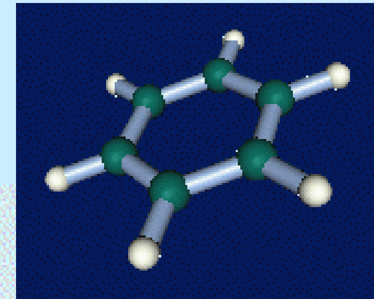
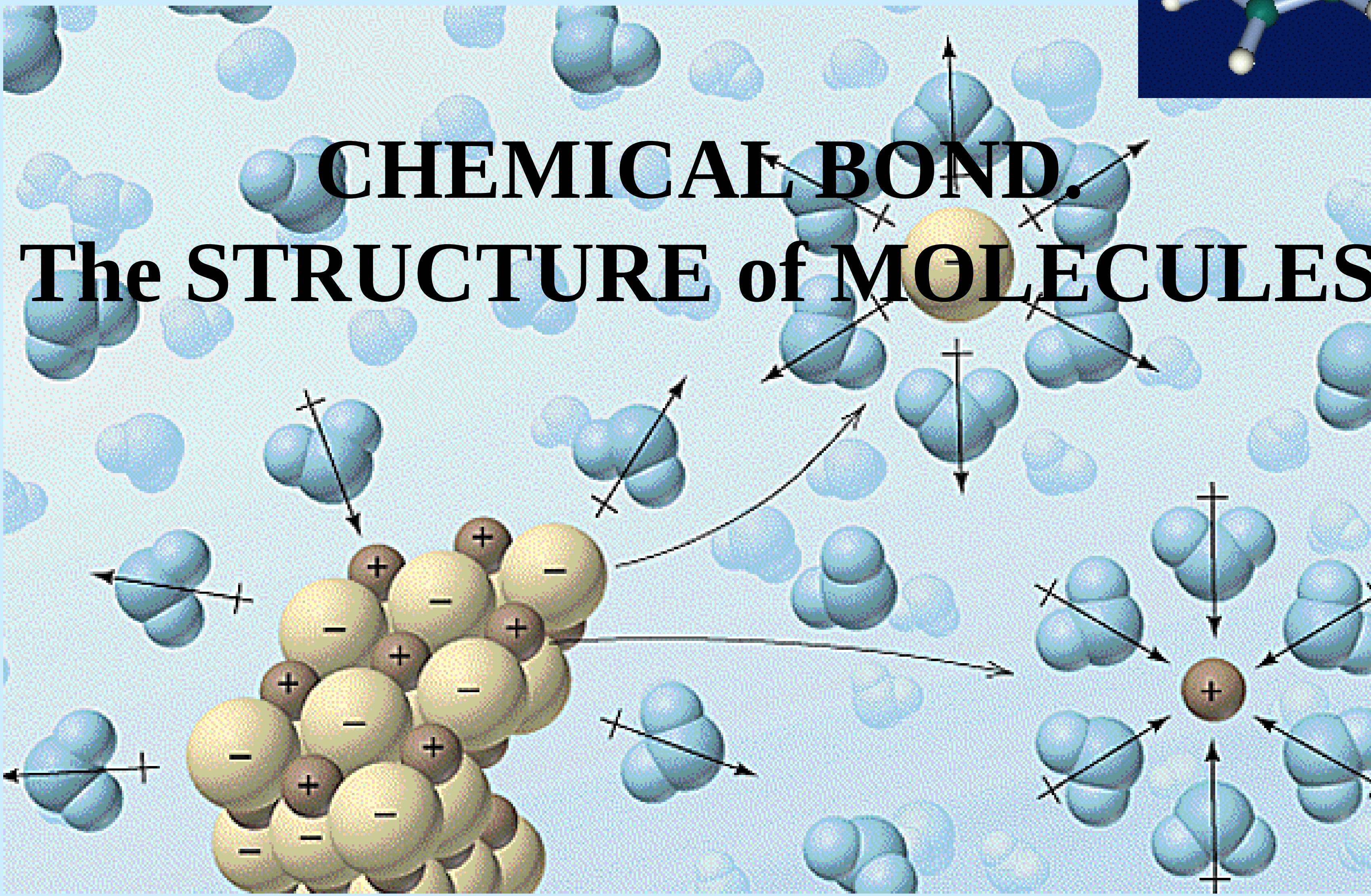
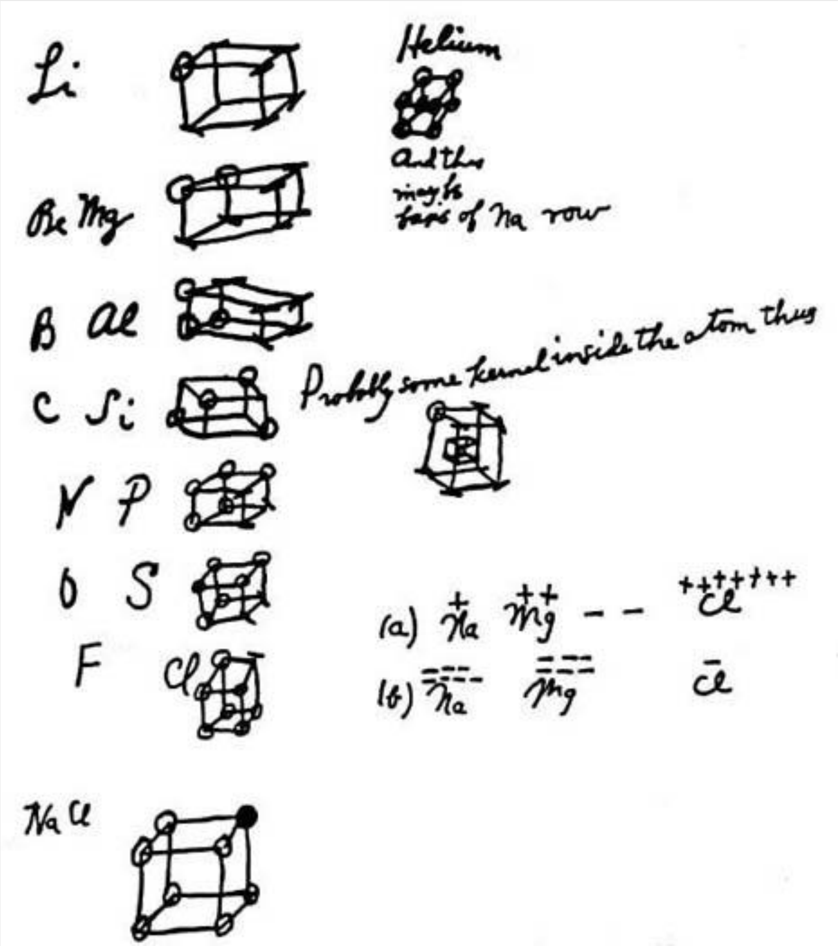
Lecture №

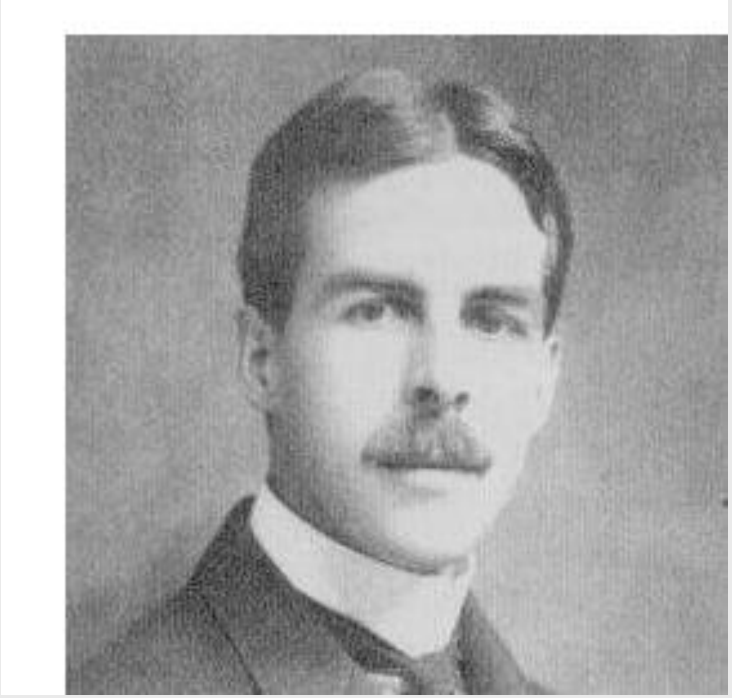
Date



CHEMICAL BOND.
The STRUCTURE of MOLECULES







- The first really successful theory of chemical bonding was formulated by **G.N.Lewis**, whose 1902 lab notes eventually led to his classic article *The Atom and the Molecule* in 1916.

- Most elements are **quite reactive:** their atoms tend to combine with those of other elements to form compounds.
- The elements that appear in nature in the uncombined form are:
  the elements in group VIII A - **noble gases**,
  gold, platinum and silver - **noble metals**.
- Air consists of nitrogen gas and oxygen gas. They contain **diatomic molecules**.

Element	at 25°C	Molecule Present
Hydrogen	colourless gas	H_2
Nitrogen	colourless gas	N_2
Oxygen	pale blue gas	O_2
Fluorine	pale yellow gas	F_2
Chlorine	yellow-green gas	Cl_2
Bromine	reddish-brown liquid	Br_2
Iodine	dark purple solid	I_2

A <u>chemical bond</u> is a force that holds group of two or more atoms together and makes them function as a unit.

Basic Parameters of Chemical Bond

- bond energy
- bond length
- valence corner

***The energy of bonding* is the energy required to break the bond.**

- energy of bonding is equal to the amount of heat, which is ***allocated*** as a result of formation the bonding from atoms under standard conditions

Atom + **Atom** = **atom – atom + Q**

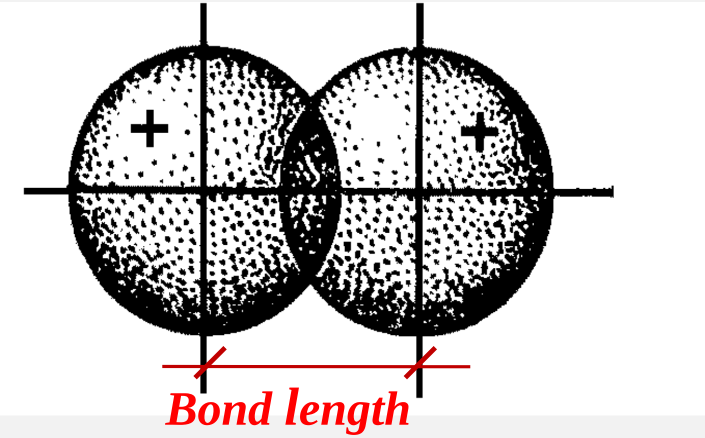
molecule

- this energy is a ***measure of the strength*** of chemical connections between atoms in a molecule.
- the energy of bonding is designated **E**,
  units of measurements **kJ/mol**.

