Atomic Theory and the Periodic Table

- Petrucci, Harwood and Herring: Chapters 8 and 9
- Aims:
  - To examine the Quantum Theory,
  - to understand the electronic structure of elements,
  - To explain the periodic table
  - To explain atomic properties

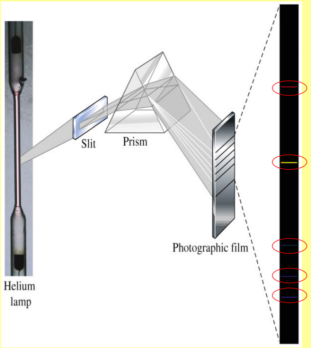
Atomic Theory and the Periodic Table

- Assumed knowledge:
  - electromagnetic radiation, frequency, wavelength, … (section 8-1)
  - introductory atomic structure (sections 2-1 to 2-6)
  - Bohr atom (section 8-4: will do some review in class)

Bohr Atom

- Observations led to the development of the Bohr model for the atom:
- In particular:
  - The spectra of atomic absorption and emission are line spectra, not continua. Atoms can only emit and absorb certain frequencies
  - Understanding black body radiation needed the ideas of quantization of energy levels (Planck)
  - Understanding some of the properties of light needed a quantum theory. (e.g. photoelectric effect)

- Emission from an atomic lamp only gives discrete wavelengths
- The energy released comes from electrons changing energy states
- This suggests the electrons can only have particular energy states



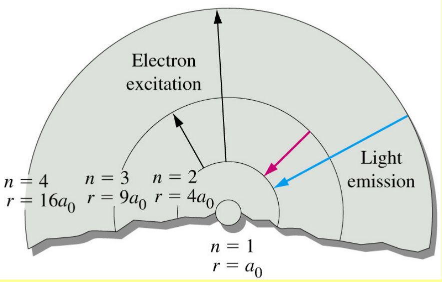
Bohr Atom

- The fundamental principles of the Bohr model of the atom are:
  - The electron moves in circular orbits around the nucleus
  - The electron has fixed orbits.
    - The electron has constant energy and no energy is emitted
  - An electron can only go from one allowed orbit to another

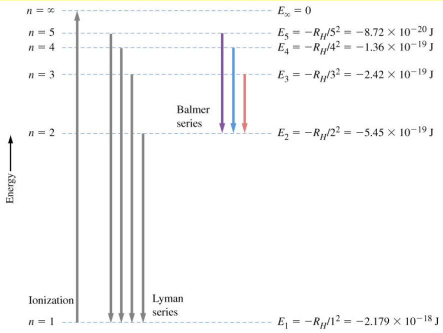
Bohr Atom

- Quantitatively
  - The radius of an orbit is $r_n=n^2a_0$
    Where n= 1,2,3,… and a_0= 53pm (determined by assuming the angular momentum is quantized in units of $h/2\pi$)
  - The electron energy in an orbit is less than if it was free and $E=-R_H/n^2$
    Where R_H= 2.179 x 10^{-18} J

Bohr Atom in space



Bohr atom in energy



Bohr atom

- This was very successful as it predicted the energy of the transitions in a hydrogen atom

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

So what’s wrong with the Bohr Model?

- Cannot explain emission spectra from multi-electron atoms
- Cannot explain the effect of magnetic fields on spectra
- No reason for the fixed, quantized orbits

Quantum Mechanics

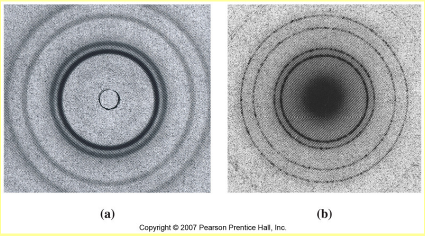
- The most important idea is that of wave-particle duality i.e. small particles display wave-like properties
  - Einstein had said light was a wave but to explain some results it has particle like properties.
  - de Broglie formulated the reverse, the wave-particle duality. Particles can display wave type properties.

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

Example of a particle having wave properties

X-rays diffracted by a metal foil

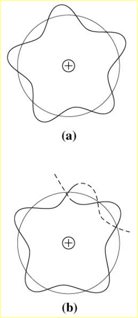
Electrons diffracted by a metal foil



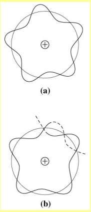
Wave Mechanics

- Wave mechanics is the description of electrons (in an atom), where the electron is considered to be a wave rather than a particle.
- The first point we need to remember is that waves can interfere.

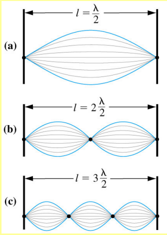
Wave Mechanics



- Think about a wave (electron) around a nucleus. (In 2-D)
- The upper wave is reasonable, the lower is not. In the lower the parts of the wave will interfere and the wave will not survive.
- Hence only standing waves make sense



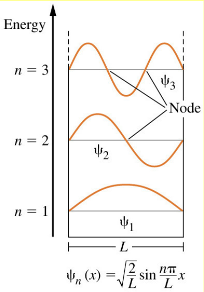
Standing Waves



- In both cases only particular wavelengths are stable.
- Each wavelength has a particular energy so only discrete energies are possible.

