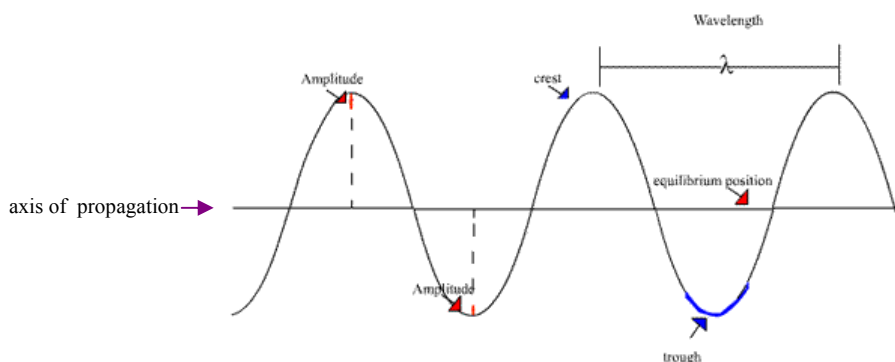
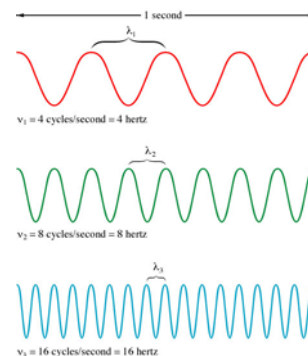


ELECTROMAGNETIC RADIATION

James Maxwell developed an elegant mathematical theory in 1864 to describe all forms of radiation in terms of oscillating or wave-like electric and magnetic fields in space.

- **electromagnetic radiation**—UV, visible light, IR, microwaves, television and radio signals, and X-rays
- **wavelength (λ)**—(lambda) length between 2 successive crests.
- **frequency (ν)**—(nu in chemistry; f in physics—either is OK), number of cycles *per second* that pass a certain point in space (Hz-cycles per second)
- **amplitude**—maximum height of a wave as measured from the axis of propagation
- **nodes**—points of *zero* amplitude (equilibrium position); always occur

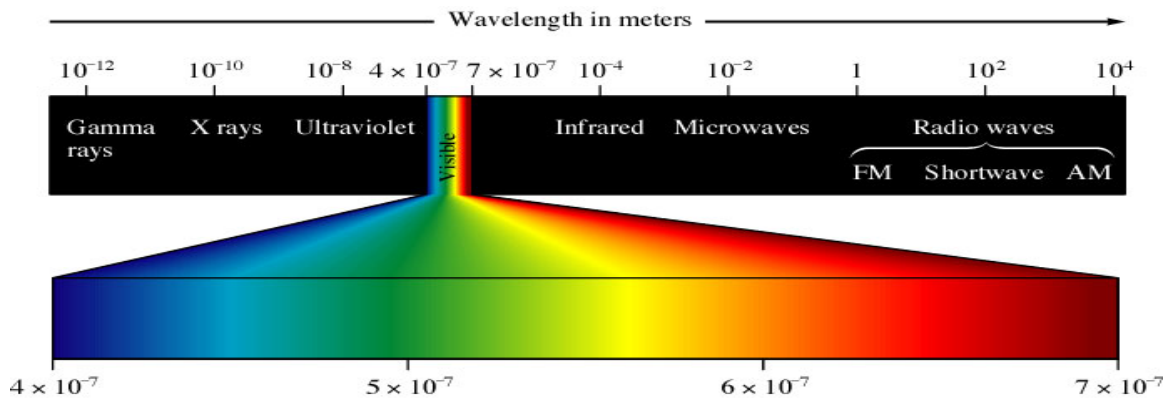


at $\lambda/2$ for sinusoidal waves
velocity—speed of the wave

$$\text{velocity} = \lambda \nu$$

“c”—the speed of light; $2.99792458 [\text{just call it } 3] \times 10^8$ m/s; ALL EM RADIATION TRAVELS AT THIS SPEED! I call it easy, you’ll call it a trick! If “light” is involved, it travels at 3×10^8 m/s

- Notice that λ and ν are inversely proportional. When one is large, the other is small.



*AP is a registered trademark of the College Board, which was not involved in the production of, and does not endorse, this product.

Exercise 1 **Frequency of Electromagnetic Radiation**

The brilliant red colors seen in fireworks are due to the emission of light with wavelengths around 650 nm when strontium salts such as $\text{Sr}(\text{NO}_3)_2$ and SrCO_3 are heated. (This can be easily demonstrated in the lab by dissolving one of these salts in methanol that contains a little water and igniting the mixture in an evaporating dish.) Calculate the frequency of red light of wavelength 6.50×10^2 nm.

$$\nu = 4.61 \times 10^{14} \text{ Hz}$$

THE NATURE OF MATTER

At the end of the 19th century, physicists were feeling rather smug. All of physics had been explained [or so they thought]. Students were being discouraged from pursuing physics as a career since all of the major problems had been solved! Matter and Energy were distinct: Matter was a collection of particles and Energy was a collection of waves. Enter Max Planck stage left...

THE QUANTIZATION OF ENERGY

"Ultraviolet catastrophe"—defined as the fact that a glowing hot object did not emit UV light as predicted.

- 1900--Max Planck solved the problem. He made an incredible assumption: *There is a minimum amount of energy that can be gained or lost by an atom, and all energy gained or lost must be some integer multiple, n , of that minimum.* (As opposed to just any old value of energy being gained or lost.)

$$\Delta \text{Energy} = n(h\nu)$$

- where h is a proportionality constant, Planck's constant, $h = 6.6260755 \times 10^{-34}$ joule • seconds. This ν is the lowest frequency that can be absorbed or emitted by the atom, and the minimum energy change, $h\nu$, is called a **quantum** of energy. Think of it as a "packet" of E equal to $h\nu$.
- No such thing as a transfer of E in fractions of quanta, only in whole numbers of quanta.
- Planck was able to calculate a spectrum for a glowing body that reproduced the experimental spectrum.
- His hypothesis applies to all phenomena on the atomic and molecular scale.

Exercise 2 **The Energy of a Photon**

The blue color in fireworks is often achieved by heating copper(I) chloride (CuCl) to about 1200°C. Then the compound emits blue light having a wavelength of 450 nm. What is the increment of energy (the quantum) that is emitted at 4.50×10^2 nm by CuCl ?

$$= 4.41 \times 10^{-19} \text{ J}$$

THE PHOTOELECTRIC EFFECT AND ALBERT EINSTEIN

In 1900 Albert Einstein was working as a clerk in the patent office in Bern, Switzerland. This left him time to work on Physics.

He proposed that EM radiation itself was quantized; he was a great fan of Planck's work! He proposed that EM radiation could be viewed as a stream of "particles" called **photons**.

- **photoelectric effect**--light bombards the surface of a metal and electrons are ejected.
- **frequency**—a minimum ν must be met or alas, no action! Once minimum is met, intensity increases the rate of ejection.
- **photon**--massless particles of light.

$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda}$$

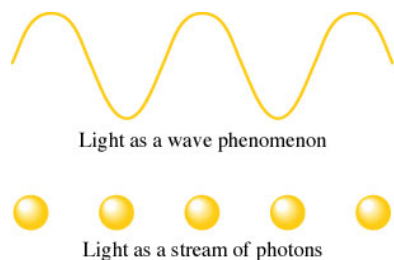
You know Einstein for the famous $E = mc^2$ from his second "work" as the special theory of relativity published in 1905. Such blasphemy, energy has mass?! That would mean:

$$m = \frac{E}{c^2}$$

therefore,

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

Does a photon have mass? Yep! In 1922 American physicist Arthur Compton performed experiments involving collisions of X-rays and electrons that showed photons do exhibit the apparent mass calculated above.