For example,

E (H_2) = 436 kJ/mol
E (HF) = 267.8 kJ/mol
E (F_2) = 159 kJ/mol

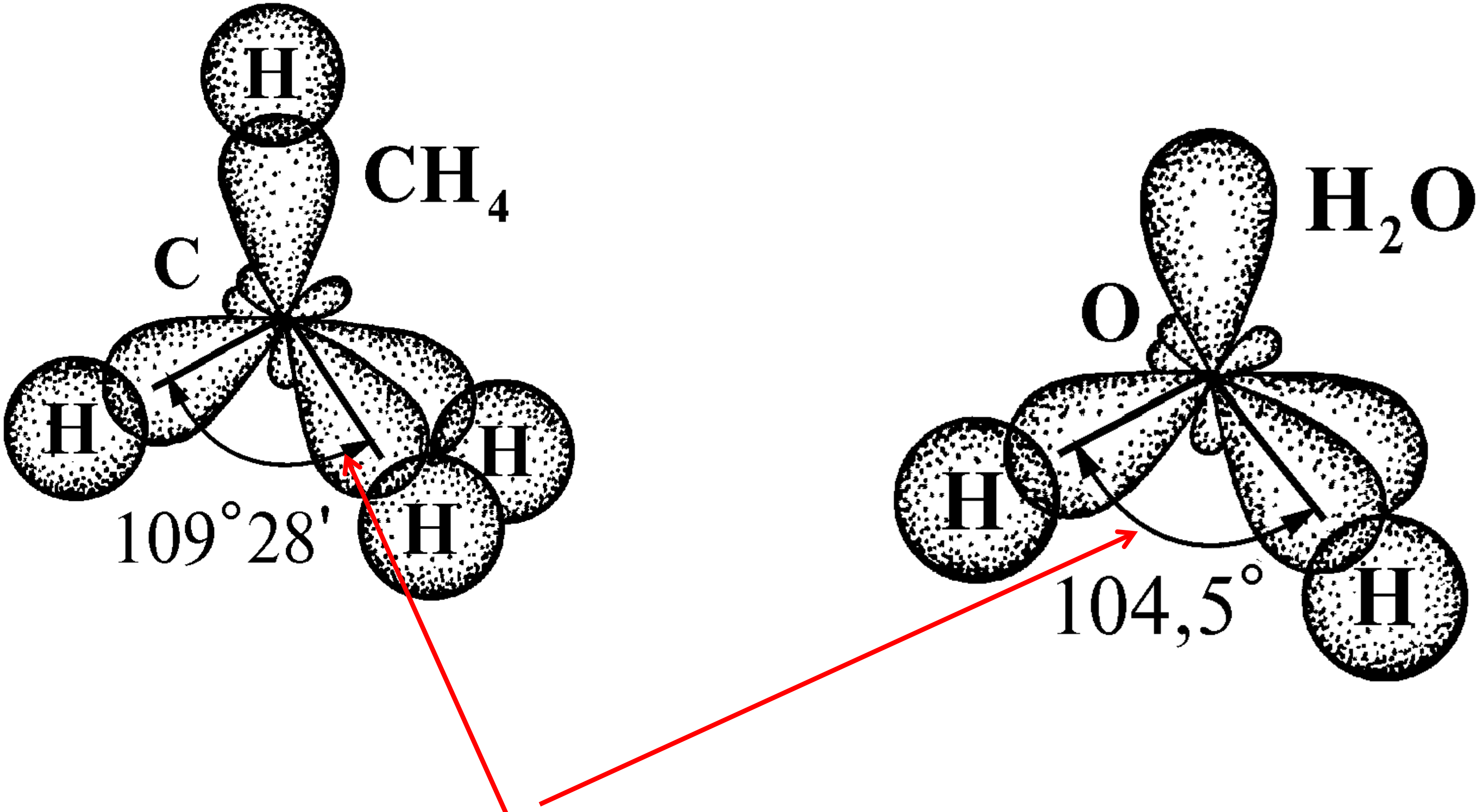
<u>The length of bond (l)</u> – is a distance between the centers of atoms in a molecule



Bond lengths depend mainly on the sizes of the atoms

Atomic radii, nm		Molecule	Bond distance, l, nm	E, kJ/mol
F	0.64	**HF**	0.100	536
Cl	0.99	**HCl**	0.127	432
Br	1.13	**HBr**	0.141	360
I	1.15	**HI**	0.162	299

The <u>stronger</u> a chemical bond, the <u>shorter</u> the bond distance



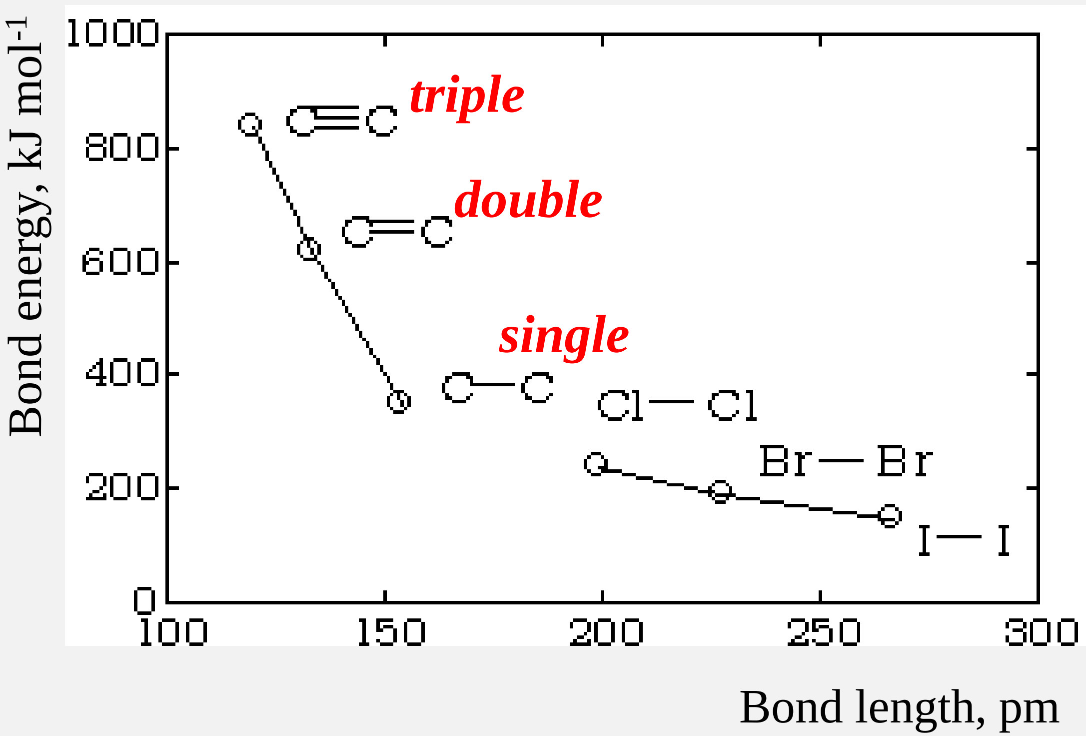
<u>The valence corner –</u>

is the corner formed by lines connecting centers of bonding atoms

multiplicity of a bond – the number of bonds between two atoms

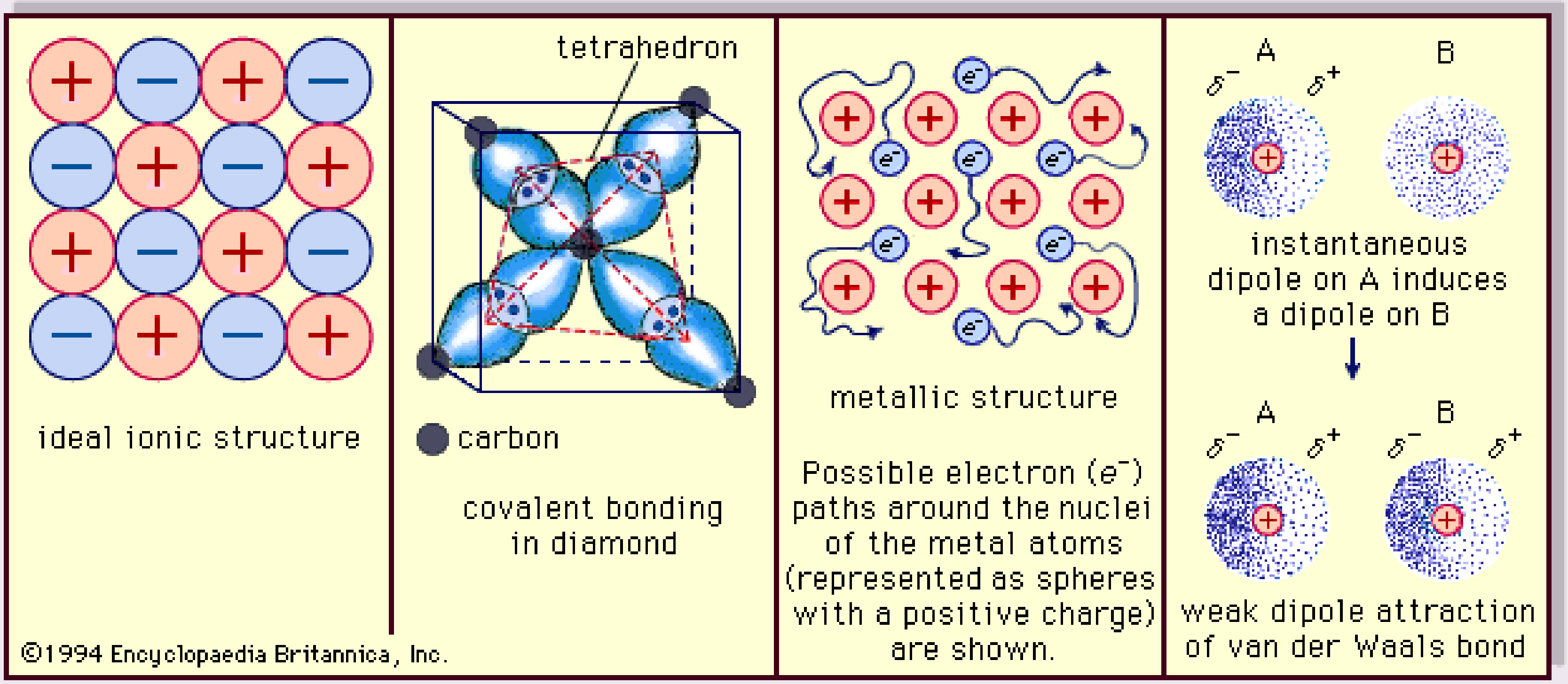
Multiply-bonded atoms are ***closer*** together than singly-bonded ones

The triple bond is ***stronger*** and shorter a chemical bond than the double and single ones.



Types of Chemical Bonding

- covalent bonding (polar, nonpolar)
- ionic bonding
- metallic bonding
- intermolecular bonding
- hydrogen bonding



Electronegativity

Electronegativity is one of atom's properties

Electronegativity **(χ)**

- is the ability of an atom to lose or gain an electron
- is the ability of an atom in a molecule to attract shared electrons to it

Electronegativities of some elements

	I	II	III	IV	V	VI	VII	VIII		
I	H 2.1									
II	Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0			
III	Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0			
IV	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			
V	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			
VI	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	Ti 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2			
VII	Fr 0.7	Ra 0.9	Ac 1.1							

The <u>type of chemical bonding</u> and its polarity <u>depends</u> on the difference between the <u>electronegativity</u> values of the atom forming the bond.

