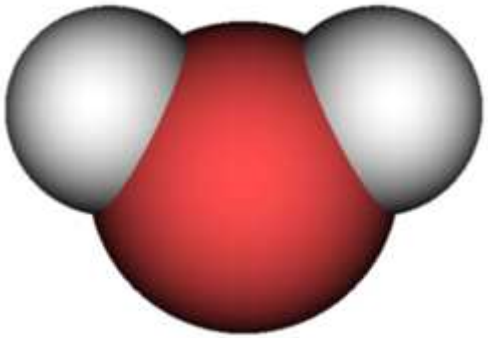
Chemical Bonding (II)



Contents

1. BASIC CONCEPTS

A) Molecular Parameters

Bond Distance

-Average distance between the nuclei of two bonded atoms.

-Factors affecting bond length:

a) Size of the bonded atoms (HI > HBr > HCl > HF)

b) Multiplicity of bond (C-C > C=C)

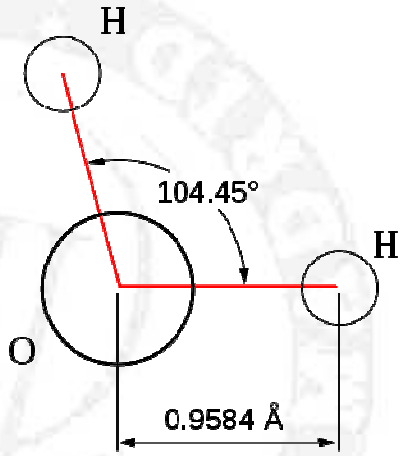


Image from: http://wikimediafoundation.org/wiki/File:Water_molecule_dimensions.svg

Bond Angle

-The internal angle between the orbitals containing electron pairs in the valence shell of the central atom in a molecule.

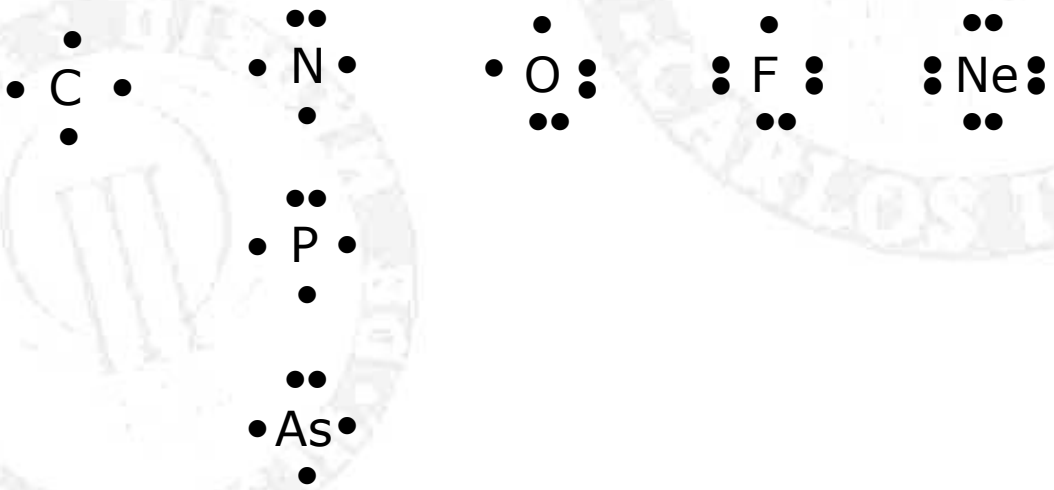
Bond Enthalpy

It is the energy required to break one mole of bonds of a particular type of substance in gaseous state.

1. BASIC CONCEPTS

B) Lewis dot symbols

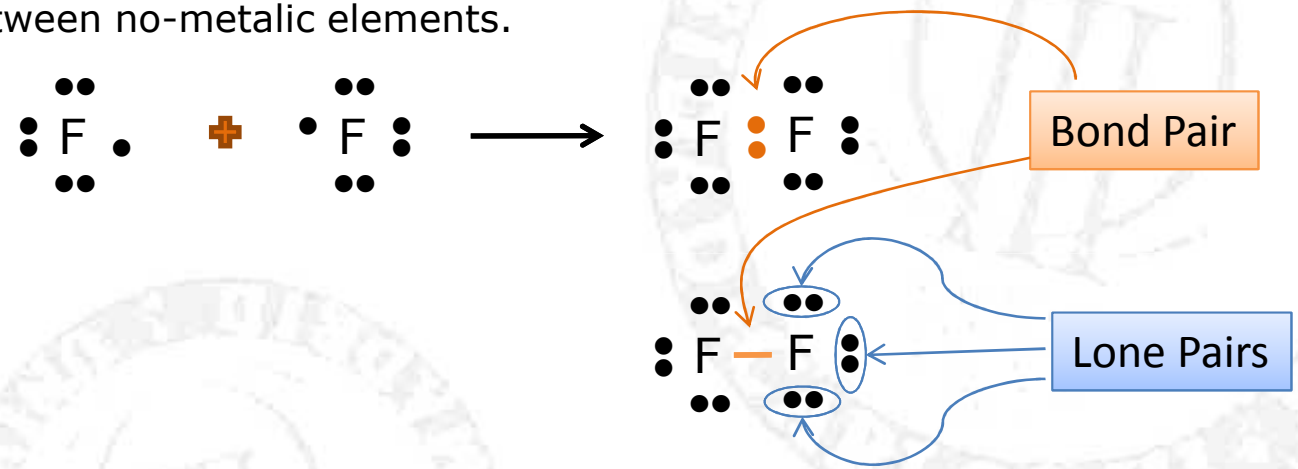
- Valence e^- play a fundamental role in chemical bonding → *the octet rule*
- *Chemical bond in terms of Lewis dot symbols*
  - ***ionic bond*** → e^- transfer
  - ***covalent bonds*** → e- sharing



2. THE COVALENT BOND

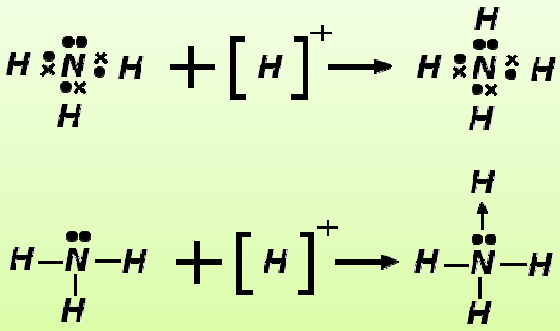
In covalent bond atoms share electrons to complete their valence shell (i.e. to reach the gas noble configuration)

It forms between no-metalic elements.



Coordinate covalent Bonds

The electron pair is provided by one of the atoms that form the covalent bond.



