Chapter 5: The Chemical Bond

Foreword: This Chemical Bond course is intended for first-year technologie science students. This presentation results from reading numerous works and documents, most of which are not cited in the bibliography.Foreword: This Chemical Liaison course is intended for first-year technologie science students. This presentation results from reading numerous works and documents, most of which are not cited in the bibliography.

Chemical bond:

Classes of chemical bonds in biological science:

The Covalent bond:

Classes of chemical bonds in biological science:

Covalent bonding occurs by a sharing of valence electrons:

Electronegativity and bond type

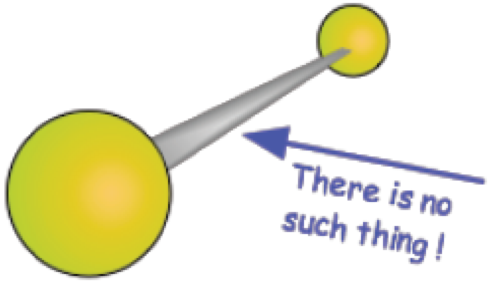
Electronegativity

Theory of hybrid orbitals (1928-)

Hybrids derived from atomic s- and p orbitals

What is a chemical bond?

Claim: chemical bonds are what hold atoms together to form the more complicated aggregates that we know as molecules and extended solids



There is no such thing !

It is more useful to regard a **chemical bond** as **an effect** that causes certain atoms to join together **to form enduring structures** that have **unique physical and chemical properties**.

Most important 1: chemical bonding occurs when one or more electrons are simultaneously attracted to two nuclei.

Most important 2: A chemical bond between two atoms forms if the resulting arrangement of the two nuclei and their electrons has a lower energy than the total energy of the separate atoms.

What is a molecule?

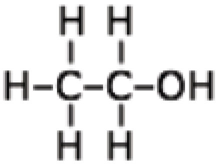
A molecule is an aggregate of atoms that possesses **distinctive observable properties**

A more **restrictive definition distinguishes** between a "true" molecule that exists as an independent particle, and an **extended solid** that can only be represented by its simplest formula.

chemical species is defined by its structure.

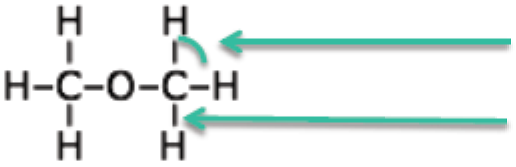
The structure of a molecule is specified by the identity of its constituent atoms and the sequence in which they are joined together, that is, by the bonding connectivity. This, in turn, defines the bonding geometry— the spatial relationship between the bonded atoms.

structural formulas reveal the very different connectivities



ethanol

C_2H_6O



bond angle

bond length

dimethyl ether

C_2H_6O

Chemical bond:

- Chemical bonding refers to the force that holds the chemical molecules or atoms together.
- Strength of the bond varies considerably, depends on the molecules or atoms involved in the process of bond formation.

Classes of chemical bonds in biological science:

1) Covalent bonds

2) Non-covalent bonds:

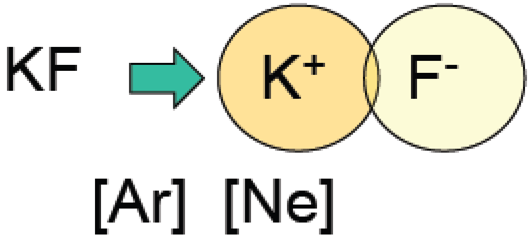
Ionic - Hydrogen - Hydrophobic - Van der waals bonds

Classical models of chemical bonding

In essence - electrostatic considerations

- ionic bond +

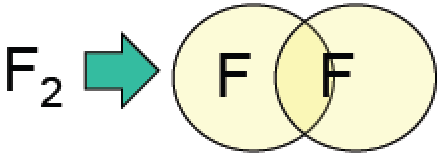
Walther Kossel, 1915, German



electron configuration
of noble (rare) gases

covalent bondig

Gilbert Newton Lewis,
1916, USA



δ- polar covalent δ +

The Covalent bond:

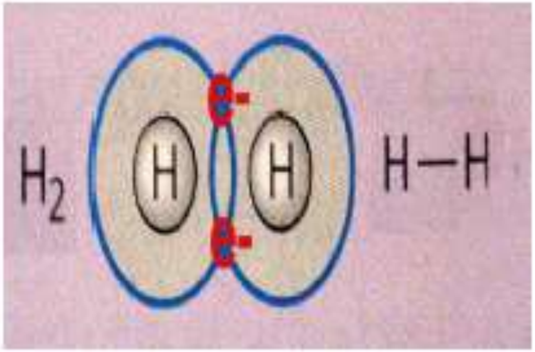
- The covalent bond is a bond formed between two atoms by electron sharing. (usually formed between two non-metal atoms by sharing electron pairs).
- Covalent Bonds are the strongest chemical bonds, formed by the sharing of a pair of electrons.
- The energy of a typical single covalent bond is ~80 kilocalories per mole (kcal/mol). However, this bond energy can vary from ~50 kcal/mol to ~110 kcal/mol depending on the elements involved.
- Once formed, covalent bonds rarely break spontaneously.

- **In a single bond, one electron pair is shared.**
- **In double bond, two electron pairs are shared.**
- **In triple bond, three electron pairs are shared.**

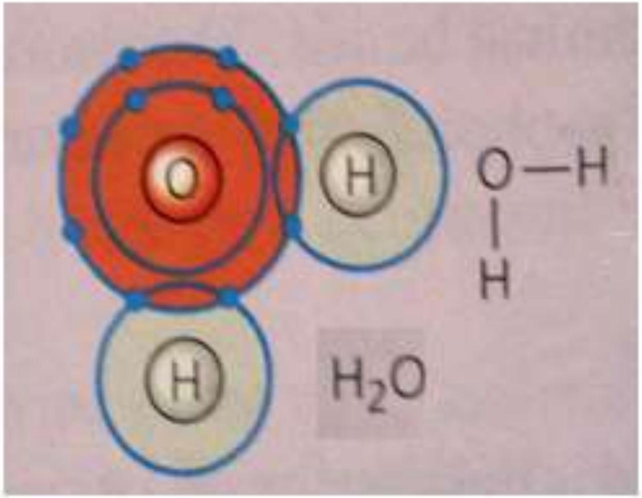
For example:

Single bond

H_2



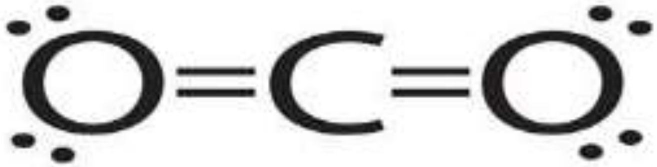
H_2O



Double bond

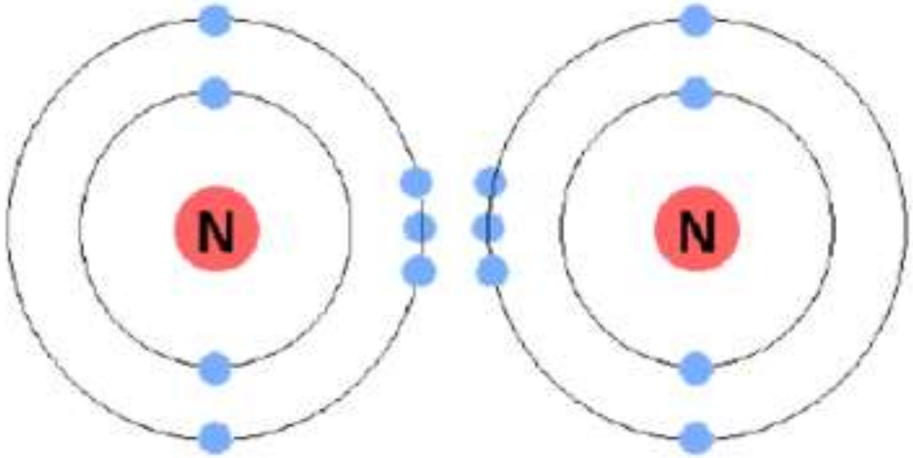
CO_2

Carbon Dioxide Molecule (CO_2)



Triple bond

N2



Covalent bond - Lewis model

Shared electron pair – a unit of the covalent bond

H· – ·H

H:H H–H

Number of shared electron pairs – valency

H $(1s)^1$ C $[He](2s)^2 (2p)^2$ N $[He](2s)^2 (2p)^3$

valency: H: 1 C: 4 N: 3

H–C≡N|

non-bonding (lone) electron pair

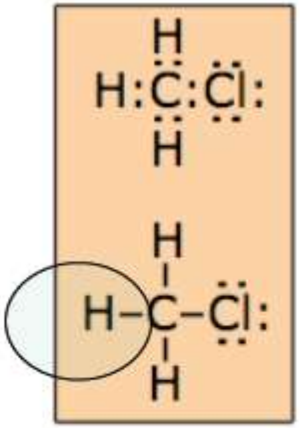
Lewis (electronic) structural formulas

(8-electron) octet rule

valence electron configuration of noble gases

– exceptions

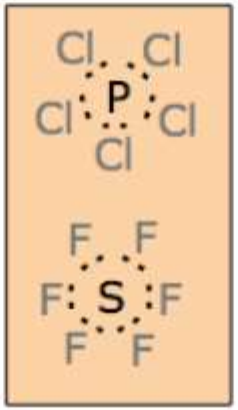
rule not always appropiate

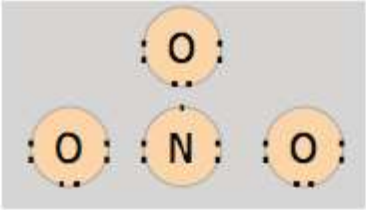


[He]

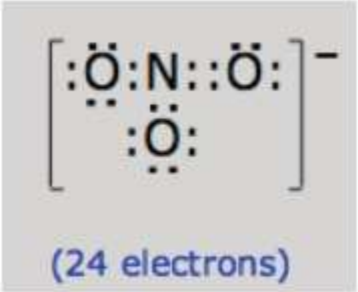
with d and f orbitals the valency is increased

