Principle



W. Heisenberg 1901-1976

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

- **Problem of defining nature of electrons in atoms explained by Heisenberg.**
- **Cannot simultaneously define the position and momentum (or energy) of an electron.**
- **We define e- energy exactly but accept limitation that we do not know exact position.**

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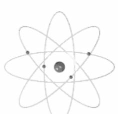
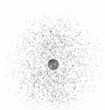
Implications of Quantum Chemistry





Current model of the atom

- **Modern view of the atom involves *probability* of electron's position (uncertainty principle) while electron's *quantized energy level* known accurately.**
- **Classic physics predicts "planets around the sun" idea, but this is incorrect.**

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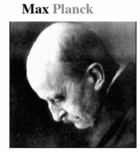
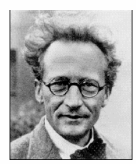
The Giants of Quantum Physics



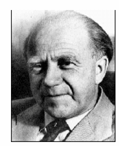
Max Planck

Niels Bohr

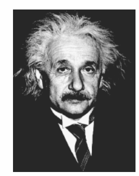
Louis Victor de Broglie



Erwin Schrödinger



Werner Heisenberg



Albert Einstein

MAR

...but great scientists are human!

Heisenberg & Bohr dining in Copenhagen, 1934
(Note the Carlsberg beer!)

They *ALL* took Chem 221 at one time - just as you are now!

'Argue for your limitations, and they are yours'

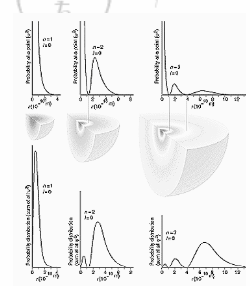
MAR

The Usefulness of Quantum Mechanics

Quantum mechanics involves math equations with calculus

We will use the results of these equations to (eventually) describe how electrons are placed in atoms and ions

First we shall look at orbitals, then shells and subshells



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Subshells & Shells

via quantum mechanics (and calculus!):

Orbitals hold electrons.

Orbitals placed in subshells which are further grouped into shells.

Each shell has a number called the PRINCIPAL QUANTUM NUMBER, n

Principal quantum number helps us to determine the energy and size of an orbital or subshell

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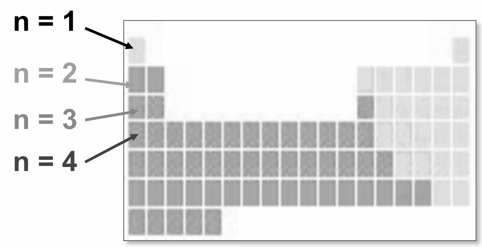
Subshells & Shells



n = Principal Quantum Number = Period Number
(for main group metals and nonmetals)

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QUANTUM NUMBERS

Via quantum mechanics, the shape, size, and energy of each orbital is a function of 4 quantum numbers:

n (principal) --> shell *(energy, size)*

l (angular) --> subshell *(shape)*

m_l (magnetic) --> **designates an orbital within a subshell** *(direction)*

m_s (spin) --> **designates the spin direction of an electron** *(Chapter 6 part 2)*

See: Quantum Numbers Handout

MAR

QUANTUM NUMBERS

Symbol	Values	Description
n (principal)	1, 2, 3, ... ∞	Orbital size and energy (*shell*)
l (angular)	0, 1, 2 .. n-1	Orbital shape or type (*subshell*)
m_l (magnetic)	-l... 0... +l	Orbital orientation

# of orbitals in subshell = 2 l + 1

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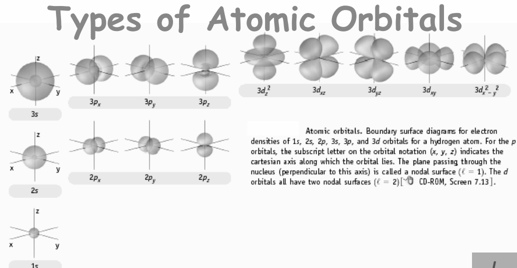
m_s covered in Chapter Six Part 2

Types of Atomic Orbitals



Atomic orbitals. Boundary surface diagrams for electron densities of 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, and 3*d* orbitals for a hydrogen atom. For the *p* orbitals, the subscript letter on the orbital notation (*x*, *y*, *z*) indicates the cartesian axis along which the orbital lies. The plane passing through the nucleus (perpendicular to this axis) is called a nodal surface ($\ell = 1$). The *d* orbitals all have two nodal surfaces ($\ell = 2$) [CD-ROM, Screen 7.13].