Polar Covalent Bonds

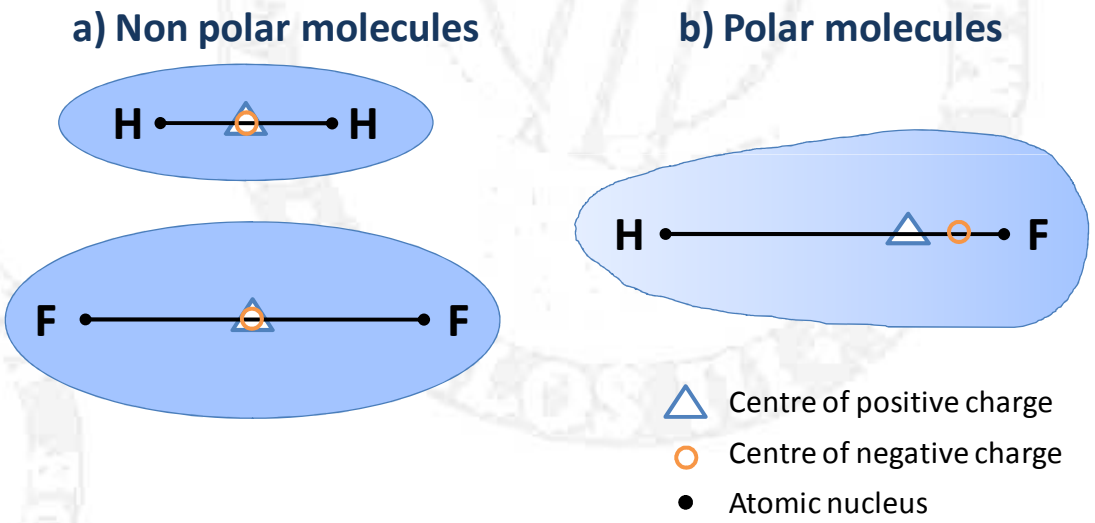
Electronegativity:
describes the ability of an atom (or, more rarely, a functional group) to attract electrons (or electron density) towards itself in a covalent bond.

Dipole moment

$\mu = Q \times r$

r = distance between atoms
Q = charge

Units Debye, D
1 D = 3.33 10^{-30} C·m



There is a shift of the electron density from H to F

General Chemistry

Polarity of molecules

Diatomic molecules

Homonuclear molecules: H_2, O_2 y F_2

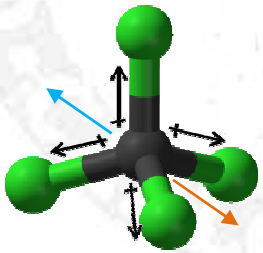
Heteronuclear molecules HCl, CO y NO

Polyatomic Molecules

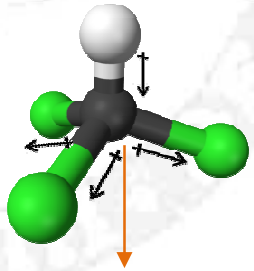
Polarity depends on:

-Polarity of the chemical bonds

-Geometry



CCl_4
A non-polar molecule



$CHCl_3$
A polar molecule

μ is the vectorial sum of the dipolar moments of the chemical bonds of the molecule.

Formal Charge

$$\text{formal charge on an atom in a Lewis structure} = \text{total number of valence electrons in the free atom} - \left[\text{total number of nonbonding electrons} + \frac{1}{2}\left(\text{total number of bonding electrons}\right)\right]$$

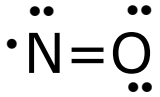
The sum of the formal charges of the atoms in a molecule or ion must equal the charge on the molecule or ion.

Practice Exercise.

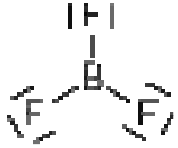
Write the Lewis structure for formaldehyde (CH_2O) using the concept of formal charge. Then compare your prediction with the real structure.

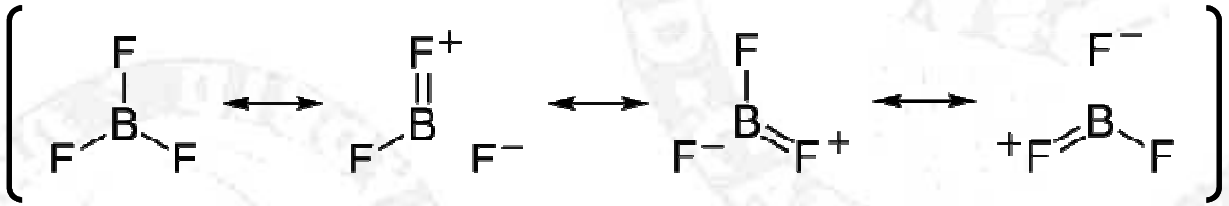
Exceptions to the Octet Rule

- Odd e^- species.

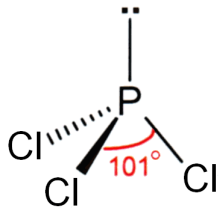


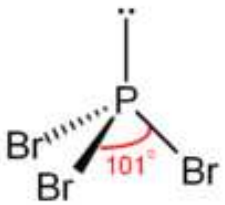
- Incomplete octets.

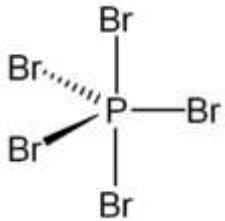


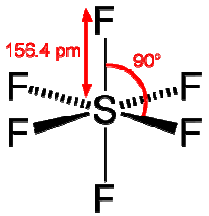


- Expanded octets.





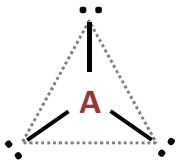
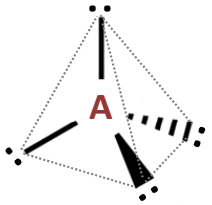
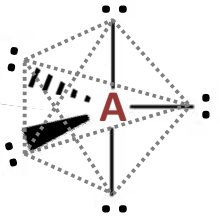
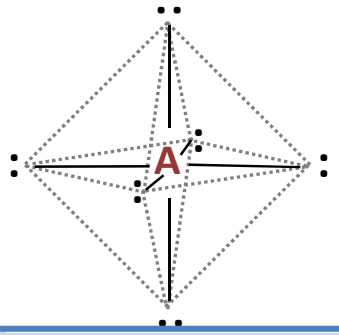