Describing the Wave

- Each wave can be described by a wave function Ψ.
  - The example is an electron in a 1-D box.
  - Ψ gives the amplitude of the wave as a function of position.
  - Note the quantum number *n=1,2,3,…*



$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x$

The wave functions

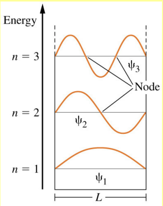
Describing the Wave

Ψ is the wave function, but this has no physical meaning (i.e. we cannot relate it to anything we can measure)

However, Ψ^2 corresponds to the electron charge density (or in terms of a particle: the probability of finding an electron in a small volume of space).

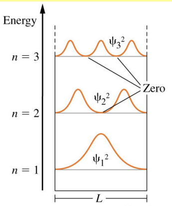
We want to know about the location of the electron so we examine Ψ^2.

The Wave Function and the Electron Charge Density



$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x$

The wave functions



$\psi_n^2(x) = \frac{2}{L} \sin^2 \left(\frac{n\pi}{L} x\right)$

The probabilities

Hydrogen Atom

- The behaviour of the electron in the hydrogen atom is described by Schödinger’s equation. This is a 3-D wave equation for the electron subjected to the attractive force between the nucleus and the electron.

- Solving Schödinger’s equation yields a set of wave functions (orbitals) for the electron.

- The solution also yields the energy associated with each of these wave functions.

Hydrogen Atom

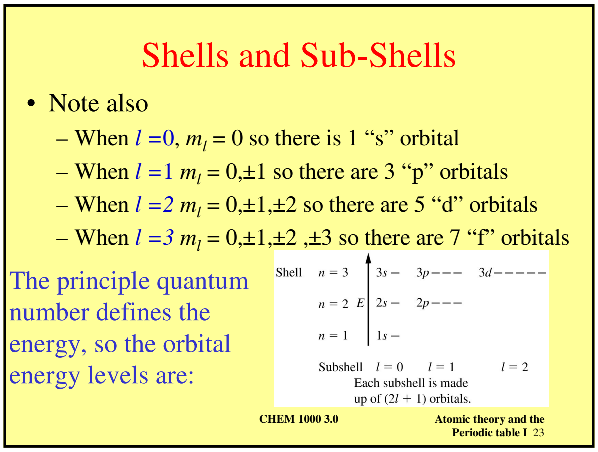
- The solutions for the hydrogen atom include 3 quantum numbers. A set of these three numbers defines the wave function.
- There are constraints on the quantum numbers, again from the solution to the Schödinger equation.

Definitions of Quantum Numbers and Constraints

- Principal quantum number n
  - $n = 1, 2, 3, \ldots$
  - (relates to energy and most probable distance of an electron from the nucleus)
- Orbital angular momentum quantum number l
  - $l = 0, 1, 2, \ldots (n-1)$
  - (relates to shape of the orbital)
- Magnetic quantum number m_l
  - $m_l = -l, -l+1, -l+2, \ldots 0 \ldots l-2, l-1, l$
  - (relates to orientation of the orbital)

Shells and Sub-Shells

- We use a shorthand to describe the orbitals
  - *n* defines the principal electronic shell and we keep the number.
  - Within each principal shell there are other possible sub-shells (as *l* varies)
    - When $l = 0$ we call the subshell s
    - When $l = 1$ we call the subshell p
    - When $l = 2$ we call the subshell d
    - When $l = 3$ we call the subshell f

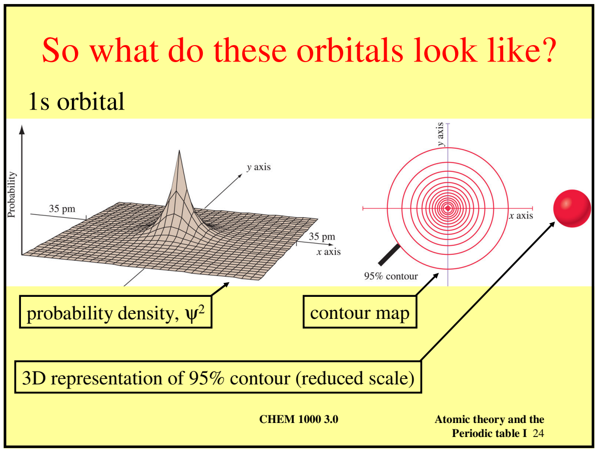


Shells and Sub-Shells

- Note also
  - When $l = 0$, $m_l = 0$ so there is 1 “s” orbital
  - When $l = 1$ $m_l = 0,\pm1$ so there are 3 “p” orbitals
  - When $l = 2$ $m_l = 0,\pm1,\pm2$ so there are 5 “d” orbitals
  - When $l = 3$ $m_l = 0,\pm1,\pm2,\pm3$ so there are 7 “f” orbitals

The principle quantum number defines the energy, so the orbital energy levels are:

Each subshell is made up of $(2l + 1)$ orbitals.



