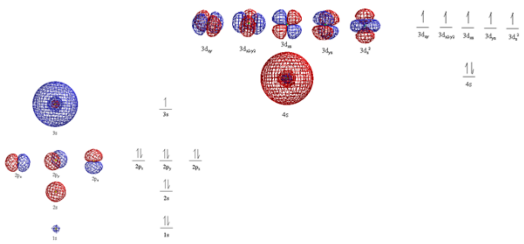
Atomic Electron Configurations and Periodicity

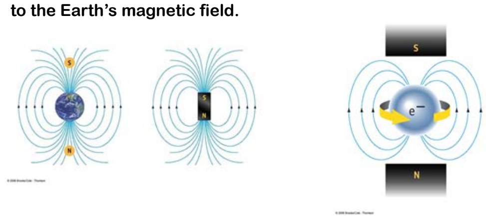


Electron Spin

The 4th quantum number is known as the "spin quantum number" and is designated by m_s. It can have the value of either + ½ or – ½

It roughly translates to refer to the magnetic spin orientation of an electron in an atom (although remember that the electron exists as a wave of probability, not a spinning particle).

The spinning electron has an associated magnetic field similar to the Earth's magnetic field.



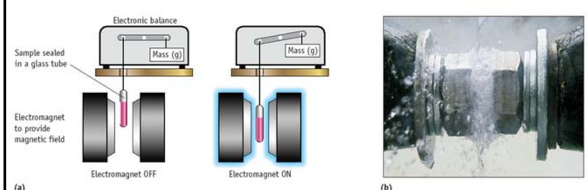
A complete description of an electron in an atom must have four quantum numbers: n, ℓ, m_ℓ, m_s

Pauli Exclusion Principle
No two electrons in an atom can have the same set of four quantum numbers (n, ℓ, m_ℓ, and m_s).
⇓ which leads to
No atomic orbital can contain more than two electrons.

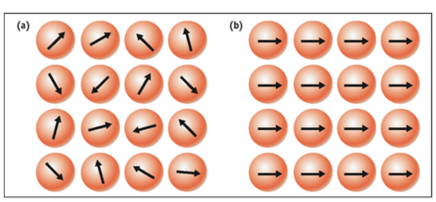
Depending on the arrangement of the electrons in an atom, the atom may be *paramagnetic* or *diamagnetic*.

Paramagnetic atoms tend to be attracted to an external magnetic field. As we will see, these atoms have one or more "unpaired" electrons in the atom.

Diamagnetic atoms are slightly repelled by an external magnetic field.



There is a third type known as ferromagnetic (iron, nickel, cobalt, neodymium, and certain alloys). These substances have permanently aligned electron spins in "domains" of the substance.



Circles represent domains. In a) (paramagnetic), the domains are not aligned until an external magnetic field is present. In b) ferromagnetic, the domains are aligned even in the absence of an external magnetic field.

There are three ways of representing the electrons in an atom.

1. Spectroscopic notation (spdf notation) given by:

$1s^22s^22p^2$, etc.

The leading numbers are the n numbers, the letters are the ℓ numbers and the superscripted number gives the total number of electrons within that suborbital.

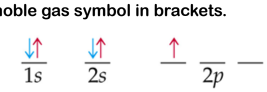
2. Condensed spectroscopic notation given by:

$[Ne]3s^23p^4$

Only the higher energy electrons are explicitly given. The core electrons are represented by the noble gas symbol in brackets.

3. Orbital box diagrams. Given by:

Where the arrows denote m_s



Two other important rules to keep in mind besides the Pauli exclusion principle:

The Aufbau ("building up") principle: Electrons should be filled in using the lowest energy state possible.

Hund's Rule: When filling in electrons in a sublevel (such as the p sublevel), one electron should be placed in each orbital with parallel spin orientations before pairing them up.

Orbital Energy and Electron Accomodation

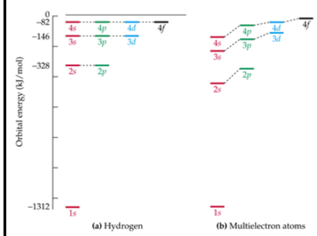
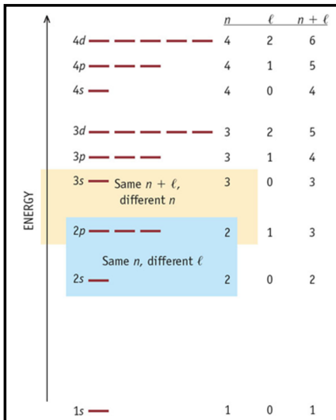
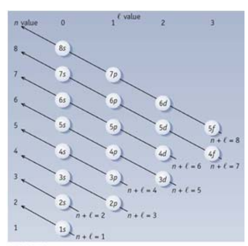