SUMMARY:

Energy is quantized.

It can occur only in discrete units called quanta [$h\nu$].

EM radiation [light, etc.] exhibits wave and particle properties.

This phenomenon is known as the **dual nature of light**.

Since light which was thought to be wavelike now has certain characteristics of particulate matter, is the converse also true? Enter Louis de Broglie [French physicist, 1923] stage right...

$$\text{IF } m = \frac{h}{\lambda c}$$

substitute v [velocity] for c for any object NOT traveling at the speed of light, then rearrange and solve for lambda

this is called the de Broglie equation:

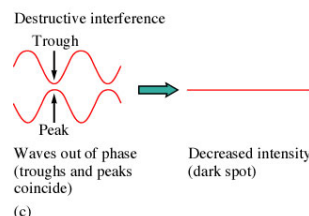
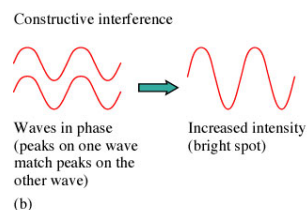
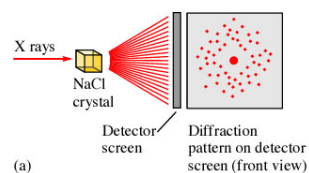
$$\lambda = \frac{h}{mv}$$

Exercise 3 Calculations of Wavelength

Compare the wavelength for an electron (mass = 9.11×10^{-31} kg) traveling at a speed of 1.0×10^7 m/s with that for a ball (mass = 0.10 kg) traveling at 35 m/s.

$$\lambda_e = 7.27 \times 10^{-11} \text{ m}$$

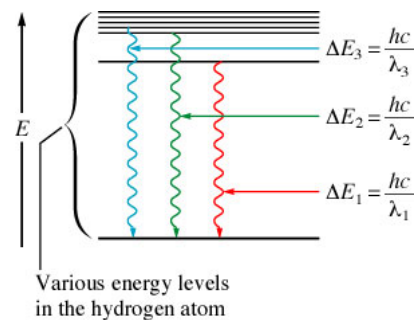
$$\lambda_b = 1.9 \times 10^{-34} \text{ m}$$



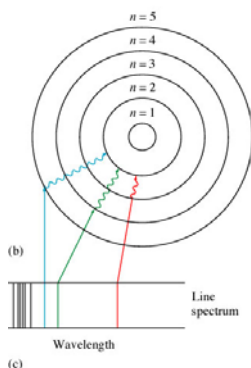
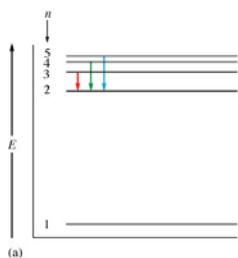
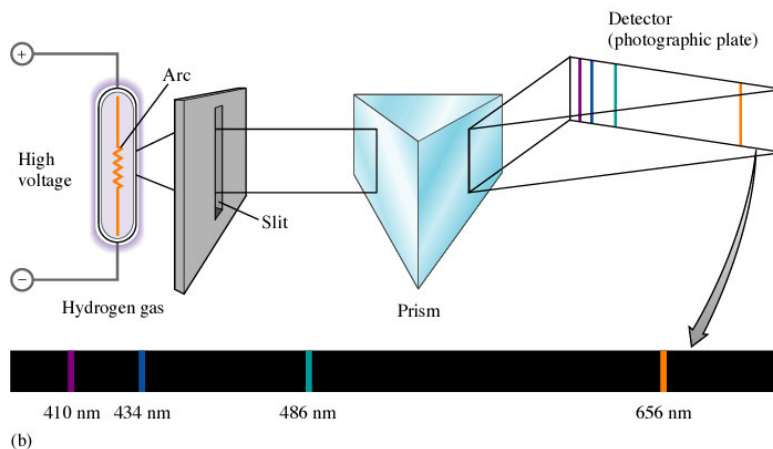
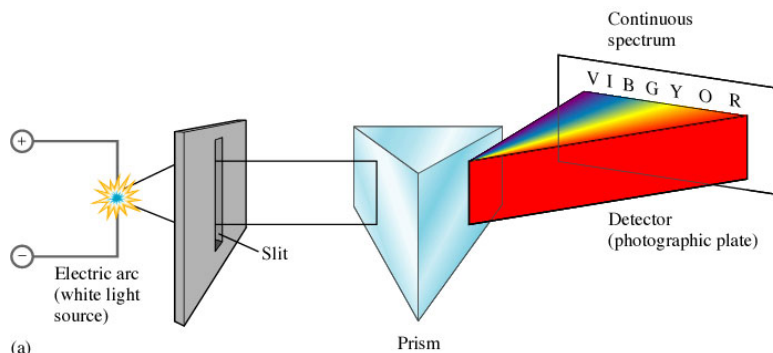
- The more massive the object, the smaller its associated wavelength and vice versa!
- Davisson and Germer @ Bell labs found that a beam of electrons was diffracted like light waves by the atoms of a thin sheet of metal foil *and* that de Broglie's relation was followed quantitatively.
- ANY moving particle has an associated wavelength.
- Silly physicists! We now know that E is really a form of matter, and ALL matter shows the same types of properties. That is, all matter exhibits both particulate and wave properties.

HYDROGEN'S ATOMIC LINE SPECTRA AND NIELS BOHR

- **emission spectrum**—the spectrum of bright lines, bands, or continuous radiation that is provided by a specific emitting substance as it loses energy and returns to its ground state OR the collection of frequencies of light given off by an "excited" electron
- **absorption spectrum**—a graph or display relating how a substance absorbs electromagnetic radiation as a function of wavelength
- **line spectrum**--isolate a thin beam by passing through a slit then a prism or a diffraction grating which sorts into discrete frequencies or lines
- Johann Balmer--worked out a mathematical relationship that accounted for the 3 lines of longest wavelength in the visible emission spectrum of H. (red, green and blue lines)



- Niels Bohr connected spectra, and the quantum ideas of Einstein and Planck: *the single electron of the hydrogen atom could occupy only certain energy states, stationary states*



"The Mother of all Assumptions"

An electron in an atom would remain in its lowest E state *unless* otherwise disturbed.

- Energy is absorbed or emitted by a change from this ground state
- an electron with $n = 1$ has the most negative energy and is thus the most strongly attracted to the *positive* nucleus. [Higher states have less negative values and are not as strongly attracted to the positive nucleus.]
- **ground state**-- $n = 1$ for hydrogen

$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda}$$

- To move from ground to $n = 2$ the electron/atom must absorb *no more or no less*

than

$0.75 Rhc$. [that's a collection of constants]

- So, a move of $n = 2$ to $n = 1$ **emits** 985 kJ of energy.
- What goes up must come down. Energy absorbed must eventually be emitted.
- *The origin or atomic line spectra is the movement of electrons between quantized energy states.*
- IF an electron moves from higher to lower E states, a photon is **emitted** and an emission line is observed.