Use *nl* notation: 3s

value of n

value of l:

l	*letter*	
0	s	*stupid*
1	p	*people*
2	d	*drink*
3	f	*freakin'*
4	g	*gas*

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Shells and Subshells

When n = 1, then l = 0 and m_l = 0

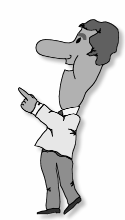
Therefore, in n = 1, there is 1 type of subshell (l)

and that subshell has a single orbital

(m_l has a single value ---> 1 orbital)

This subshell is labeled 1s ("ess")

Each shell has 1 orbital labeled s, and it is SPHERICAL in shape.



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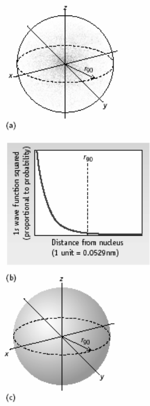
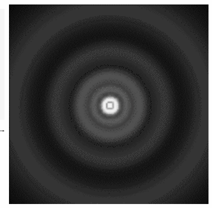
German: sphere = "sphäre", spherical = "sphärisch"



s Orbitals (l = 0)

All *s* orbitals are *spherical* in shape.

s orbitals have *n-l-1 spherical nodes*



a 6s orbital with 6-0-1 = 5 spherical nodes

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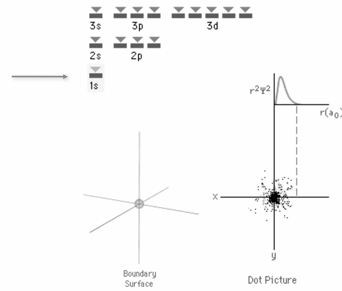
1s Orbital (n=1, l=0)



No spherical nodes in 1s

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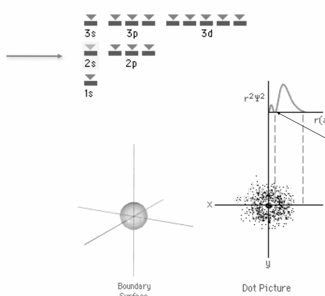
2s Orbital (n=2, l=0)



One spherical node in 2s = n-l-1 in s orbitals

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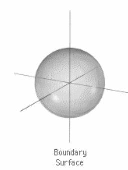
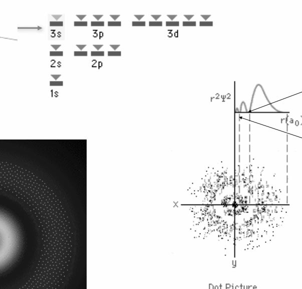
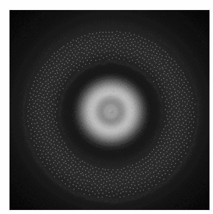
3s Orbital (n=3, l=0)







Two spherical nodes in 3s

Number of spherical nodes = n-l-1 in s orbitals

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p Orbitals (l=1)

When n = 2, then l = 0 and 1

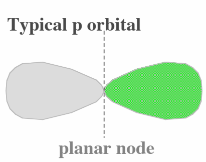
Therefore, in n = 2 shell there are *2 types of orbitals* or 2 subshells

For l = 0 m_l = 0

this is a 2s subshell

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

this is a 2p subshell with 3 orbitals



When l = 1, there is a PLANAR NODE through the nucleus.

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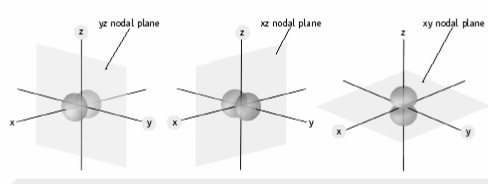
p Orbitals (l=1)



The three p orbitals lie 90º apart in space

Each p orbital has 1 planar node

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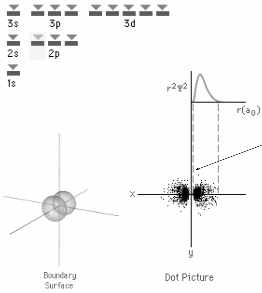
$2p_x$ Orbital (n=2, l=1)



One planar node in $2p_x$

$2p_y$ and $2p_z$ similar

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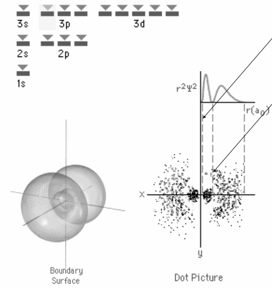
$3p_x$ Orbital (n=3, l=1)



One planar node in $3p_x$

One spherical node in $3p_x$

 # spherical nodes = n - l - 1

$3p_x$ *(n = 3)* larger than $2p_x$ *(n = 2)*

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d Orbitals (l=2)

When n = 3, what are the values of l?

l = 0, 1, 2

and so there are 3 subshells in the shell.

