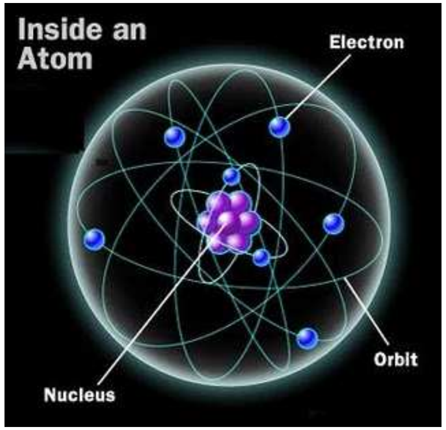
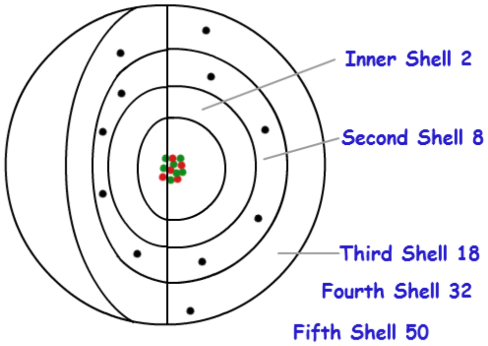
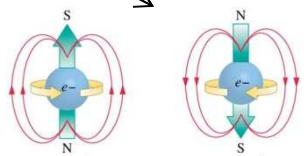
Atoms

Atomic electron distribution

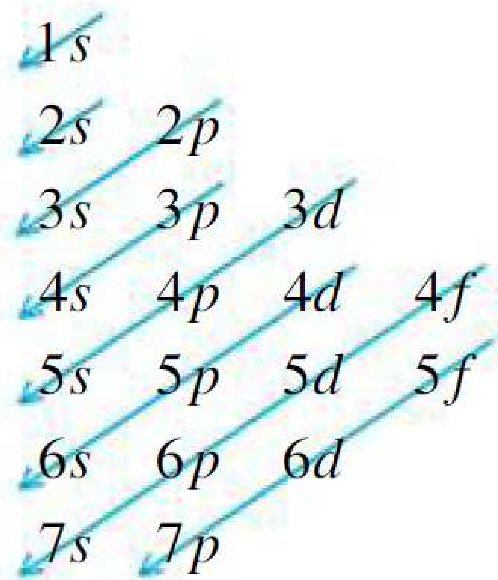


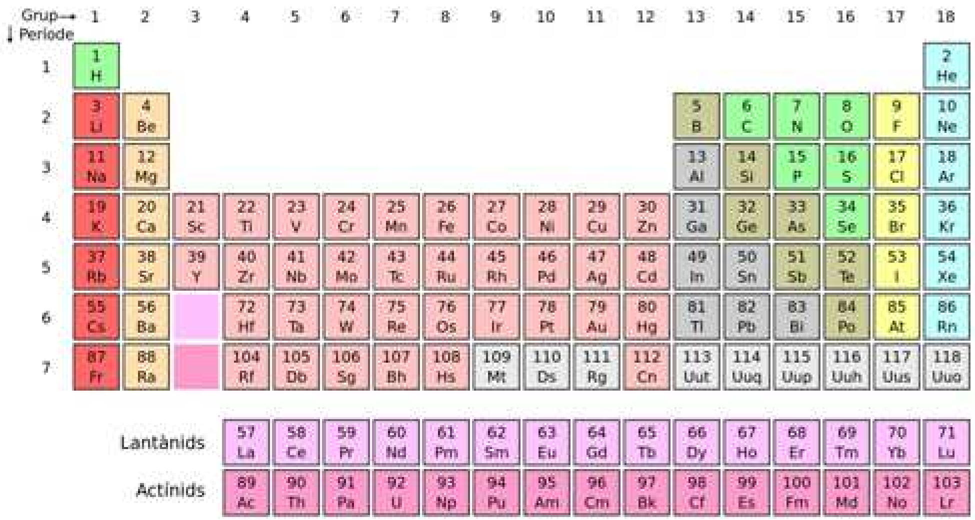


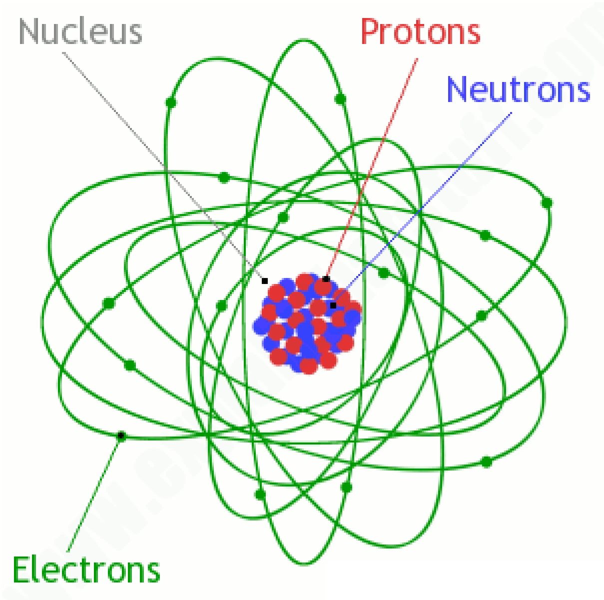
Shell:	n=1, 2, 3, 4......
Sub-Shell:	ℓ=0, 1, 2, 3,... (n-1)
	s p d f .....
Orbital:	m= $-\ell$, ... 0 .... ℓ
Spin:	ms = + or –



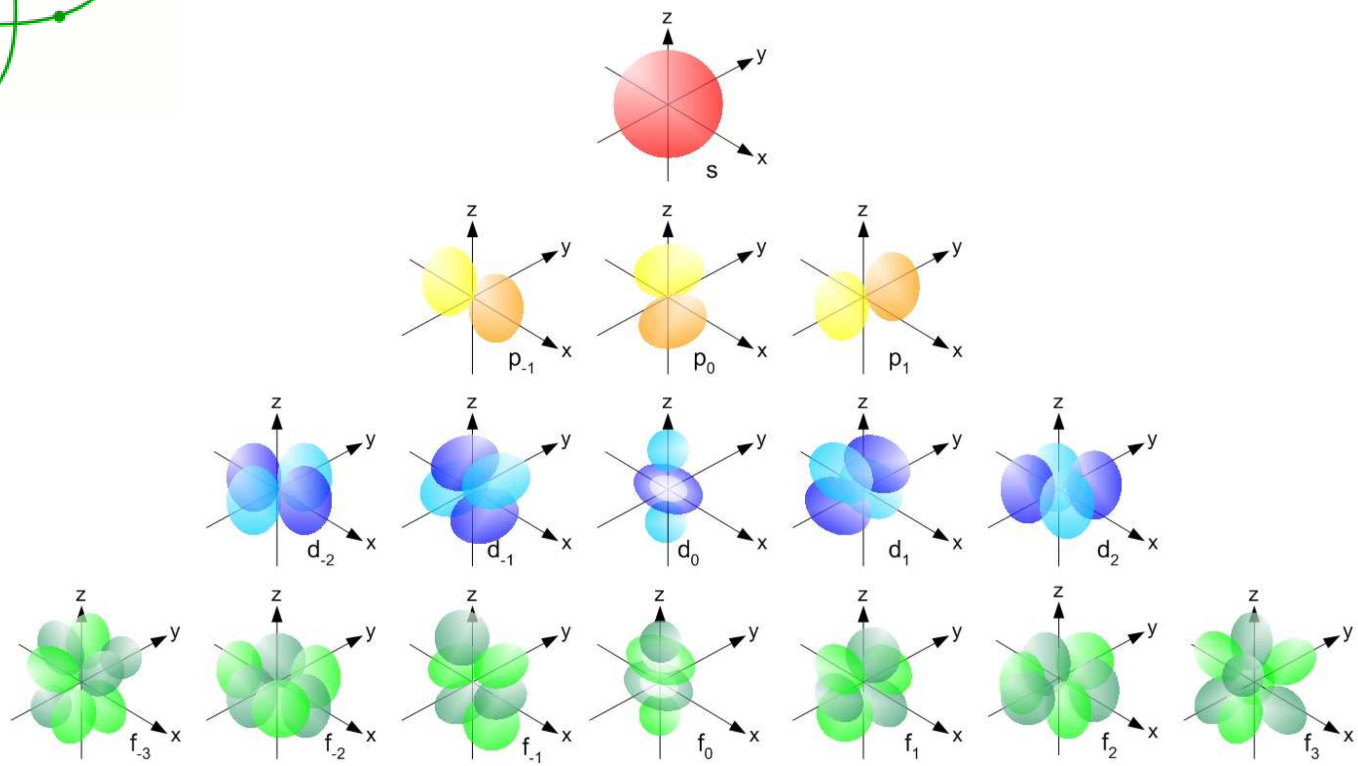
Sequence:	s	s p	s p	s d p	s d p	s f d p	...
	2	8	8	18	18	32	...
	2	10	18	36	54	86	....