3. VSEPR MODEL

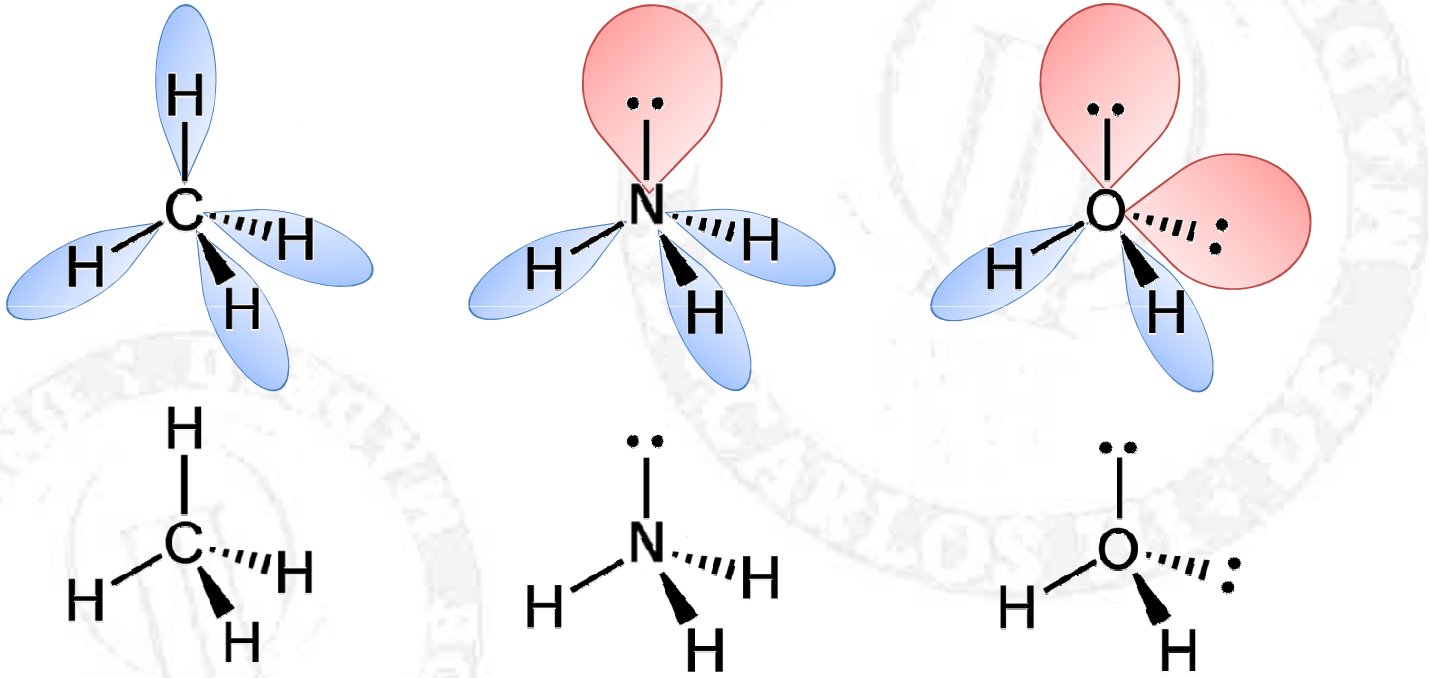
Electron pairs repel each other whether they are in chemical bonds (bond pairs) or unshared (lone pairs). Electron pairs assume orientations about an atom to minimize repulsions.

A) Molecules with no lone pairs on the central atom

No. of electron pairs or charge clouds		Distribution of the charge clouds (Molecular Shape)	
2	$BeCl_2$		Linear
3	BF_3		Trigonal planar
4	CH_4		Tetrahedral
5	PCl_5		Trigonal bipyramidal
6	SF_6		Octahedral

3. VSEPR MODEL

B) Molecules with lone pairs on the central atom



bond pairs *vs.* Bond pairs	lone pairs *vs.* bond pairs	Lone pairs *vs.* Lone pairs

3. VSEPR MODEL

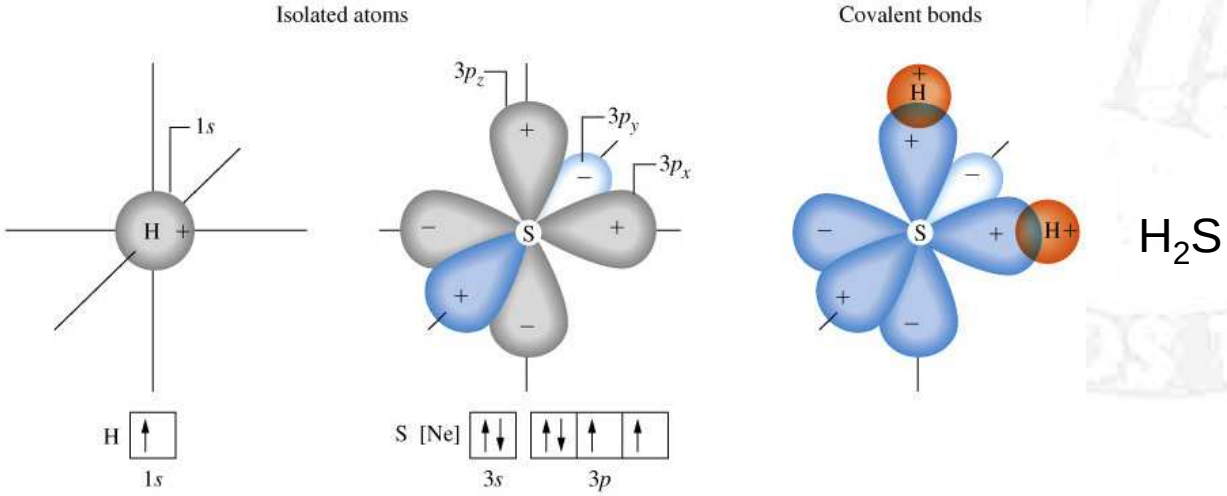
B) Molecules with lone pairs on the central atom

Number of bond pairs ("x")	Number of Lone pairs of electrons("y")	Number of group of electrons (n = x+y)	VSEPR Notation (AB_xE_y)	Electron group geometry	Example	Ideal bond angles	Molecular geometry
2	0	2	AB_2	Linear	$BeCl_2$	180º	Linear
2	1	3	AB_2E_1	Trigonal planar	SO_2	120º	Angular
4	0	4	AB_4	Tetrahedral	CH_4	109.5º	Tetrahedal
3	1		AB_3E_1		NH_3		Piramidal
2	2		AB_2E_2		H_2O		Angular
5	0	5	AB_5	Trigonal Bipyramidal	PCl_5	90º; 120º	Trigonal pyramidal
4	1		AB_4E_1		SF_4		Seesaw
3	2		AB_3E_2		ClF_3		T- shaped
2	3		AB_2E_3		XeF_2		Linear
6	0	6	AB_6	Octahedral	SF_6	90º	Octahedral
5	1		AB_5E_1		ICl_5, BrF_5 $XeOF_4$		Square pyramidal
4	2		AB_4E_2		XeF_4; ICl_4^-		Square planar

4. BOND THEORIES

Valence Bond Theory

- Atomic orbital overlap describes covalent bonding.
- Area of overlap of orbitals is *in phase.*
- A *localized* model of bonding.