$0 < \Delta\chi < 0.4$	*nonpolar covalent bond*
$0.5 < \Delta\chi < 1.9$	*polar covalent bond*
$\Delta\chi > 2.0$	*ionic bond*

<u>For example</u>

The difference in electronegativity values in the molecules H_2, HF, NaCl:

$\Delta\chi(H - H) = \chi(H) - \chi(H) = 2.1 - 2.1 = 0$ ***covalent nonpolar bond***

$\Delta\chi(H - F) = \chi(F) - \chi(H) = 4.0 - 2.1 = 1.9$ ***covalent polar bond***

$\Delta\chi(Na - Cl) = \chi(Cl) - \chi(Na) = 3.0 - 0.9 = 2.1$ ***ionic bond***

Valence Bond (VB) Method

The basic rules of the VB method are:

- - the chemical bond is produce by ***valence electrons***;
- - the chemical bond can be between ***two atoms***;
- - the chemical bond in a molecule is carried out with the help by one or several shared ***electronic pairs***.

- The method of VB uses an ***electron dots diagram*** to picture the transfer or sharing of valence electrons.
- ***Symbol*** of the element represents the nucleus of the atom plus its inner shells of electrons
- ***Dots*** around the symbol stand for the valence electrons

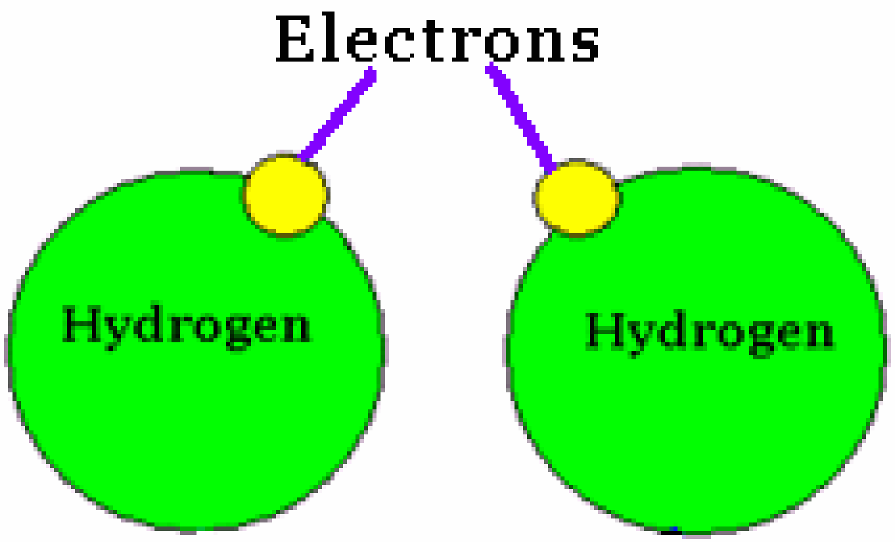
The covalent bond

Covalent bonds are formed between atoms through simultaneous 'sharing' of electrons

a pair of electrons shared between two atoms

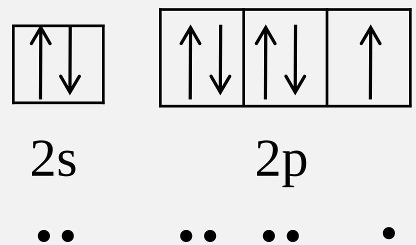
Let us consider the mechanism of covalent bond formation by the example of the hydrogen molecule:

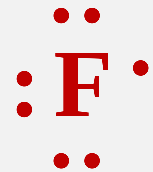
H· + H· = H_2,   ΔH = – 436 кJ/mol

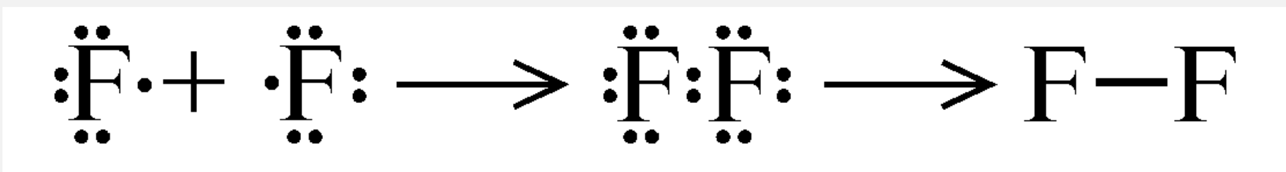


fluorine molecule $\boldsymbol{F_2}$

F $1s^2\underline{2s^2 2p^5}$

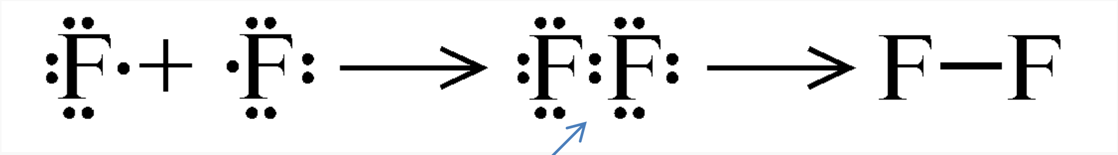






(single bond)

Formation of covalent bonding between fluorine atoms in a molecule F_2

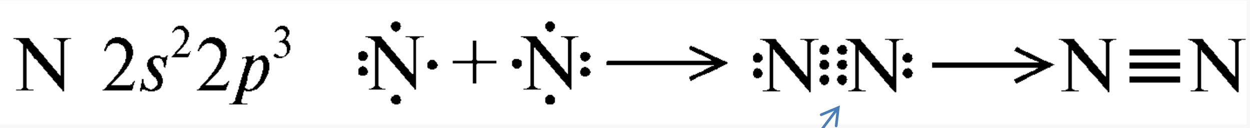


(single bond)

one pair of electrons shared between two atoms

It is possible that two atoms in a molecule will share ***more than one pair*** of electrons in order ***to make octet*** for each atom.

Formation of covalent bonding between nitrogen atoms in a molecule N_2



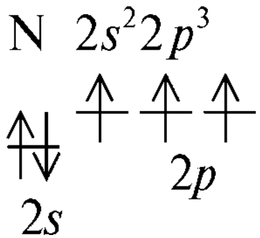
(triple bond)

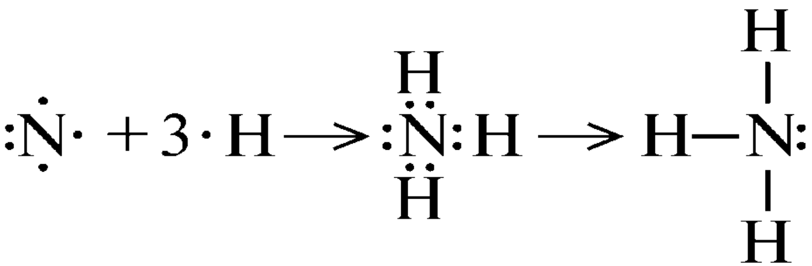
free pairs of electron are shared

Mechanism of the Chemical Bond Formation

- **exchange mechanism**

each atom gives ***one electron*** to produce a common electronic pair

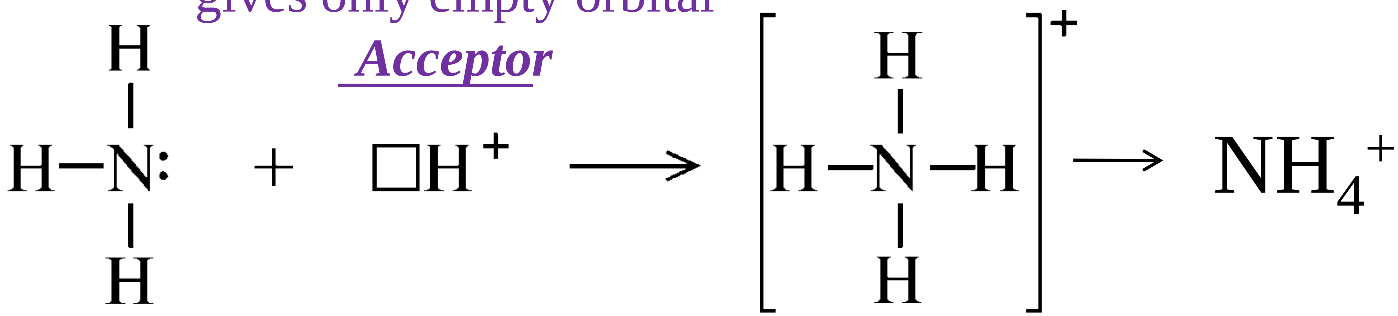




- **donor-acceptor mechanism**

gives only empty orbital

Acceptor

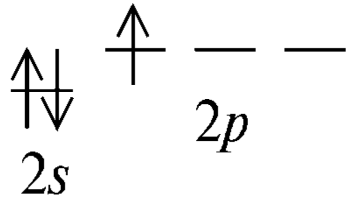


Donor

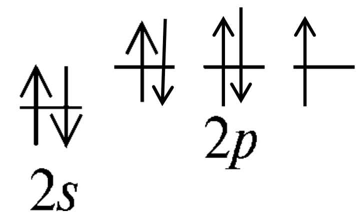
gives a pair of electrons

Formation BF_3 и BF^- according to the method of VB

B $2s^2 2p^1$

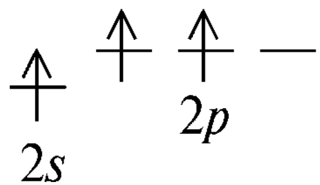


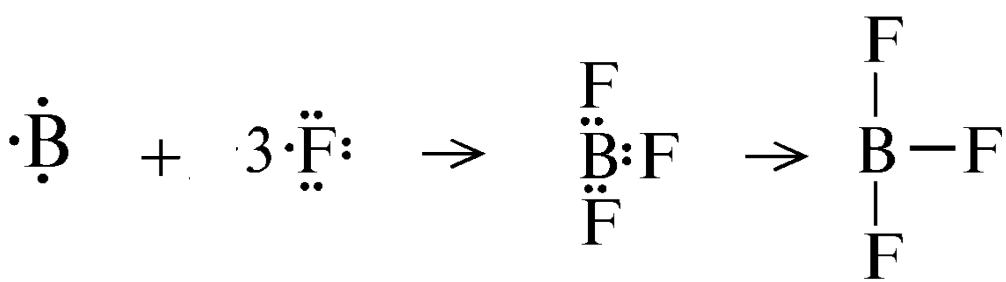
F $1s^2 \underline{2s^2 2p^5}$



excited state

B^* $2s^1 2p^2$

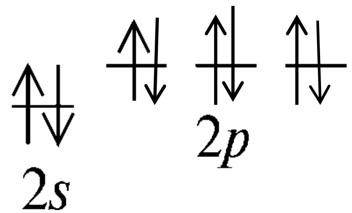


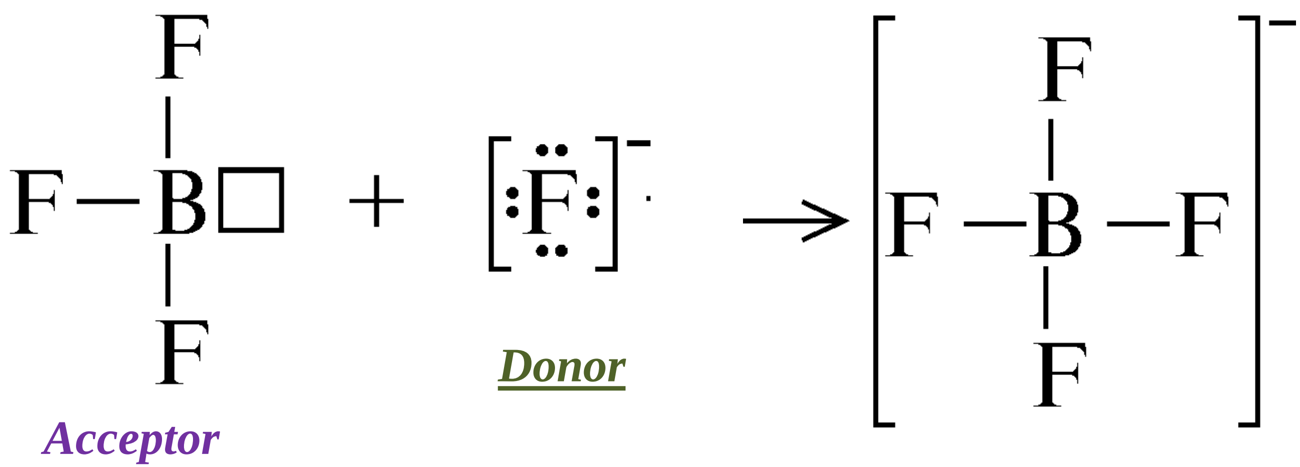


Valence of boron atom III

BF_4^-

F^- $1s^2\underline{2s^22p^6}$



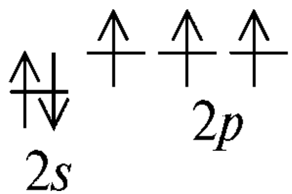


Valence of boron atom IV

Task 1. Write the orbital diagram of nitrogen atom. What is the valence and the oxidation state of nitrogen in HNO_3?