So what do these orbitals look like?

1s orbital

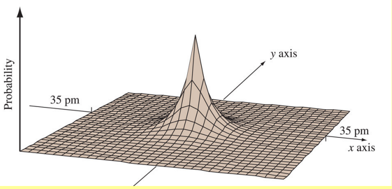
probability density, ψ^2

contour map

3D representation of 95% contour (reduced scale)

How Does This Model Fit With the Bohr Atom?

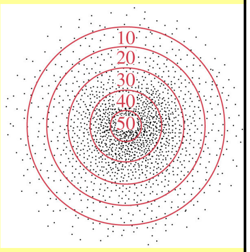
- We need to look at the electron density a bit differently.



- This picture gives the electron density at a point. What we want is the electron density in a shell of constant distance from the nucleus, that is, we need to consider a 3D region of space.

How Does This Model Fit With the Bohr Atom?

- Analogy with the dart board
  - In the centre the density of hits is high
  - In a ring around the centre (say the 30) the density is lower but the area is larger so the number of hits within a ring is higher
  - For hydrogen the electron density is also high in the centre



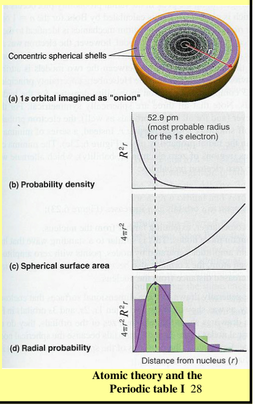
How Does This Model Fit With the Bohr Atom?

- To get the radius corrected number of hits on the dart board for a 3D orbital we need to multiply the hit density by the distance from the centre (i.e. the radius).
- To get the radius corrected electron density in hydrogen we need to multiply the electron density at a particular radius by the surface area of a spherical shell at that radius.

e.g. 1s orbital

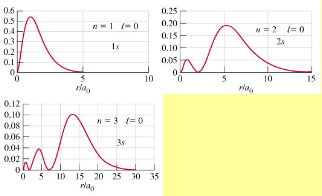
$$\psi(1s) = R(r) \times Y(\theta,\phi) = \frac{2e^{-r/a_0}}{{a_0}^{3/2}} \times \frac{1}{\sqrt{4\pi}} = \frac{e^{-r/a_0}}{\sqrt{(\pi a_0^3)}}$$

- The wave function, ψ, consists of a radial component, $R(r)$, and an angular component, $Y(\theta,\varphi)$.
- The surface area of a sphere with radius r is $4\pi r^2$.
- The radial probability is therefore given by $4\pi r^2 R^2(r)$.

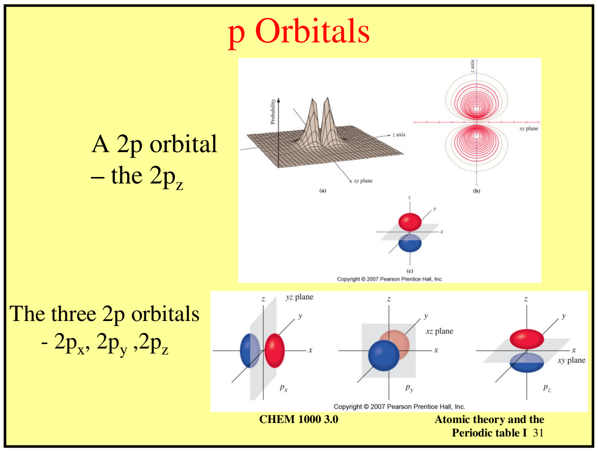


Radial Probability Distributions

- These are radial probability distributions for “s” orbitals.
- Note for the 1s orbital the maximum is at a_0 the Bohr radius
- The distance of the maximum from the nucleus increases with n (although not as n^2)



Back to:
So what do these orbitals look like?



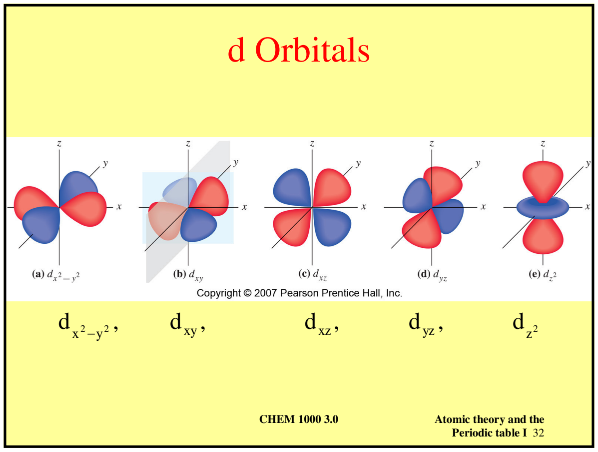
p Orbitals

A 2p orbital
– the $2p_z$

Copyright © 2007 Pearson Prentice Hall, Inc.