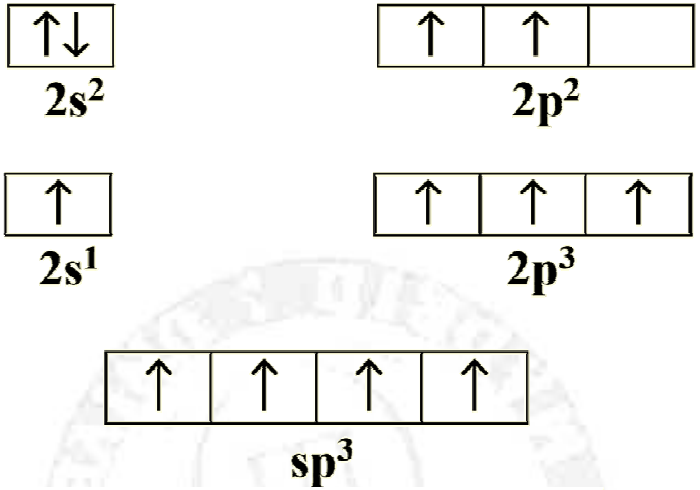
General Chemistry: Principles and Moderns Applications (R.H. Petrucci)

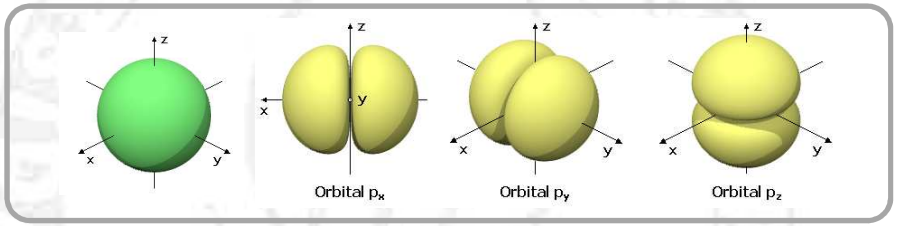
4. BOND THEORIES

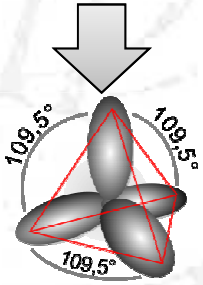
Valence Bond Theory

Hybridization of Atomic Orbitals

CH_4







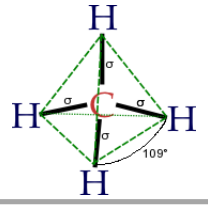
Hybridization: term applied to the mixing of atomic orbitals in a atom (i.e. linear combination of the wavefunctions).

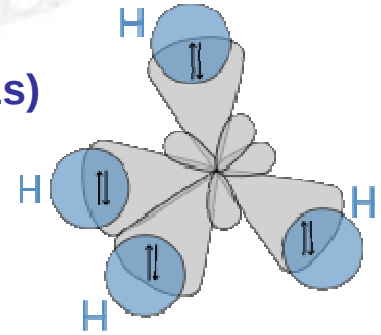
-Promotion
-Hybridization

CH_4 molecule

4 σ bonds: C(sp^3)-H(1s)

Bond angle: 109.5 º





4. BOND THEORIES

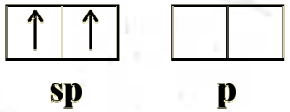
Valence Bond Theory

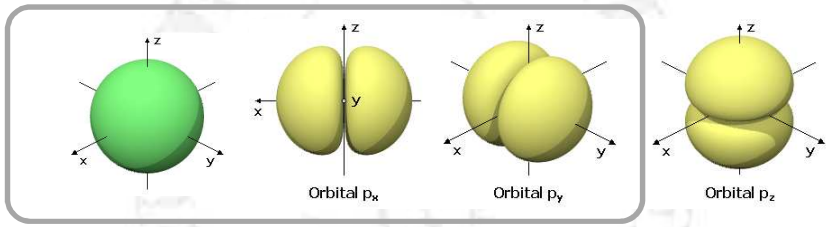
BF_3

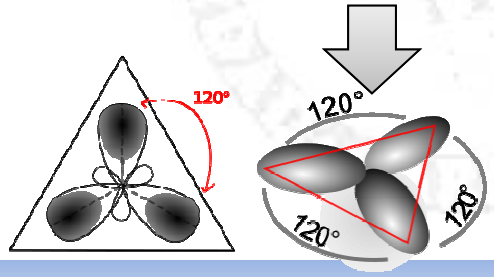
Orbital diagram B (ground state)

Promotion of one electron (2s →2p) (Excitation)

Mixing of orbitals (2s & 2p) (Hybridization)





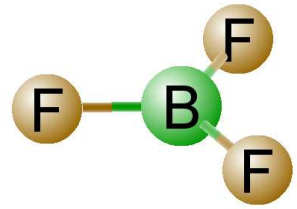


$3sp^2$ orbitals
+
Unhybridised 2p

BF_3 molecule

3 σ bonds: B(sp^2)-F(2p)

Bond angle: 120º

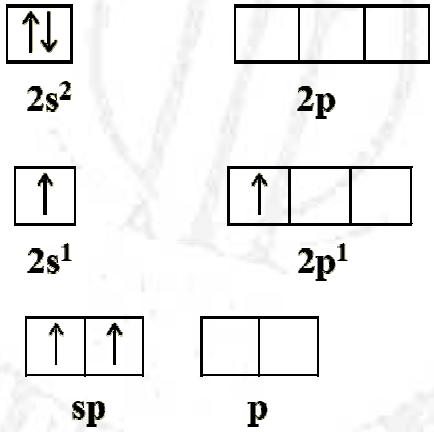


4. BOND THEORIES

Valence Bond Theory

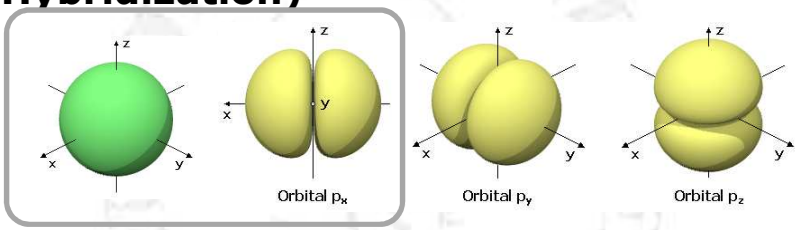
$BeCl_2$

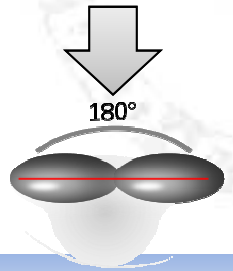
Orbital diagram Be (ground state)



Promotion of one electron (2s →2p) (Excitation)

Mixing of orbitals (2s & 2p) (Hybridization)



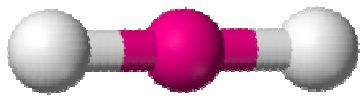


2sp orbitals
+
2 Unhybridised 2p

$BeCl_2$ molecule

2 σ bonds: Be(sp)-Cl(3p)