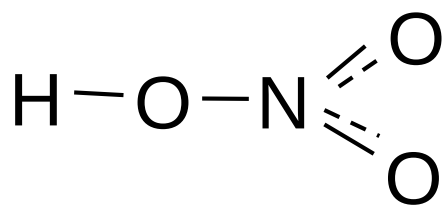
$\overset{+1}{H}\overset{+5}{N}\overset{-2}{O}_3$

N $2s^2 2p^3$



H $\underline{1s^1}$

O $1s^2\underline{2s^2 2p^4}$

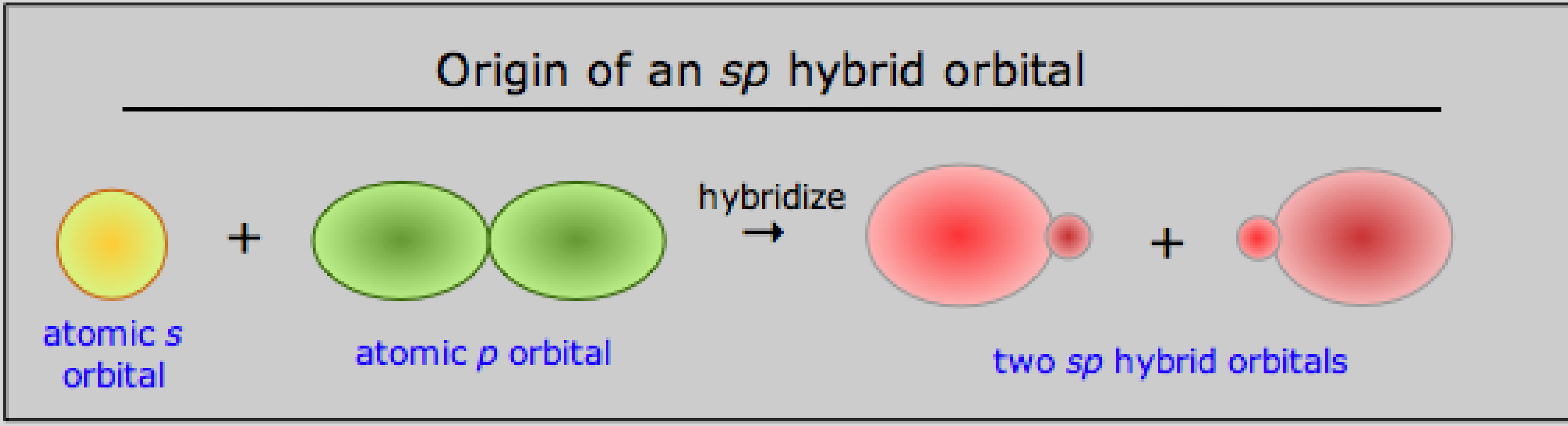


valence of nitrogen ***IV***
oxidation state of nitrogen ***+5***

The Hybridization Theory

All types of the electron orbital, which take part in the bond formation ***mixing according their type and energy***

Types of hybridization		***Molecular structure***		***Valence corner***
sp	→	line	→	180°
sp^2	→	triangle	→	120°
sp^3	→	tetrahedron	→	109°28’


Origin of an sp hybrid orbital
atomic s orbital
atomic p orbital
hybridize
two sp hybrid orbitals

Formation of $BeCl_2$ molecule

Beryllium atom in the ground state

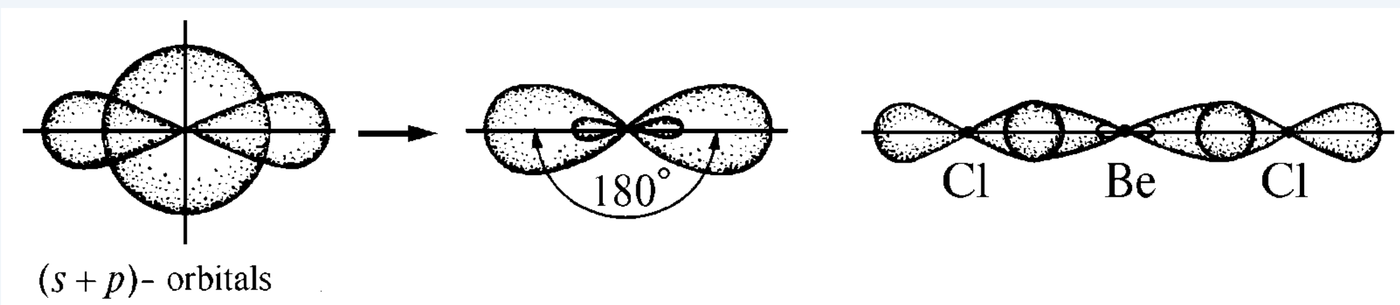
Be $1s^2\underline{2s^22p^0}$ ↑↓ — — —

2s 2p

- in the exiting state (excess of energy)

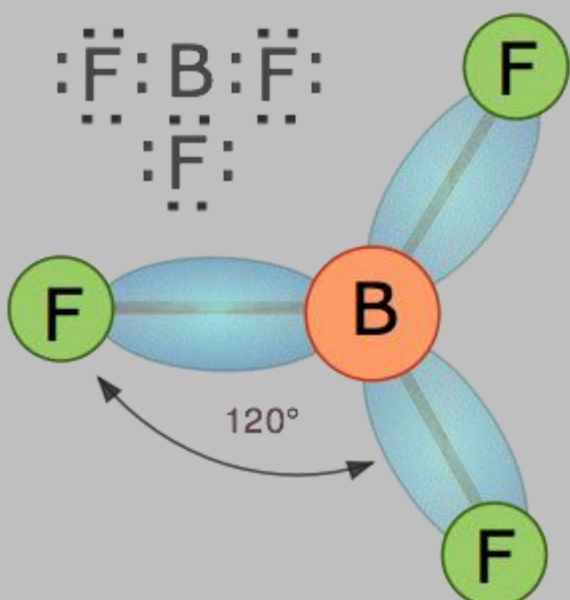
Be* $1s^2\underline{2s^12p^1}$ ↑ ↑ — —

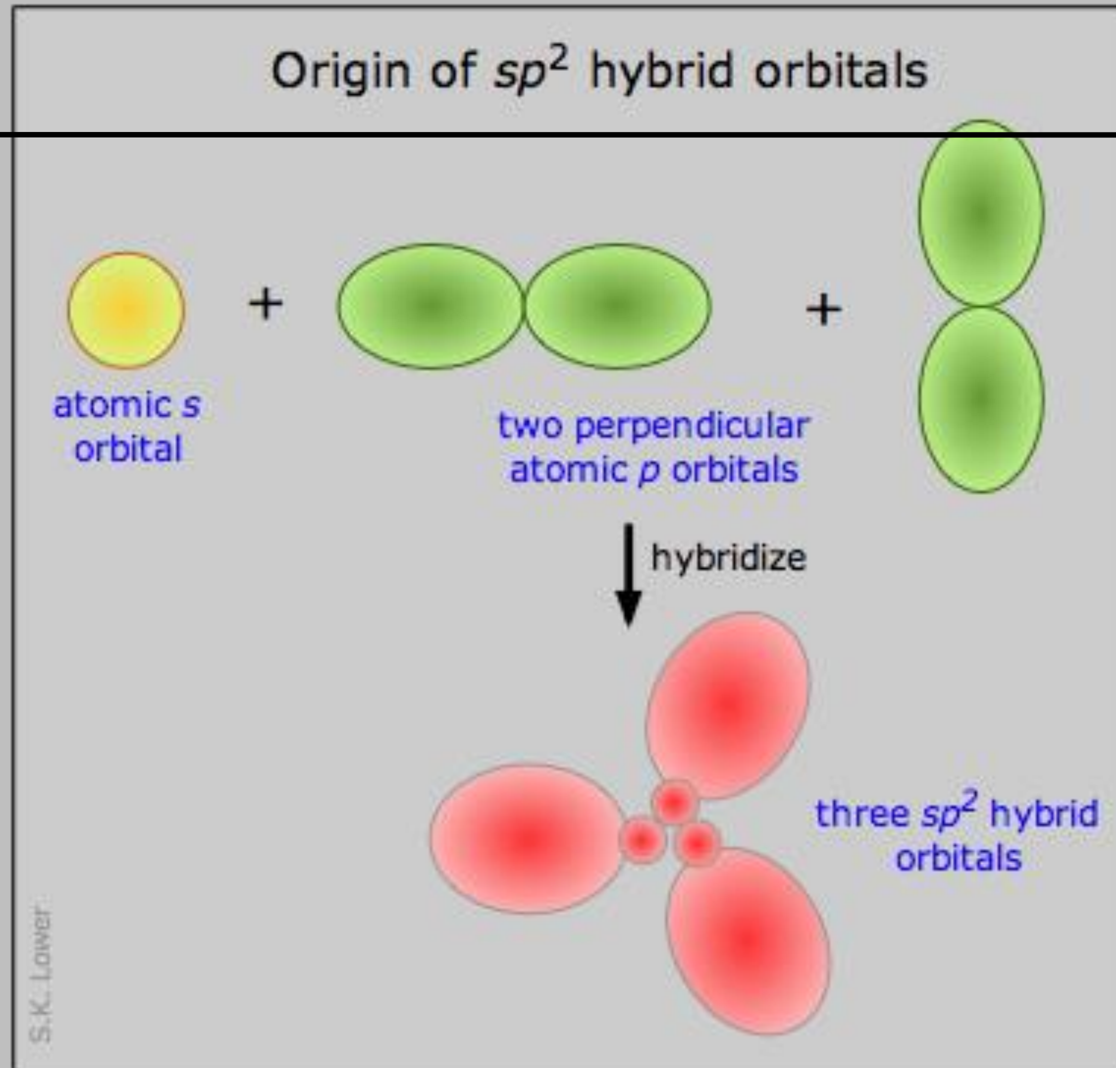
2s 2p

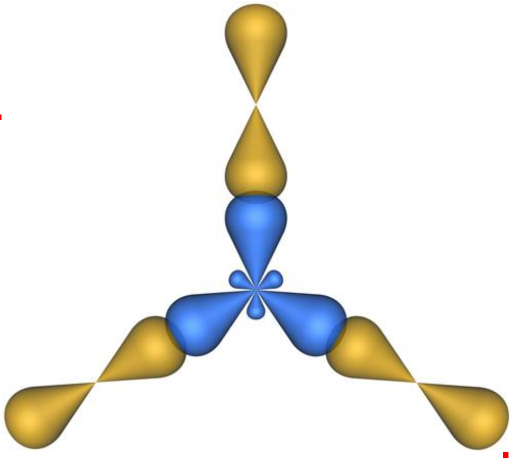


<u>Conclusion:</u>

the atomic orbital (AO) of beryllium (central atom) has **sp-type** of hybridization