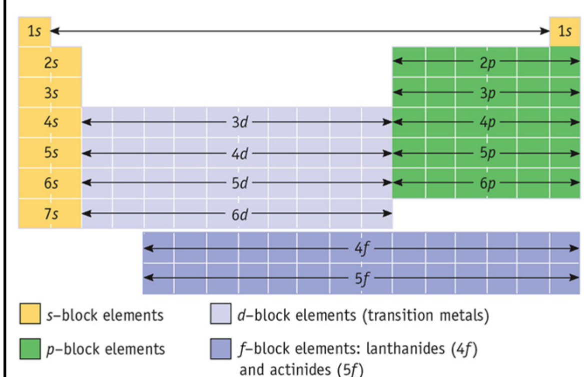
Table 8.1 Number of Electrons Accommodated in Electron Shells and Subshells with $n = 1$ to 6

Electron Shell (n)	Subshells Available	Orbitals Available ($2\ell + 1$)	Number of Electrons Possible in Subshell [$2(2\ell + 1)$]	Maximum Electrons Possible for nth Shell ($2n^2$)
1	s	1	2	2
2	s	1	2	8
	p	3	6	
3	s	1	2	18
	p	3	6	
	d	5	10	
4	s	1	2	32
	p	3	6	
	d	5	10	
	f	7	14	
5	s	1	2	50
	p	3	6	
	d	5	10	
	f	7	14	
	g*	9	18	
6	s	1	2	72
	p	3	6	
	d	5	10	
	f	7	14	
	g*	9	18	
	h*	11	22	