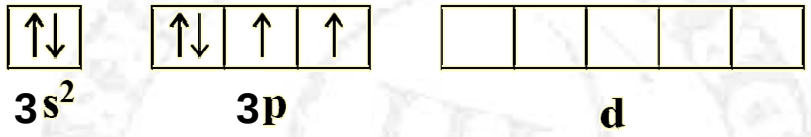
Bond angle: 180º



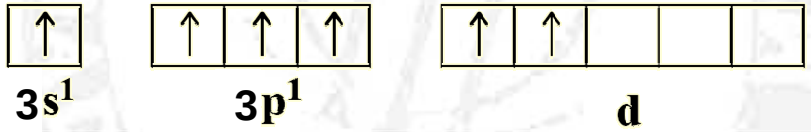
4. BOND THEORIES

SF_6

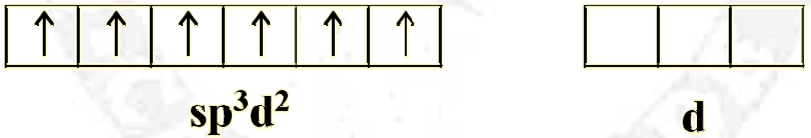
Orbital diagram S (ground state)

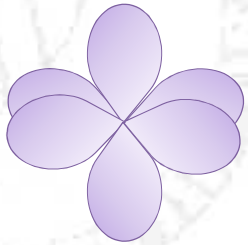


Promotion of 2 electron (3s →3p, 3d) (Excitation)

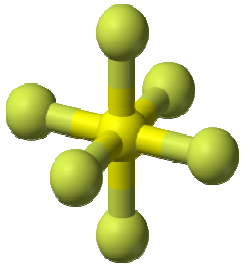


Mixing of orbitals (3s, 3p & 3d) (Hybridization)





sp^3d^2 orbitals



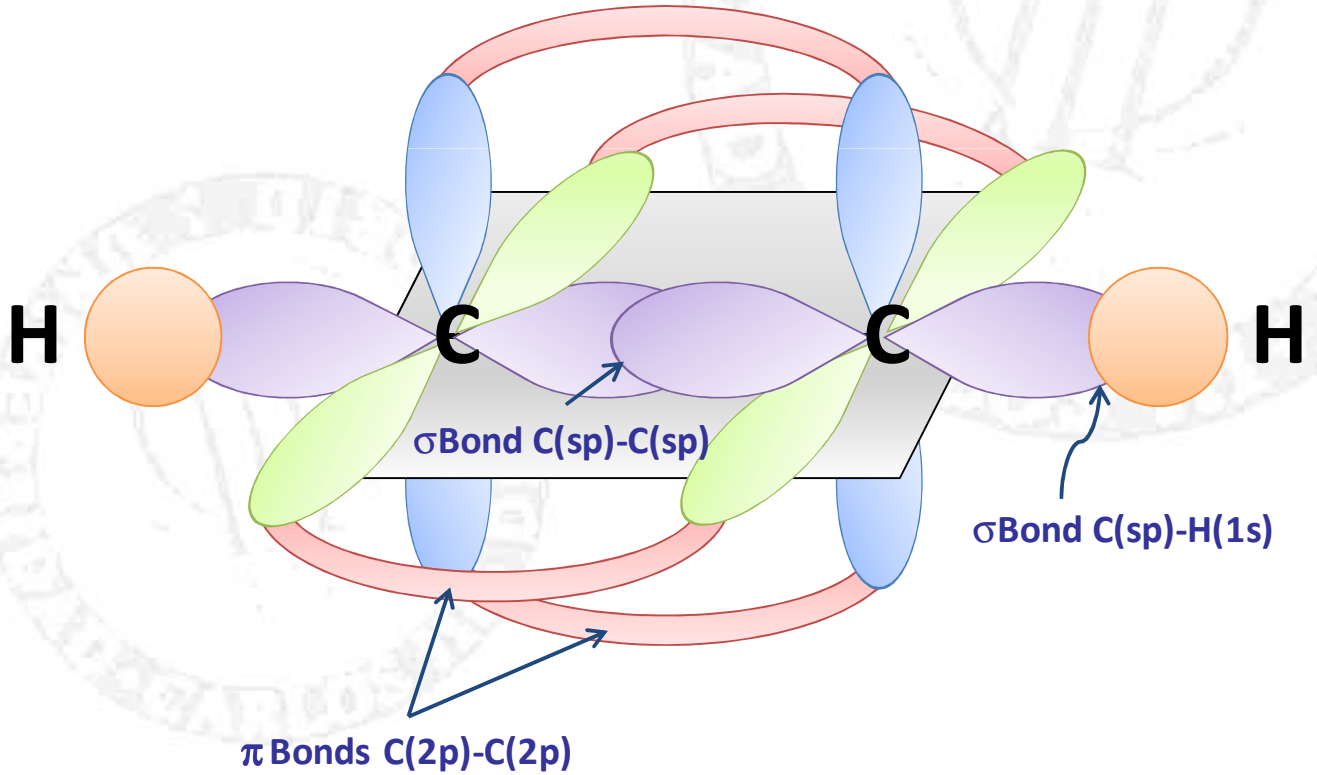
SF_6 molecule

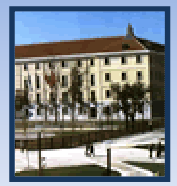
4. BOND THEORIES

Valence Bond Theory

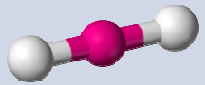
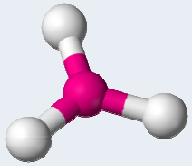
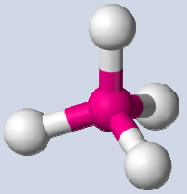
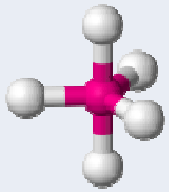
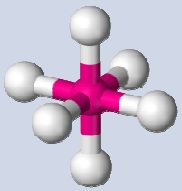
Hybridization of Atomic Orbitals.
Geometry of Organic Molecules.

B) Geometry in acethylene molecule C_2H_2





General Chemistry

Hybridization	Ideal bond angles	Molecular geometry	Stick and balls Model
sp	180º	Linear	
sp^2	120º	Trigonal	
sp^3	109.5º	Tetrahedral	
sp^3d	90º; 120º	Trigonal pyramidal	
sp^3d^2	90º	Octahedral	

4. BOND THEORIES

Molecular Orbital Theory

Explains the formation of the H-H bond in H_2 molecule.

Description of the model:
When the 1s wave functions of the **two hydrogen atoms (H)** are combined, one sigma (σ) bonding orbital (named σ_{1s}) is obtained. It is known as **linear combination of atomic orbitals (LCAO)**.

-The sum of the two 1*s* orbitals (one for each atom) yields the **bonding orbital**. In terms of wave mechanics, this corresponds to a ***constructive interaction*** .