- hypervalence





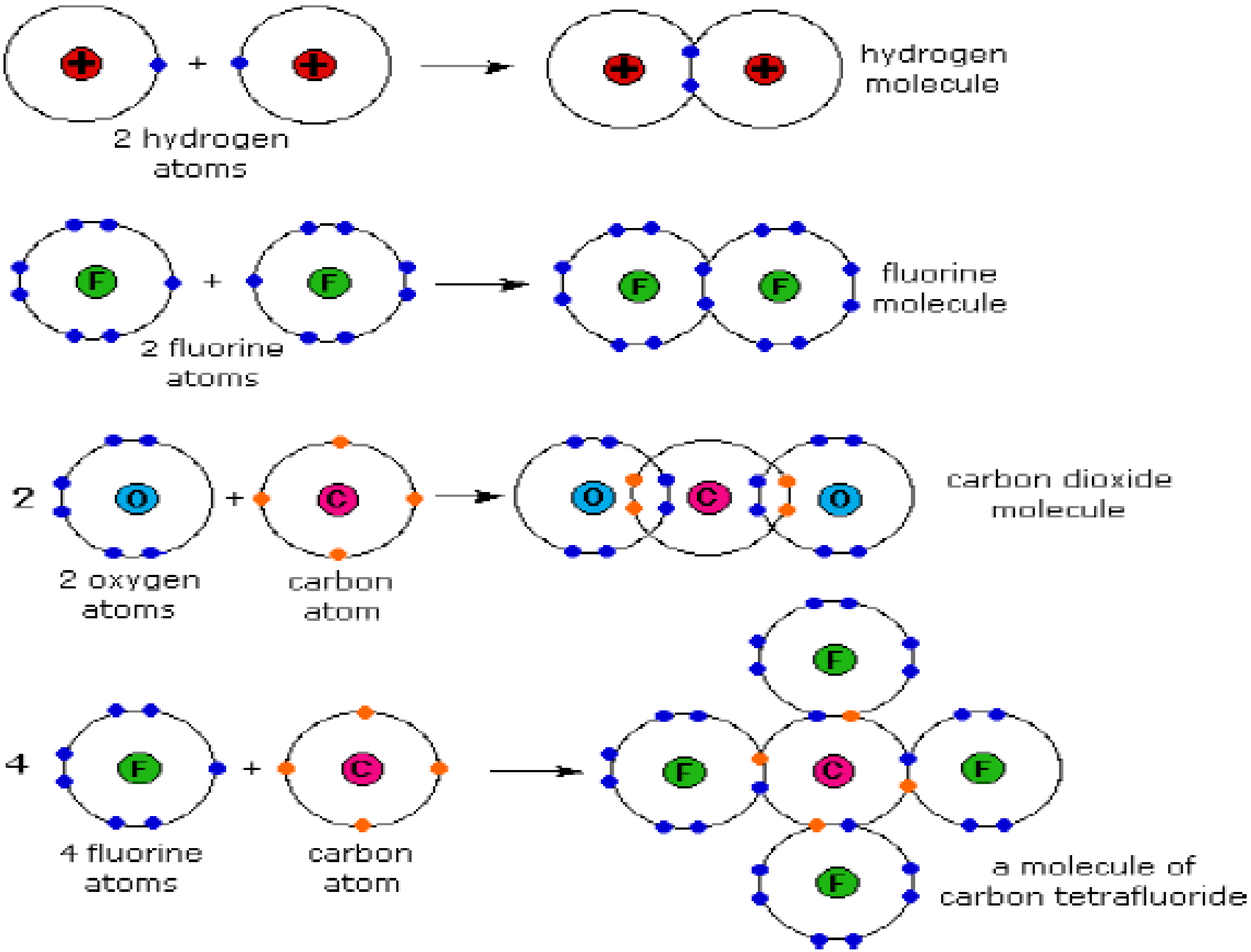
+ 1 electron

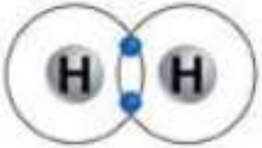


(24 electrons)

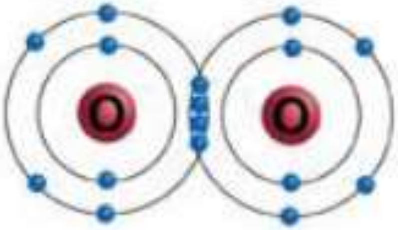
Covalent bonding occurs by a sharing of valence electrons:

Examples of covalent bonding:

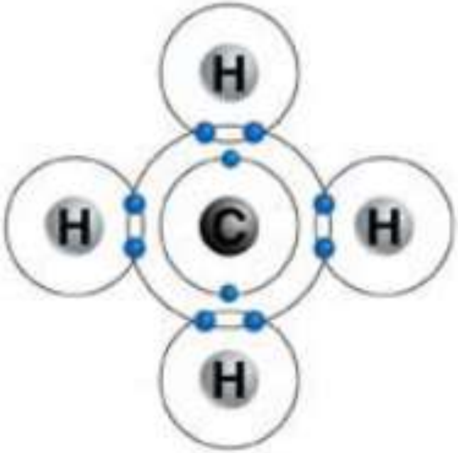


Electron Model	Structural Formula	Molecular Formula
	$H-H$	H_2

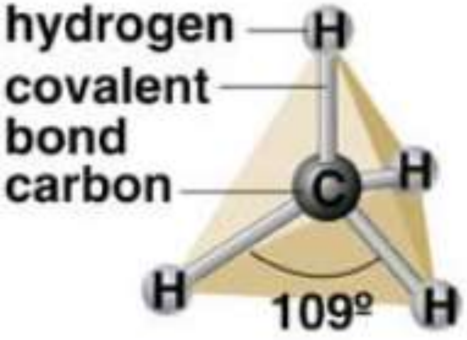
a. Hydrogen gas

	$O=O$	O_2

b. Oxygen gas

	$\begin{array}{c} H \\ \vert \\ H-C-H \\ \vert \\ H \end{array}$	CH_4

c. Methane

Ball–and–stick Model


Space-filling Model


d. Methane, cont'd.

Covalent bond - Lewis model

does not explain the nature of „bonding“ orbitals

„implicitly“ works with localized (unchanged) atomic orbitals

Limitation to two-center bonds

does not explain the geometric structure of molecules

Lewis model does not explain the structure!

VSEPR model – 1960 Ronald Gillespie

Valence-Shell Electron-Pair Repulsion

Regions of high electron density

bond

lone pair

rule: multiple bond is a single region

rule: any of the resonant structures can be used

geometric structure is determined by the repulsion of these regions!

Types of covalent bonds:

1) Non-polar covalent bond.

2) polar covalent bond.

1) Non-polar covalent bond

- It is a covalent bond in which electrons are shared equally between two atoms.
- Non-polar covalent bonds are formed, when the sharing atoms have the same electronegativity → so the electrons are shared equally.

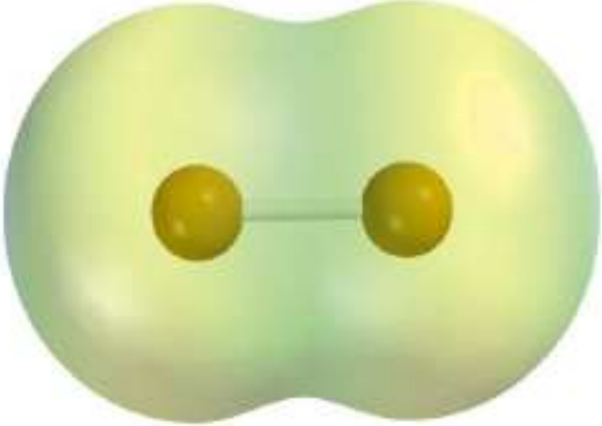
→ Electron cloud is not displaced

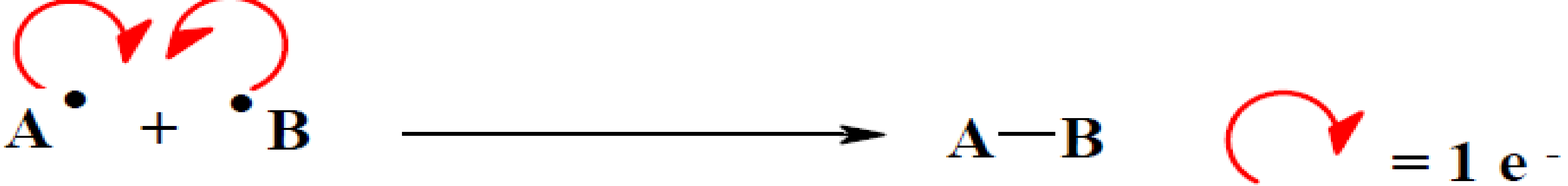
Example

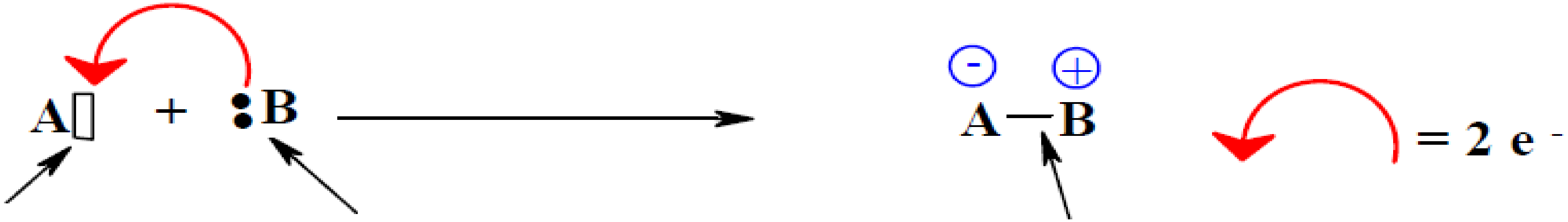
Covalent bonds that are formed between identical atoms, as in oxygen gas (O_2) and hydrogen gas (H_2), Cl_2

[Since the electrons are equally shared between the two identical atoms, these molecules are said to be nonpolar and the bonds between them are nonpolar covalent bonds].

Cl:Cl A nonpolar covalent bond







2) Polar covalent bond

A type of covalent bond between two different atoms in which electrons are shared unequally. The shared electrons tend to be pulled more toward one atom than the other (because of electronegativity) → and results on partial charges on the atom (i.e one end of the molecule has a slightly negative charge and the other a slightly positive charge.

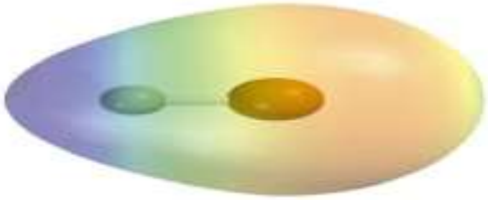
Example

bond between the two atoms H and Cl

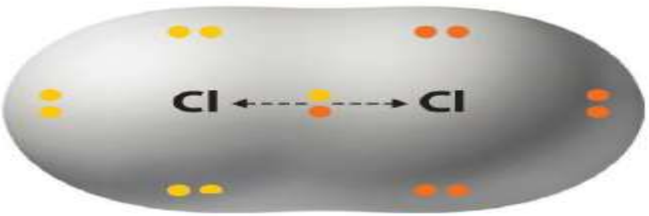
$^{\delta+}\mathrm{H}-\mathrm{Cl}^{\delta-}$

$[\mathrm{H}\ \mathrm{:Cl}]$

A polar covalent bond.
The bonding electrons are attracted more strongly by Cl than by H.

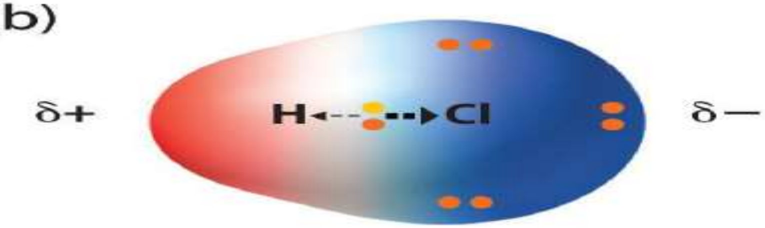


(a)



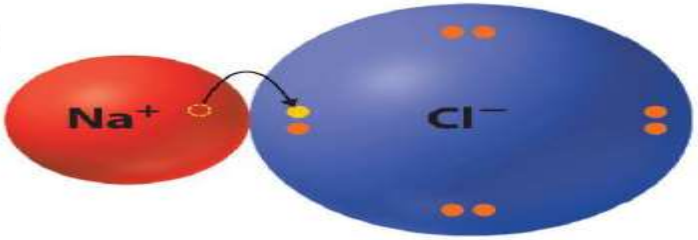
Nonpolar covalent bond
Bonding electrons shared equally between two atoms.
No charges on atoms.