When filling orbitals of the same n+ℓ value, the lower n value is filled first



Orbital Filling

H – $1s^1$

He – $1s^2$

Li – $1s^22s^1$

Be – $1s^22s^2$

B – $1s^22s^22p^1$

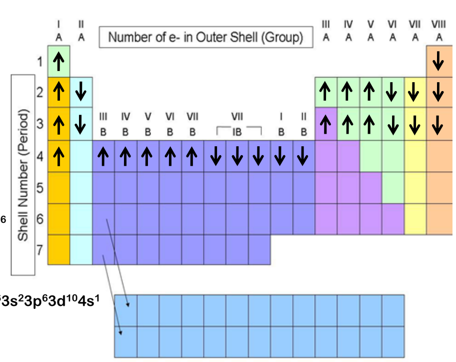
C – $1s^22s^22p^2$

N – $1s^22s^22p^3$

O – $1s^22s^22p^4$

F – $1s^22s^22p^5$

Ne – $1s^22s^22p^6$



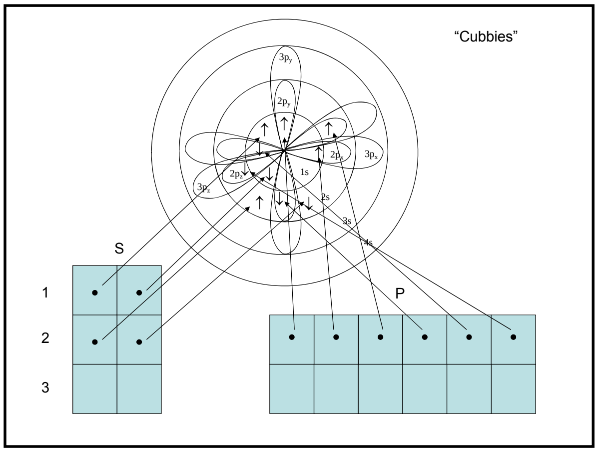
Cu – $1s^22s^22p^63s^23p^63d^{10}4s^1$

Exceptions to the Aufbau principle

Note Cr and Cu

Table 8.4 Orbital Box Diagrams for the Elements Ca Through Zn

		3d	4s
Ca	$[Ar]4s^2$	[ ][ ][ ][ ][ ]	[↑↓]
Sc	$[Ar]3d^14s^2$	[↑][ ][ ][ ][ ]	[↑↓]
Ti	$[Ar]3d^24s^2$	[↑][↑][ ][ ][ ]	[↑↓]
V	$[Ar]3d^34s^2$	[↑][↑][↑][ ][ ]	[↑↓]
Cr*	$[Ar]3d^54s^1$	[↑][↑][↑][↑][↑]	[↑]
Mn	$[Ar]3d^54s^2$	[↑][↑][↑][↑][↑]	[↑↓]
Fe	$[Ar]3d^64s^2$	[↑↓][↑][↑][↑][↑]	[↑↓]
Co	$[Ar]3d^74s^2$	[↑↓][↑↓][↑][↑][↑]	[↑↓]
Ni	$[Ar]3d^84s^2$	[↑↓][↑↓][↑↓][↑][↑]	[↑↓]
Cu*	$[Ar]3d^{10}4s^1$	[↑↓][↑↓][↑↓][↑↓][↑↓]	[↑]
Zn	$[Ar]3d^{10}4s^2$	[↑↓][↑↓][↑↓][↑↓][↑↓]	[↑↓]



Example:

Give the proper spectroscopic, condensed spectroscopic and orbital box notations for the following elements:

Oxygen, Gallium and Calcium

Predict whether each is expected to be paramagnetic or diamagnetic.

Oxygen
$1s^2 2s^2 2p^4$ $[He]2s^2 2p^4$ [↑↓] [↑↓] [↑↓][↑][↑] paramagnetic
1s 2s 2p

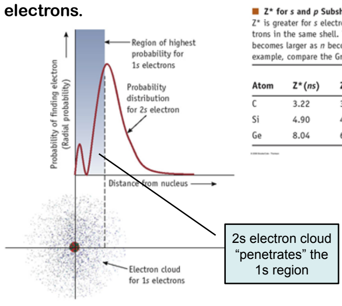
Gallium
$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^1$
$[Ar]\ 3d^{10} 4s^2 4p^1$
[↑↓] [↑↓] [↑↓][↑↓][↑↓] [↑↓] [↑↓][↑↓][↑↓] [↑↓] [↑↓][↑↓][↑↓][↑↓][↑↓] [↑][ ][ ]
1s 2s 2p 3s 3p 4s 3d 4p
paramagnetic

Calcium
$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
$[Ar]4s^2$
[↑↓] [↑↓] [↑↓][↑↓][↑↓] [↑↓] [↑↓][↑↓][↑↓] [↑↓]
1s 2s 2p 3s 3p 4s diamagnetic

Effective Nuclear Charge Z*:

How much positive charge from the nucleus does an electron actually see?

Depends on the distance from the nucleus and shielding from other electrons.



Z* for s and p Subshells
Z* is greater for s electrons than for p electrons in the same shell. This difference becomes larger as n becomes larger. For example, compare the Group 4A elements.

Atom	Z*(ns)	Z*(np)	Value of n
C	3.22	3.14	2
Si	4.90	4.29	3
Ge	8.04	6.78	4

Nuclear charge increases as the number of protons in the nucleus increases but not as much as expected because of shielding

Table 8.2 Effective Nuclear Charges, Z*, for n = 2 Elements

Atom	Z*(2s)	Z*(2p)
Li	1.28	
B	2.58	2.42
C	3.22	3.14
N	3.85	3.83
O	4.49	4.45
F	5.13	5.10

Electron Configurations of Ions

When cations are formed, electrons are removed from the highest n number first.

Ex. The ground state electron configuration for zinc is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$.
When it becomes a 2+ ion, the electrons are removed from the 4s sublevel to become $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$.

All common transition metal *cations* have electron configurations of the general type [noble gas core]$(n-1)d^x$.
In the process of ionization, the ns electrons are lost first.

The paramagnetic properties of transition metal ions can provide clues as to which sublevel the electrons are removed from.

Example:

Depict the electron configurations for V^{2+}, V^{3+}, and Co^{3+}. Use orbital box diagrams and noble gas notation. Are any of the ions paramagnetic? If so, give the number of unpaired electrons.

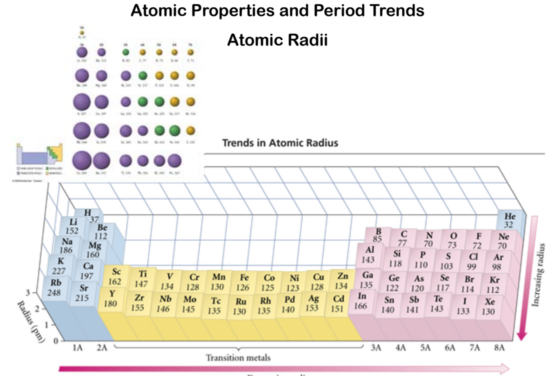
V^{2+}
$[Ar]3d^3$ [Ar] [↑][↑][↑][ ][ ] paramagnetic, 3 unpaired
3d