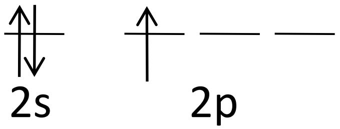

:F:B:F:
:F:
F
F
B
F
120°


Origin of sp2 hybrid orbitals
atomic s orbital
+
two perpendicular atomic p orbitals
+
hybridize
three sp2 hybrid orbitals
S.K. Lower

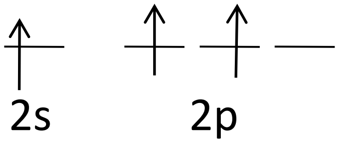


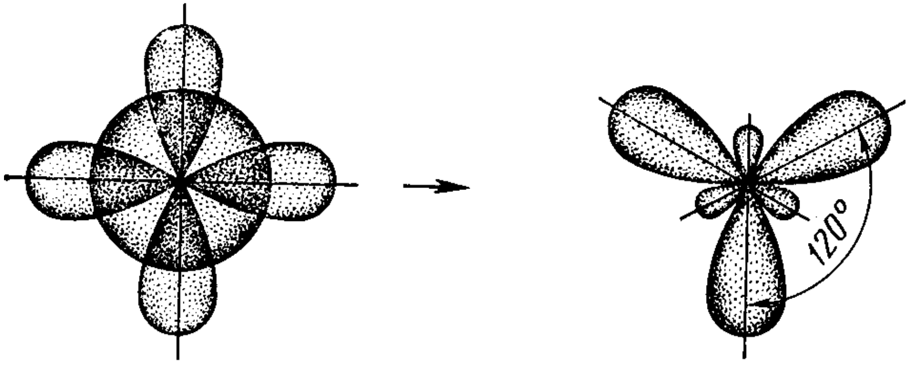
BCl_3

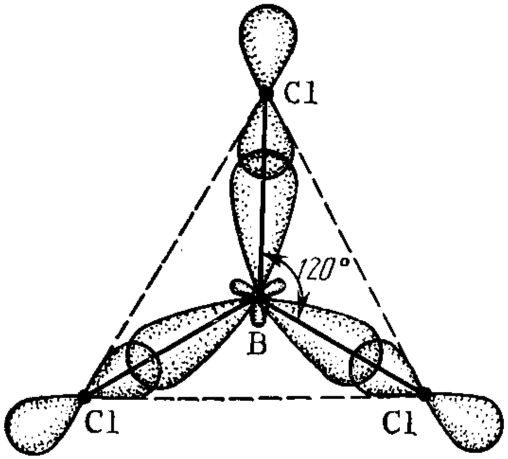
B $1s^2\underline{2s^22p^1}$



B* $1s^2\underline{2s^12p^2}$

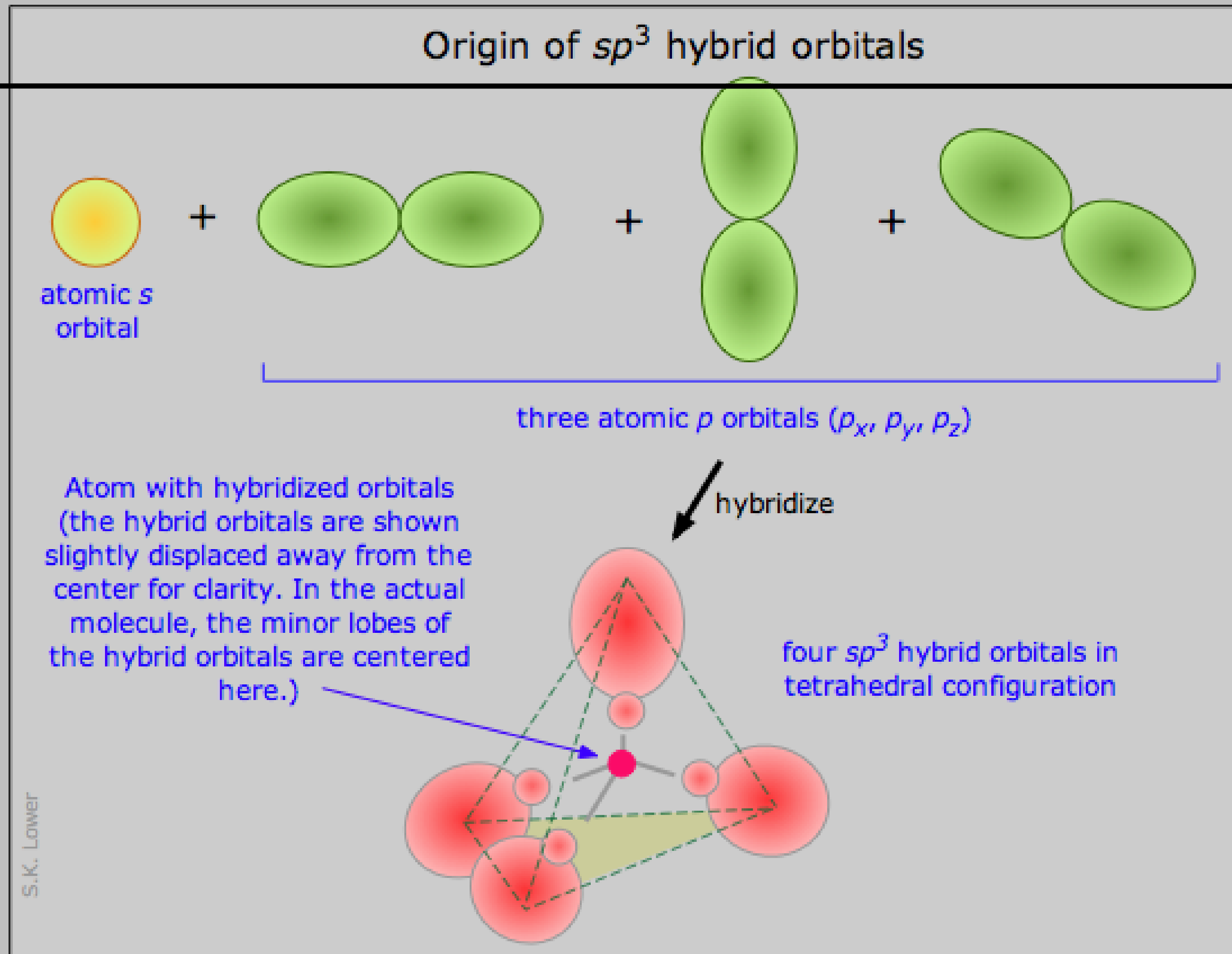


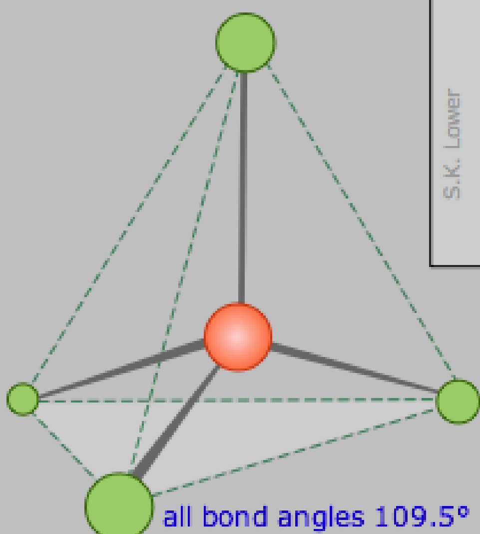




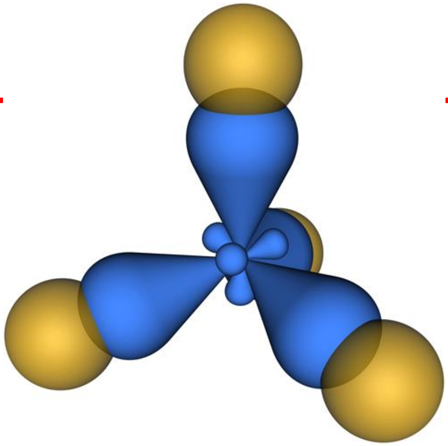
<u>Conclusion:</u>

the atomic orbital (AO) of boron (central atom) has **sp^2 -type** of hybridization

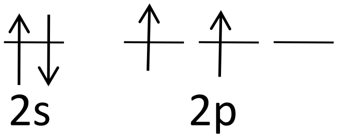

Origin of sp3 hybrid orbitals
+
atomic s orbital
three atomic p orbitals (px, py, pz)
hybridize
Atom with hybridized orbitals (the hybrid orbitals are shown slightly displaced away from the center for clarity. In the actual molecule, the minor lobes of the hybrid orbitals are centered here.)
four sp3 hybrid orbitals in tetrahedral configuration
S.K. Lower