(b)



Polar covalent bond
Bonding electrons shared unequally between two atoms.
Partial charges on atoms.

(c)

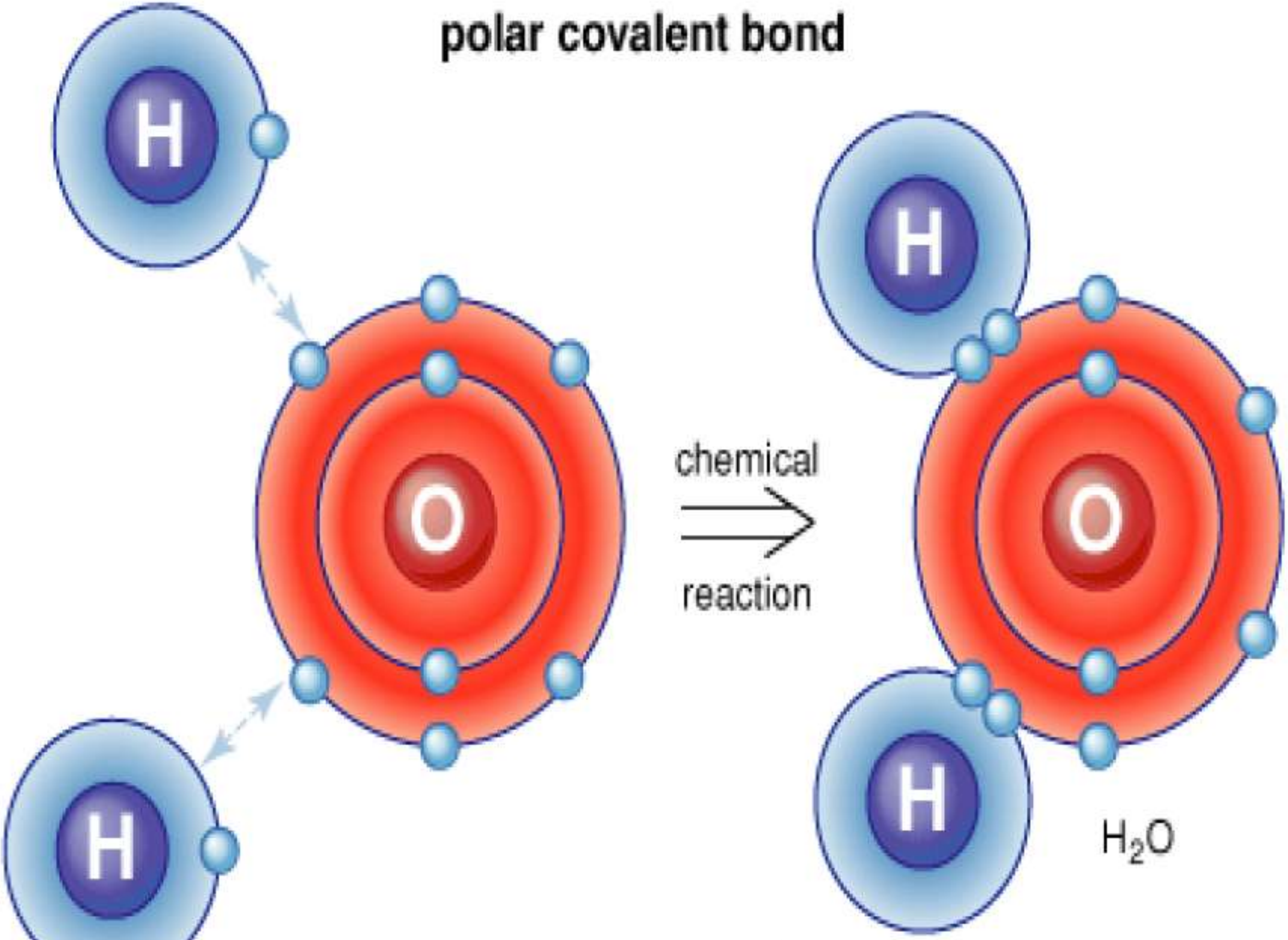


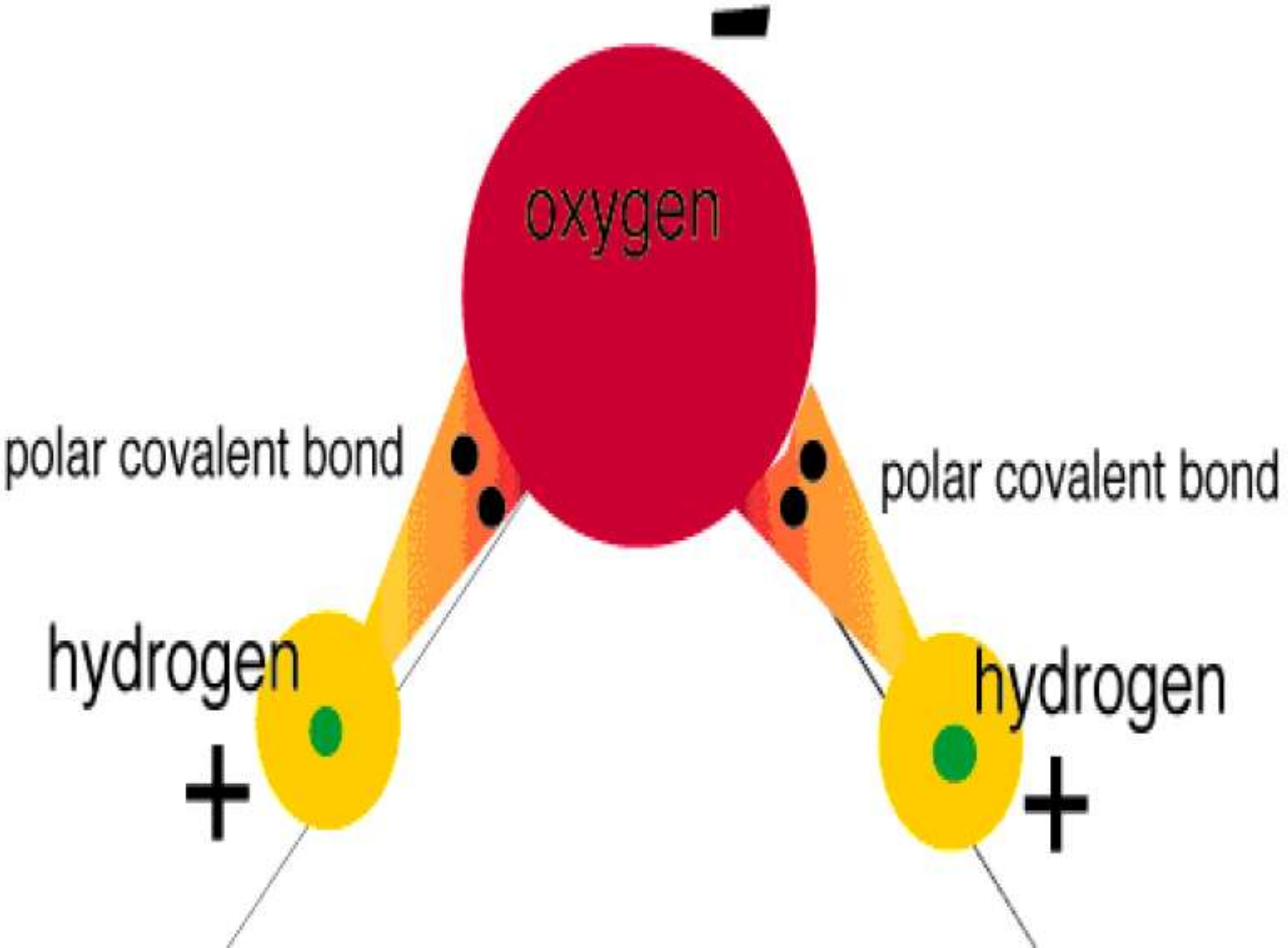
Ionic bond
Complete transfer of one or more valence electrons.
Full charges on resulting ions.

Note: Atoms of oxygen, nitrogen and phosphorus have a particularly strong tendency to pull electrons toward themselves when they bond with other atoms.

- Water is the most abundant molecule in the body and serves as the solvent for body fluids.
- Water is a good example because it is polar; the oxygen atom pulls electrons from the two hydrogens toward its side of the water molecule, so that the oxygen side is more negatively charged than the hydrogen side of the molecule.