- Bohr's equation for calculating the energy of the E levels available to the electron in the hydrogen atom:

$$E = -2.178 \times 10^{-18} \text{ J} \left(\frac{Z^2}{n^2} \right)$$

- where n is an integer [larger n means larger orbit radius, farther from nucleus], Z is the nuclear charge
- The NEGATIVE sign simply means that the E of the electron bound to the nucleus is lower than it would be if the electron were at an infinite distance [$n = \infty$] from the nucleus where there is NO interaction and the energy is zero.
- ΔE is simply the subtraction of calculating the energy of two different levels, say $n=6$ and $n=1$. If the difference is negative, E was lost. If the difference is positive, E was gained.
- TWO Major defects in Bohr's theory: 1) Only works for elements with ONE electron.
2) The one, lonely electron **DOES NOT** orbit the nucleus in a fixed path!!

Exercise 4

Energy Quantization in Hydrogen

Calculate the energy required to excite the hydrogen electron from level $n = 1$ to level $n = 2$. Also calculate the wavelength of light that must be absorbed by a hydrogen atom in its ground state to reach this excited state.

$$\Delta E = 1.633 \times 10^{-18} \text{ J}$$

$$\lambda = 1.216 \times 10^{-7} \text{ m}$$

Exercise 5

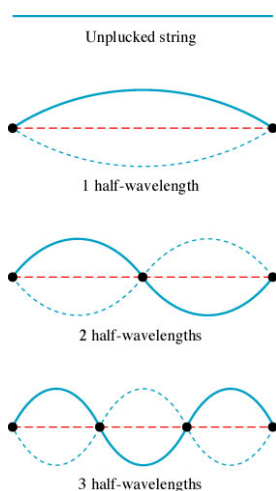
Electron Energies

Calculate the energy required to remove the electron from a hydrogen atom in its ground state.

$$\Delta E = 2.178 \times 10^{-18} \text{ J}$$

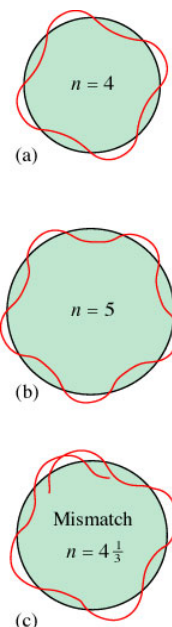
THE WAVE PROPERTIES OF THE ELECTRON SCHRODINGER, HEISENBERG, AND QUANTUM NUMBERS

- After World War I--Niels Bohr assembled a group of physicists in Copenhagen hoping to derive a comprehensive theory for the behavior of electrons in atoms from the viewpoint of the electron as a particle
- Erwin Schrodinger--independently tried to accomplish the same thing but focused on de Broglie's eqn' and the electron as a wave. Schrodinger's approach was better; explained more than Bohr's and met with more success. Quantum mechanics was born!
- de Broglie opened a can of worms among physicists by suggesting the electron had wave properties
- *the electron has dual properties*
- Werner Heisenberg and Max Born provided the **uncertainty principle**
 - if you want to define the momentum of an electron, then you have to forego knowledge of its exact position at the time of the measurement
- Max Born on the basis of Heisenberg's work suggested: *if we choose to know the energy of an electron in an atom with only a small uncertainty, then we must accept a correspondingly large uncertainty about its position in the space about the atom's nucleus.* So What? We can only calculate the **probability** of finding an electron within a given space.



THE WAVE MECHANICAL VIEW OF THE ATOM

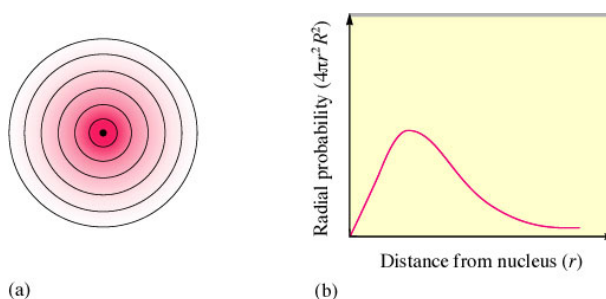
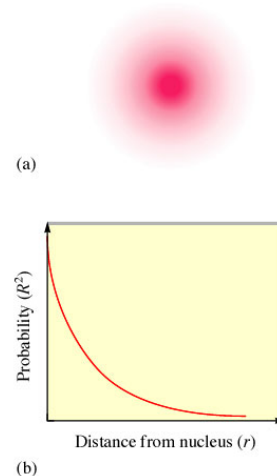
- Schrodinger equation: solutions are called wave functions--chemically important. The electron is characterized as a matter-wave
- sort of standing waves--*only certain allowed wave functions* (symbolized by the Greek letter, ψ , pronounced "sigh")
- Each ψ for the electron in the H atom corresponds to an allowed energy ($-Rhc/n^2$). For each integer, n , there is an atomic state characterized by its own ψ and energy E_n .
- In English? Points 1 & 2 above say that the energy of electrons is quantized.



Notice in the figure to the right, that only whole numbers of standing waves can "fit" in the proposed orbits.

The hydrogen electron is visualized as a standing wave around the nucleus [above right]. The circumference of a particular circular orbit would have to correspond to a whole number of wavelengths, as shown in (a) and (b) above, OR else destructive interference occurs, as shown in (c). This is consistent with the fact that only certain electron energies are allowed; the atom is quantized. (Although this idea encouraged scientists to use a wave theory, it does not mean that the electron really travels in circular orbits.)

- the square of ψ gives the intensity of the electron wave or the probability of finding the electron at the point P in space about the nucleus—the intensity of color in (a) above represents the probability of finding the electron in that space, the darker the color—the more probable it is we would find the electron in that region.
- electron density map, electron density and electron probability ALL mean the same thing! When we say “orbital” this image at right is what we picture in our minds.
- matter-waves for allowed energy states are also called (drum roll please...) orbitals.
- To solve Schrodinger's equation in a 3-dimensional world we need the quantum numbers n , ℓ , and m_ℓ
- **The amplitude of the electron wave at a point depends on the distance of the point from the nucleus.**



- Imagine that the space around a H nucleus is made up of a series of thin “shells” like the layers of an onion, but these “shells” as squishy (Very scientific word, that “squishy”!)
- Plot the total probability of finding the electron in each shell versus the distance from the nucleus and you get the radial probability graph you see in (b) above
- The maximum in the curve occurs because of two opposing effects. 1) the probability of finding an electron is greatest near the nucleus [electrons just can't resist the attraction of a proton!], BUT 2) the volume of the spherical shell increases with distance from the nucleus, SO we are summing more positions of possibility, so the TOTAL probability increases to a certain radius and then decreases as the electron probability at EACH position becomes very small.

Try not to stress over this introduction stuff! Learn to do the calculations in the practice exercises & do the best you can with the “theory” stuff. It's my moral obligation to TRY to explain it to you. Stress over quantum numbers and electron configurations and periodicity if you must—that's the important stuff in this chapter! I just feel the need to give you a complete education!

QUANTUM NUMBERS & ATOMIC ORBITALS

There are 4 quantum numbers that describe the “address” and “spin” of an electron. The value of n limits the possible values of ℓ , which in turn limit the values of m_ℓ .