The three 2p orbitals
- $2p_x$, $2p_y$,$2p_z$

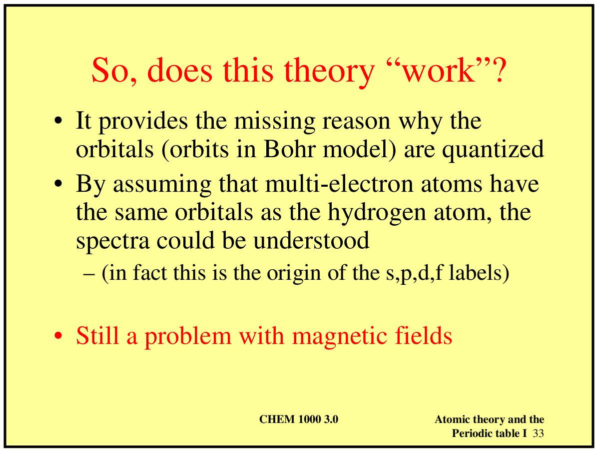
Copyright © 2007 Pearson Prentice Hall, Inc.



d Orbitals

Copyright © 2007 Pearson Prentice Hall, Inc.

$d_{x^2-y^2}$, d_{xy} , d_{xz} , d_{yz} , d_{z^2}



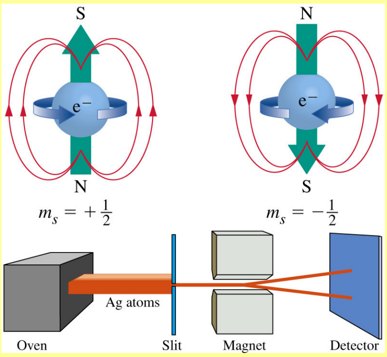
So, does this theory “work”?

- It provides the missing reason why the orbitals (orbits in Bohr model) are quantized
- By assuming that multi-electron atoms have the same orbitals as the hydrogen atom, the spectra could be understood
  - (in fact this is the origin of the s,p,d,f labels)
- Still a problem with magnetic fields

Electron spin

- For atoms with an odd number of electrons, the atom experiences a force when placed in a magnetic field.
  - This is best explained using the particle nature of the electron if the electron can spin. This spin induces a magnetic field.
  - The spin is described by an additional electron spin quantum number m_s with values of +½ or -½
  - For 2 electrons of opposing spin the net field is zero

Electron spin



Electronic States

- The electronic state of an atom is usually represented by the principal quantum number *(n),* the letter associated with the angular momentum quantum number (s,p,d..), and the number of electrons in the orbital.
- For hydrogen we can have states such as $1s^1$, $2p^1$, $3s^1$.

Multielectron Atoms

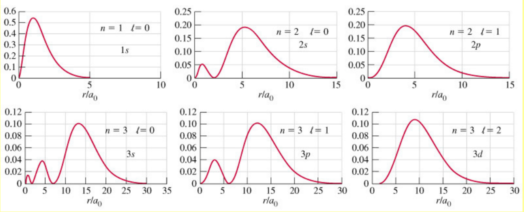
- Schrödinger's equation for a multi-electron atom has the additional terms for the repulsion between electrons. This prevents an exact solution.
- One way around the problem is to consider one electron at a time, in an environment established by the nucleus and the other electrons.
- This then looks like a "big" hydrogen atom where the outer electron sees a "nucleus" that includes the nuclear charge, shielded (screened) by the other electrons.

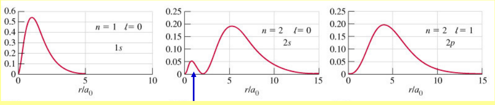
Multielectron Atoms

- Solving the Schrödinger equation for this system gives hydrogen-like orbitals.
  - The same shape
  - Different sizes
- At large distances from the nucleus this works fine, however at close distances we see effects because the shielding is not done by only spherical orbitals

Shielding in Multielectron Atoms

- Return to the radial probability distribution for an electron in an orbital.
  - (The probability multiplied by the surface area at distance r)

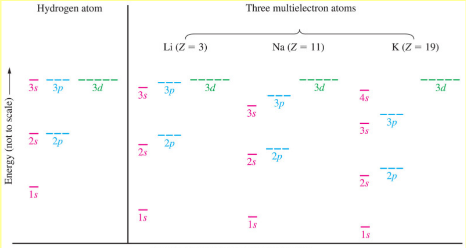




- Compare the 2s and 2p orbitals, assuming the 1s is full
  - The peak in electron density at around a_0 means the 2s orbital can penetrate closer to the nucleus than the 2p
  - The nuclear attraction at the closer distance means the 2s electron is held tighter than the 2p, so the 2s orbital will be at lower energy
  - Also this means that the 2s orbital is less effectively shielded (screened) by the inner orbitals

Multielectron Atoms

The consequence of penetration/shielding is that the s,p,d,f orbitals within a shell (same n) no longer have the same energy.