polar covalent bond




-
oxygen
polar covalent bond
polar covalent bond
hydrogen
hydrogen
+
+

Electronegativity and bond type

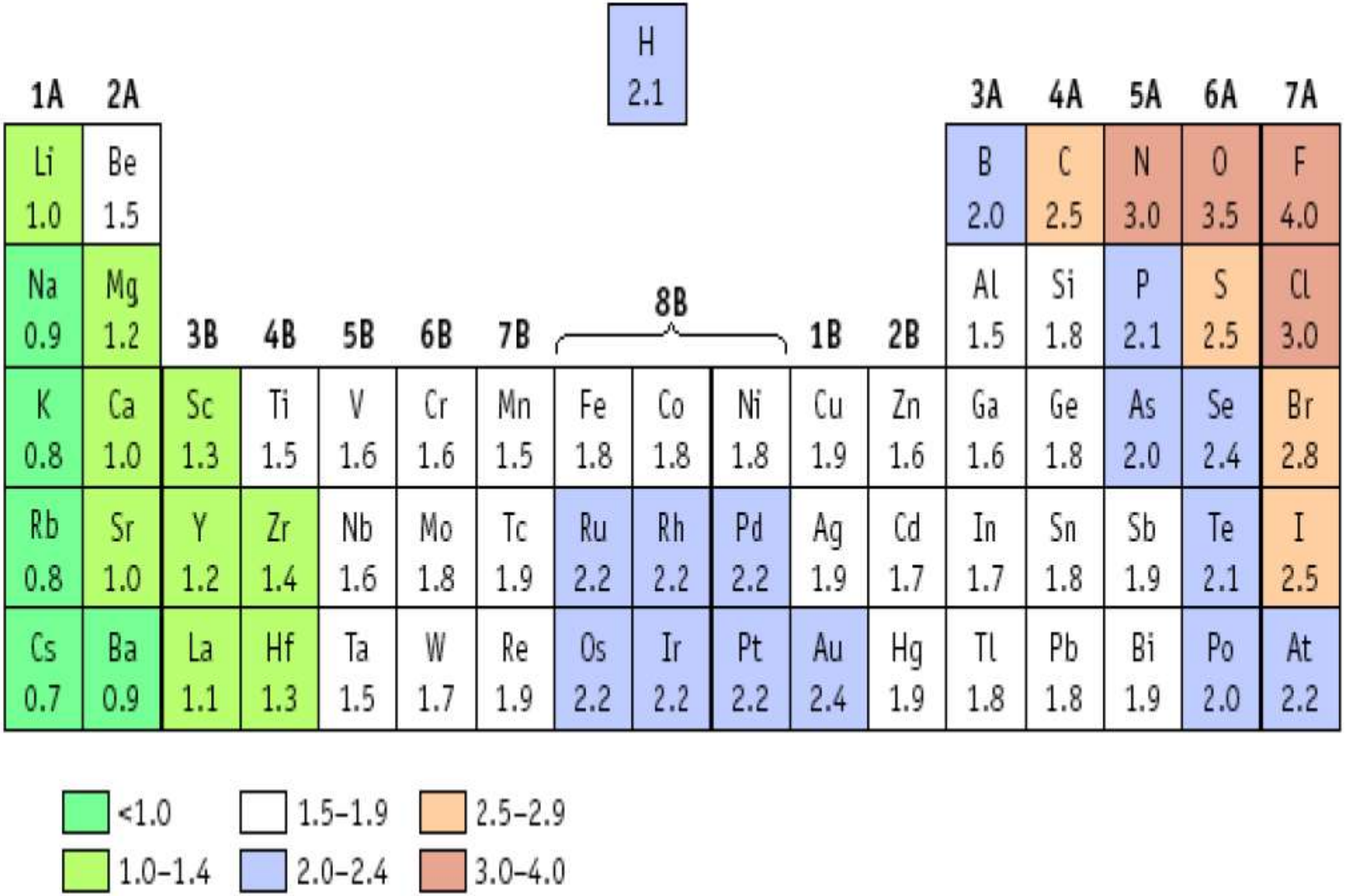
Electronegativity

- Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons.
- The difference in electronegativity's of two elements can be used to predict the nature of the chemical bond.
  - If the difference in electronegativity's is between:

    1.7 to 4.0: Ionic

    0.3 to 1.7: Polar Covalent

    0.0 to 0.3: Non-Polar Covalent



1A	2A	3B	4B	5B	6B	7B	8B	8B	8B	1B	2B	3A	4A	5A	6A	7A
								H 2.1								
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.7	Ba 0.9	La 1.1	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2

🟩 <1.0
🟩 1.0–1.4
⬜ 1.5–1.9
🟦 2.0–2.4
🟧 2.5–2.9
🟥 3.0–4.0

Figure 9.9 Electronegativity values for the elements according to Pauling. Trends for electronegativities are the opposite of the trends defining metallic character. Nonmetals have high values of electronegativity, the metalloids have intermediate values, and the metals have low values.

Example

Na Cl

Na = 0.9, Cl = 3.0

Difference in electronegativity (ΔEN) is 2.1, so → this is an ionic bond

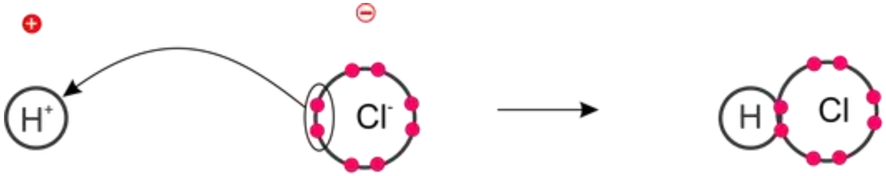
Ionic bond

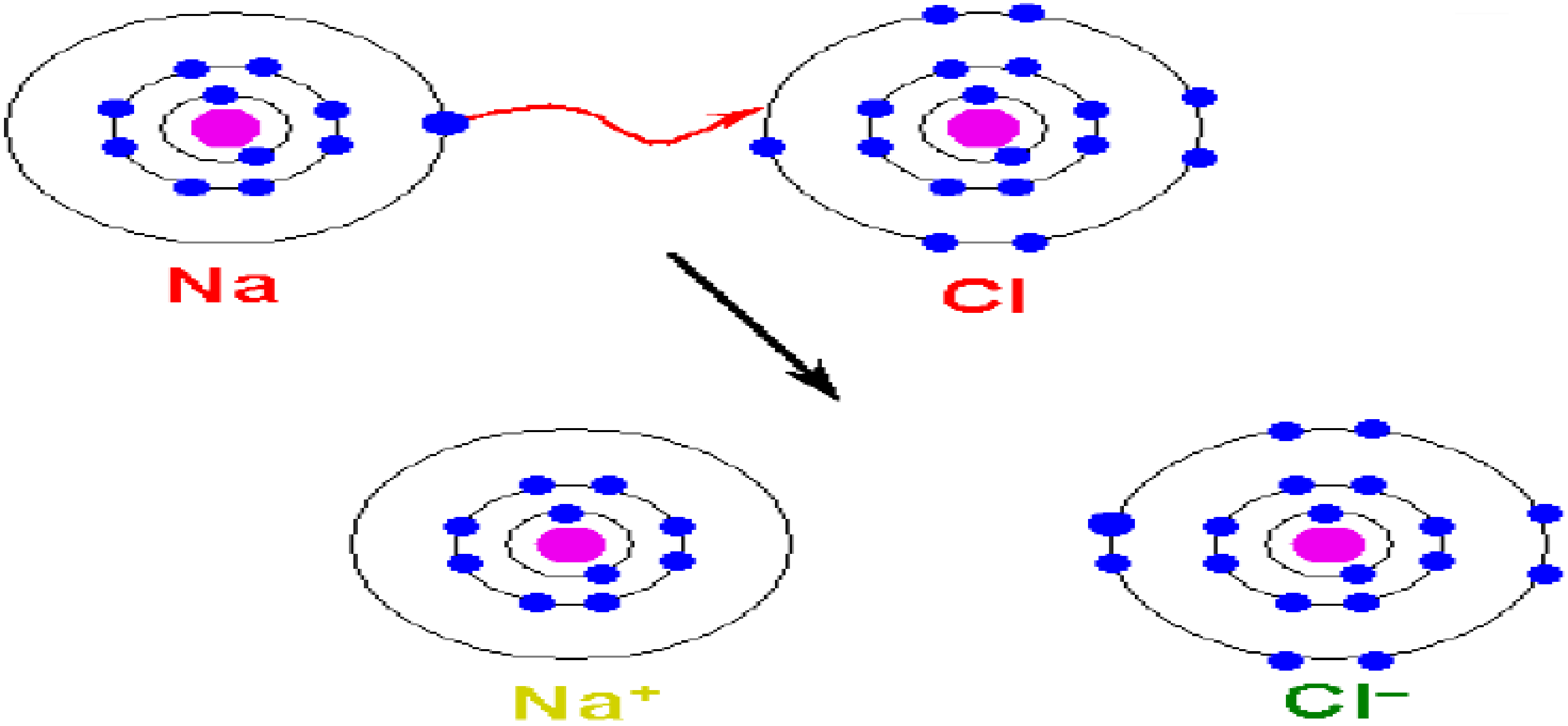
Ionic bond result when one or more valence electrons from one atom are completely transferred to a second atom. Thus, the electrons are not shared at all.

- **The first atom loses electrons → so that its number of electrons become smaller than its number of protons → it becomes a positively charged ion.**
- **The second atom now has more electrons than it has protons → and becomes a negatively charged ion.**

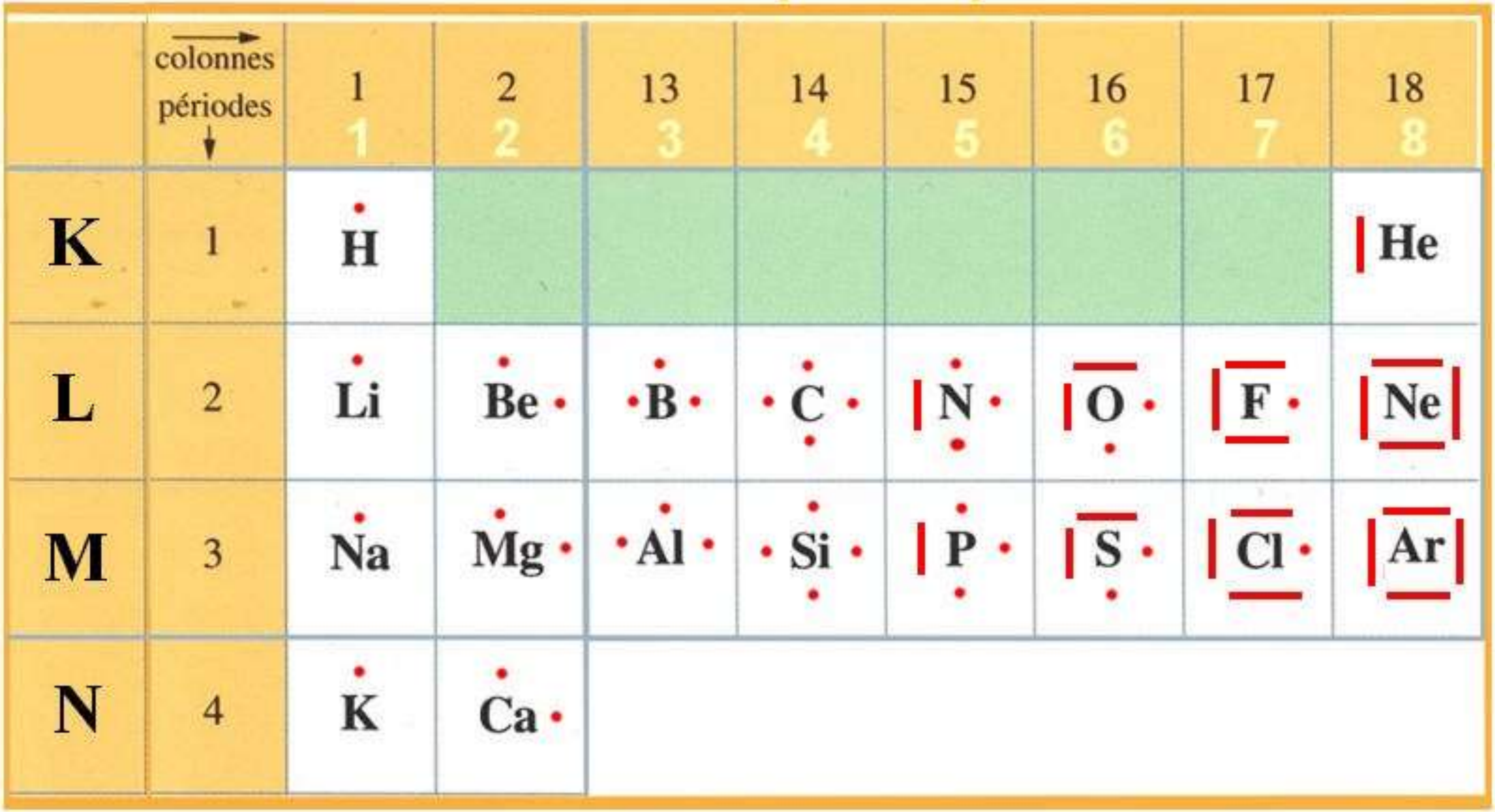
- Atoms that has positive or negative charges are called ions
  - Positively charged ions are called cations.
  - Negatively charged ion are called anions.