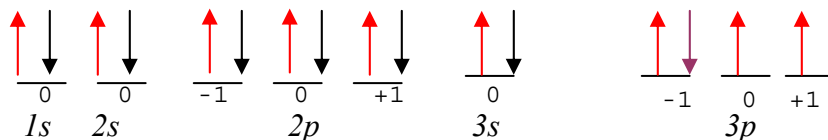
- **n —principal energy level**--1 to infinity. Determines the total energy of the electron. It indicates the most probable [within 90%] distance of the electron from the nucleus. A measure of the orbital size or diameter. $2n^2$ electrons may be assigned to a shell. *It's simply the Energy level that electron is in. If it's a 3s electron, $n = 3$, if it's a 4d electron, $n = 4$, etc.*
- **ℓ —angular momentum**--0,1,2,...($n-1$) electrons w/in shell may be grouped into subshells [or sublevels, same thing!], each characterized by its certain wave shape. Each ℓ is a different orbital shape or orbital type.
 - n limits the values of ℓ to no larger than $n-1$. Thus, the number of possibilities for ℓ is equal to n . (English translation: 3 sublevels for 3rd E level, 4 for 4th E level, etc.)
 - s,p,d,f sublevels \rightarrow 0,1,2,3 **ℓ -values respectively** (So, what do $spdf$ stand for? Sharp, principle, diffuse, fundamental--early days of atomic spectroscopy)

Table 7.1 The Angular Momentum Quantum Numbers and Corresponding Letters Used to Designate Atomic Orbitals

Value of ℓ	0	1	2	3	4
Letter Used	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>g</i>

You can keep going from $g...$

- **m_ℓ —magnetic**—assign the “blanks” in orbital notation with zero on the middle blank and then $-\ell$ through zero to $+\ell$. I'll bet this looks familiar for Sulfur from Chem. I!



- that means that the range of orbitals is from $+\ell$ to $-\ell$
- it describes the orientation of an orbital in a given subshell
- The down arrow in the $3p, -1$ slot is the last electron placed [valence electron], so far it's set of quantum numbers is 3, 1, -1

DON'T
try to
make this
hard!

Embrace
the elegant
patterns!

Table 7.2 Quantum Numbers for the First Four Levels of Orbitals in the Hydrogen Atom

n	ℓ	Orbital Designation	m_ℓ	Number of Orbitals
1	0	1s	0	1
2	0	2s	0	1
	1	2p	-1, 0, +1	3
3	0	3s	0	1
	1	3p	-1, 0, 1	3
	2	3d	-2, -1, 0, 1, 2	5
4	0	4s	0	1
	1	4p	-1, 0, 1	3
	2	4d	-2, -1, 0, 1, 2	5
	3	4f	-3, -2, -1, 0, 1, 2, 3	7

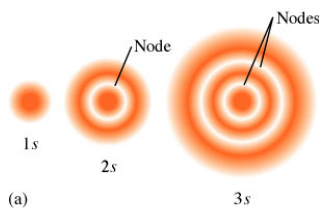
Exercise 6**Electron Subshells**

For principal quantum level $n = 5$, determine the number of allowed subshells (different values of ℓ), and give the designation of each.

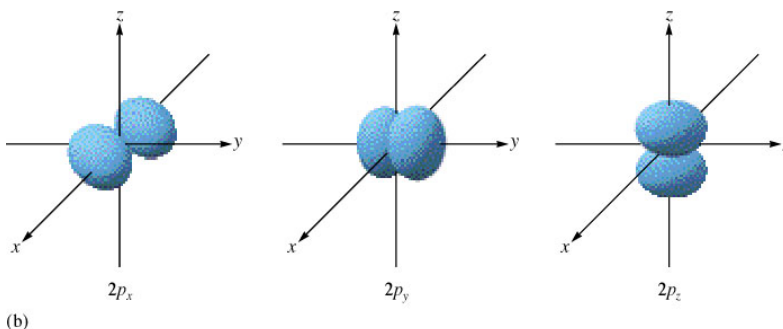
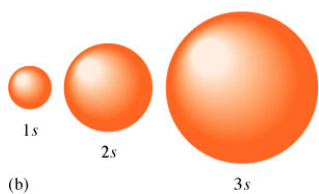
$\ell = 0$; 5s
 $\ell = 1$; 5p
 $\ell = 2$; 5d
 $\ell = 3$; 5f
 $\ell = 4$; 5g

THE SHAPES OF ATOMIC ORBITALS

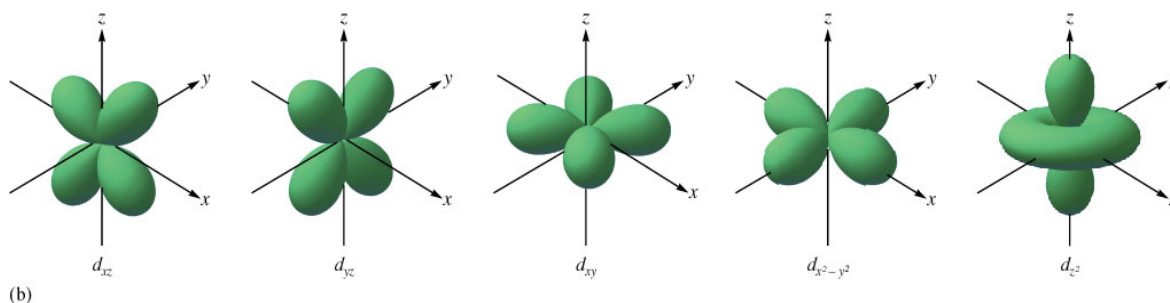
There is no sharp boundary beyond which the electrons are never found!!



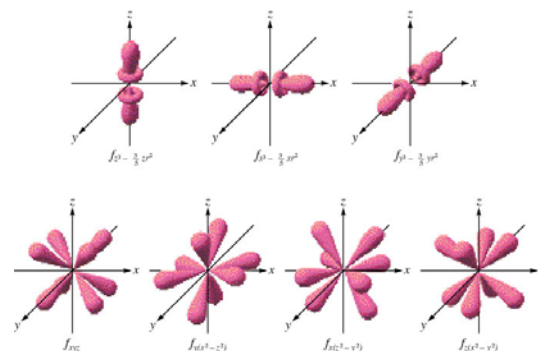
- s --spherical; the size increases with n . The nodes you see at left represent ZERO probability of finding the electron in that region of space. The number of nodes equals $n-1$ for s orbitals.
- p --have one plane that slices through the nucleus and divides the region of electron density into 2 halves. **Nodal plane**--the electron can never be found there!!
- 3 orientations: p_x , p_y , and p_z .



- d --2 nodal planes slicing through the nucleus to create four sections; 5 orbitals.
 - The d_{z^2} orbital is really strange!



- f --3 nodal planes slicing through the nucleus; eight sections; 7 orbitals

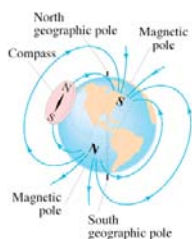
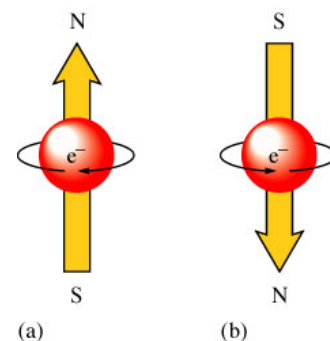


ELECTRON CONFIGURATIONS

Chemical properties depend on the number and arrangement of electrons in an atom. Usually only the valence electrons play the reaction game.