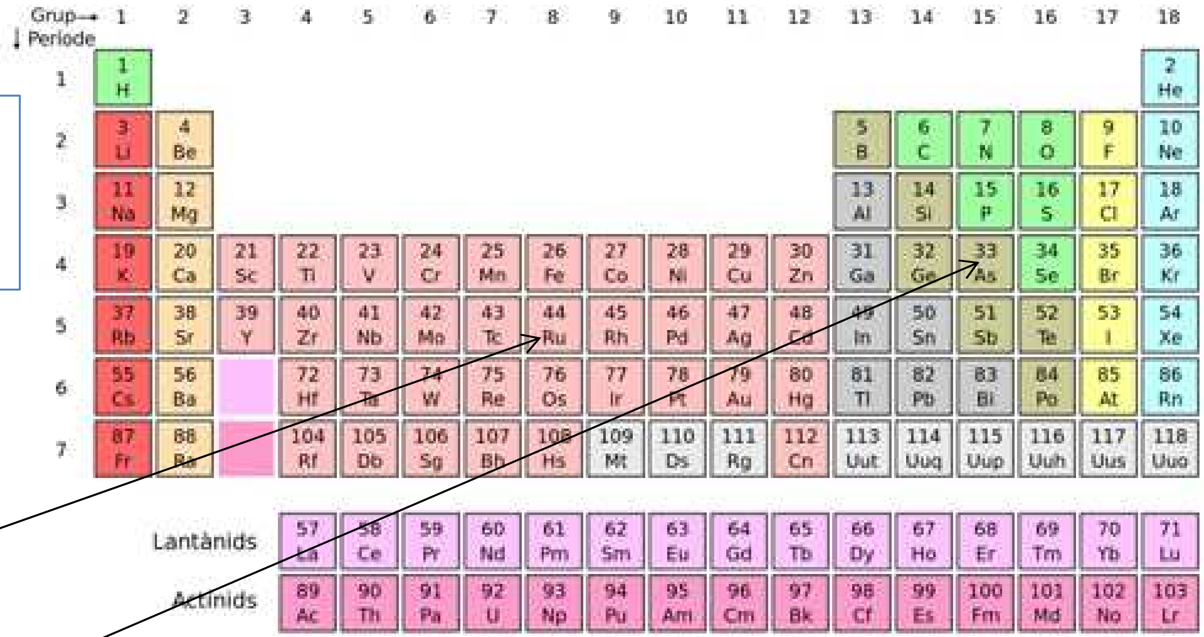


Orbitals are not planetary orbits!



Electron Configurations

s	s p	s p	s d p	s d p	s f d p	...
2	8	8	18	18	32	...
2	10	18	36	54	86	....



Ru (N=44)   44-36= 8 $5s^2\ 4d^6$

As (N=33)   33-18= 15 $4s^2\ 3d^{10}\ 4p^3$

Anomalous configurations: filling or half-filling shells

e.g.   Cu (N=29)   29-18= 11 $4s^1\ 3d^{10}$

Some definitions

- Atom: An atom is the smallest constituent unit of ordinary matter that has the properties of a chemical element.

- Chemical element: The chemical elements are pure substances that can not be decomposed into any other pure substance by simple chemical methods.

- Molecule: A molecule is an electrically neutral group of two or more atoms held together by chemical bonds.

  A molecule can be decomposed by chemical methods into other simpler pure substances.

  Molecules are distinguished from ions by their lack of electrical charge.

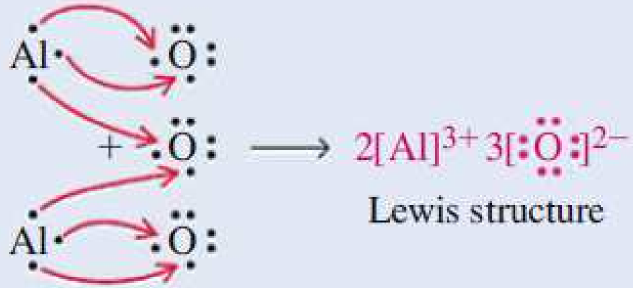
Molecules

Lewis Theory: An Overview

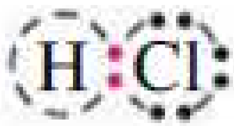
1. Electrons, especially those of the outermost (valence) electronic shell, play a fundamental role in chemical bonding.
2. In some cases, electrons are *transferred* from one atom to another. Positive and negative ions are formed and attract each other through electrostatic forces called **ionic bonds**.
3. In other cases, one or more pairs of electrons are *shared* between atoms. A bond formed by the sharing of electrons between atoms is called a **covalent bond**.
4. Electrons are transferred or shared in such a way that each atom acquires an especially stable electron configuration. Usually this is a noble gas configuration, one with eight outer-shell electrons, or an **octet**.

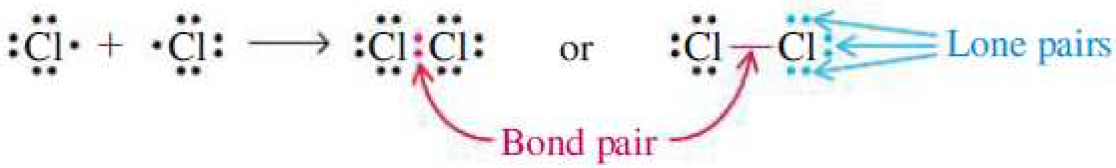
Lewis Structures for Ionic Compounds

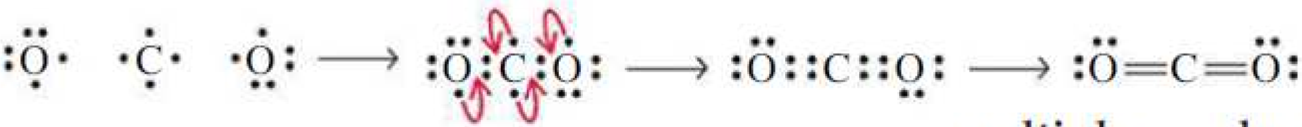
The formula of aluminum oxide follows directly from the Lewis structure. The combination of one Al atom, which loses three electrons, and one O atom, which gains two, leaves an excess of one lost electron. To match the numbers of electrons lost and gained, the formula unit must be based on *two* Al atoms and *three* O atoms.