all bond angles 109.5°

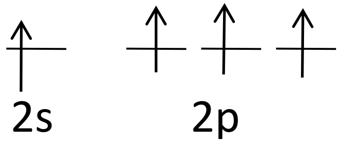
CH_4

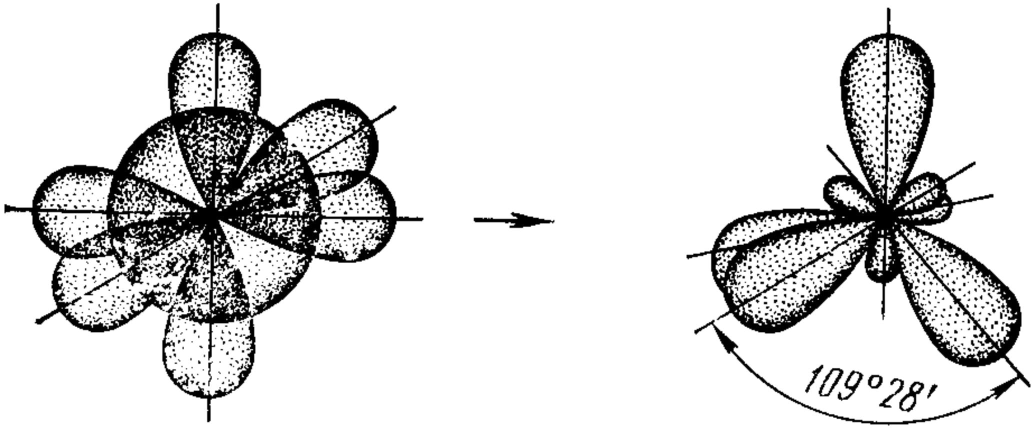


C $1s^2\underline{2s^22p^2}$



C* $1s^2\underline{2s^12p^3}$

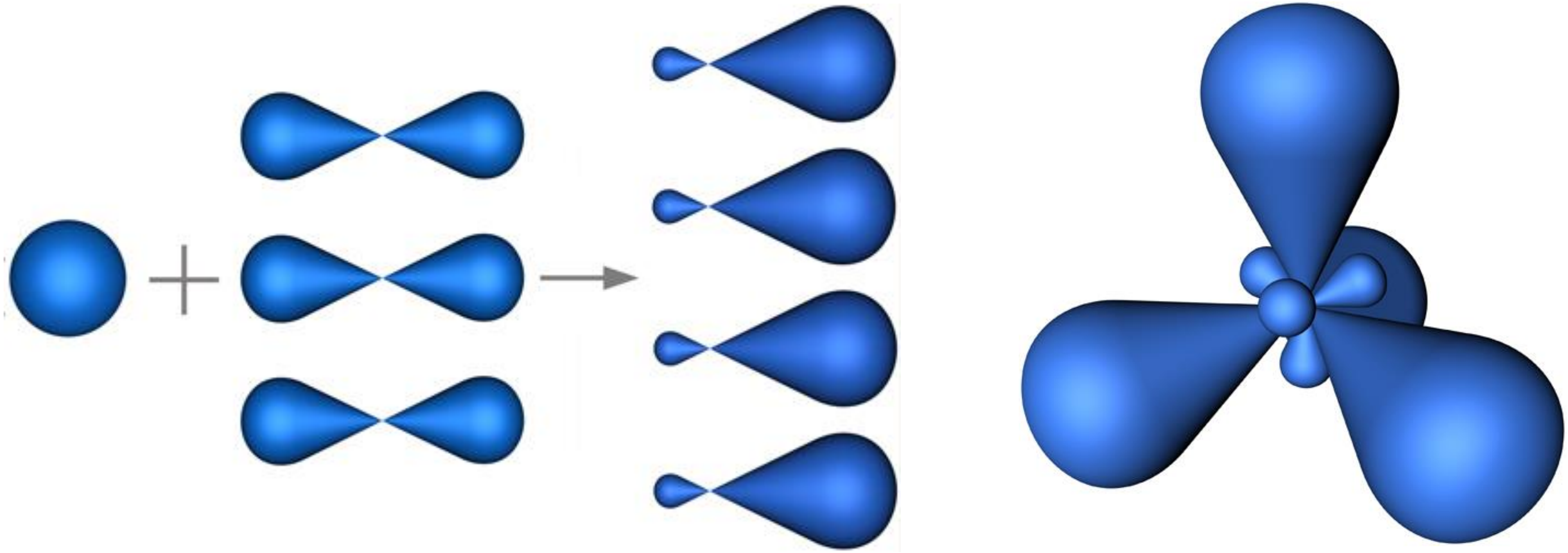




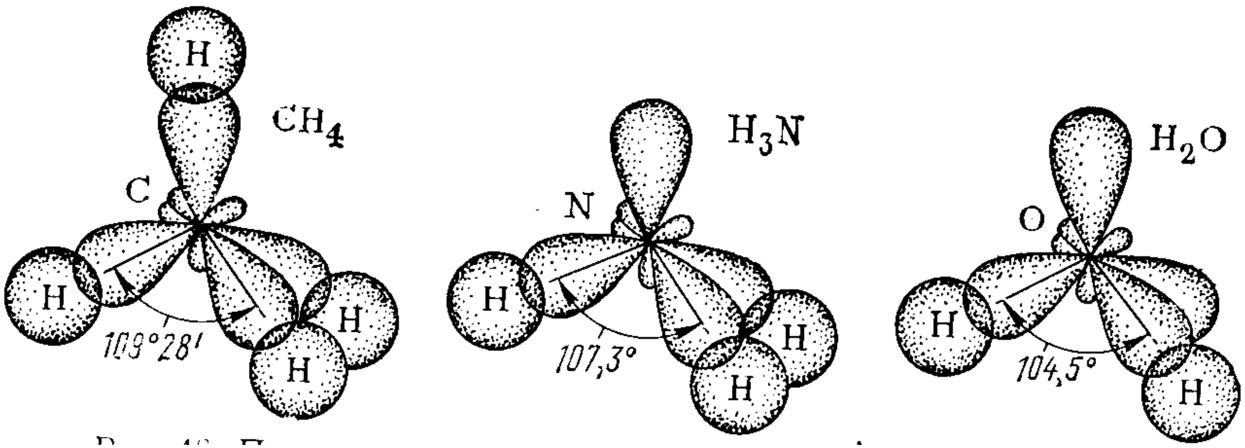
<u>Conclusion:</u>

the atomic orbital (AO) of carbon (central atom) has **sp^3 -type** of hybridization

sp^3- Hybridization atomic orbital of carbon



sp^3-Hybridization of atomic orbitals due to the equivalence of the four bonds of the carbon atom in compounds CH_4, CF_4, CCl_4, $C(CH_3)_4$ and their orientation under the same (tetrahedral) angles.

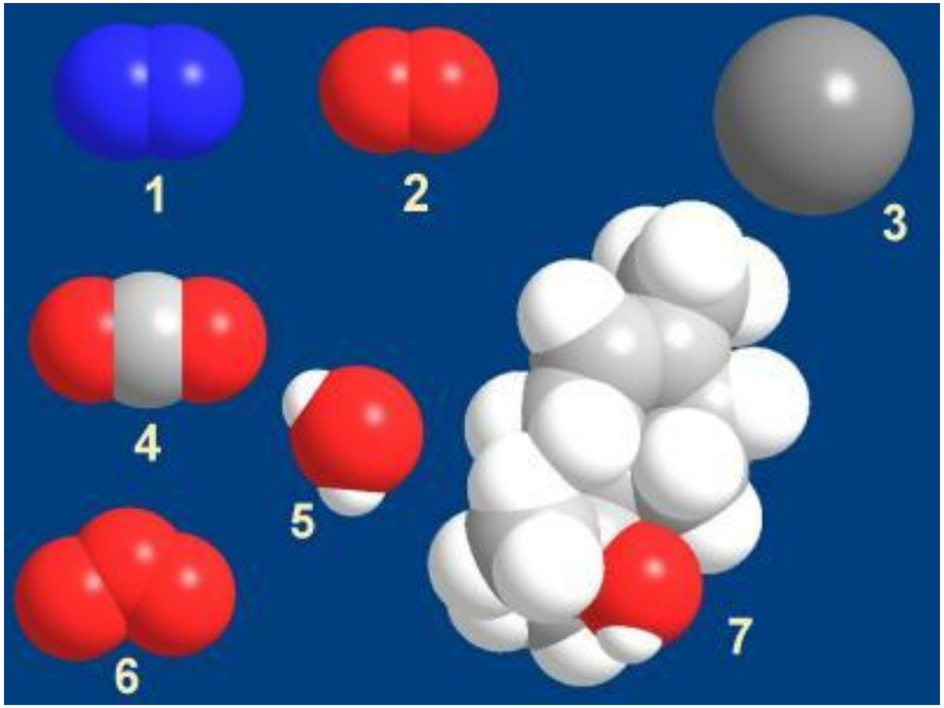


The basic properties of the covalent bonding

- ***saturation*** is an ability of atoms to form the limited amount of chemical bonding (due to its valence)
- ***orientation***
- ***polarityes***

Saturation is a limit of number of covalent bonds that a given atom can form with other atoms

Because of saturation covalent molecules have a well-defined chemical composition and exist as discrete particles with a certain structure (H_2, H_2O, CH_4).

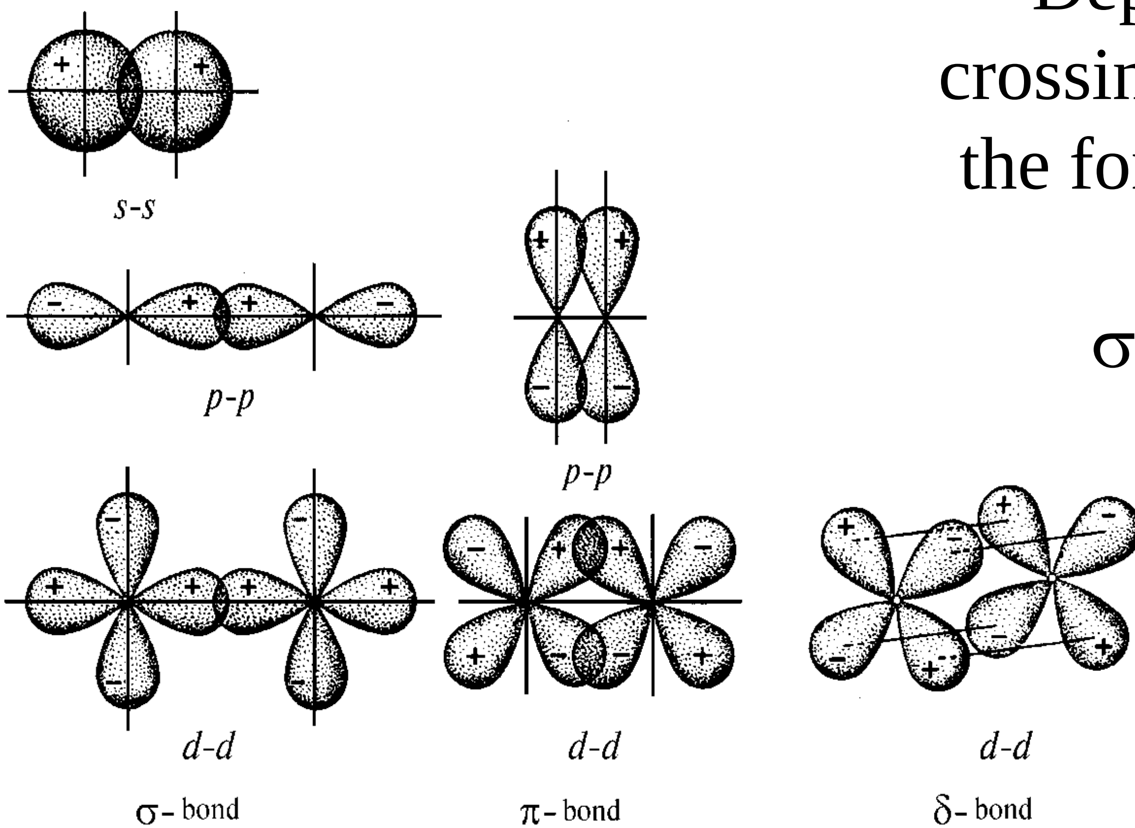


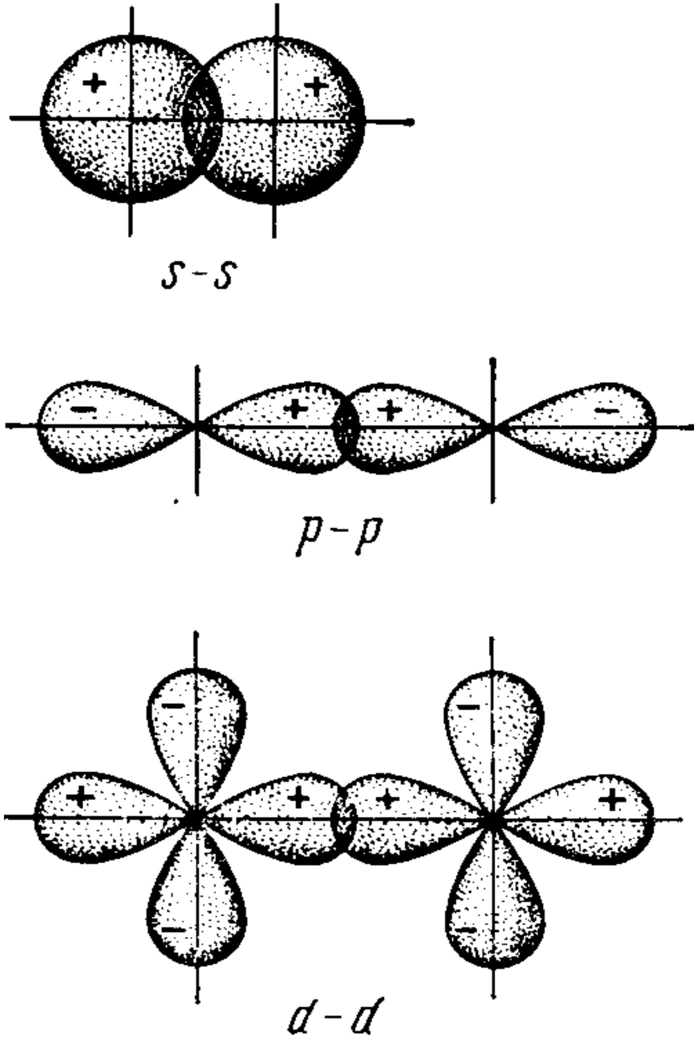
Molecular models (forest air):