V^{3+}
$[Ar]3d^2$ [Ar] [↑][↑][ ][ ][ ] paramagnetic, 2 unpaired
3d

Co^{3+}
$[Ar]3d^6$ [Ar] [↑↓][↑][↑][↑][↑] paramagnetic, 4 unpaired
3d

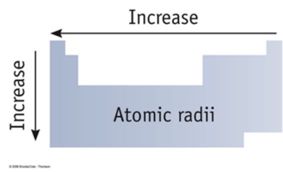
Atomic Properties and Period Trends

Atomic Radii



The trend for the sizes of the atoms on the periodic table is influenced by two factors:

a. As you work your way across a row (period) on the periodic table you are filling up electrons within the same principal energy level, which means that the electrons are all being added to approximately the same distance away from the nucleus. As this is occurring, each successive element is also adding more positively charged protons to the nucleus, thus increasing the force on each electron. The combined effect causes the electrons to be pulled closer to the nucleus as you move across the row and the radius gets smaller.



b. As you work your way down a column (group or family), the principal energy level is increasing for each successive element. This means that the average distance from the nucleus is also increasing. This is similar to the different layers of an onion. Also, there are more core electrons (electrons between the valence electrons and the nucleus) causing the repulsion on the outer electrons to be greater and the pull from the nucleus to be weaker. These combined effects cause the radius to increase as you move down the group.

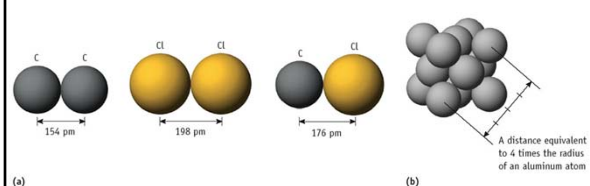
In summary, although there are some exceptions, the general rule for atomic radii is that:

The atomic radii of the elements decrease as you go right and up on the periodic table.

Generally speaking, a jump up or down on the periodic table has a larger effect on the atomic radii that a jump to the left or right.

a) Using ½ the internuclear distance between atoms in a diatomic molecule allows approximate atomic radii to be determined.

b) Knowing the arrangement of atoms in a metallic crystal allows determination of the radii of metals.



Ionization Energy: The energy required to remove an electron from an atom in the gas phase.

$$\text{Atom in ground state}_{(g)} \rightarrow \text{Atom}^{+}_{(g)} + e^{-}$$

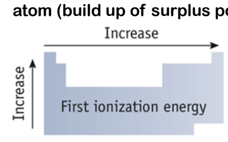
$$\Delta E = \text{ionization energy, IE}$$

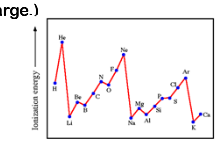
All ionization energies are endothermic.

It is more difficult (i.e. higher ionization energy) to remove electrons from stable and semi-stable electron configured atoms.

Such As:

Filled Sublevel, half-filled sublevel or noble gas configuration. Also IE increases for each successive electron removed from an atom (build up of surplus positive charge.)





Electron Affinity (EA): The energy involved in the process of an atom (in its gas phase) gaining an electron. Values range from 0 (for atoms that do not form stable anions in their gas phase) to large negative numbers (indicating a high "affinity" or attraction for electrons). The larger the negative number, the more exothermic the process is.

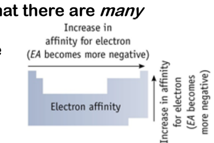
$$A_{(g)} + e^{-} \rightarrow A^{-}_{(g)} \quad \Delta E = \text{Electron affinity.}$$

Units: J/atom or more commonly kJ/mol.

Based on the definitions of EA and IE, elements with high ionization energies generally have high electron affinities.

The general trend is that *electron affinity increases to the right and up on the periodic table* (i.e. the values become more negative.), however it should be noted that there are *many* exceptions to this trend.
(Alkaline earth metals and nitrogen have values of 0 as do the noble gases)
See App. F on page A-19

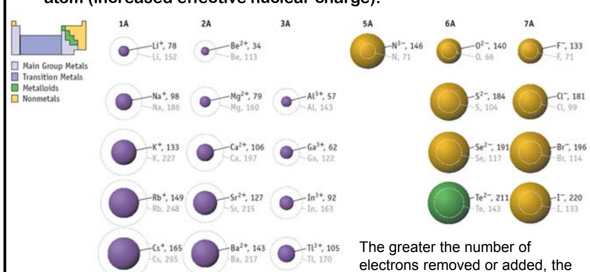
No element has a negative electron affinity for a second electron.