Covalent Bonding







multiple covalent bonds

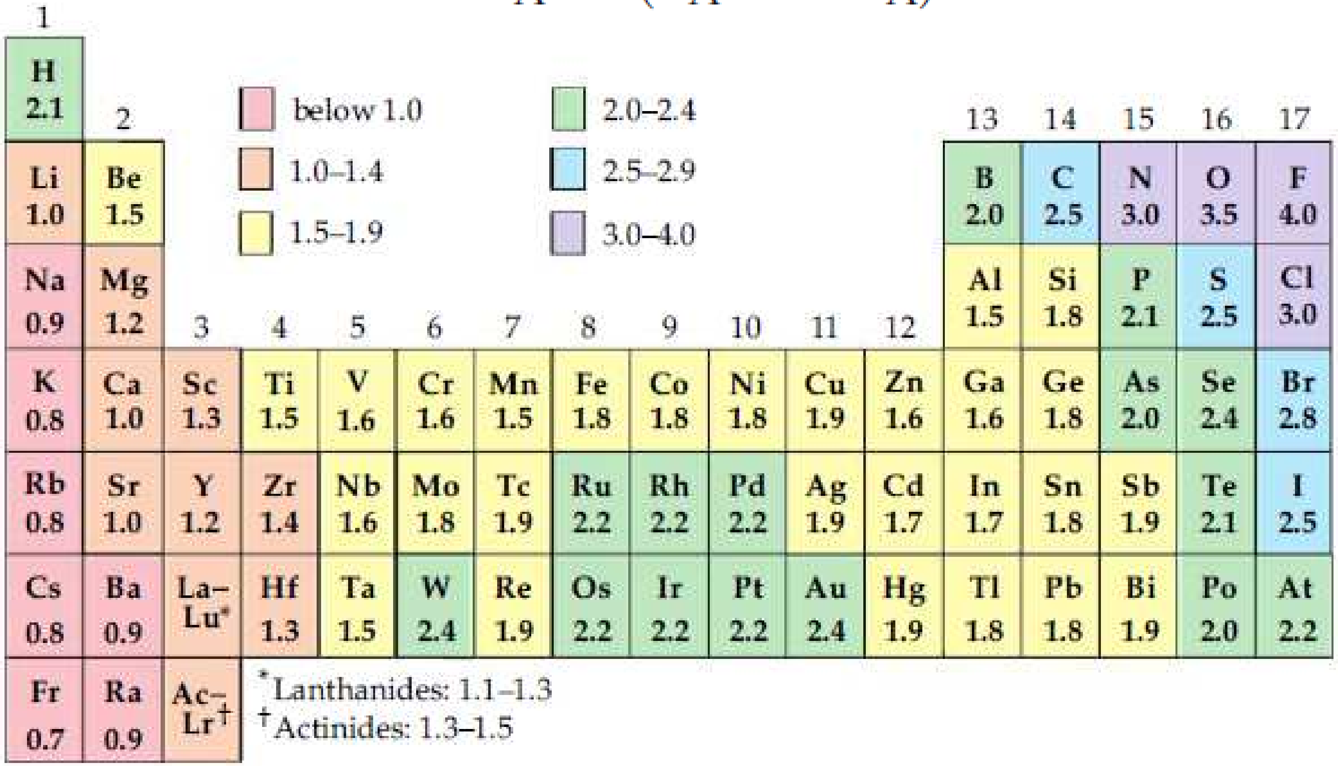
Electronegativity atom's ability to compete for electrons

$$A + B \longrightarrow A^{+}B^{-} \qquad \Delta E_1 = (I_A + EA_B)$$

$$A + B \longrightarrow A^{-}B^{+} \qquad \Delta E_2 = (I_B + EA_A)$$

nonpolar $(I_A + EA_B) = (I_B + EA_A) \longrightarrow (I_A - EA_A) = (I_B - EA_B)$

$$EN_A \propto (I_A - EA_A)$$



Formal Charge

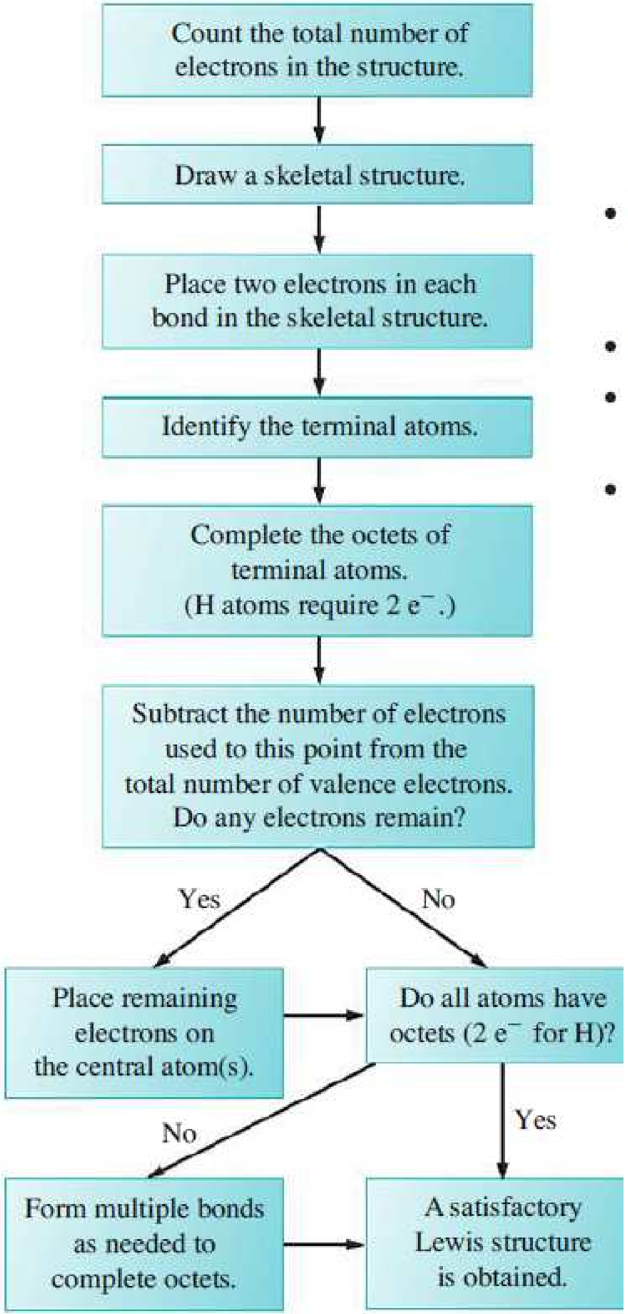
$:O\equiv$ FC = *6* valence e^- in O − *2* lone-pair e^- − $\frac{1}{2}$ (*6* bond-pair e^-) = 6 − 2 − 3 = +1

$\equiv N-$ FC = *5* valence e^- in N − *0* lone-pair e^- − $\frac{1}{2}$ (*8* bond-pair e^-) = 5 − 0 − 4 = +1

$-\ddot{O}:$ FC = *6* valence e^- in O − *6* lone-pair e^- − $\frac{1}{2}$ (*2* bond-pair e^-) = 6 − 6 − 1 = −1

	Interpretation	Comments
Oxidation state	The charge an atom would have if the bonding electrons in each bond were *transferred* to the more electronegative atom.	• The oxidation state concept tends to exaggerate the ionic character of the bonding between atoms. • Oxidation states are used to predict and rationalize chemical properties of compounds.
Formal charge	The charge an atom would have if the bonding electrons in each bond were *divided equally* between the two atoms involved.	• The formal charge concept tends to exaggerate the covalent character of the bonding between atoms. • Formal charges are used to assess which Lewis structure is the most satisfactory representation of the true structure.

A Strategy for Writing Lewis Structures



Formal Charge

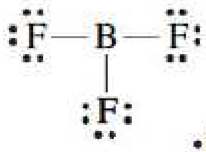
- The sum of the formal charges in a Lewis structure must equal *zero* for a neutral molecule and must equal the magnitude of the charge for a polyatomic ion.
- Where formal charges are required, they should be as small as possible.
- Negative formal charges usually appear on the most electronegative atoms; positive formal charges, on the least electronegative atoms.
- Structures having formal charges of the same sign on adjacent atoms are unlikely.