1 - nitrogen
2 - oxygen
3 - argon
4 – CO_2
5 – H_2O
6 – O_3
7 - terpineol

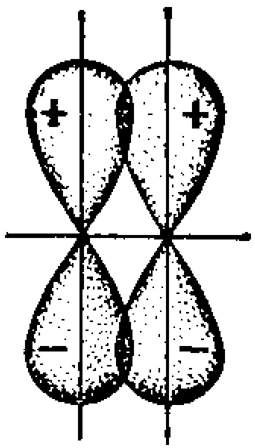
Orientation of covalent bond determines the spatial structure of molecules - the geometry of the molecules.

Depending on a way of crossing and the symmetry of the formed electronic cloud, distinguish
σ-, π- and δ- bonds

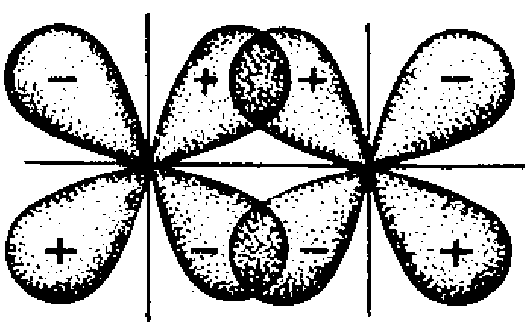




σ-Bonds are formed by head-on overlapping between atomic orbitals. The overlap region lies directly between the two nuclei**.**



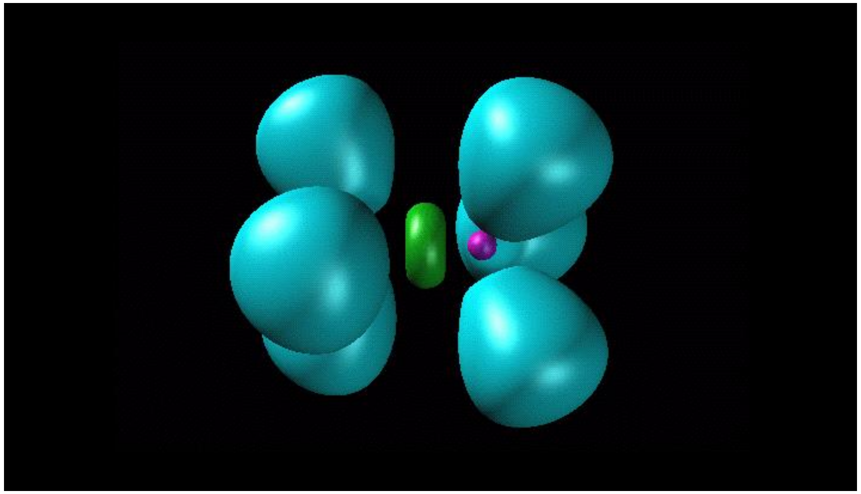
p-p

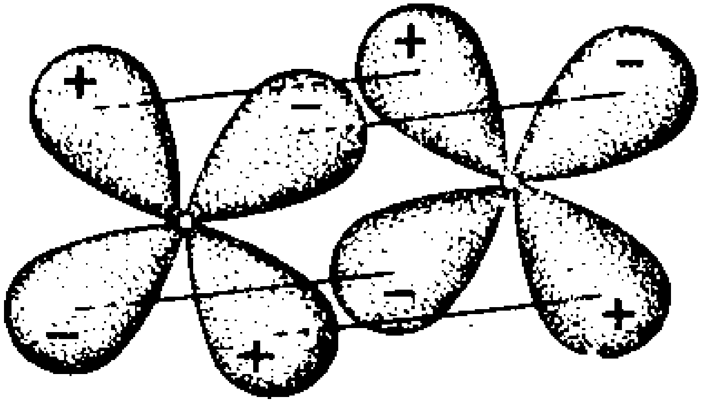


d-d

π-Bonds are formed by overlapping electron clouds, oriented perpendicular to the axis of communication, forming two areas of overlap on each side of the line connecting the centers of the atoms.

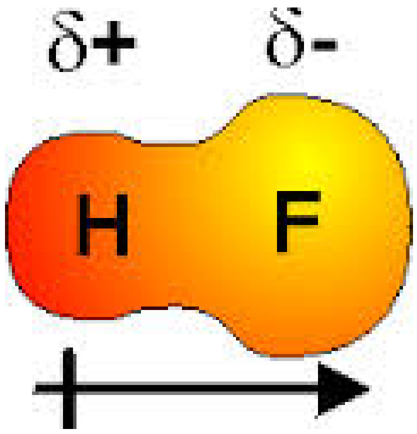
δ-Bonds are formed by overlapping of four lobes of each two d-atomic orbital arranged in parallel planes.





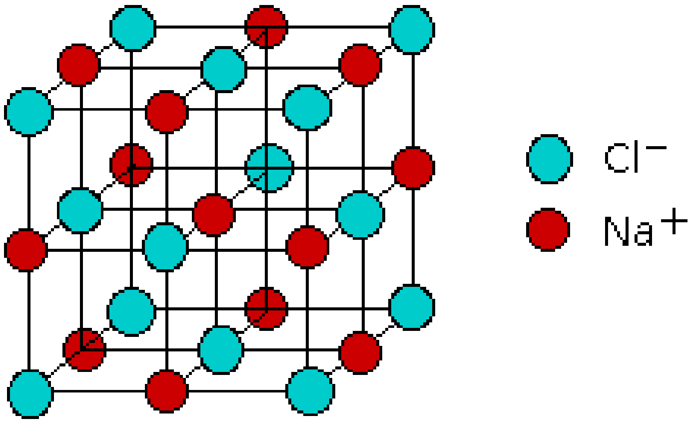
d – d

Polarity of covalent bonds is the shift of the electron pair to the more electronegative atom



The bond polarity means that the electrons in the bonds are not shared equally. Fluorine atom has a stronger attraction than the hydrogen atom for the shared electrons. This type of bonding produces the partial positive and partial negative charges on the fluorine and hydrogen atoms.

IONIC BONDING



NaCl

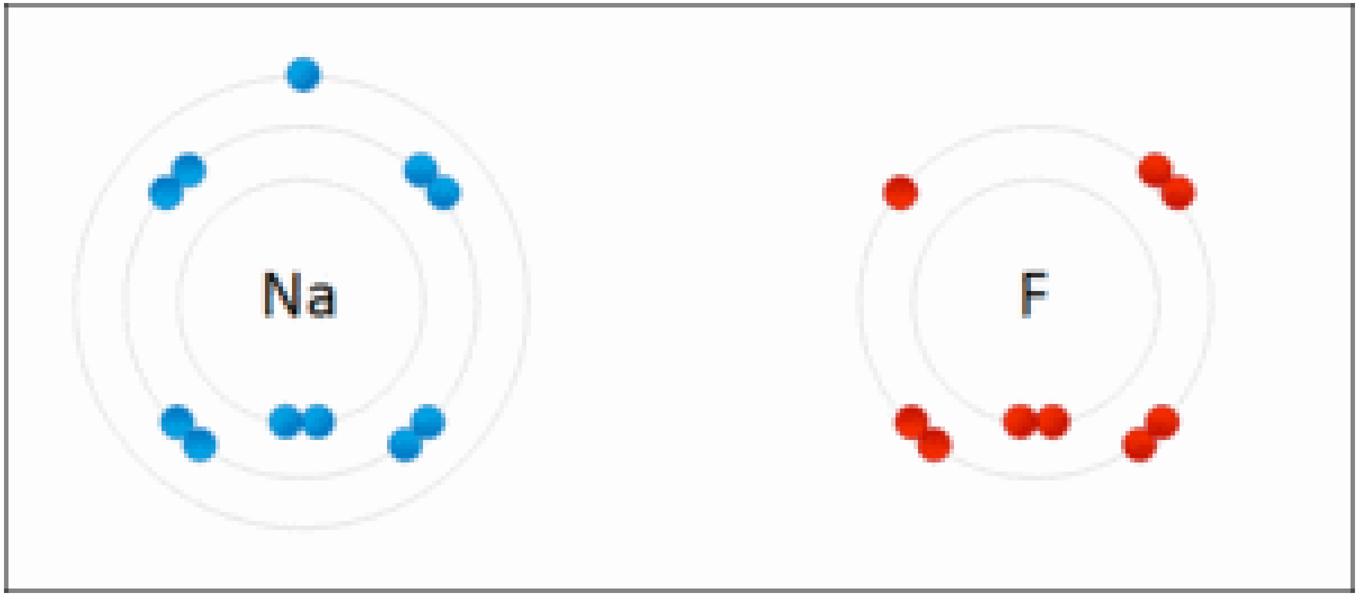
$Na - e^- = Na^+$

cation

$Cl + e^- = Cl^-$

anion

- The attraction between ions are based on a mutual electrostatic attraction and pushing away.
- The ions can be presented as the charged spheres.
- Each ion is able to draw ions of an opposite charge, that is ionic bond is **unsaturated** and **undirection**.



Sodium and fluorine undergoing a redox reaction to form sodium fluoride. Sodium loses its outer electron to give it a stable electron configuration, and this electron enters the fluorine atom exothermically. The oppositely charged ions – typically a great many of them – are then attracted to each other to form a solid.

Task 3.