ELECTRON SPIN

- 1920--chemists realized that since electrons interact with a magnetic field, there must be one more concept to explain the behavior of electrons in atoms.
- m_s --the 4th quantum number; accounts for the reaction of electrons in a magnetic field

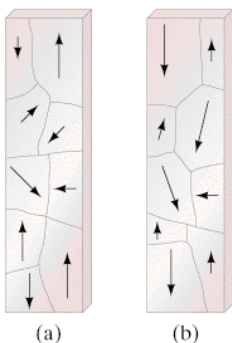


MAGNETISM

- **magnetite**-- Fe_3O_4 , natural magnetic oxide of iron
- 1600--William Gilbert concluded the earth is also a large spherical magnet with *magnetic south* at the geographic North Pole (Santa's habitat).
- NEVER FORGET: opposites attract & likes repel whether it's opposite poles of a magnet or opposite electrical charges

PARAMAGNETISM AND UNPAIRED ELECTRONS

- **diamagnetic**--not magnetic [magnetism **dies**]; in fact they are *slightly* repelled by a magnetic field. Occurs when all electrons are PAIRED.
- **paramagnetic**--attracted to a magnetic field; lose their magnetism when removed from the magnetic field; HAS ONE OR MORE UNPAIRED ELECTRONS
- **ferromagnetic**--retain magnetism upon introduction to, then removal from a magnetic field
- All of these are explained by electron spins
 - Each electron has a magnetic field with N & S poles
 - *electron spin is quantized such that, in an external magnetic field, only two orientations of the electron magnet and its spin are possible*
 - $+1/2$ and $-1/2$
 - H is paramagnetic; He is diamagnetic, WHY?
 - H has one *unpaired* electron
 - He has **NO** *unpaired* electrons; all spins offset and cancel each other out



What about ferromagnetic?

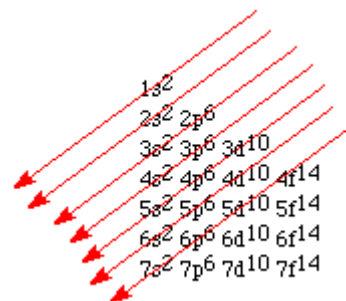
- clusters of atoms have their unpaired electrons aligned within a cluster, clusters are more or less aligned and substance acts as a magnet. **Don't drop it!!**
- When all of the domains, represented by these arrows are aligned, it behaves as a magnet.
- This is what happens if you drop it: The domains go in all different directions and it no longer operates as a magnet.

THE PAULI EXCLUSION PRINCIPLE

In 1925 Wolfgang Pauli stated: *no two electrons in an atom can have the same set of four quantum numbers*. This means no atomic orbital can contain more than 2 electrons & for two electrons to occupy the same orbital, they must be of opposite spin!!

ATOMIC ORBITAL ENERGIES AND ELECTRON ASSIGNMENTS

- Order of orbital energies--the value of n ($E = -Rhc/n^2$) determines the energy of an electron
- "many-electron" atoms depend on both n & ℓ
- Use the diagonal rule or Aufbau series
- Orbital radius changes slightly with ℓ as well as with n
- subshell orbitals contract toward the nucleus as the value of ℓ increases
- contraction is partially into the volume of space occupied by the *core* electrons
- the energy of the electrons in these subshells is raised due to the repulsions between the subshell electrons and the core electrons.



- *a subshell's energy rises as its ℓ quantum number increases when inner electrons are present*

- Order of Orbital Assignments
- each electron is lazy and occupies the lowest energy space available
- based on the assumption inner electrons have no effect on which orbitals are assigned to outer or valence electrons
 - not exactly true (use diagonal rule)—note that the one pictured shows the lowest energy state ($1s$) at the top of the diagram—some variations show $1s$ at the bottom of the diagram
- electron configurations (spectroscopic notation)
- clump the $1s$, $2s$, etc. TOGETHER rather than written in the order the orbitals fill

HUNDS RULE

The most stable arrangement of electrons is that with the maximum number of unpaired electrons; WHY?? it minimizes electron-electron repulsions (*everyone gets their own room*)

- all single electrons also have parallel spins to reduce e^-/e^- repulsions (aligns micromagnets)
- When 2 electron occupy the same orbital they must have opposite spins (Pauli exclusion principle); this also helps to minimize e^-/e^- repulsions

Personally, I think this whole quantum number thing is easiest when we start with the electron configurations THEN write the quantum numbers.

Allow me to recap: Don't try to make this hard! It just isn't.

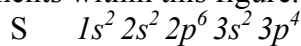
Energy Level	1	2	3	4	5	6	7....
# of sublevels	1	2	3	4	5	6	7....
Names of sublevels	<i>s</i>	<i>s, p</i>	<i>s, p, d</i>	<i>s, p, d, f</i>	<i>s, p, d, f, g</i>	<i>s, p, d, f, g, h</i>	<i>s, p, d, f, g, h, i</i>
n, principal quantum number	1	2	3	4	5	6	7....

Name of sublevel	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>g</i>	<i>h</i>	<i>i...</i>
ℓ , angular momentum quantum number [= n-1]	0	1	2	3	4	5	6
# of orbitals [= - ℓ to + ℓ]	1	3	5	7	9	11	13
m_ℓ for each orbital within a sublevel	$\overline{0}$	$\overline{-1} \overline{0} \overline{+1}$	$\overline{-2} \overline{-1} \overline{0} \overline{+1} \overline{+2}$	And so on, just pretend you are in second grade and make a number line with negative numbers on the left, ZERO in the middle, and positive numbers on the right.			

The first electron placed in an orbital is assigned the +1/2 and the second one is assigned the -1/2.

Let's practice: Give the electron configurations for the elements within this figure. I'll get you started!

Period	1A	2A	Group										3A	4A	5A	6A	7A	8A	
1	1s																	1s	
2	2s																	2p	
3	3s																	3p	S
4	4s																	4p	
5	5s																	5p	Cd
6	6s	La	Hf															6p	
7	7s	Ra	Ac																



Cd

La

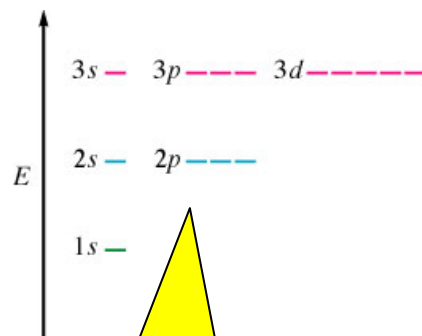
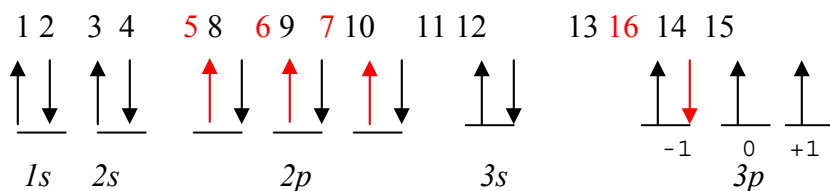
Hf

Ra

Ac

And their Orbital Notation:

Sulfur



As electrons enter these sublevels their wave functions interfere with each other causing the energy of these to change and separate. Do not be misled by this diagram, there ARE INDEED energy differences between all of these sublevels. See below.