Resonance

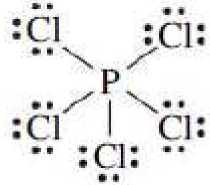
Exceptions to the Octet Rule

Odd-Electron Species

Incomplete Octets



Expanded Valence Shells

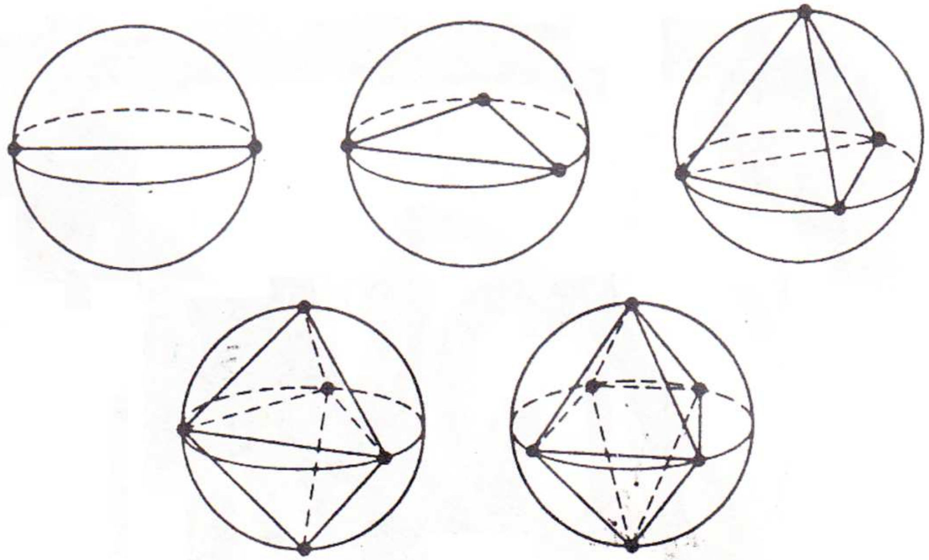


Shapes of Molecules Valence-Shell Electron-Pair Repulsion (VSEPR) Theory

Electron pairs repel each other, whether they are in chemical bonds (bond pairs) or unshared (lone pairs). Electron pairs assume orientations about an atom to minimize repulsions.

Possibilities for Electron-Group Distributions

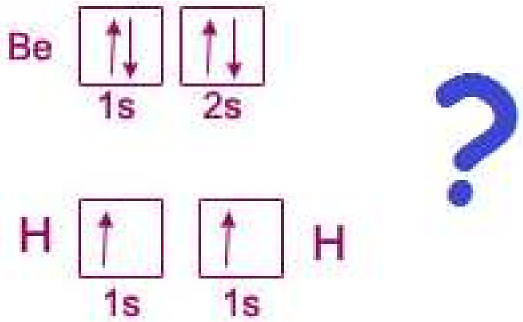
- two electron groups: linear
- three electron groups: trigonal planar
- four electron groups: tetrahedral
- five electron groups: trigonal bipyramidal
- six electron groups: octahedral

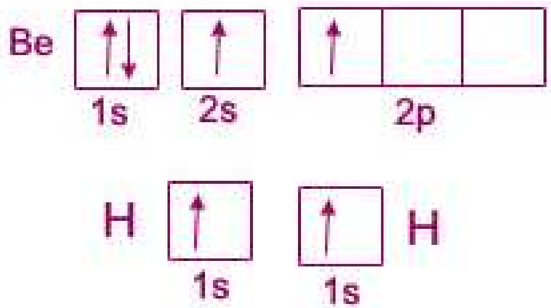


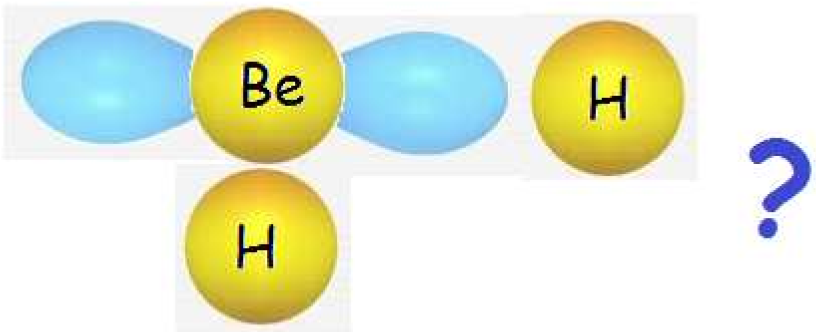
Hybrid orbitals and molecular geometry

H:Be:H or H—Be—H

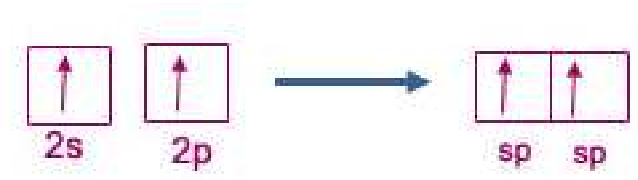
Lewis structure

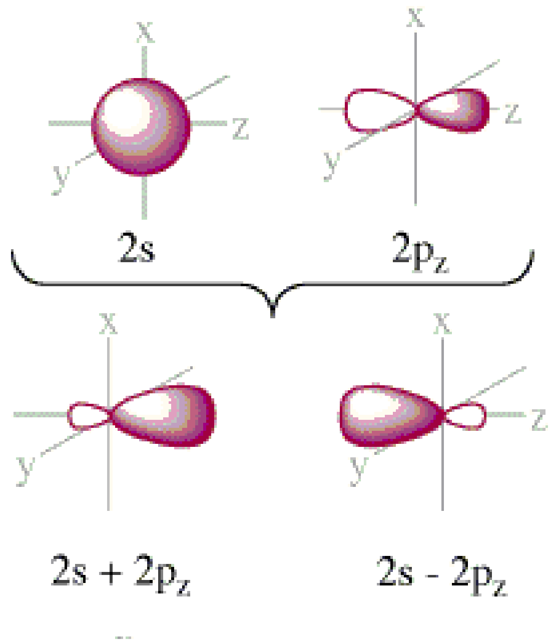


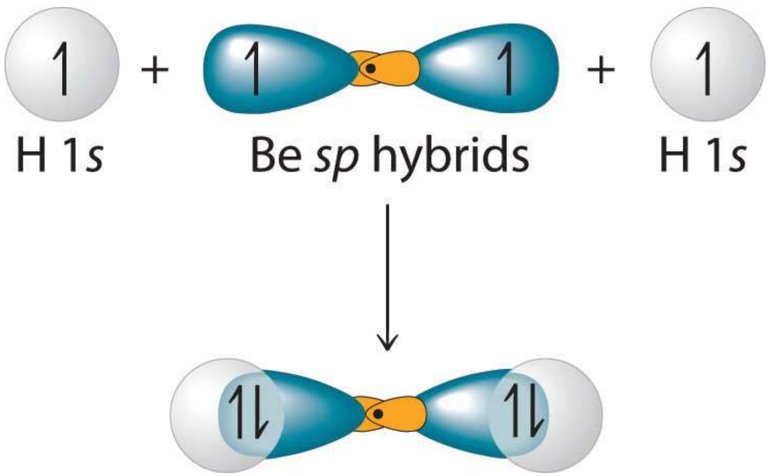




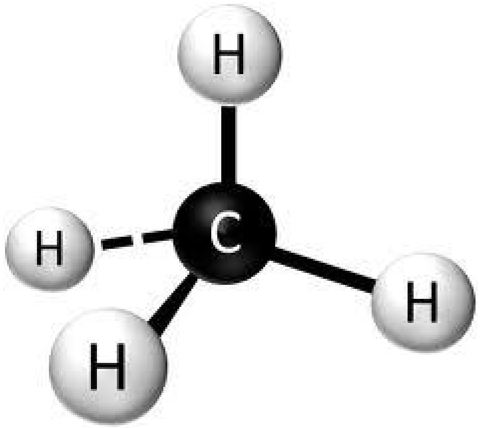
Hybrid orbitals (cont.)