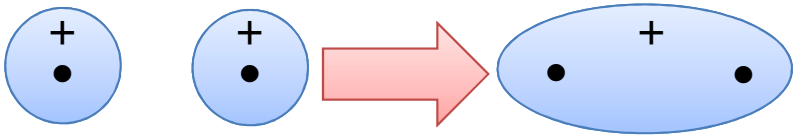
-The difference of the two orbitals forms the **antibonding orbital**, s_{1s}*, i.e. in terms of wave mechanics, this corresponds to a ***destructive interference***.

4. BOND THEORIES

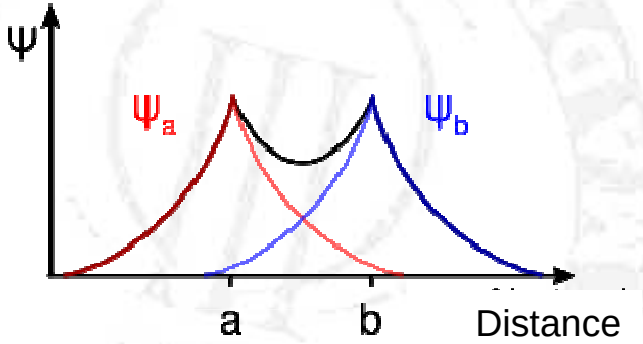
Molecular Orbital Theory

Bonding interaction

Addition



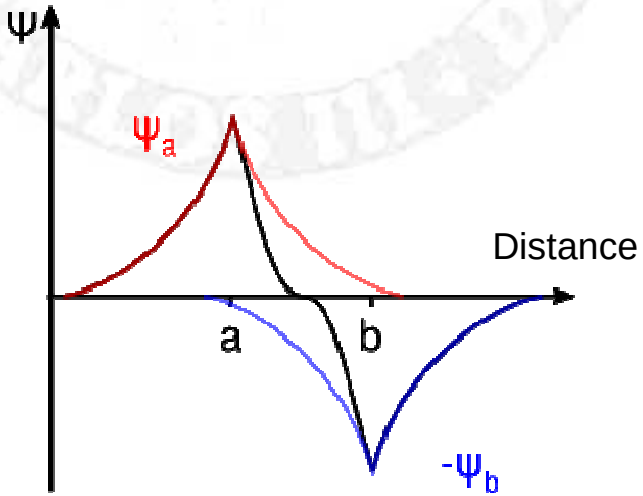
$1s_A + 1s_B$ σ



Antibonding interaction

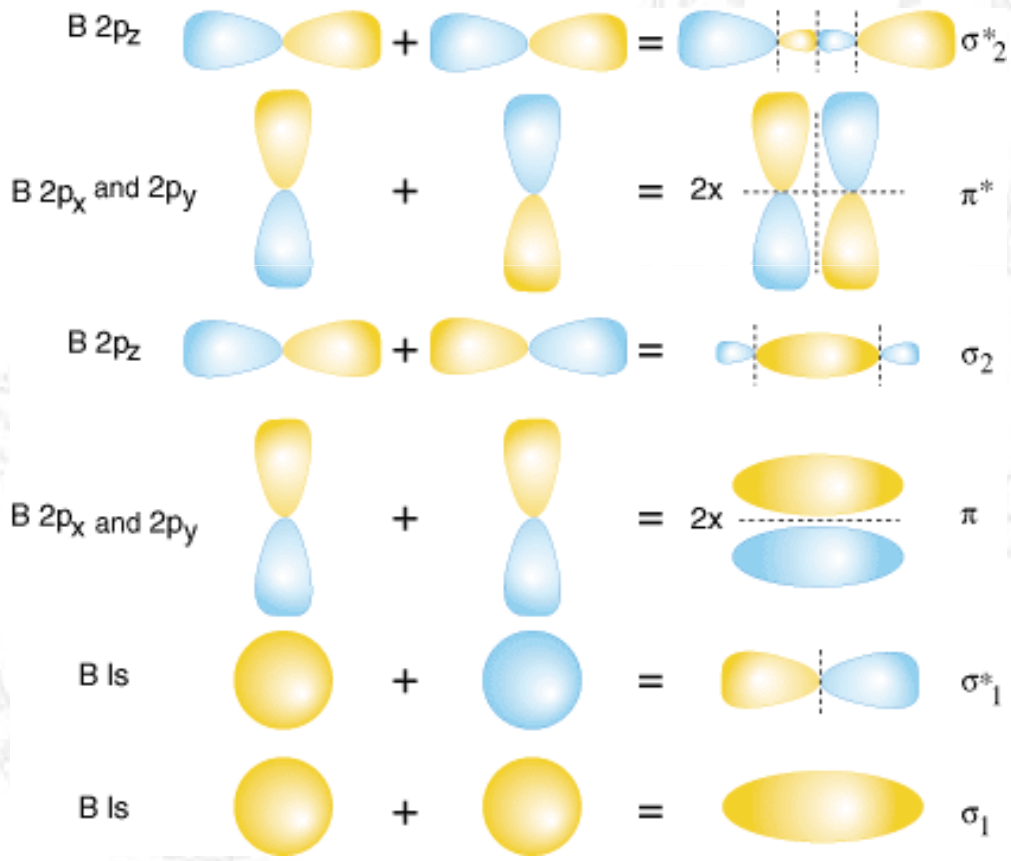
Substraction

$1s_A - 1s_B$ σ^*



4. BOND THEORIES

Molecular Orbital Theory



Images from http://www.sparknotes.com/chemistry/bonding/molecularorbital/section1.html

4. BOND THEORIES

Molecular Orbital Theory

Molecular orbital for Homonuclear Diatomic Molecules of the second period (Li_2 - N_2)