Example NaCl

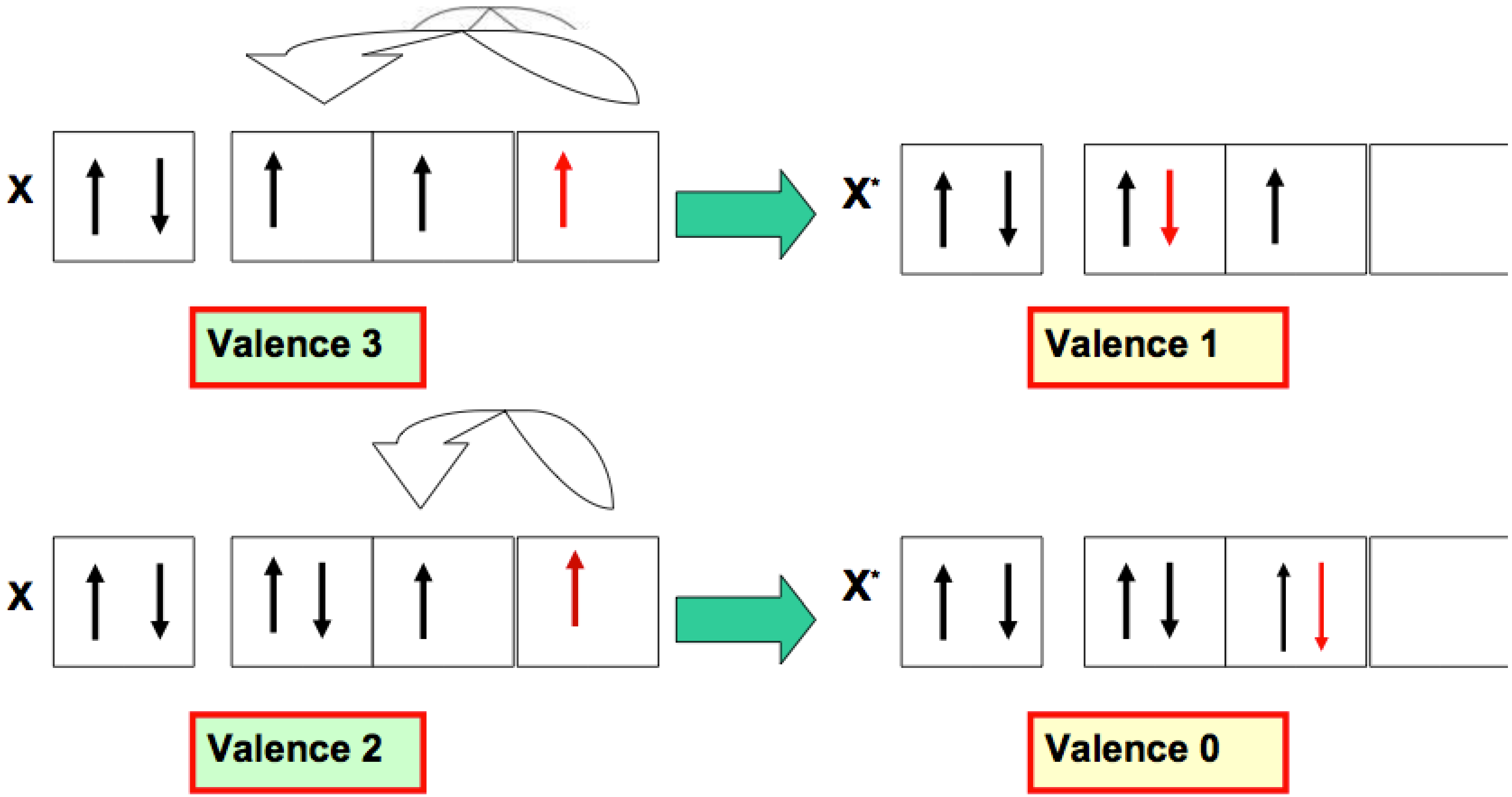




Classification périodique réduite



	colonnes → périodes ↓	1 1	2 2	13 3	14 4	15 5	16 6	17 7	18 8
K	1	**H**							**He**
L	2	**Li**	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
M	3	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
N	4	**K**	**Ca**						

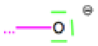
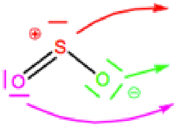
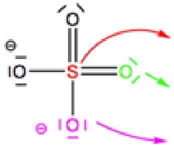


Valence 3

Valence 1

Valence 2

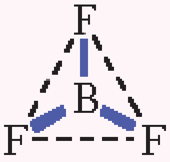
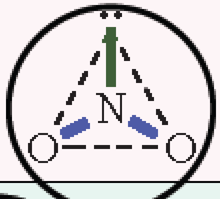
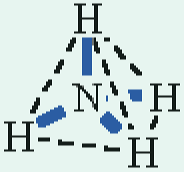
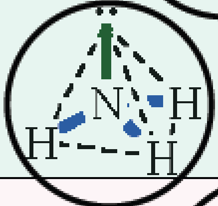
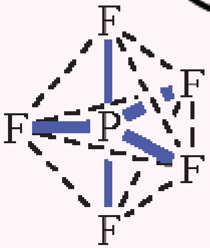
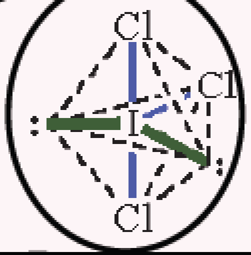
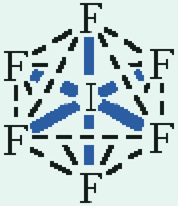
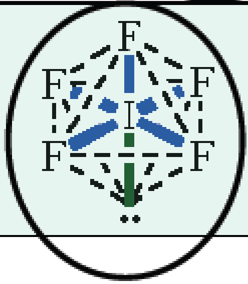
Valence 0

	O: $1s^2\ 2s^2\ 2p^4$; 6 électrons de valence ; $Cf = 6 - 2 - 2 \times 2 = 0$; Dans une molécule l'oxygène divalent est neutre.
	O: $1s^2\ 2s^2\ 2p^4$; 6 électrons de valence ; $Cf = 6 - 1 - 2 \times 3 = -1$; Dans une molécule l'oxygène monovalent porte une charge formelle -1. In a molecule, monovalent oxygen carries a formal charge -1.
	S: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$; 6 électrons de valence ; 6 valence electrons; $Cf = 6 - 3 - 2 \times 1 = +1$ O: $1s^2\ 2s^2\ 2p^4$; 6 électrons de valence ; $Cf = 6 - 1 - 2 \times 3 = -1$ O: $1s^2\ 2s^2\ 2p^4$; 6 électrons de valence ; $Cf = 6 - 2 - 2 \times 2 = 0$
	S: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$; 6 électrons de valence ; $Cf = 6 - 6 - 2 \times 0 = 0$ O: $1s^2\ 2s^2\ 2p^4$; 6 électrons de valence ; $Cf = 6 - 2 - 2 \times 2 = 0$ O: $1s^2\ 2s^2\ 2p^4$; 6 électrons de valence ; $Cf = 6 - 1 - 2 \times 3 = -1$

Règle :

La somme des charges formelles est toujours égale à la charge globale de l'édifice. The sum of the formal loads is always equal to the overall load of the building.

VSEPR structures

regions with high densitties	most favorable arrangement		
2	linear	Cl—Be—Cl	
3	planar trigonal		
4	tetrahedral		
5	trigonal bypiramidal		
6	octahedral		

Predicting the shapes of molecules with general formula AX_nE_m

-Repulsion: LP-LP > LP-BP > BP-BP

-Lone pairs occupy the largest site (e.g. equatorial in a trigonal bipyramid)

-If all sites are equal (e.g. octahedral geometry) then lone pairs will be trans to each other (i.e. forming a 180° angle)

-Double bonds occupy more space than single bonds - Bonding pairs to electronegative substituents occupy less space than those to more electropositive substituents.

Pseudostructure

Structure

Tetrahedral

Trigonal pyramidal

AX_3E

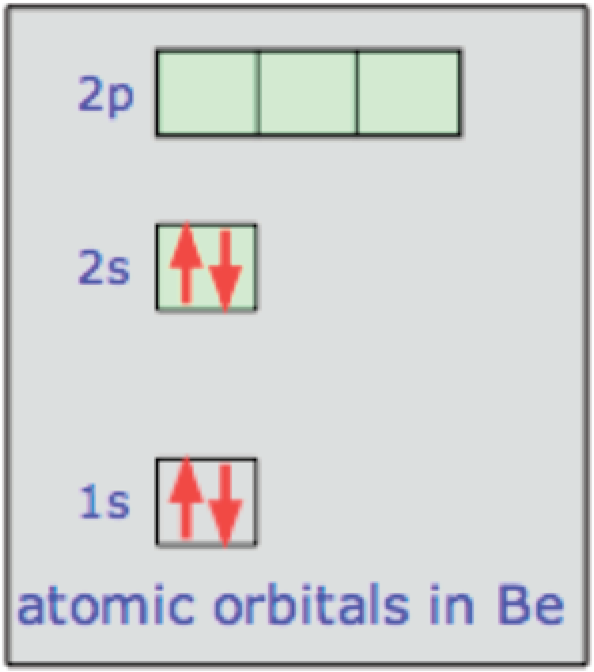
trigonal (bent)

AX_2E_2

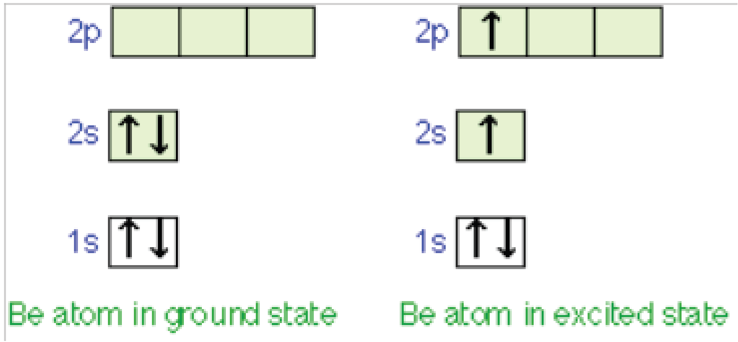
Why atomic orbitals don't work for molecules