For l = 0, m_l = 0

---> 3s subshell with single orbital

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

---> 3p subshell with 3 orbitals

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

---> 3d subshell with 5 orbitals

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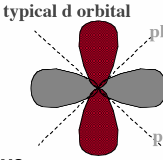
d Orbitals (l=2)



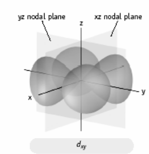
s orbitals have no planar node (l = 0) and so are spherical.

p orbitals have l = 1 and have 1 planar node ("dumbbell" shaped)

This means d orbitals (with l = 2) have 2 planar nodes

 # planar nodes = l

 # spherical nodes = n - l - 1



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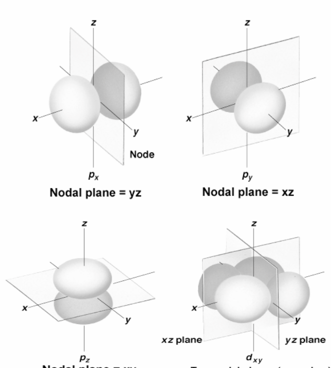

Nodal Planes in p and d Orbitals

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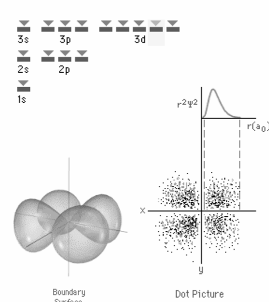
$3d_{xy}$ Orbital (n=3, l=2)



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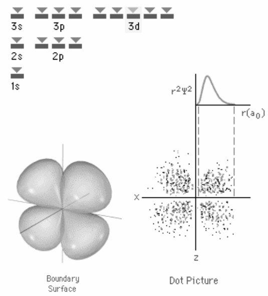
$3d_{xz}$ Orbital (n=3, l=2)



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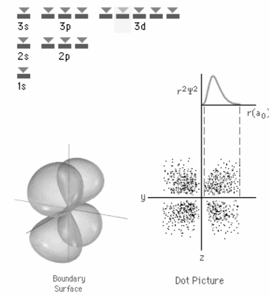
$3d_{yz}$ Orbital (n=3, l=2)



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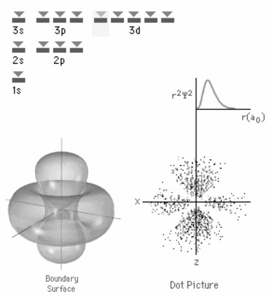
$3d_{z^2}$ Orbital (n=3, l=2)



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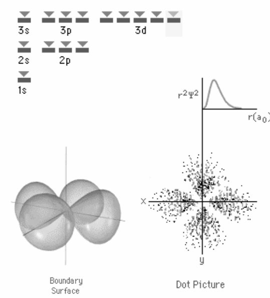
$3d_{x^2-y^2}$ Orbital (n=3, l=2)



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The n = 3 shell *(example)*

l values			
subshell letter			
nl notation			
m_l values			
# orbitals			

***three subshells** when n=3*

***l*: 0, 1, ... (n-1)**

m_l : -l...0...+l

subshell:
s p d f
l: 0 1 2 3

\# orbitals =
1 + 3 + 5 = 9
Total orbitals = n²

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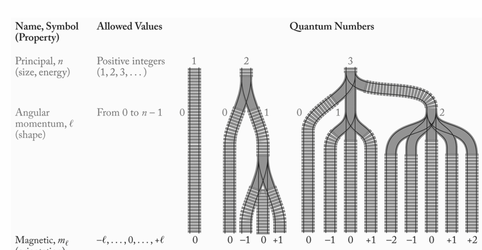
The Train Track Model



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f Orbitals (l = 3)

When n = 4, l = 0, 1, 2, 3 so there are 4 subshells in the shell.