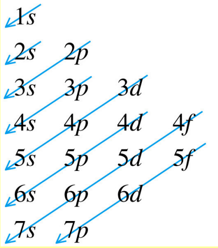


Copyright © 2007 Pearson Prentice Hall, Inc.

Multielectron Atoms

The order of energies up to n=4 is then

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d…



Electron Configuration

- Electron Configuration is the description of how the electrons are distributed through the orbitals.

Rules for Assigning Electrons to Orbitals

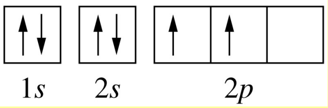
1. Electrons occupy orbitals to minimize the energy of the atom
    - The electrons in the atom fill up from the bottom
2. No two electrons can have the same four quantum numbers
    - Pauli exclusion principle, alternatively-you can only have 2 electrons per orbital and then they must have opposite spin

Rules for Assigning Electrons to Orbitals

3. When orbitals have the same energy, electrons initially occupy them singly.
    - Hunds rule: alternatively
        - an atom tries to have as many unpaired electrons as possible, or
        - it costs energy to pair up electrons

Representing Electron Configurations

- For carbon (6 electrons)
  - $1s^2\ 2s^2\ 2p^2$
- Or more explicitly
  - $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1$
- or



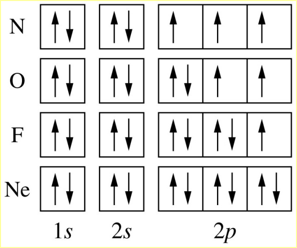
- We are now in a position to describe how electrons are distributed through the available orbitals.
- This is normally thought of as a building process. You put the first electron in the lowest energy orbital, then the next and so on. This is usually called the aufbau process

Aufbau process

- Z=1,H. $1s^1$
- Z=2,He. $1s^2$
- Z=3,Li. $1s^2\ 2s^1$
- Z=4,Be. $1s^2\ 2s^2$
- Z=5,B. $1s^2\ 2s^2\ 2p^1$
- Z=6,C. $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1$
- Z=7,N. $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$

Aufbau process

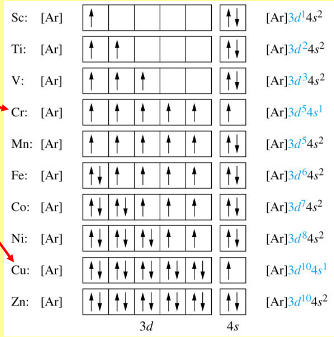
- Z=7-10 N-Ne



Aufbau process

- Z=11-18, this is the same as Z=3-10 but with the 3s and 3p orbitals. End with Ar
- One would expect the 3d orbitals to fill next but remember that 4s is lower
- Z=19,20 fill the 4s orbital
- Z=21-30 fill the 3d orbitals. There are two exceptions where the full and ½ full d orbital is especially stable and you get $4s^1$ not $4s^2$

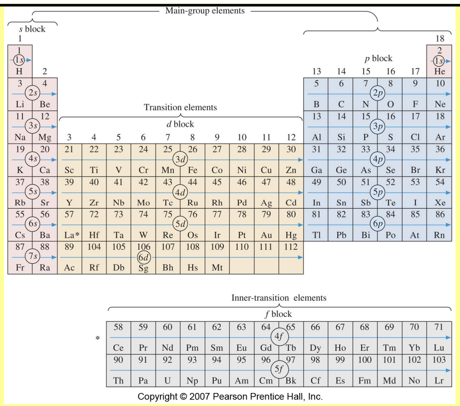
$4s^1$



- Note the nomenclature here: [Ar] shows the Ar shell. The electrons shown are the valence electrons

Periodic Table

- We can now see the electron configuration rationale for the periodic table.



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110	111	112						

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

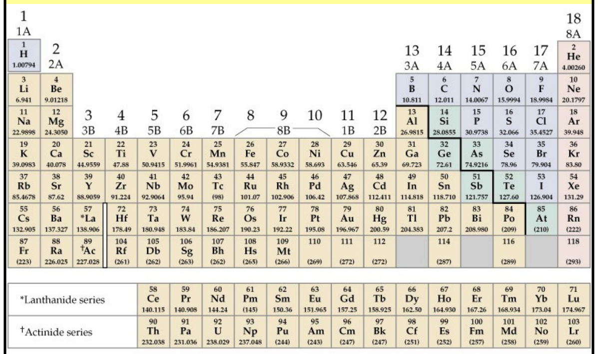
The Periodic Table and Atomic Properties

- The periodic table originally came from the observation that when the elements are arranged by atomic mass, properties recur periodically. (Mendeleev)
- Now we understand the periodic table in terms of atomic number and electronic structure.
- We will look at the properties of elements from this viewpoint.