Bonding in beryllium hydride

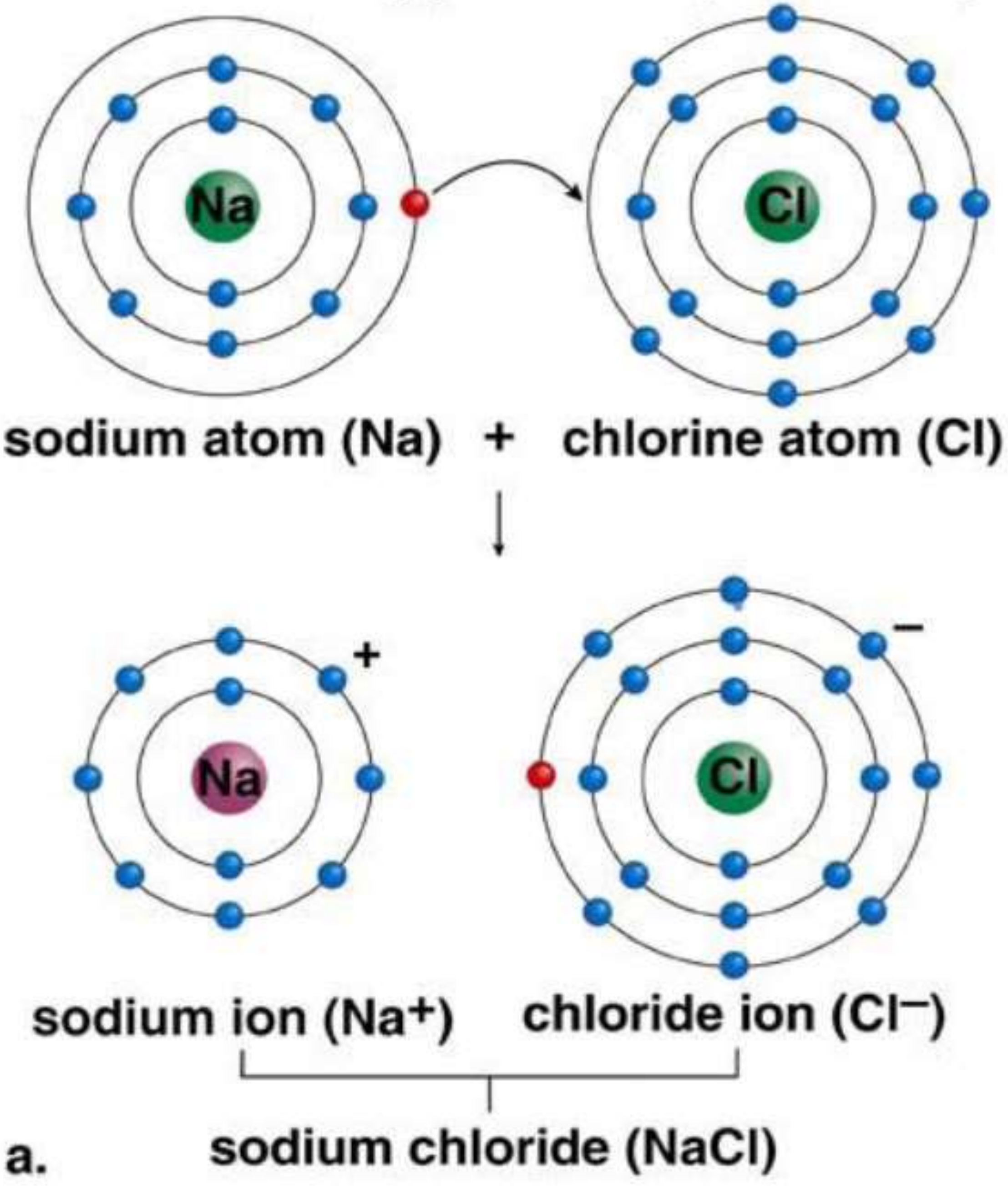
Consider how we might explain the bonding in a compound of divalent beryllium, such as beryllium hydride, BeH_2. The beryllium atom, with only four electrons, has a configuration of $1s^2 2s^2$. Note that the two electrons in the 2s orbital have opposite spins and constitute a stable pair that has no tendency to interact with unpaired electrons on other atoms.

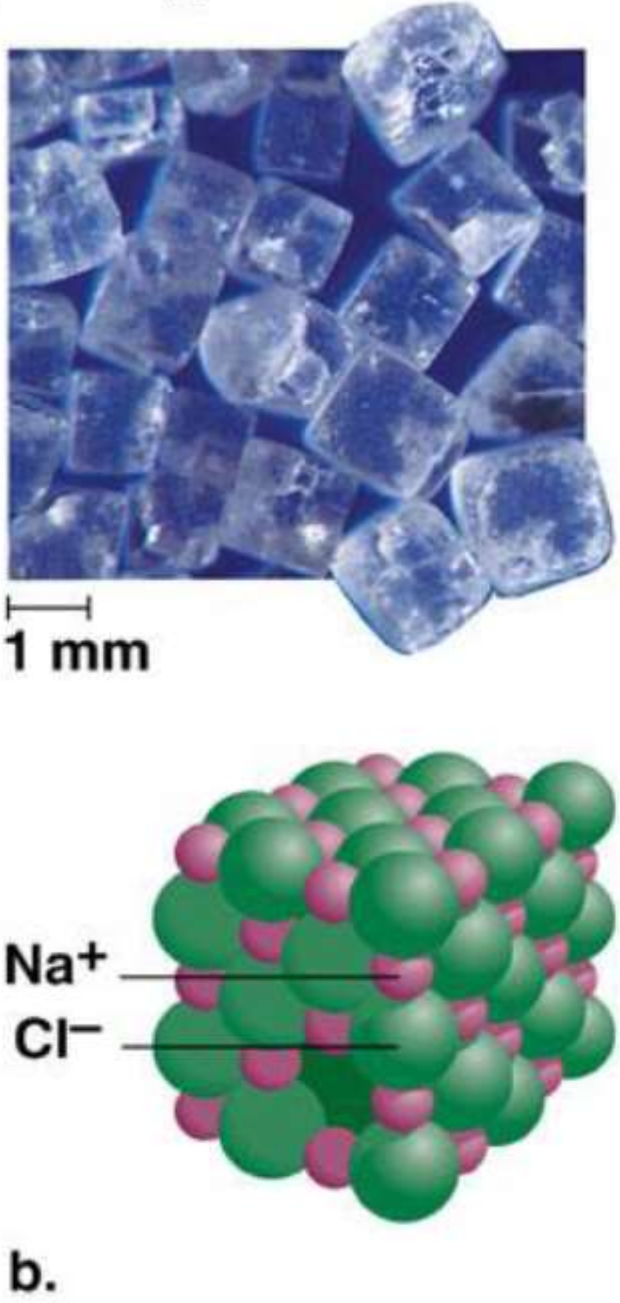


The only way that we can obtain two unpaired electrons for bonding in beryllium is to promote one of the 2s electrons to the 2p level. However, the energy required to produce this excited-state atom would be sufficiently great to discourage bond formation. It is observed that Be does form reasonably stable bonds with other atoms. Moreover, the two bonds in BeH_2 and similar molecules are completely equivalent; this would not be the case if the electrons in the two bonds shared Be orbitals of different types, as in the "excited state" diagram above.



These facts suggest that it is incorrect to assume that the distribution of valence electrons that are shared with other atoms can be described by atomic-type s, p, and d orbitals at all.


Na
Cl
sodium atom (Na) + chlorine atom (Cl)
Na
+
Cl
–
sodium ion (Na^+)
chloride ion (Cl^-)
sodium chloride (NaCl)
a.


1 mm
Na^+
Cl^-
b.

- **The sodium ion and the chloride ion will be attracted to each other and form an ionic bond.**

→ **The ionic bond is due to the attractive forces between the positively charged sodium & the negatively charged chloride.**

→ **Therefore, ionic compounds are usually between metals and nonmetals (opposite ends of the periodic table).**

Hydrogen bond

- A hydrogen bond is a type of attractive interaction between an electronegative atom and a hydrogen atom bonded covalently to another electronegative atom.

Examples

N – H -------------- O=C -

O – H -------------- O=C -

[a chemical bond consisting of a hydrogen atom between two electronegative atoms (e.g., oxygen or nitrogen) with one side be a covalent bond and the other being an ionic Bond]

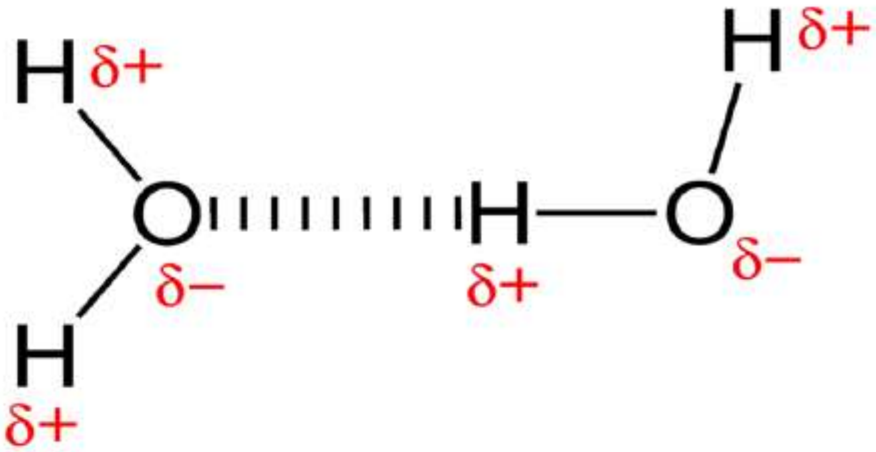
- **This bond always involves a hydrogen atom.**
- **Hydrogen bonds can occur between molecules or within parts of a single molecule. [When a hydrogen atom forms a polar covalent bond with an atom of oxygen or nitrogen, the hydrogen gains a slight positive charge as the electron is pulled towards the other atom. This other atom is thus described as being electronegative. Since the hydrogen has a slight positive charge, it will have a weak attraction for a second electronegative atom (oxygen or nitrogen) that may be located near it. This weak interaction is called a hydrogen bond].**

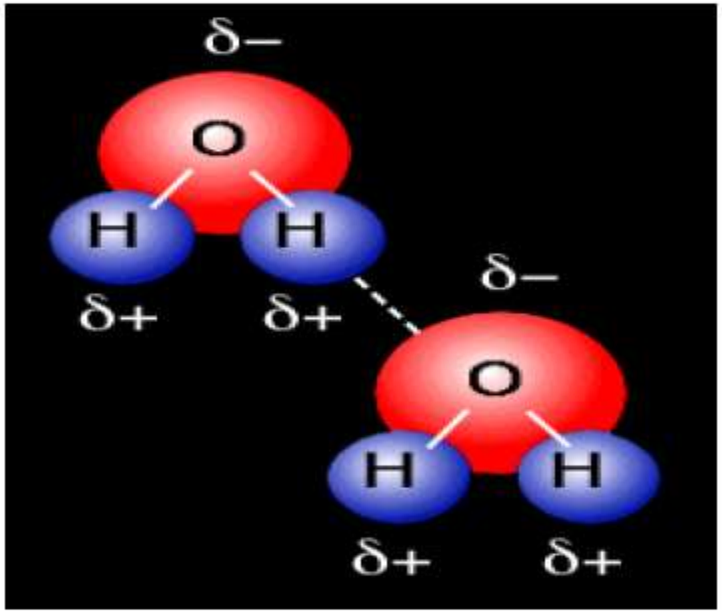
- A hydrogen bond tends to be stronger than van der Waals forces, but weaker than covalent bonds or ionic bonds.
- Although each hydrogen bond is relatively weak, the sum of their attractive forces is largely responsible for:
  - The folding and bonding of long organic molecules such as proteins, and for the holding together of the two strands of a DNA molecule

➡ hydrogen bonds are weak bonds, but there are so many! So, as a collective force, they can be quite strong.

Example

The hydrogen bonding between water molecules.