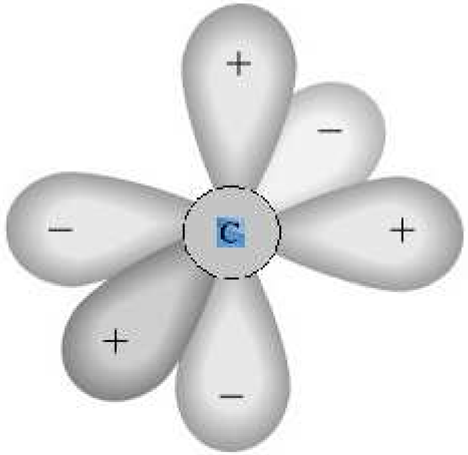


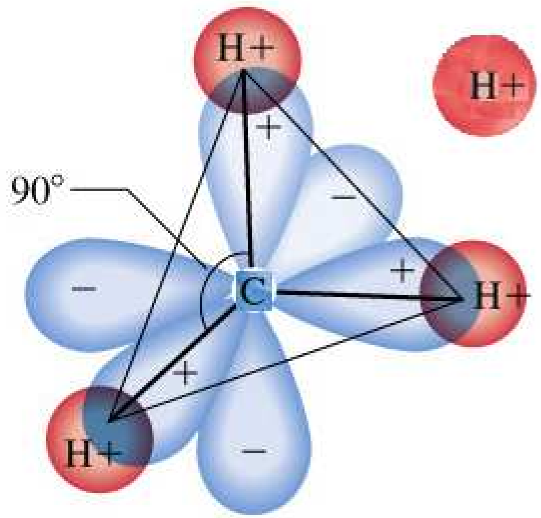


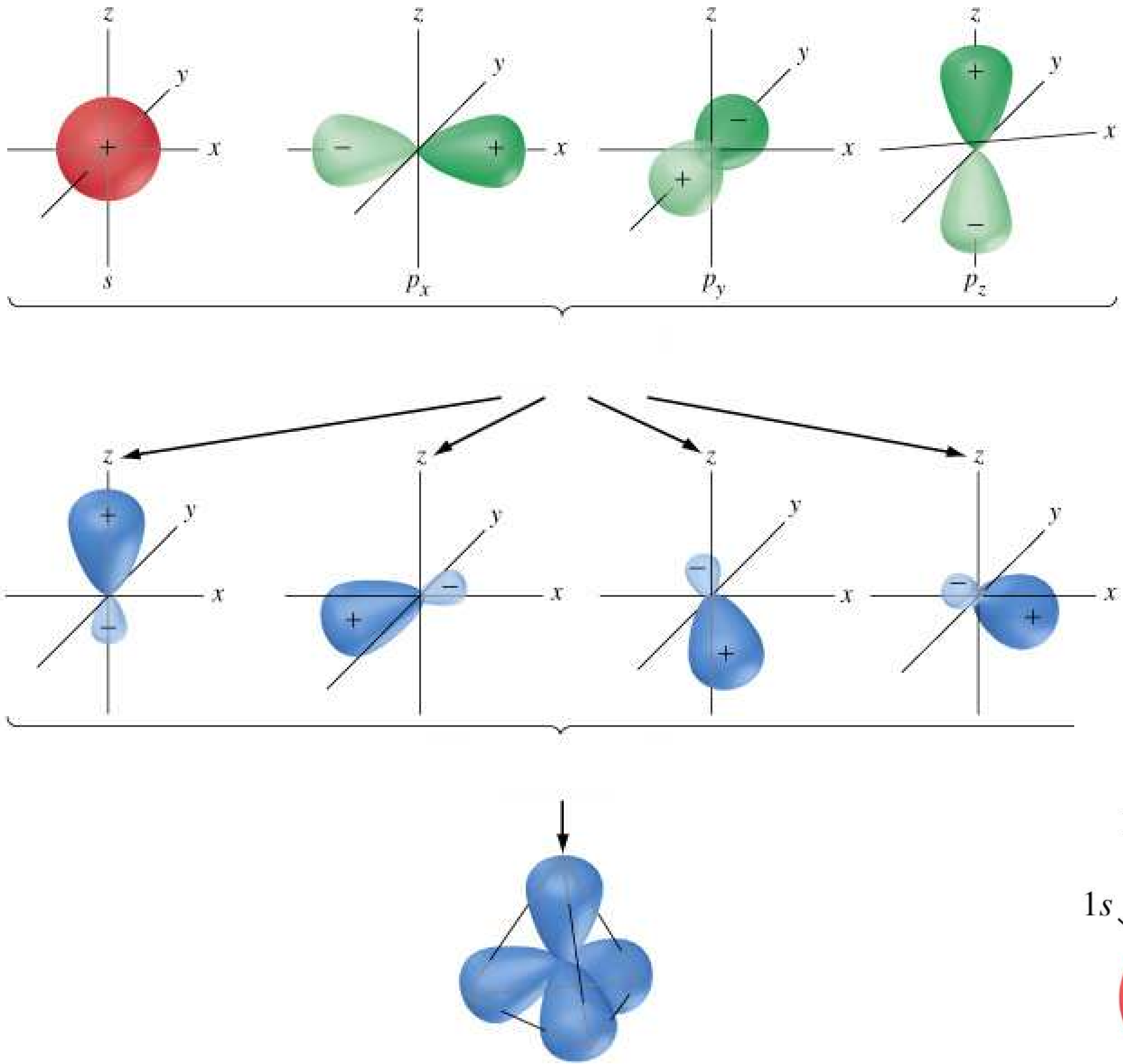


Hybrid orbitals (cont.) Methane case

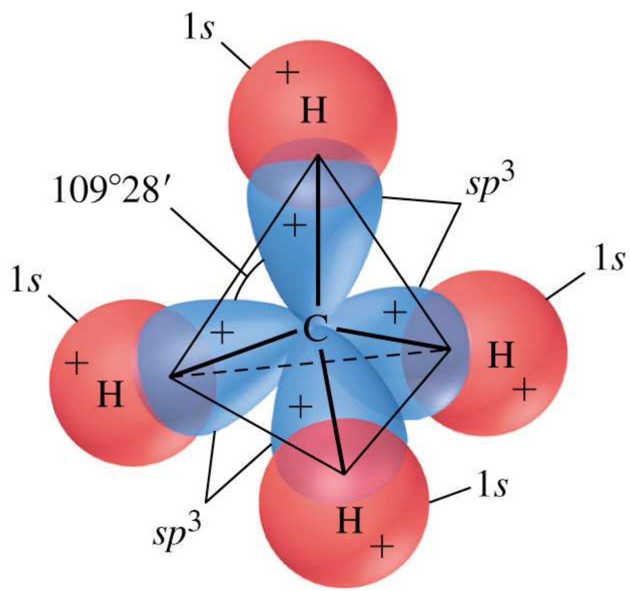






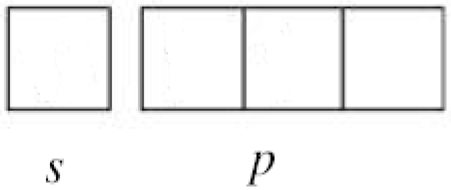


s
p_x
p_y
p_z

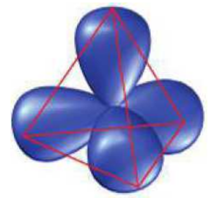


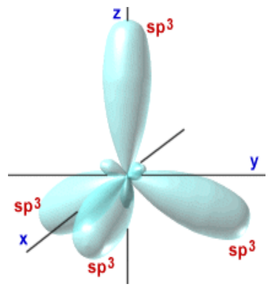
1s
H
C
109°28′
sp^3

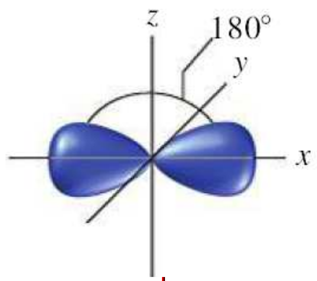
Hybrid Orbitals



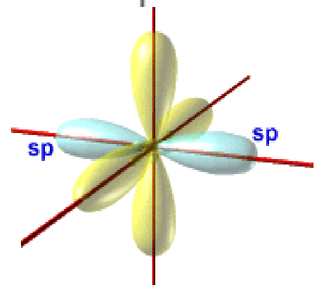
sp^3



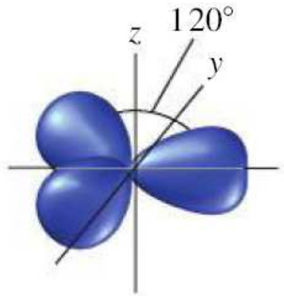


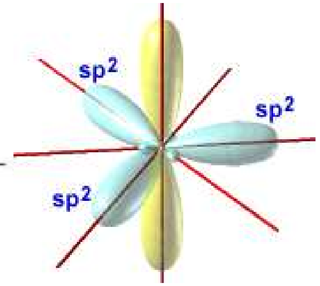


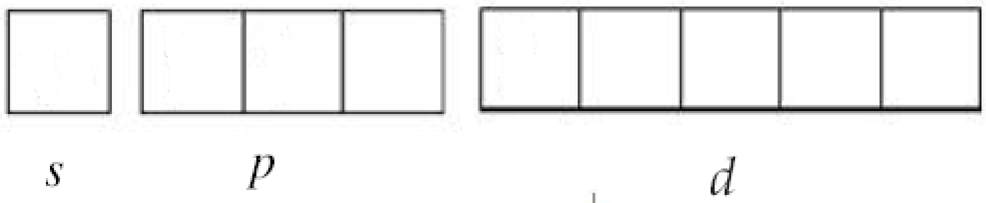
sp



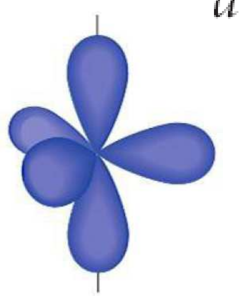
sp^2



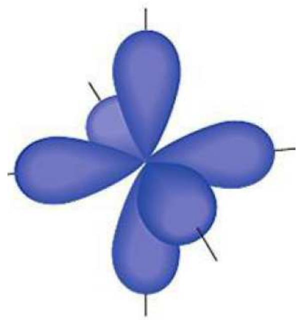


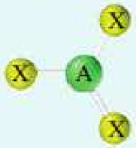
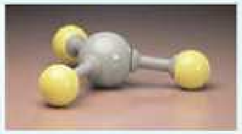
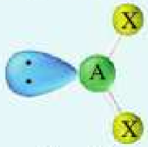
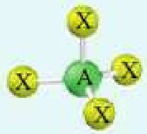
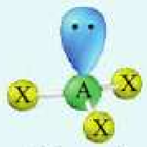
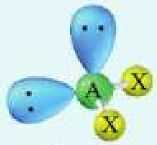
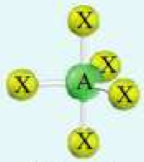


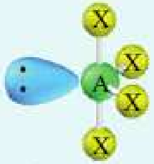