Metals and Nonmetals

- Metals have the properties:
  - – Good conductors of heat and electricity
  - – Malleable and ductile
  - – High melting points
- Non-metals have the properties:
  - – Poor conductors of heat and electricity
  - – Brittle
  - – Low melting points (some are even gases at room temperature)

Metals and Nonmetals



1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9	10	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 H 1.00794																	2 He 4.00260
3 Li 6.941	4 Be 9.01218											5 B 10.811	6 C 12.011	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.1797
11 Na 22.9898	12 Mg 24.3050											13 Al 26.9815	14 Si 28.0855	15 P 30.9738	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.9559	22 Ti 47.88	23 V 50.9415	24 Cr 51.9961	25 Mn 54.9381	26 Fe 55.847	27 Co 58.9332	28 Ni 58.693	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.906	46 Pd 106.42	47 Ag 107.868	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.757	52 Te 127.60	53 I 126.904	54 Xe 131.29
55 Cs 132.905	56 Ba 137.327	57 *La 138.906	72 Hf 178.49	73 Ta 180.948	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.967	80 Hg 200.59	81 Tl 204.383	82 Pb 207.2	83 Bi 208.980	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.025	89 †Ac 227.028	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 (269)	111 (272)	112 (272)		114 (287)		116 (289)		118 (293)

*Lanthanide series	58 Ce 140.115	59 Pr 140.908	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.965	64 Gd 157.25	65 Tb 158.925	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.967
†Actinide series	90 Th 232.038	91 Pa 231.036	92 U 238.029	93 Np 237.048	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

Metals and Nonmetals

- Non metals:
  - – To the right of the periodic table
  - – Includes the noble (inert) gases as a special case
- Metals
  - – Most elements are metals
- Metalloids
  - – In between metal and non-metals, have some properties of metals and non-metals

Correlations between electronic configuration and properties

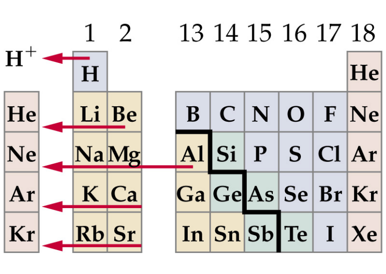
- Noble Gases:
  - All have a full valence shell
  - This gives extreme stability and chemical inertness

- It appears most elements try to achieve this stability by acquiring or losing electrons

Group 1 and 2 metal ions

- These have 1 or 2 electrons more than a Noble gas
  - They can lose these electrons (through reaction for example) to produce very stable ions
  - Aluminum (Group 13) will actually lose 3 electrons to achieve the stable ion

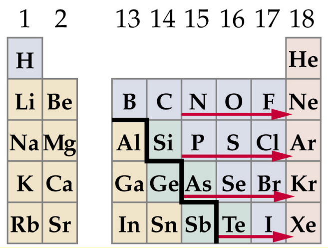
Group 1 and 2 metal ions



Group 16 and 17 non-metal ions

- These have 1 or 2 electrons less than a Noble gas
  - They can gain these electrons (through reaction for example) to produce very stable ions

Group (15),16, and 17 non-metal ions



1	2	13	14	15	16	17	18
H							He
Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar
K	Ca	Ga	Ge	As	Se	Br	Kr
Rb	Sr	In	Sn	Sb	Te	I	Xe

Transition Metal Ions

- The electrons are lost from Transition metals in a different order than the aufbau principle would suggest
  - **They lose the "s" orbital electrons first**
  - Often they also lose "d" orbital electrons to give a half filled "d" subshell which has special stability.
  - e.g Fe $[Ar]3d^6 4s^2$ gives Fe^{3+} $[Ar]3d^5$

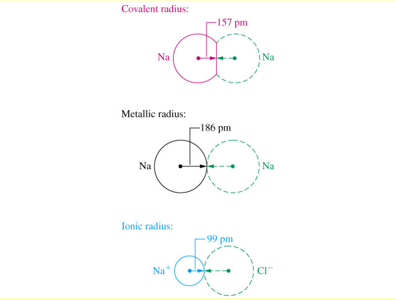
Sizes of Atoms and Ions

- Atomic and ionic radii cannot easily be described as the electron density extends to infinity
- Usually we use the measured distances in compounds to infer sizes, but even these are not all the same

Sizes of Atoms and Ions

- Definitions
  - Covalent radius
    - Half the distance between identical atoms in a covalent compound
  - Ionic radius
    - Determined from separation between ions joined by ionic bonds
  - Metallic Radius
    - Half the distance between metal atoms in crystalline solid