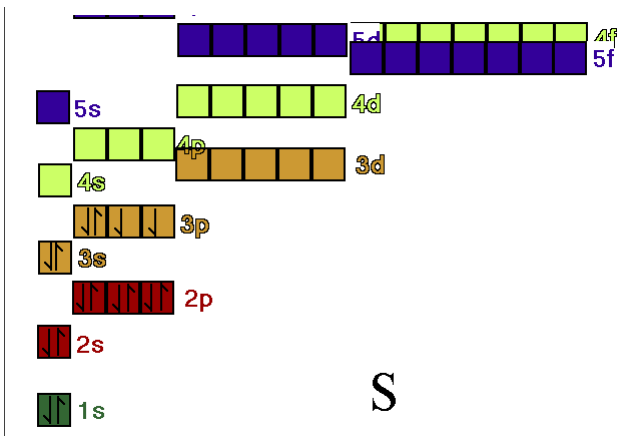
Cd

La

Hf

Ra

Ac



There is a super cool animation that illustrates this concept. The website is from the Chief Reader of the AP Exam. This site is <http://intro.chem.okstate.edu/APnew/Default.html> Click on Electron Configuration Animation. You'll need the shockwave plug-in. Once the animation comes up, click on the screen to advance from Hydrogen on up by atomic number.

What are the quantum numbers for the outermost [valence] electron?

S--since the last electron put in is #16 and it is in the $3p$ sublevel, $n = 3$ and $\ell = 2$. It's in the -1 slot, the $m_\ell = -1$ and since it's the second arrow placed [down arrow] its $m_s = -1/2$. So the set of quantum numbers for the 16th electron in sulfur is: 3,2,-1, -1/2. You'll find this really easy IF you draw the orbital notation for the last sublevel!

Cd

La

Hf

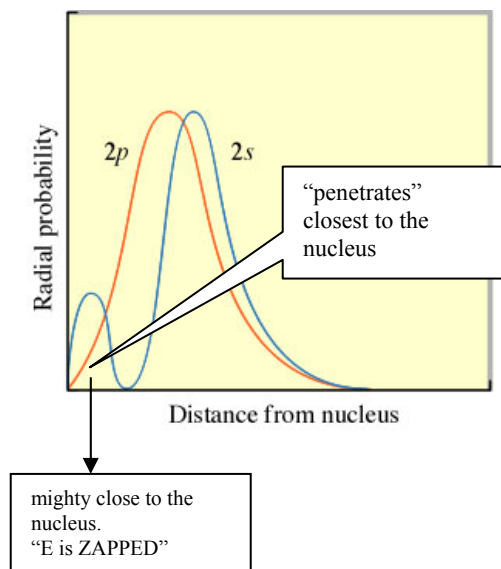
Ra

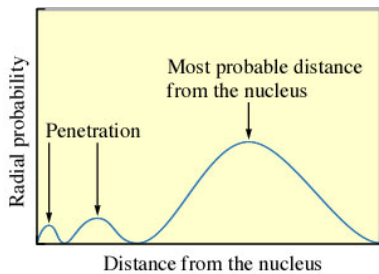
Ac

- You accepted that the sublevels had differences in energies long ago.
- You even know the increasing order of energies:

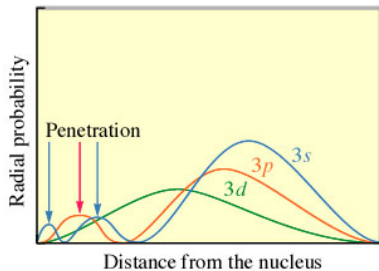
$$s < p < d < f < g \dots$$

- Now you have to be able to EXPLAIN it on the AP test. Throughout this discussion keep some fundamental scientific principles close at hand
 - electrons repel each other
 - electrons are negative and thus, attracted by the positive nucleus
 - forces (attractive & repulsive) dissipate with increasing distance.
- We need to examine the graph at the right, radial probabilities again.
 - See the small hump near the origin? That's the distance from the nucleus that a $2s$ electron occupies a small but significant amount of the time—we say the $2s$ electron “penetrates to the nucleus” more than for the $2p$ orbital. This causes a $2s$ electron to be ATTRACTED to the nucleus more than a $2p$ electron making the $2s$ orbital LOWER in E than the $2p$ orbital.
 - Think of the nucleus as “zapping” the energy of the electrons that penetrate closer to it. [Just don't write that!] Imagine a hyper child—it's on its best behavior, sitting still, being quiet, etc. when it's close to Mom. The closer to the Mother Nucleus the hyper electron is, the less hyper or energetic it is. Don't EVER write this as an answer to an essay question! It's just a model to help you get your teeth into this concept!





(a)



(b)

- Same song second verse—the last hump represents the greatest probability for predicting the distance of an electron from the nucleus, BUT the first humps determine the order of the energy.
 - The top graph is for 3s—note it has 2 humps close to the nucleus
 - The bottom graph is for 3s, 3p and note that 3d only has one hump.
 - 3s penetrates most [has least energy], then 3p [higher E than 3s, lower E than 3d] then 3d penetrates least [so it has the highest energy].
 - MORAL: The greater the penetration, the less energy that orbital has. Since you already knew the order with respect to energy, $s < p < d < f$, the degree of penetration is s 's penetrate most and f 's penetrate least.

ION ORBITAL ENERGIES AND ELECTRON CONFIGURATIONS

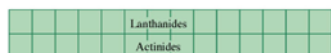
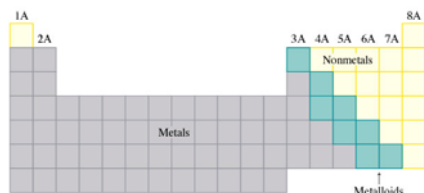
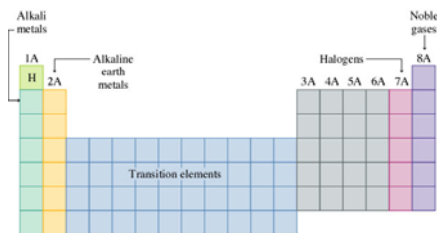
The *dfs* overlay [that thing that happens when the configurations don't fit the pattern in transition metals and rare earth metals] does not occur in ion configurations since the valence (*outermost n*) electrons are the first to go! THE SHELL ENERGY RANGES SEPARATE MORE WIDELY AS ELECTRONS ARE REMOVED.

- Atoms and ions with unpaired electrons are paramagnetic (attracted to a magnetic field)
- Transition metals with +2 or higher have no ns electrons
- Fe^{+2} is paramagnetic to the extent of 4 unpaired electrons and Fe^{+3} is paramagnetic to the extent of 5 unpaired electrons

THE HISTORY OF THE PERIODIC TABLE

1800ish—Johann Dobereiner, triads; 1864 John Newlands octaves; 1870--Dmitrii Mendeleev & Julius Lothar Meyer--by mass; 1913 Mosley--by number of protons.