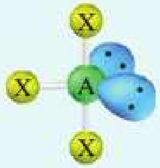
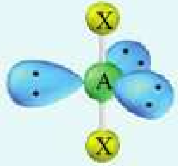
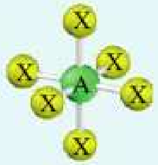
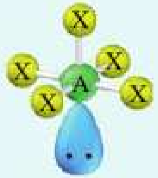
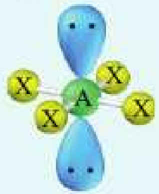
sp^3d



sp^3d^2



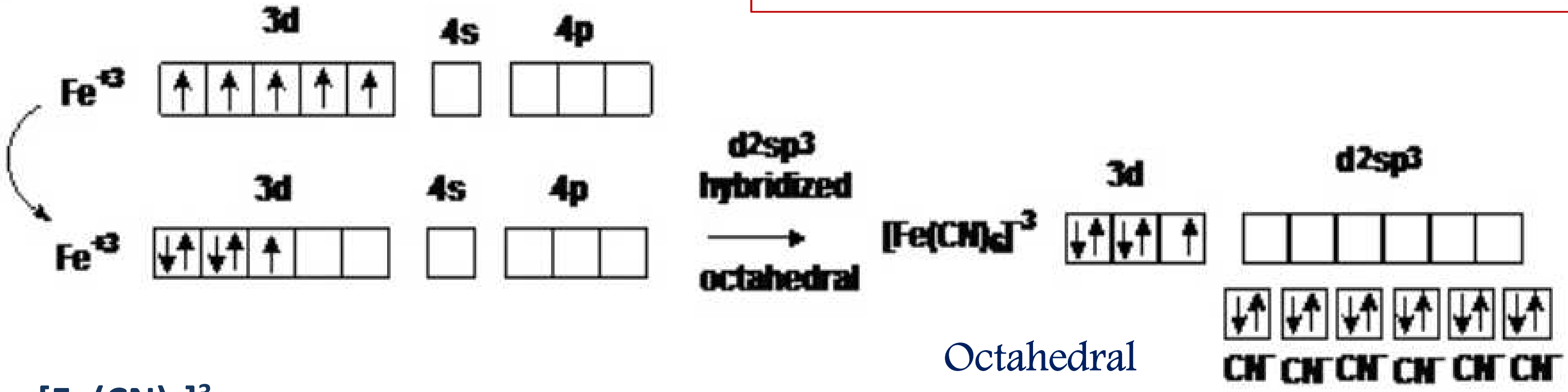
2	linear	0	AX_2	 (linear)	180°	$BeCl_2$		*sp*
3	trigonal planar	0	AX_3	 (trigonal planar)	120°	BF_3		sp^2
	trigonal planar	1	AX_2E	 (bent)	120°	SO_2[a]		sp^2
4	tetrahedral	0	AX_4	 (tetrahedral)	109.5°	CH_4		sp^3
	tetrahedral	1	AX_3E	 (trigonal pyramidal)	109.5°	NH_3		sp^3
	tetrahedral	2	AX_2E_2	 (bent)	109.5°	OH_2		sp^3
5	trigonal bipyramidal	0	AX_5	 (trigonal bipyramidal)	90°, 120°	PCl_5		sp^3d

	trigonal bipyramidal	1	AX_4E[b]	 (seesaw)	90°, 120°	SF_4	sp^3d
	trigonal bipyramidal	2	AX_3E_2	 (T-shaped)	90°	ClF_3	sp^3d
	trigonal bipyramidal	3	AX_2E_3	 (linear)	180°	XeF_2	sp^3d
6	octahedral	0	AX_6	 (octahedral)	90°	SF_6	sp^3d^2
	octahedral	1	AX_5E	 (square pyramidal)	90°	BrF_5	sp^3d^2
	octahedral	2	AX_4E_2	 (square planar)	90°	XeF_4	sp^3d^2