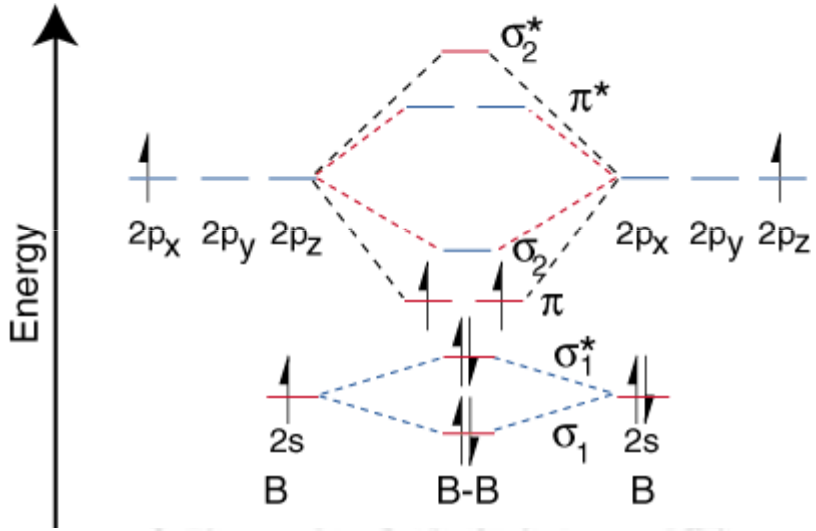
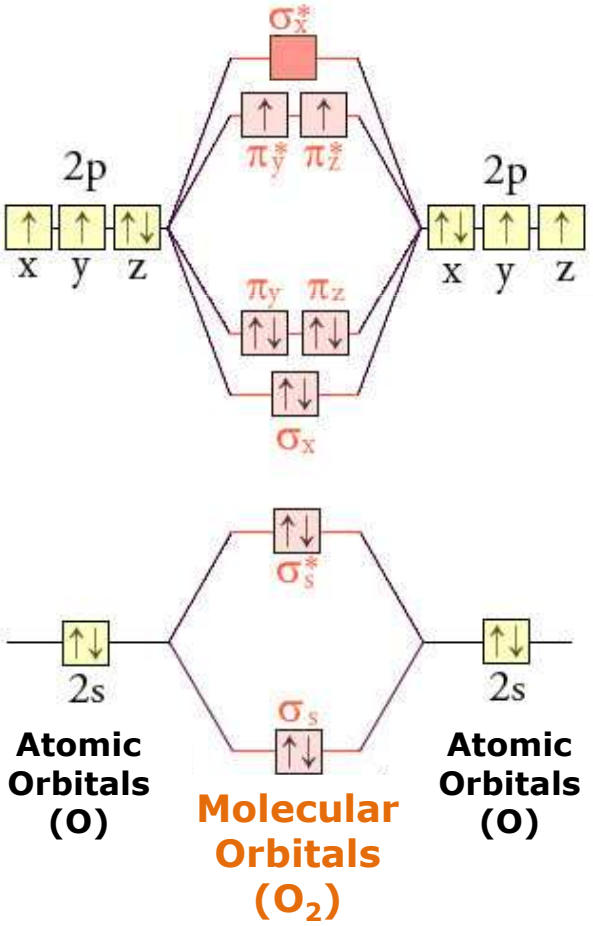


Image from
http://www.sparknotes.com/chemistry/bonding/molecularorbital/section1.html

$$\text{Bond Order} = \frac{\text{No. } e^- \text{ in bonding MOs - No. } e^- \text{ in antibonding MOs}}{2}$$

Molecular orbital for Homonuclear Diatomic Molecules of the second period (O_2 , F_2, Ne_2)



4. BOND THEORIES

Molecular Orbital Theory

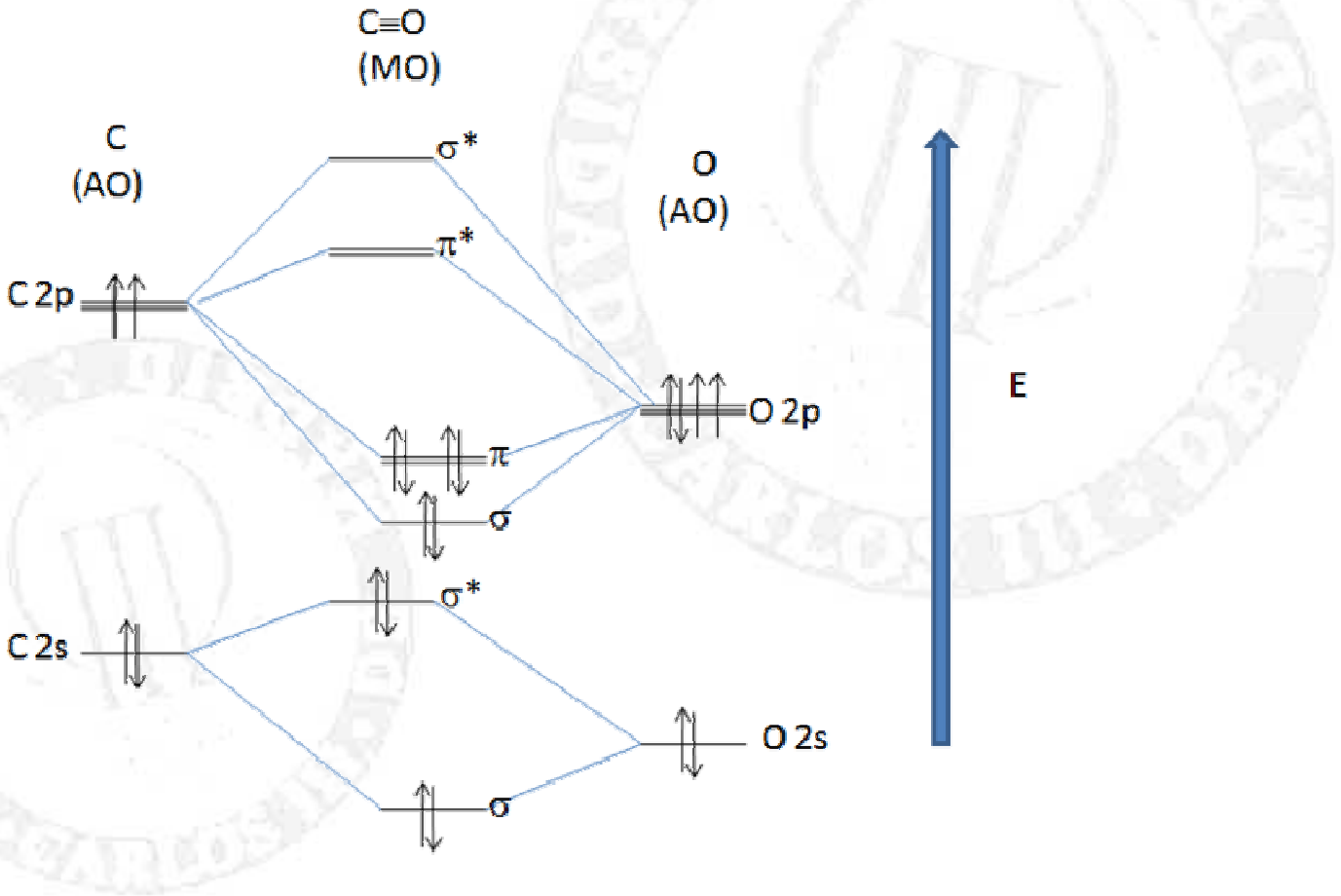
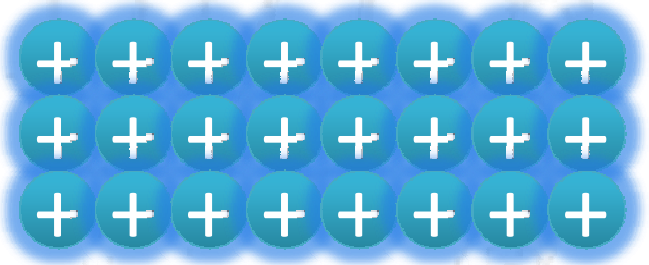