For l = 0, m_l = 0

---> **4s** *subshell with single orbital*

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

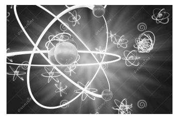
---> **4p** *subshell with 3 orbitals*

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

---> **4d** *subshell with 5 orbitals*

For l = 3, m_l = -3, -2, -1, 0, +1, +2, +3

---> 4f subshell with 7 orbitals



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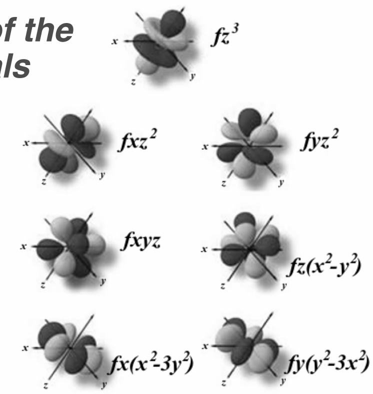
Pictures of the f Orbitals



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Quick & Dirty Quantum Chemistry

memorize c = 2.998 x 10^8 m/s

memorize h = 6.626 x 10^{-34} J s

E = hν = hc/λ $\quad$ *ν = frequency (Hz)*

λ = h / mv $\quad$ *v = velocity (m/s)*

 # orbitals in a shell = n^2

 # orbitals in a subshell = 2l + 1

stupid people drive freakin' gas hogs

0 1 2 3 4 5 *(l values)*

so a 4d *subshell would have* n = 4, l = 2

 # planar nodes = l

 # spherical nodes = n - l - 1

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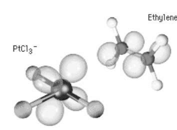
Importance of Orbitals

Knowledge of orbitals critical when understanding bonding in molecules (we'll see this in CH 222)



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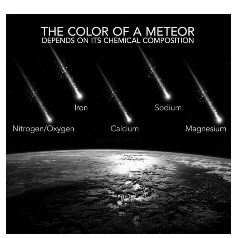
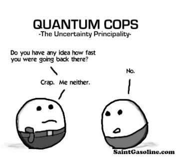
End of Chapter Six Part 1

See also:

- *Chapter Six Part 1 Study Guide*
- *Chapter Six Part 1 Concept Guide*
- *Important Equations (following this slide)*
- *End of Chapter Problems (following this slide)*





"More decisive? How can I be more decisive? - I live by the uncertainty principle!"

MAR

Important Equations, Constants, and Handouts from this Chapter:

- *know relationship between* **frequency, wavelength, energy, speed of light, energy per mole**
- *know the* **regions** *and* **relative energies** *within the* **electromagnetic spectrum**
- *know about* **sharp line spectra, absorbance** *and* **emission spectra**
- *know about* **wave particle duality** **(***including* **de Broglie)**
- **quantum numbers:** *know the origin and meaning of* **n, l, m_l**
- *know* **"nl" notation** *(4s, 3d, etc.)*
- *know how to find* **spherical** *and* **planar nodes, number of orbitals,** *etc.*

c = 2.998 x 10^8 m/s

h = 6.626 x 10^{-34} J s

E = hν = hc/λ *(E/M)*

λ = h / mv *(particles)*

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End of Chapter Problems: *Test Yourself*

1. Place the following types of radiation in order of increasing energy per photon: **yellow light, x-rays, microwaves** and your favorite FM music **radio** station at 92.3 MHz.
2. Aluminum has an emission line at 396.15 nm. What is the frequency of this line? What is the energy of one photon with this wavelength? Of 1.00 mol of these photons?
3. A rifle bullet (mass = 1.50 g) has a velocity of 7.00×10^2 miles per hour. What is the wavelength associated with this bullet? (0.6214 miles = 1 km)
4. a. When $n = 4$, what are the possible values of ℓ?
   b. When ℓ is 2, what are the possible values of m_ℓ?
   c. For a 4*s* orbital, what are the values of n and ℓ?
5. Explain why these sets of quantum numbers are incorrect.
   a. n = 3, l = 3, m_l = 0, ms = +1/2
   b. n= 4, l = 3, m_l = -4, ms = -1/2
6. How many nodal surfaces (planar and spherical) are associated with each of the following atomic orbitals? **5f** *and* **4s**

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End of Chapter Problems: *Answers*

1. radio, microwave, yellow light, x-rays
2. $\upsilon = 7.568 \times 10^{14}$ Hz, E = 5.014×10^{14} J/ph, E = 3.02×10^5 J/mol
3. 1.41×10^{-33} m
4. a. 0, 1, 2 or 3. b. 0, ±1, ±2. c. n = 4, l = 0.
5. a. l cannot equal n. b. m_l can only equal ±l (+3 to -3 only)
6. **5f**: three planar and one spherical node. **4s**: zero planar and three spherical nodes.

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