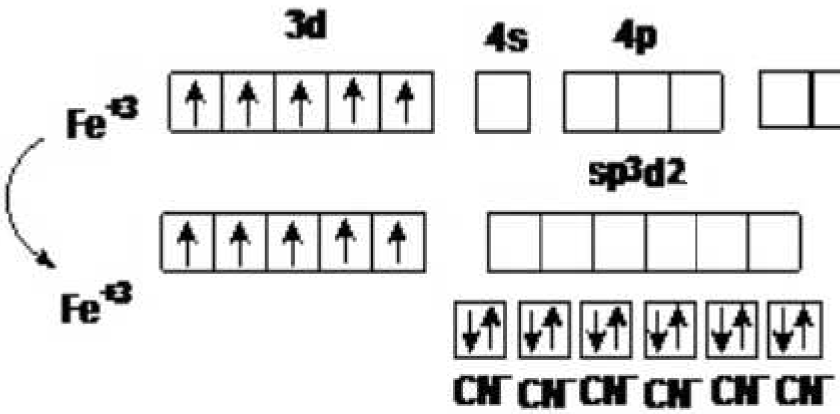
Further reading:

Metal Complexes

> **Inner shell Lone pairs of electrons are ignored.** Since lone pairs are in the inner shell, **they are believed to have little effect on molecular geometry**



$[Fe(CN)_6]^{3-}$

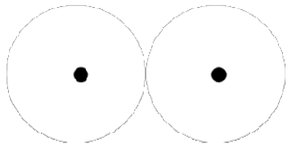


Octahedral

Bonding in Metals

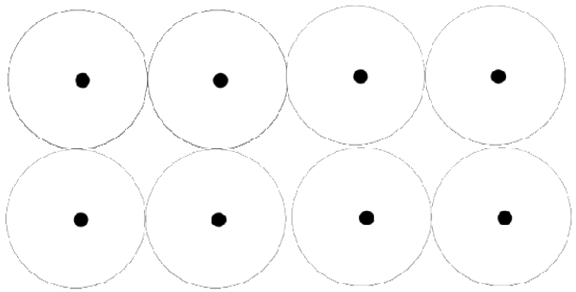
Na [Ne] $3s^1$

Na_2

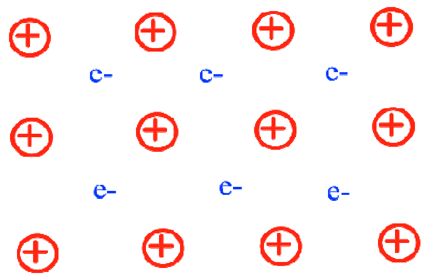


Covalent

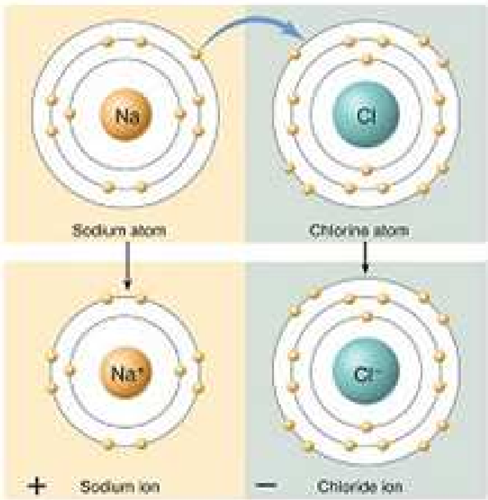
Na_n



The Electron Sea Model

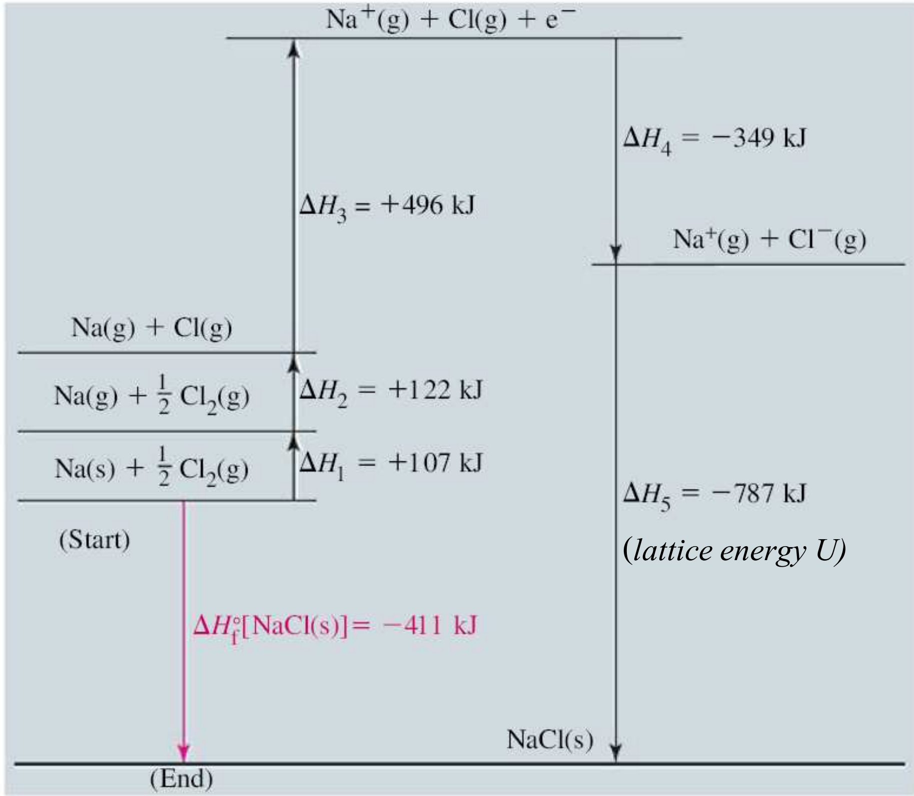


Ionic Bonds and ionic Crystals

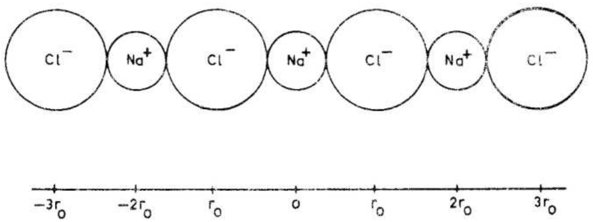


NaCl crystal

Born–Haber cycle



Lattice Energy



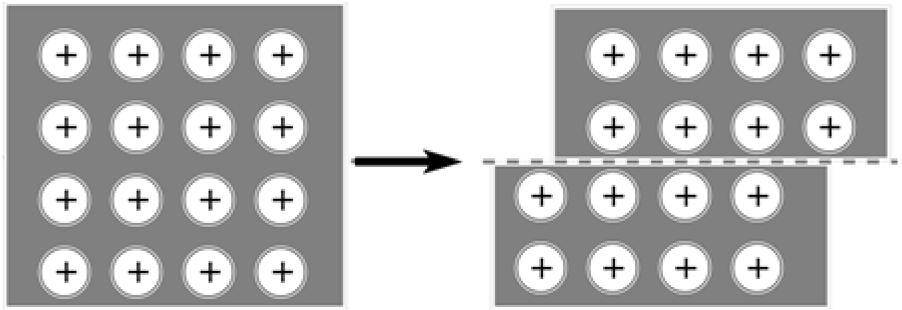
A hypothetical one-dimensional $NaCl$ lattice.

$$U = -\frac{2e^2}{4\pi\varepsilon_0 (r_0)} + \frac{2e^2}{4\pi\varepsilon_0 (2r_0)} - \frac{2e^2}{4\pi\varepsilon_0 (3r_0)} + \frac{2e^2}{4\pi\varepsilon_0 (4r_0)}$$