Theory of hybrid orbitals (1928-)

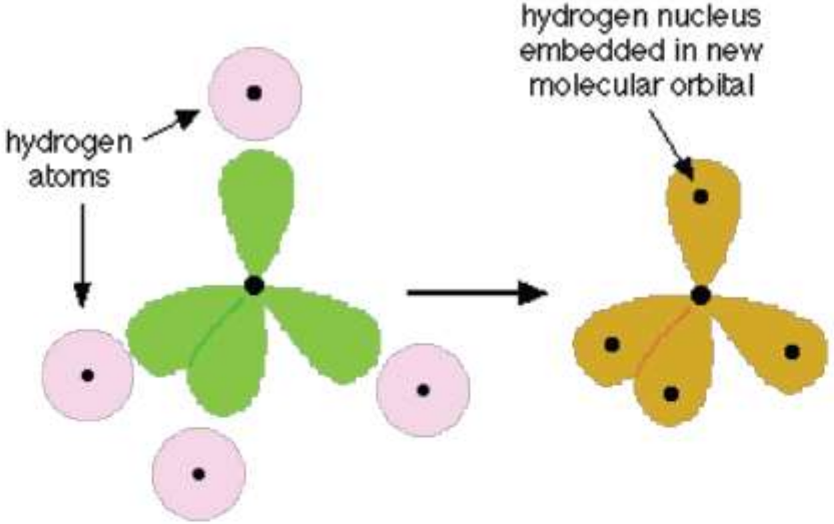
Linus Pauling (USA, 1901-1994)

Most known american chemist of 20th century,
Nobel prize: for chemistry 1954, for peace 1962

hybrid orbitals
- principle

atomic orbitals
do combine

if *s*, *p*, *d* orbitals occupied by the valence electrons of adjacent atoms are combined in a suitable way, the hybrid orbitals that result will have the character and directional properties that are consistent with the bonding pattern in the molecule.



What are hybrid orbitals?

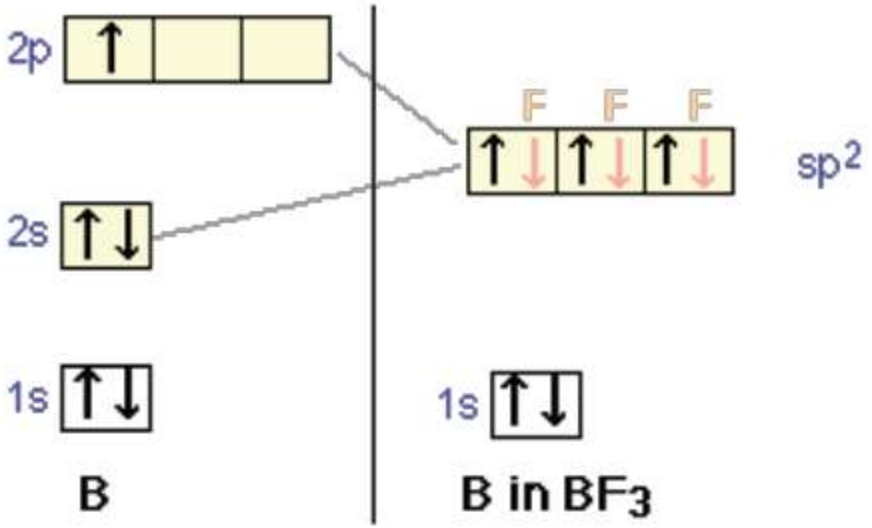
we will look at a model that starts out with the familiar valence-shell atomic orbitals, and allows them to combine to form **hybrid orbitals** whose shapes **conform** quite well to **the bonding geometry** that we observe in a wide **variety of molecules**.

orbital:	region of space around the nucleus in which the probability of finding the electron exceeds some arbitrary value, such as 90% or 99%.

Orbitals of all types are mathematical functions that describe particular standing-wave patterns that can be plotted on a graph but have no physical reality of their own. Because of their wavelike nature, two or more orbitals (i.e., two or more functions ψ) can be combined both in-phase and out-of-phase to yield a pair of resultant orbitals which, to be useful, must have squares that describe actual electron distributions in the atom or molecule.

Hybrids derived from atomic s- and p orbitals

Trigonal (sp^2) hybridization



2p ↑

2s ↑↓

1s ↑↓

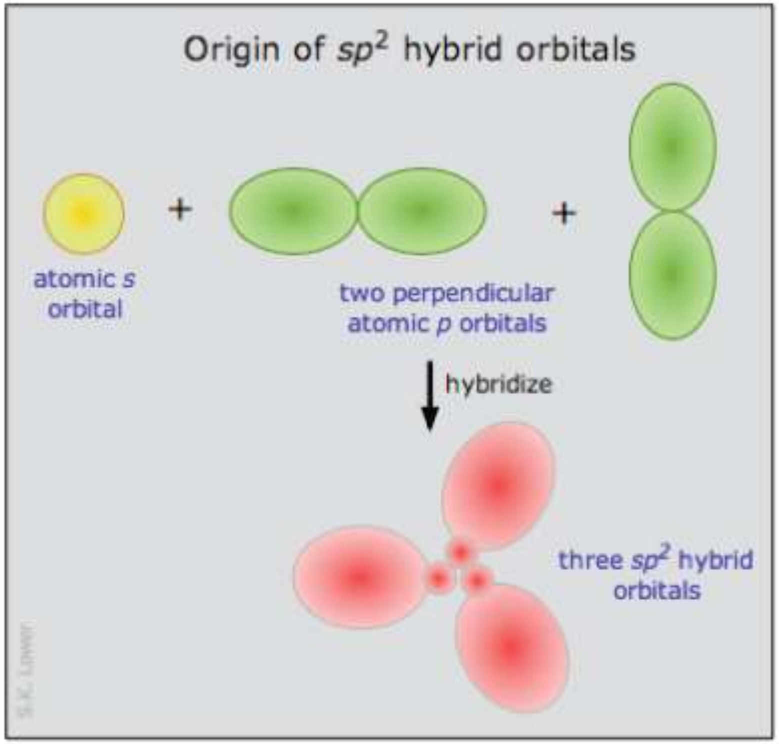
B

F F F

↑↓ ↑↓ ↑↓ sp^2

1s ↑↓

B in BF_3

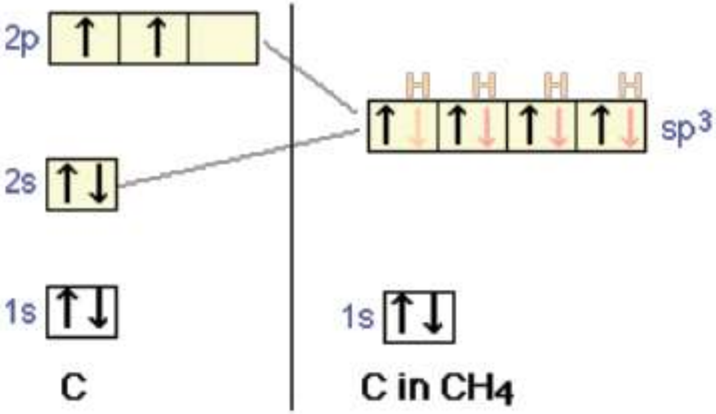


The molecule has plane trigonal geometry.

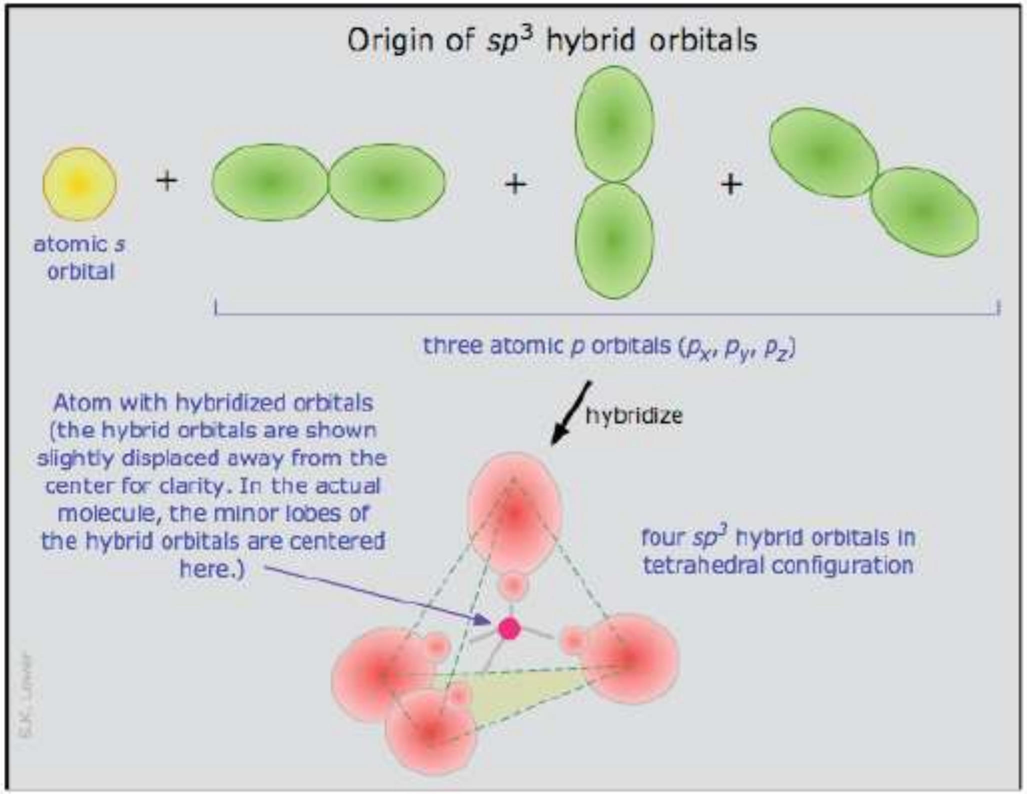
Hybrids derived from atomic s- and p orbitals