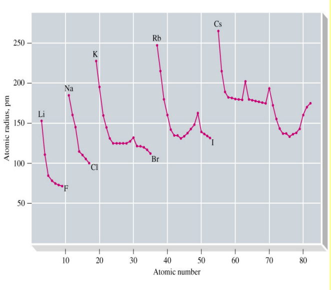
Sizes of Atoms and Ions



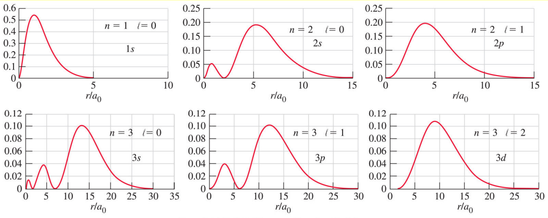
Sizes of Atoms and Ions

Can we explain this variation in radii?

- Down a group radii increase
- Across a period radii decrease
- Transition metal radii don't change much

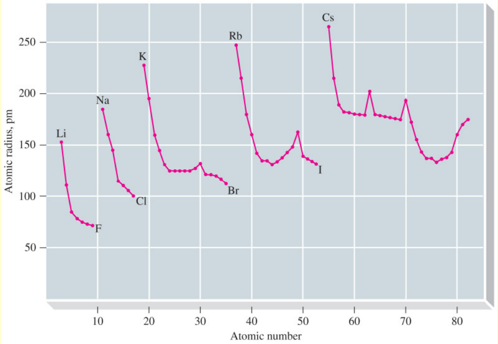


Sizes of Atoms and Ions



- Within (Down) a Group
  - The probability of finding an electron at larger distances is higher for higher n
  - Hence the more electronic shells the larger the atom

Sizes of Atoms and Ions



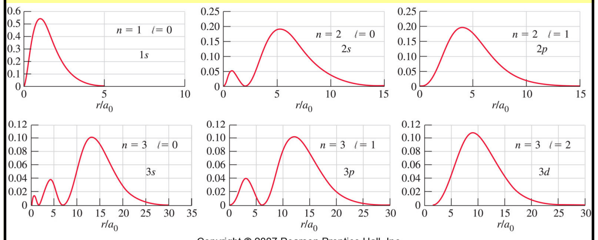
Sizes of Atoms and Ions

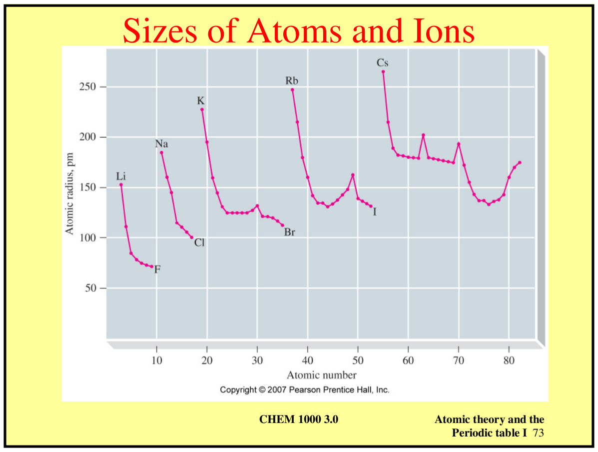
- Across a period
  - – The nuclear charge and the number of electrons increase while the *n* stays the same.
    - Across a period the electrons go into the outer orbitals. The amount of screening is about the same, so successive electrons see higher effective nuclear charges so the radius decreases across a period.

Sizes of Atoms and Ions

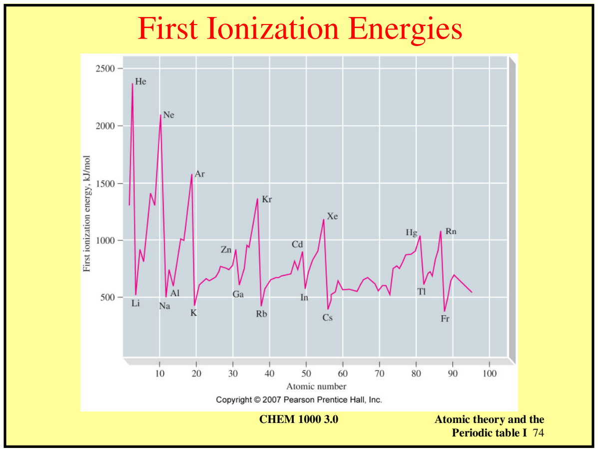
- Across a period (ctd)
  - – The nuclear charge and the number of electrons increase while the *n* stays the same.
    - For transition metals the electrons are going into an INNER shell so the screening is more pronounced. The number of outer shell electrons stays the same. The increase in the nuclear charge is balanced by the increased screening. The outer electrons see the same effective nuclear charge. Since the size is determined by the outer electrons the radius remains similar across a transition metal series