Radius of Ions:

Anions will always have radii that are larger than their neutral atom (increased repulsive electron forces).

Cations will always have radii that are smaller than their neutral atom (increased effective nuclear charge).

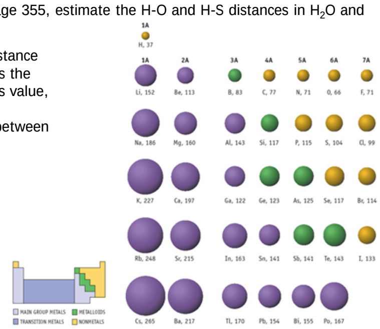


The greater the number of electrons removed or added, the greater this effect becomes.

Example:
Place the three elements Al, C and Si in order of increasing atomic radius.

Example:
a. Using figure 8.11 Page 355, estimate the H-O and H-S distances in H_2O and H_2S, respectively.

b. If the interatomic distance in Br_2 is 228pm, what is the radius of Br? Using this value, and that for Cl (99pm), estimate the distance between atoms in BrCl.



Supplemental Problems:

1. Gallium lies under aluminum in Group 3A (13), but it has a smaller radius. What causes this deviation from the general trend in atomic size? What other atomic property of Ga might also be affected by this?

2. Calculate the longest wavelength of electromagnetic radiation that could ionize an atom of Au; IE_1 = 889.9kJ/mol

3. Theorize as to why palladium (Pd) is unexpectedly diamagnetic.

4. Give a reasonable set of quantum numbers for the outermost (most energetic) ground state electron in scandium (Sc).

5. When sodium chloride is strongly heated in a flame, the flame takes on the yellow color associated with the emission spectrum of sodium atoms. The reaction that occurs in its *gaseous* state is:
$Na^+_{(g)} + Cl^-_{(g)} \rightarrow Na_{(g)} + Cl_{(g)}$
Calculate ΔH for this reaction.

Answers:

1. Because of the penetration by the 4p orbitals through the 3d sublevel, the $4p^1$ electron feels an increased Z_{eff} due to the additional protons added during the 3d transition series, and this is slightly smaller than aluminum. This should also result in an IE_1 greater than expected.

2. 889.9kJ/mol (1,000J/1kJ)(1mol/6.022x10^{23}atoms) = 1.4777x10^{-18}J/atom Au
λ = hc/E = (6.626x10^{-34}Js)(3.00x10^8m/s)/(1.4777x10^{-18}J/atom)
= 1.345x10^{-7}m = 135nm

3. Both of its 5s electrons are promoted into the 4d sublevel, filling the 4d and leaving the 5s vacant.

4. n = 3, ℓ = 2, m_ℓ = -2,-1,0,1 or 2, m_s = +1/2 or -1/2

5. IE_1 for sodium = 496kJ/mol
EA_1 for chlorine = -349.0kJ/mol
Since you are doing the opposite:
ΔH = -496kJ/mol + 349.0kJ/mol = -147kJ/mol

Supplemental Problem:

1. Match each of the lettered items on the left with an appropriate numbered item on the right. All the numbered items should be used, and some more than once.

a) Z = 32	**1. two unpaired p electrons**
b) Z = 8	**2. diamagnetic**
c) Z = 53	**3. more negative electron affinity than elements on either side of it in the same period**
d) Z = 38	**4. first ionization energy lower than that of Ca but greater than that of Cs**
e) Z = 48	
f) Z = 20	

2. The production of gaseous bromide ions from bromine molecules can be considered a two-step process in which the first step is
$Br_{2(g)} \rightarrow 2Br_{(g)}$ ΔH = +193kJ
Is the formation of $Br^-_{(g)}$ from $Br_{2(g)}$ an endothermic or exothermic process? What is the value?

Answers: (See appendix F on page A-19)

1.

a) Z = 32 1	**1. two unpaired p electrons**
b) Z = 8 1	**2. diamagnetic**
c) Z = 53 3	**3. more negative electron affinity than elements on either side of it in the same period**
d) Z = 38 2, 4	
e) Z = 48 2	**4. first ionization energy lower than that of Ca but greater than that of Cs**
f) Z = 20 2	

2. Exothermic
EA for bromine is -324.7kJ/mol
(2)(-324.7kJ/mol) + (193kJ/mol) = -456.4 = -456kJ/mol