Tetrahedral (sp^3) hybridization

several tetravalent molecules

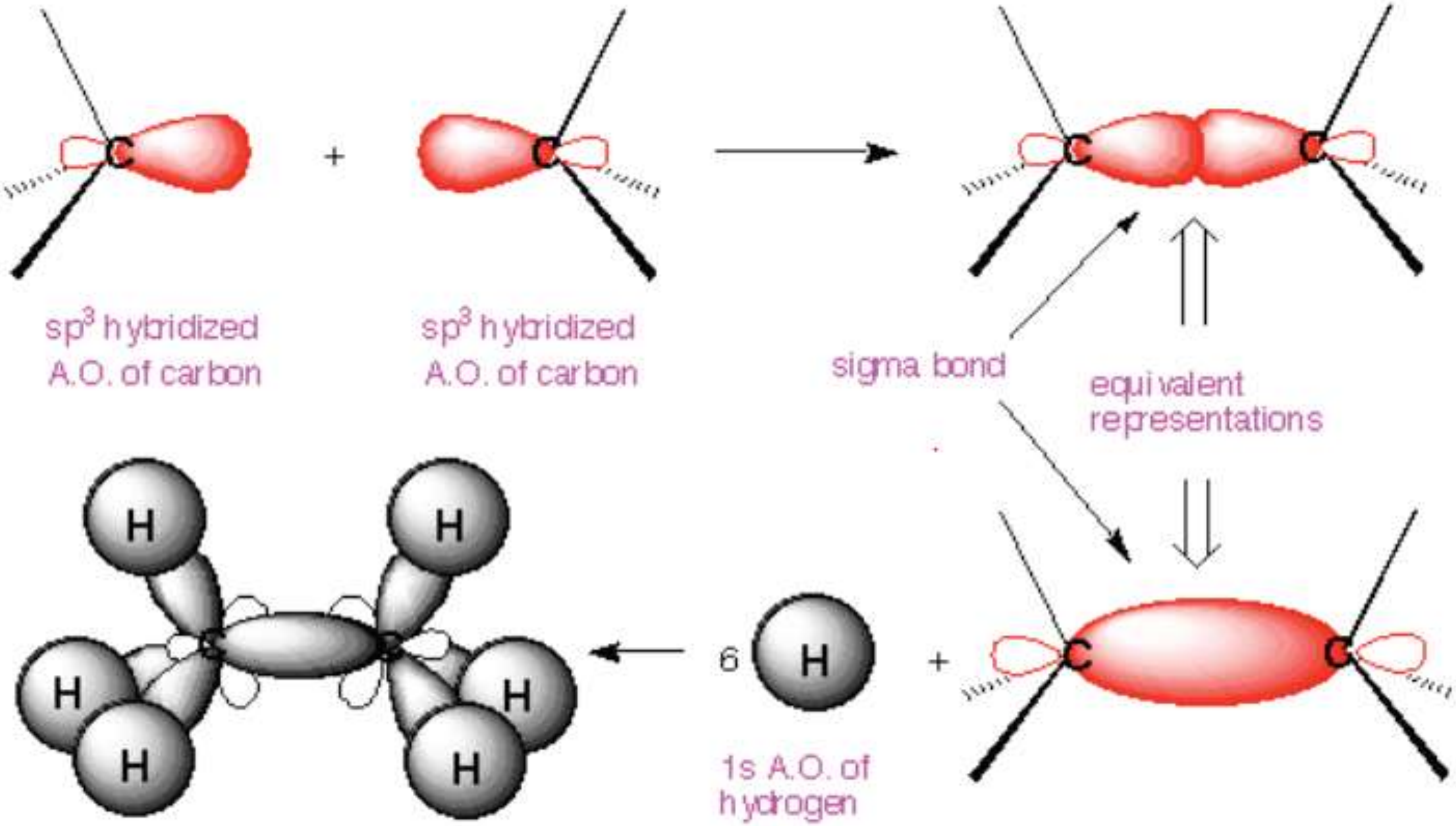


In the ground state of the free carbon atom, there are two unpaired electrons in separate 2p orbitals. In order to form four bonds (tetravalence), need four unpaired electrons in four separate but equivalent orbitals. We assume that the single 2s, and the three 2p orbitals of carbon mix into four sp^3 hybrid orbitals which are chemically and geometrically identical



Bonding with hybrid orbitals

The M.O.s of Ethane



sp^3 hybridized
A.O. of carbon

sp^3 hybridized
A.O. of carbon

sigma bond

equivalent
representations

1s A.O. of
hydrogen

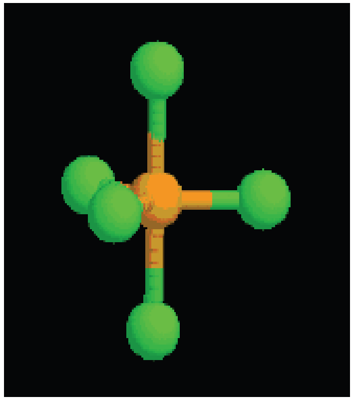
ethane
CC bond 1.54 Å, 88kcal/mol
CH bond 1.10 Å, 98 kcal/mol

Structure: **trigonal bipyramid**

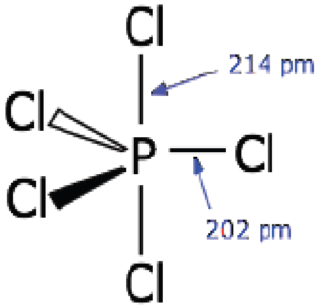
sp^3d (dsp^3) hybrid orbitals

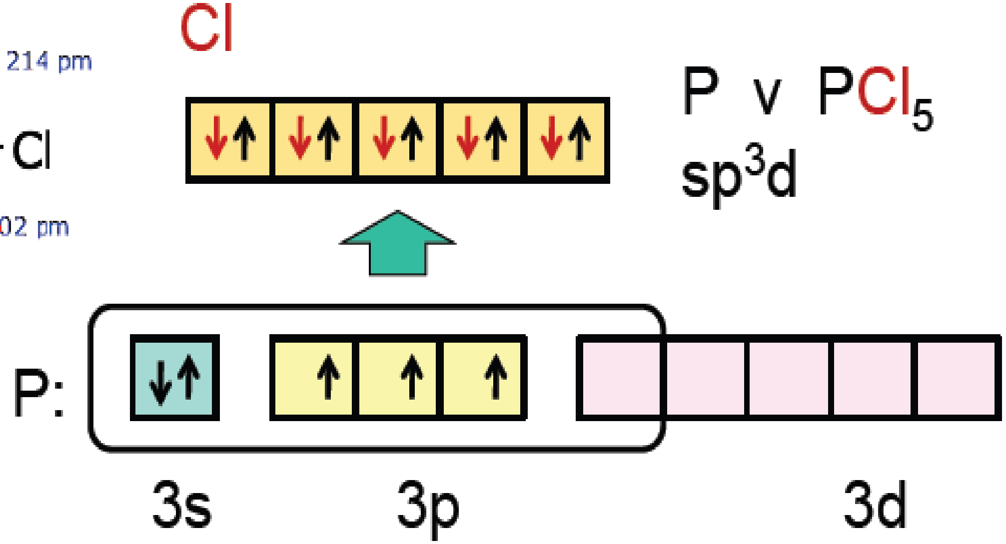
If the energies of s, p, d are close

$$s+p_x+p_y+p_z+d_{z^2}\ (n) \longrightarrow 5\ (sp^3d)$$



PCl$_5$

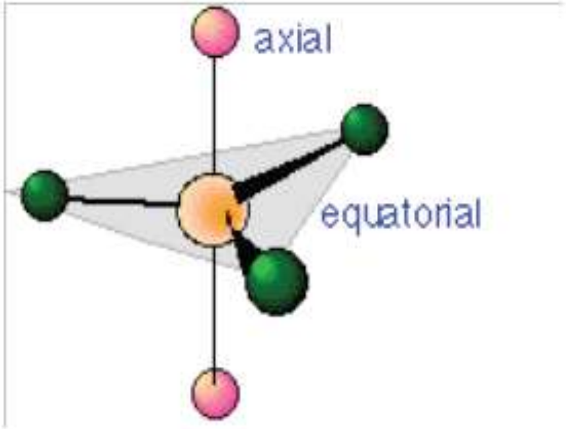




P v PCl$_5$

sp^3d

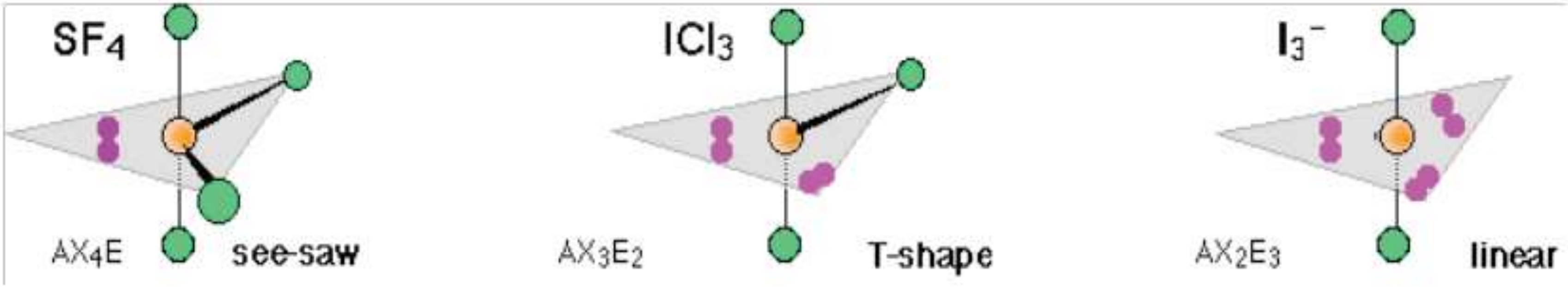
$$dsp^3 \longleftarrow d_{z^2}\ (n-1) +s+p_x+p_y+p_z$$



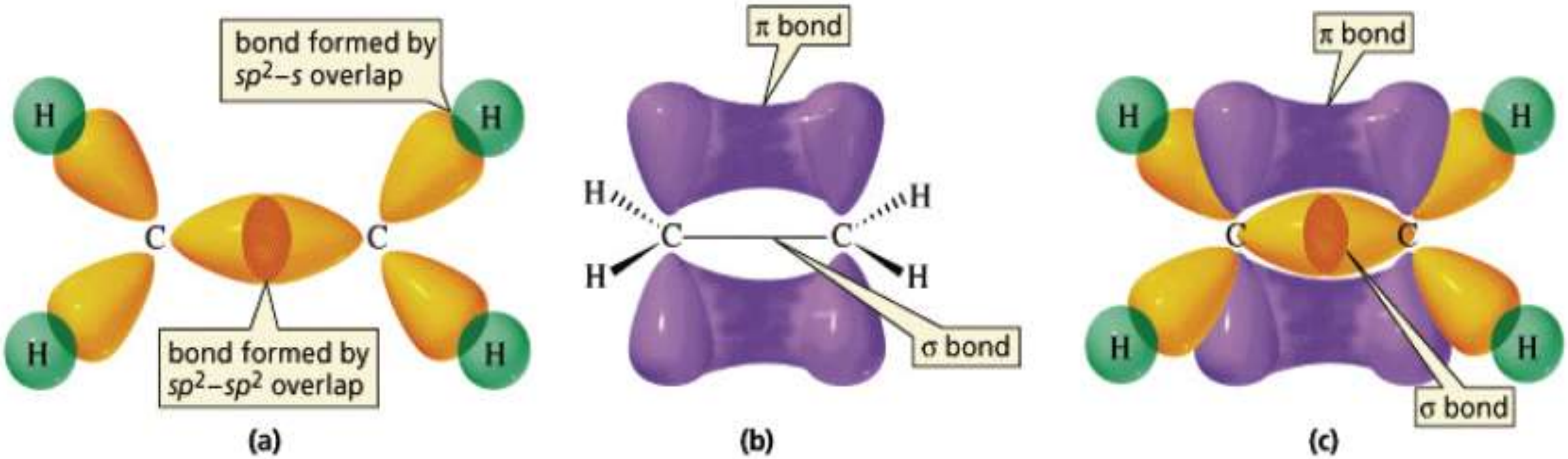
The shape of PCl_5 and similar molecules is a **trigonal bipyramid**

sp^3d hybrids

With lone (non-bonding) pairs:



Double bond between carbon atoms sp^2



Triple bond between carbon atoms sp