Sizes of Atoms and Ions

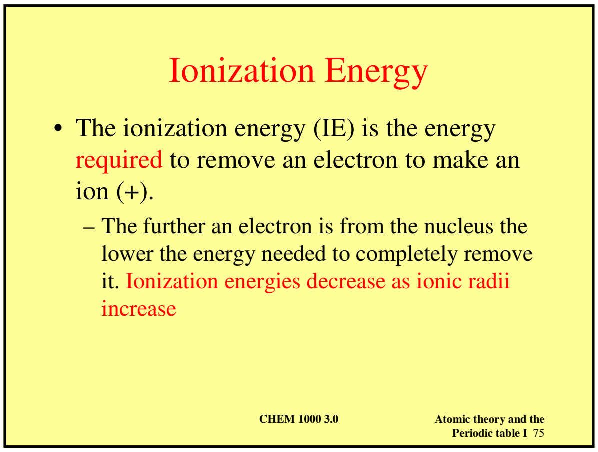




Sizes of Atoms and Ions



First Ionization Energies



Ionization Energy

- The ionization energy (IE) is the energy required to remove an electron to make an ion (+).
  - – The further an electron is from the nucleus the lower the energy needed to completely remove it. Ionization energies decrease as ionic radii increase

Ionization Energy

- The ionization energy (IE) is the energy required to remove an electron to make an ion (+).
  - There are 2nd and 3rd ionization energies to remove successive electrons. Since the ion is smaller than the atom and there is a net charge, the successive IEs are higher

$Mg(g) \rightarrow Mg^{+}(g) + e^{-}$ $I_1 = 738$ kJ mol^{-1}

$Mg^{+}(g) \rightarrow Mg^{2+}(g) + e^{-}$ $I_2 = 1451$ kJ mol^{-1}

Electron Affinity

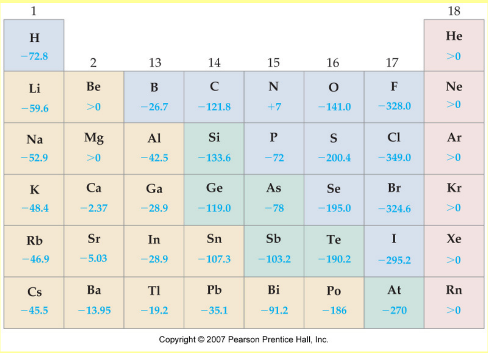
- The electron affinity (EA) is the energy change when an atom gains an electron to make an ion (-).

$F(g) + e^{-} \rightarrow F^{-}(g)$ EA = -328 kJ mol^{-1}

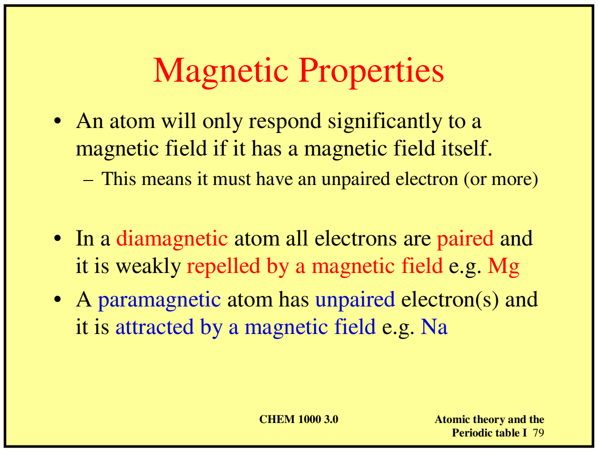
The atom releases energy when it gains the electron

- Atoms that have high EA are those where adding an electron stabilize a shell
  - Group 17 elements gain an electron to fill the shell
  - Group 1 elements gain an electron to fill the “s” orbital

Electron Affinities



1	2	13	14	15	16	17	18
H −72.8							He >0
Li −59.6	Be >0	B −26.7	C −121.8	N +7	O −141.0	F −328.0	Ne >0
Na −52.9	Mg >0	Al −42.5	Si −133.6	P −72	S −200.4	Cl −349.0	Ar >0
K −48.4	Ca −2.37	Ga −28.9	Ge −119.0	As −78	Se −195.0	Br −324.6	Kr >0
Rb −46.9	Sr −5.03	In −28.9	Sn −107.3	Sb −103.2	Te −190.2	I −295.2	Xe >0
Cs −45.5	Ba −13.95	Tl −19.2	Pb −35.1	Bi −91.2	Po −186	At −270	Rn >0



Magnetic Properties

- An atom will only respond significantly to a magnetic field if it has a magnetic field itself.
  - This means it must have an unpaired electron (or more)

- In a diamagnetic atom all electrons are paired and it is weakly repelled by a magnetic field e.g. Mg
- A paramagnetic atom has unpaired electron(s) and it is attracted by a magnetic field e.g. Na