Image from http://commons.wikimedia.org/wiki/File:MOdiagramCO.png

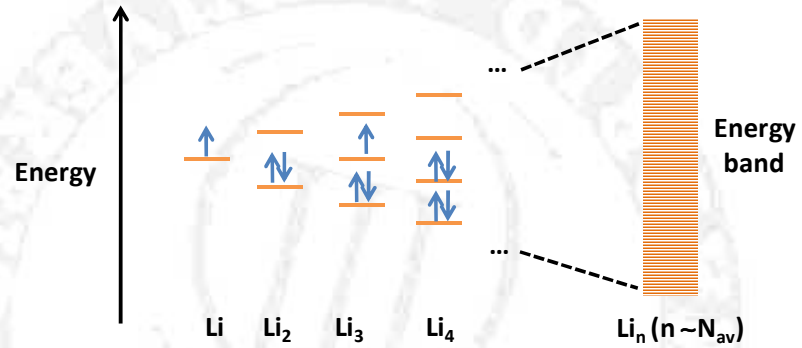
5. THE METALLIC BOND

- First approach to explain the metallic bond: the **electron sea model**
  - Nuclei are in a sea of electrons (the valence electrons)
  - It explains metallic luster and malleability



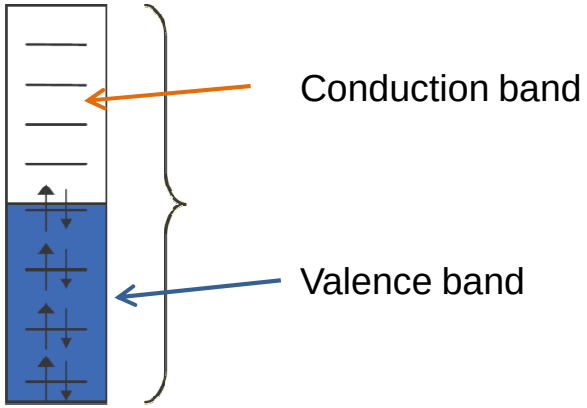
5. THE METALLIC BOND

- Bond theories: **the Band theory**
  - It is an extension of the MO theory
  - "N" atoms give "N" orbitals with very close energies → a **band** is formed.



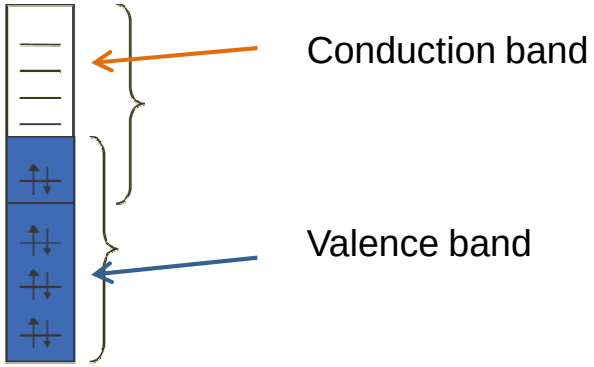
Band theory in alkaline metals

Outer shell electron configuration: ns^1
"N" orbitals, "N" levels → N/2 filled levels

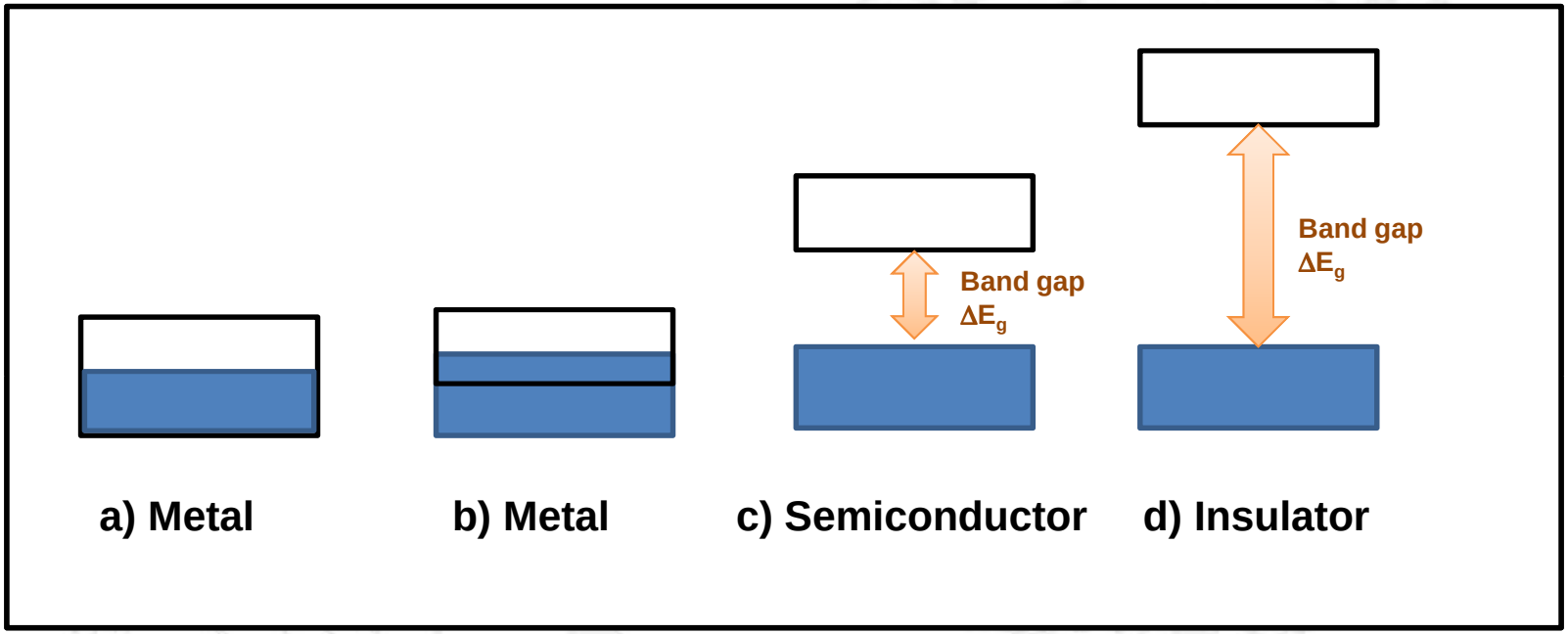


Band theory in alkaline earths metals

Outer shell electron configuration: **ns^2**
"N" orbitals, "N" levels → "N" filled levels
"p" and "s" bands overlap in energy.



5. THE METALLIC BOND



Elements of Group 14

	Tin	Germanium	Silicon	C (Diamond)
Gap (eV):	0,08	0,72	1,11	6,0

Bibliography

- ✓ R. H. Petrucci, W. S. Harwood, F. G. Herring, J. Madura. *General Chemistry. Principles and Modern Applications*. Prentice Hall, Ninth edition. Chapters 10-11.
- ✓ R. Chang. *Chemistry*. McGrawHill, Ninth edition. Chapters 9- 11.
- ✓ J. McMurry, R.C. Fay. Chemistry. Pearson, Fourth edition. Chapters 6, 7.