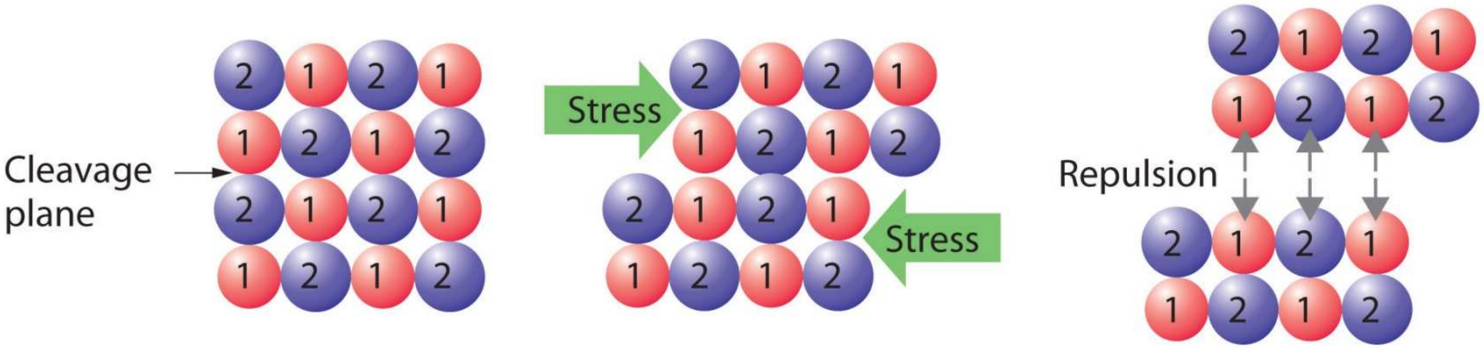
$$= -\frac{e^2}{4\pi\varepsilon_0 r_0}\left[2\left(1-\frac{1}{2}+\frac{1}{3}-\frac{1}{4}+\dots\right)\right] = -\frac{e^2 A}{4\pi\varepsilon_0 r_0} \times \left(1-\frac{1}{n}\right)$$

Repulsion correction

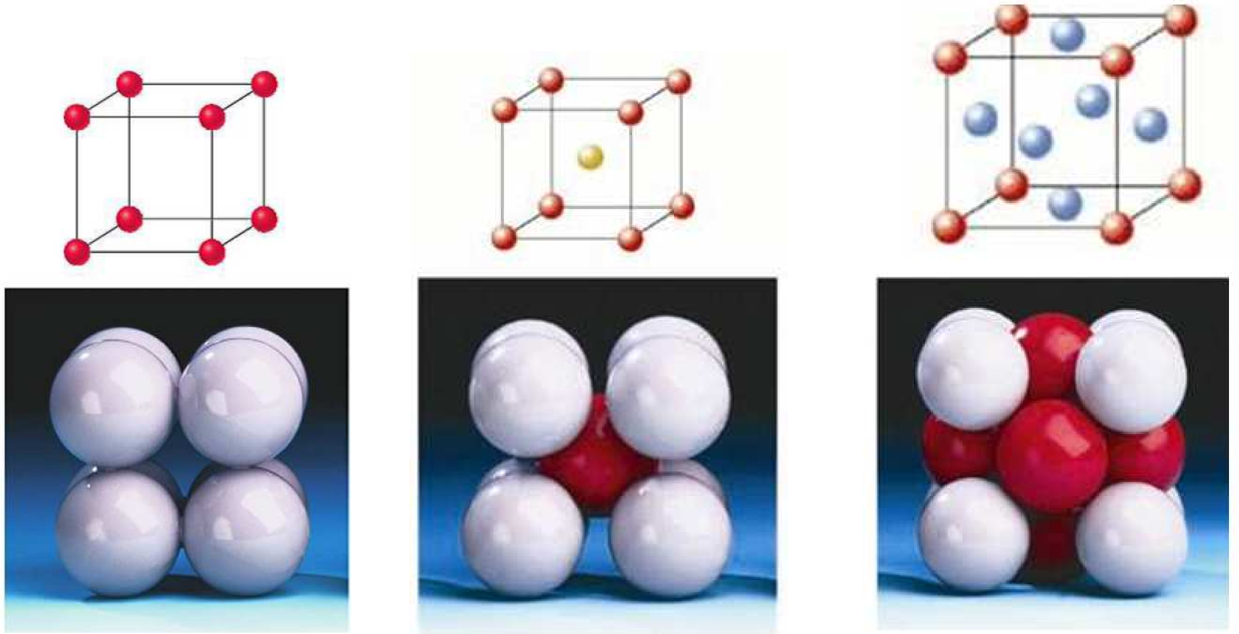
Metal crystal: ductile and malleable



Ionic crystal: hard but brittle

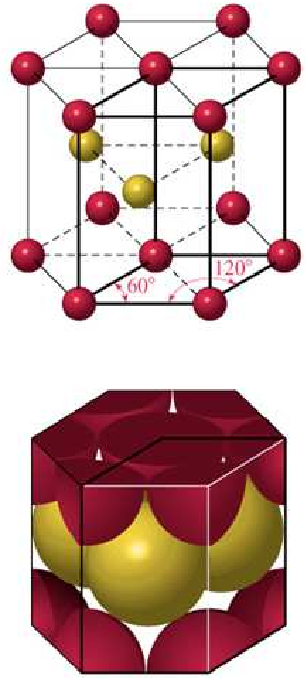


Arranging atoms or ions in solids



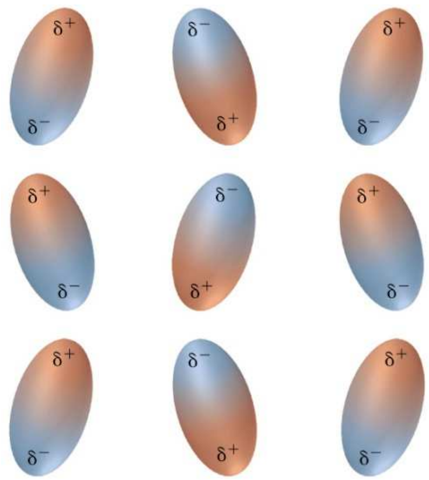
Simple cubic　　Body-centered cubic　　Face-centered cubic

cubic crystal

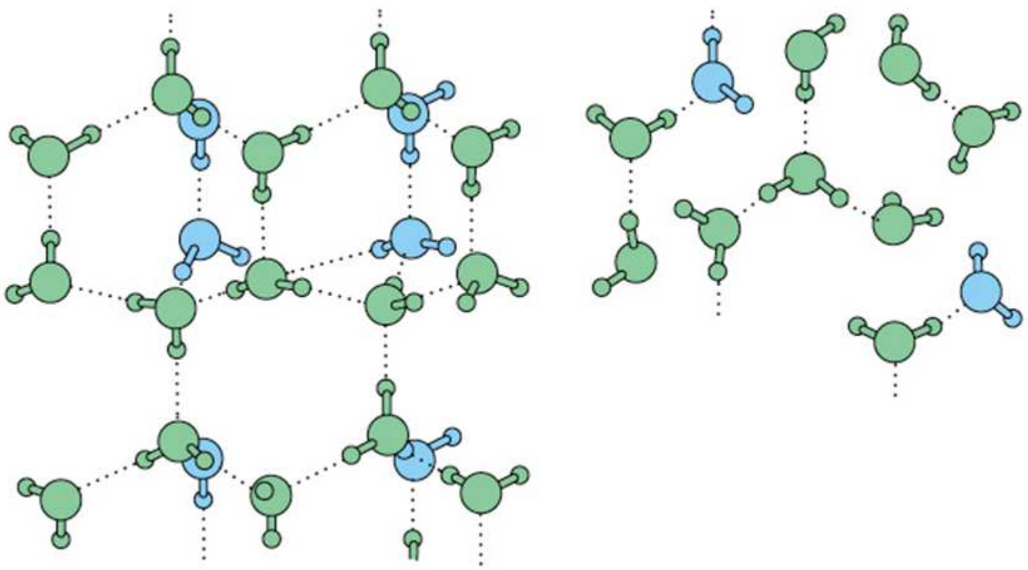


hexagonal crystal

Intermolecular Forces: Liquids and Solids



Hydrogen bonding in water



ice

liquid