TABELLE II								
REIHE	GRUPPE I R10	GRUPPE II R0	GRUPPE III R103	GRUPPE IV RH4 R07	GRUPPE V RH5 R105	GRUPPE VI RH2 R03	GRUPPE VII RH R107	GRUPPE VIII R04
1	H1							
2	Li = 7	Be = 9,4	B = 11	C = 12	N = 14	O = 16	F = 19	
3	Na = 23	Mg = 24	Al = 27,3	Si = 28	P = 31	S = 32	Cl = 35,5	
4	K = 39	Ca = 40	— 44	Ti = 48	V = 51	Cr = 52	Mn = 55	
5	[Cu = 63]	Zn = 65	— 68	— 72	As = 75	Se = 78	Br = 80	
6	Rb = 85	Sr = 87	Yt = 88	Zr = 90	Nb = 94	Mo = 96	— 100	
7	[Ag = 108]	Cd = 112	In = 113	Sn = 118	Sb = 122	Te = 125	J = 127	
8	Cs = 133	Ba = 137	La = 138	Ce = 140	—	—	—	
9	[—]							
10			Pr = 139	La = 138	Ta = 182	W = 184		
11	[Au = 198]	Hg = 200	Tl = 204	Pb = 207	Bi = 208			
12				Th = 231		U = 240		



- Group IA(1A or 1)--alkali metals
- Group IIA(2A or 2)--alkaline earth metals
- Group VIA(6A or 16)--Chalcogens
- Group VIIA(7A or 17)—Halogens
- Group VIIIA (8A or 18)—Noble gas

1											18						
1	2											18					
3	4											10					
11	12											18					
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72
87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104
Fr	Ra	Ac ⁺	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub						

SOME PROPERTIES OF COMMON GROUPS:

- Alkali metals—the most reactive metal family; must be stored under oil; react with water violently!
- Alkaline-earth metals-- except for Be(OH)₂, the metal hydroxides formed by this group provide basic solutions in water ; pastes of these used in batteries
- Chalcogen family – many found combined with metal ores
- Halogen family – known as the “salt-formers” ; used in modern lighting
- Noble Gas family – known for their disinterest in other elements; once thought to never react; neon used to make bright RED signs
- Transition metals—fill the d orbitals.
 - Anomalies occur at Chromium and Copper to *minimize electron/electron repulsions*. If you learned that there is special stability associated with a half-filled sub-level, IT’S A LIE!! No such stability exists! NEVER, EVER write that! It’s all about lowering energy by minimizing electron/electron repulsions.

*Lanthanide series													
58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
**Actinide series													
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
4s ¹	4s ²	3d ¹	3d ²	3d ³	4s ¹ 3d ⁵	3d ⁵	3d ⁶	3d ⁷	3d ⁸	4s ¹ 3d ¹⁰	3d ¹⁰	4p ¹	4p ²	4p ³	4p ⁴	4p ⁵	4p ⁶

- Rare Earth metals—fill the f sublevels. Lanthanides and Actinides. These sometimes put an electron in d [just one or two electrons] before filling f . This is that dsf overlay referred to earlier—the energies of the sublevels are very similar.

PERIODIC TRENDS:
 A trend is **NOT** an
 EXPLANATION!

The diagram shows a periodic table with sublevels labeled: 1s, 2s, 3s, 4s, 5s, 6s, 7s, 3d, 4d, 5d, 6d, 4f, 5f, 2p, 3p, 4p, 5p, 6p. Groups are labeled 1A, 2A, 3A, 4A, 5A, 6A, 7A, 8A. The lanthanide (La) and actinide (Ac) series are shown below the main table, with arrows indicating their placement between the 6s and 7s sublevels.

This is an important section—there is almost always an essay involving this topic on the AP exam. There are several arguments you will evoke to EXPLAIN a periodic trend. Remember opposites attract and likes repel. The trick is learning **which argument to use when** explaining a certain trend!

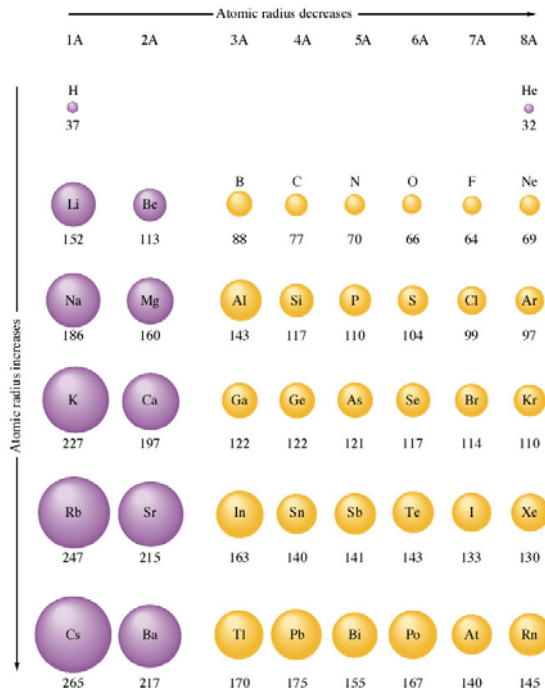
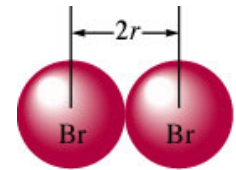
THE ARGUMENTS:

1. Effective nuclear charge, Z_{eff} —essentially equal to the group number. Think of the IA's having a Z_{eff} of one while the VII A's have a Z_{eff} of 7! The idea is that the higher the Z_{eff} , the more positive the nucleus, the more attractive force there is emanating from the nucleus drawing electrons in or holding them in place. Relate this to ENERGY whenever possible.
2. Distance—attractive forces dissipate with increased distance. Distant electrons are held loosely and thus easily removed. Relate this to ENERGY whenever possible.
3. Shielding—electrons in the “core” effectively shield the nucleus’ attractive force for the valence electrons. Use this ONLY when going up and down the table, NOT across. There is ineffective shielding within a sublevel or energy level. Relate this to ENERGY whenever possible. {I can’t help but think of dodge ball, such a barbaric ritual—since you’re the smart kids, you figured out in elementary school to stay behind the bigger kids to keep from getting hit! The electrons in the first or second energy level, shield the outer valence electrons from the Mother Nucleus’ attractive force. }
4. Minimize electron/electron repulsions—this puts the atom at a lower energy state and makes it more stable. Relate this to ENERGY whenever possible.

Here we go!

1. ATOMIC RADIUS--No sharp boundary beyond which the electron never strays!!

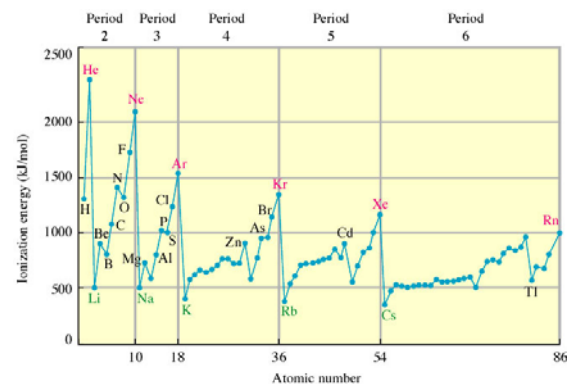
- Use diatomic molecules and determine radius then react with other atoms to determine the radius of those atoms
- ATOMIC radii decreases (↓) moving across a period AND increases (↑) moving down a row (family)



- WHY ↓ **across**? The effective nuclear charge (Z_{eff}) increases (more protons for the same number of energy levels) as we move from left to right across the periodic table, so the nucleus has a greater positive charge, thus the entire electron cloud is more strongly attracted and “shrinks”.
 - This shrinks the electron cloud *until*...
 - ...the point at which electron/electron repulsions overcome the nuclear attraction and stop the contraction of the electron cloud.
- WHY ↑ **down**? The principal level, n , determines the size of an atom—add another principal level and the atoms get MUCH larger radii
- As we move down a family, the attractive force the nucleus exerts on the valence electrons dissipates.
- Shielding is only a valid argument when comparing elements from period to period (up and down the table) since shielding is incomplete *within* a period—use this argument with extreme caution! It should NOT be your favorite!

2. IONIZATION ENERGY--energy required to remove an electron from the atom IN THE GAS PHASE. Costs Energy.

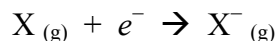
- Removing each subsequent electron requires more energy: Second IE, Third IE, etc.
- Some subsequent IEs cost more E than others!! A **HUGE** energy price is paid if the subsequent removal of electrons is from another sublevel or, Heaven forbid, another principal E level (core).
 - ↓ down a family—increased distance from the nucleus and increased shielding by full principal E levels means it requires less E to remove an electron
 - ↑ across a period—due to increasing Z_{eff} . The higher the Z_{eff} , the stronger the nucleus attracts valence electrons, the more energy required to remove a valence electron. Let's talk EXCEPTIONS!!



	1A	2A	3A	4A	5A	6A	7A	8A
1	H 1311							He 2377
2	Li 520	Be 899						Ne 2088
3	Na 495	Mg 735						Ar 1527
4	K 419	Ca 590						Kr 1356
5	Rb 409	Sr 549						Xe 1176
6	Cs 382	Ba 503						Rn 1042
			B 800	C 1086	N 1402	O 1314	F 1681	
			Al 580	Si 780	P 1060	S 1005	Cl 1255	
			Ga 579	Ge 761	As 947	Se 941	Br 1143	
			In 558	Sn 708	Sb 834	Te 869	I 1009	
			Tl 589	Pb 715	Bi 703	Po 813	At (926)	

- an anomaly occurs at “messing up a half-filled or filled sublevel” There’s nothing magical about this and electrons are not “happier” as a result. The simple truth is that when electron pairing first occurs within an orbital, there is an increase in electron/electron repulsions which makes it require less energy [easier] to remove an electron thus the IE drops. NEVER, EVER write about the fictitious stability of a $\frac{1}{2}$ -filled shell—even though you may see it in books!
- Look at oxygen vs. nitrogen—it requires less energy to remove an electron from oxygen’s valence IN SPITE OF AN INCREASING Z_{eff} because oxygen’s p^4 electron is the first to pair within the orbital thus experiencing increased repulsion. The increased repulsion lowers the amount of energy required to remove the newly paired electron!
- Also, look at the drop in IE from any s^2 to p^1 . This is also IN SPITE OF AN INCREASING Z_{eff} . This drop in the energy required to remove a valence electron is due to the fact that you are removing a p electron rather than an s electron. The p ’s are less tightly held BECAUSE they do not penetrate the electron cloud toward the nucleus as well as an s electron. The general trend is that s is held most tightly since it penetrates more than p , d and f ...

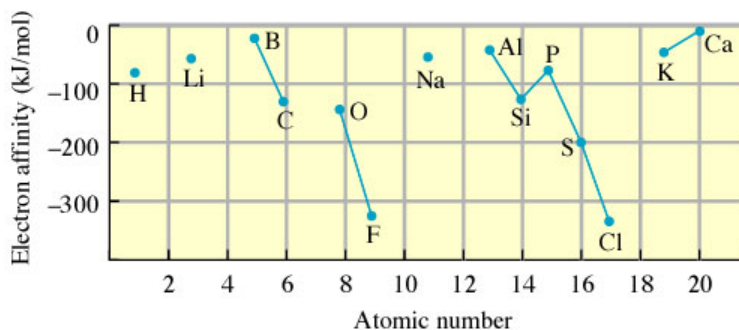
3. ELECTRON AFFINITY—an affinity or “liking” for electrons—force feeding an element an electron—Energy associated with the addition of an electron to a gaseous atom:



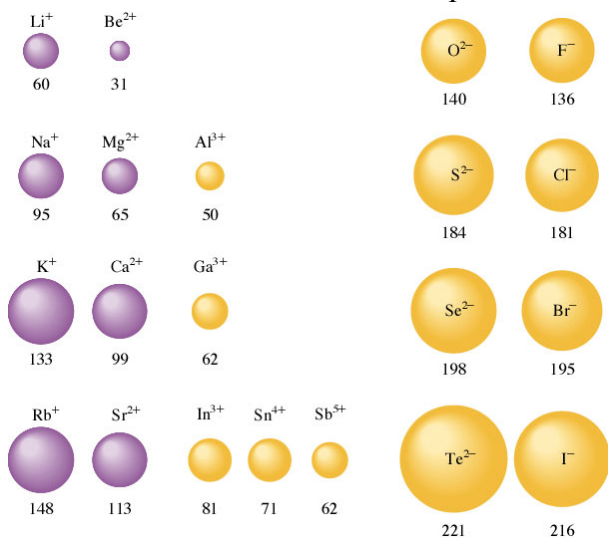
If the addition of an electron is exothermic, then you’ll see a negative sign on the energy change and the converse is also true. The more negative the quantity, the more E is released. This matches our sign convention in thermodynamics.

- ↓ down a family [that means becomes less negative a.k.a. more positive, giving off less energy]—due to increased distance from the nucleus with each increasing principal E level. The nucleus is farther from the valence level and more shielded.
- ↑ across a period [that means become more negative, giving off more energy]—Again the increasing Z_{eff} more strongly attracts the electron. The interactions of electron/electron repulsions wrecks havoc with this generalization as we shall soon see!

- Let's talk EXCEPTIONS!! First the lines on the diagram below connect adjacent elements. The absence of a line indicates missing elements whose atoms do not add an electron exothermically and thus do not form stable isolated anions [remember these are all -1 ions at this point].



- an anomaly—No N^- yet there is a C^- --this is due to their electron/electron repulsions compared to their electron configurations. N is p^3 while C is p^2 . C adds an electron WITHOUT PAIRING which does NOT increase the e^-/e^- repulsions and therefore, carbon forms a stable -1 ion while N would have to pair p electrons and the increased e^-/e^- repulsions overcome the increasing attractive force due to the increase in Z_{eff} and no -1 N ion forms! [horrid sentence structure!]
- O^{2-} doesn't exist in isolated form [gasp] for the same reason. It's p^4 , so adding the first electron causes a subsequent pairing BUT it has a greater Z_{eff} than N, so it can form O^- . BUT adding the second electron fills the p 's and that increased e^-/e^- repulsion overpowers the Z_{eff} of oxygen. Never fear, oxide ions exist in plenty of compounds so we haven't exactly been lying to you!
- F is weird, it has really strong e^-/e^- repulsion since the p orbitals are really small in the second level therefore repulsions are high. In subsequent halogen orbitals, it's not as noticeable.



4. IONIC RADII

- Cations**—shrink big time since the nucleus is now attracting fewer electrons
- Anions**—expand since the nucleus is now attracting MORE electrons than there are protons AND there is enhanced electron/electron repulsion to boot.
- Isoelectronic**—ions containing the same number of electrons
 - consider the # of protons to determine size. Oxide vs. Fluoride. Fluoride has one more proton which further attracts the electron cloud, so it is smaller.

Exercise 9**Ionization Energies**

Consider atoms with the following electron configurations:

- a. $1s^2 2s^2 2p^6$
- b. $1s^2 2s^2 2p^6 3s^1$
- c. $1s^2 2s^2 2p^6 3s^2$

Identify each atom. Which atom has the largest first ionization energy, and which one has the smallest second ionization energy? Explain your choices.

A: Ne; largest IE
B: Na
C: Mg; smallest IE₂

Exercise 10**Trends in Radii**

Predict the trend in radius for the following ions: Be^{2+} , Mg^{2+} , Ca^{2+} , and Sr^{2+} .

$\text{Be}^{2+} < \text{Mg}^{2+} < \text{Ca}^{2+} < \text{Sr}^{2+}$