Write the electronic formula of ions Br^-, Li^+

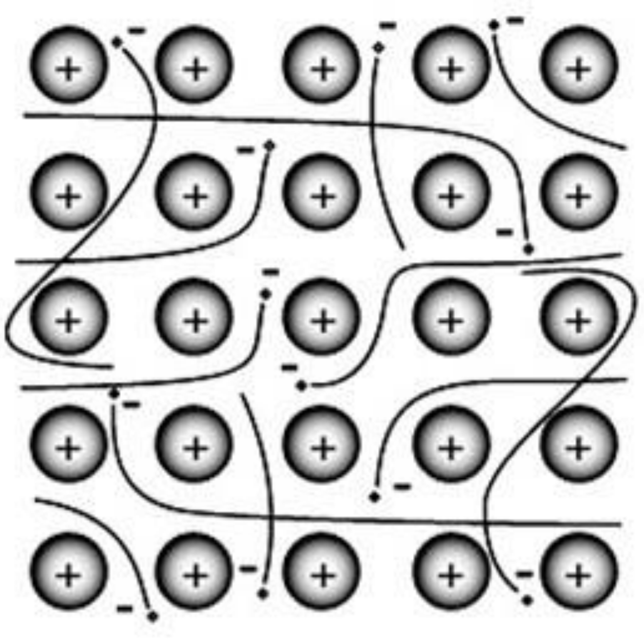
$\overset{0}{Br}$ $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} \underline{4s^2 4p^5}$

$\overset{-1}{Br}$ $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} \underline{4s^2 4p^6}$ $\overset{-1}{Br}$ [Xe]

$\overset{0}{Li}$ $1s^2 \underline{2s^1}$

$\overset{+1}{Li}$ $1s^2 \underline{2s^0}$ $\overset{+1}{Li}$ [He]

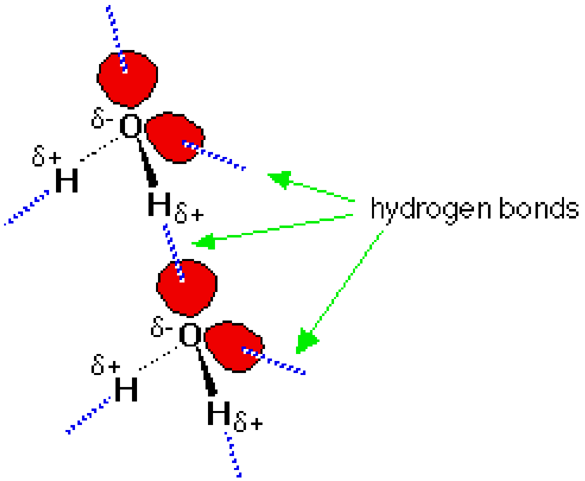
Metallic bond

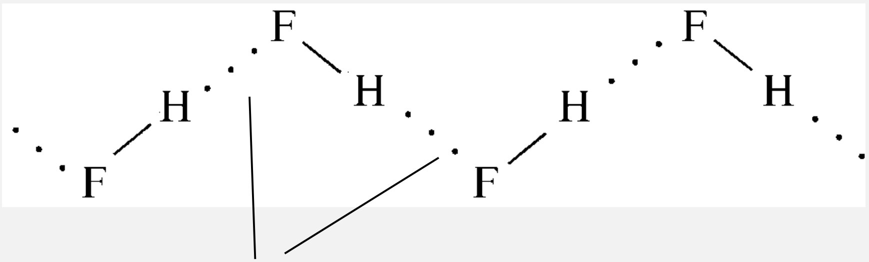


--Metallic- a chemical bond where electrons are shared over multiple nuclei. In the bond, the outer atoms are attached to eachother in a way that allows electrons to flow easily from atom to atom.

hydrogen bond

- A **hydrogen bond** is the electromagnetic attractive interaction between polar molecules, in which hydrogen (H) is bound to a highly electronegative atom, such as nitrogen (N), oxygen (O) or fluorine (F).

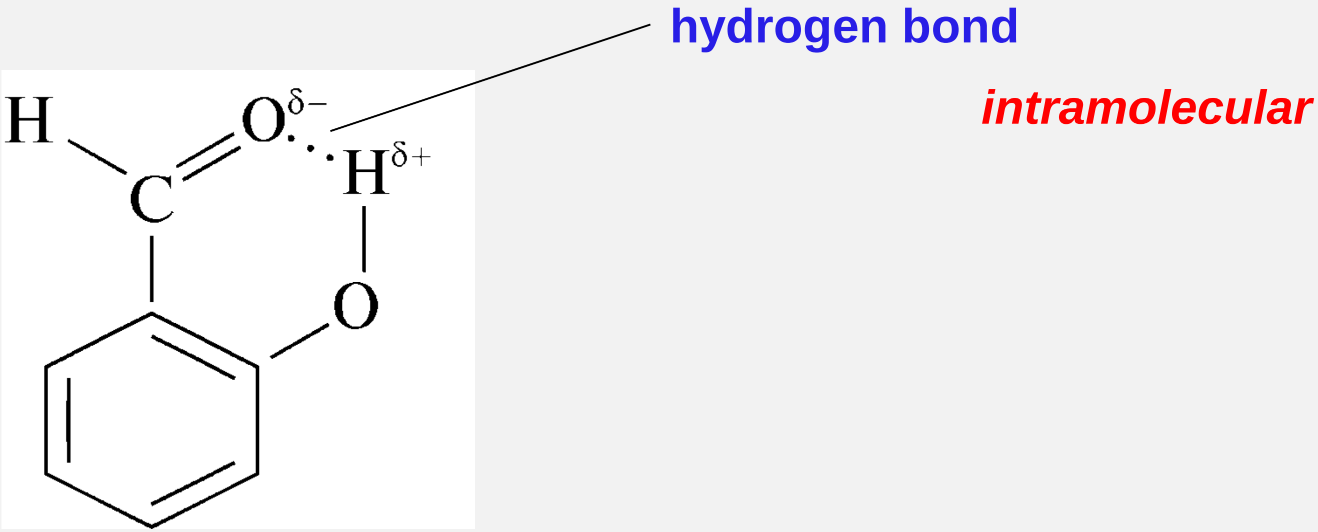




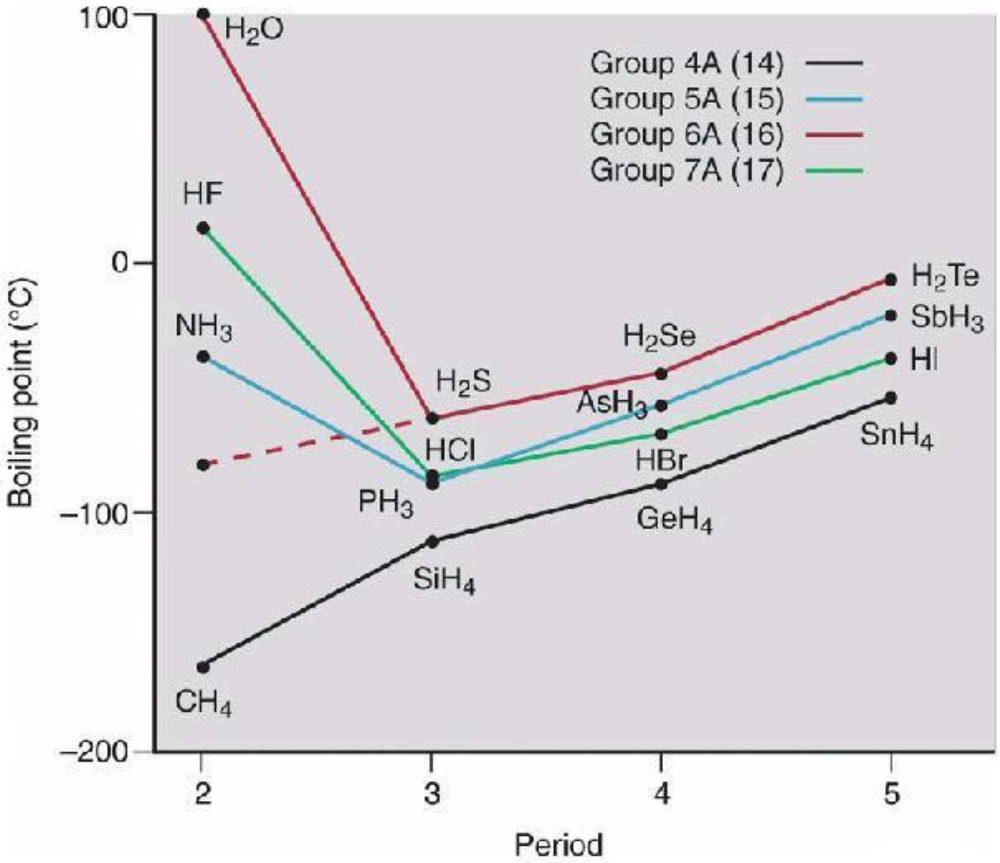
hydrogen bond in *HF*

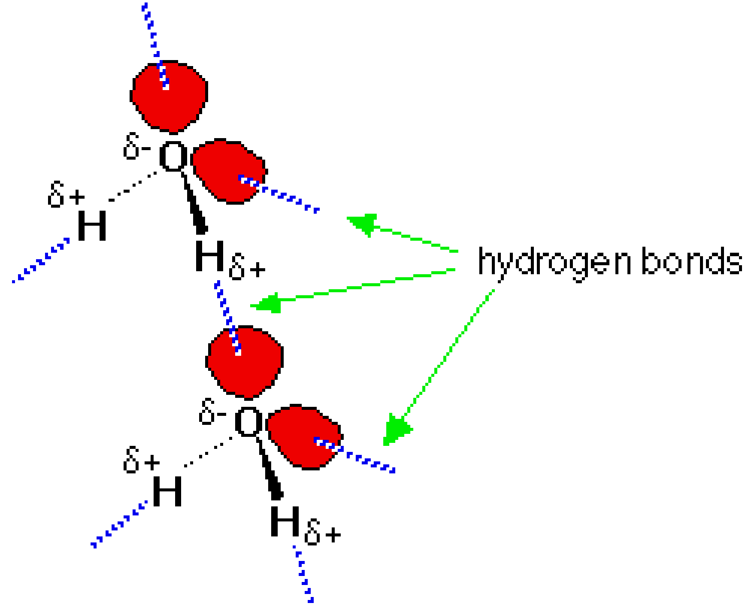
intermolecular

These hydrogen-bond attractions can occur between molecules (*intermolecular*) or within different parts of a single molecule (*intramolecular*).



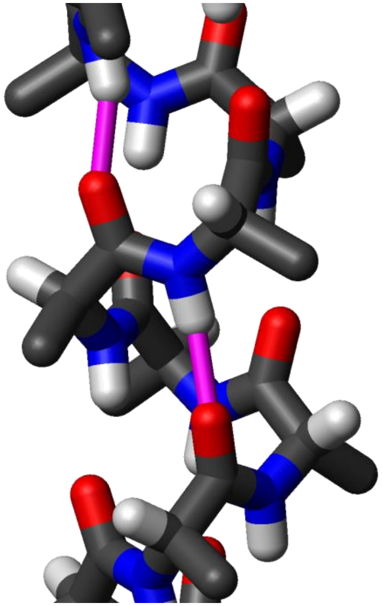
Hydrogen Bonds

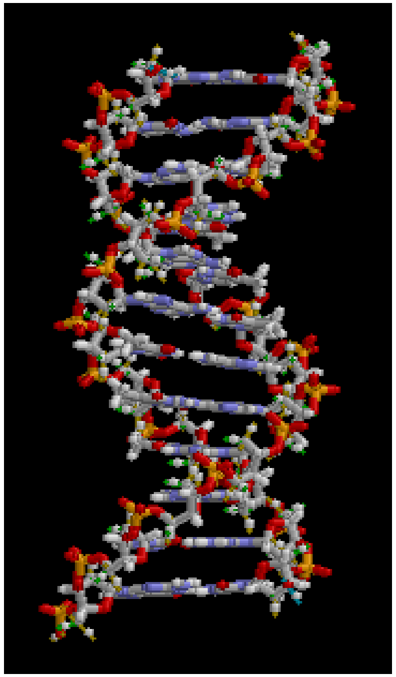




The hydrogen bond (5 to 30 kJ/mole) is stronger than a van der Waals interaction, but weaker than covalent orionic bonds.

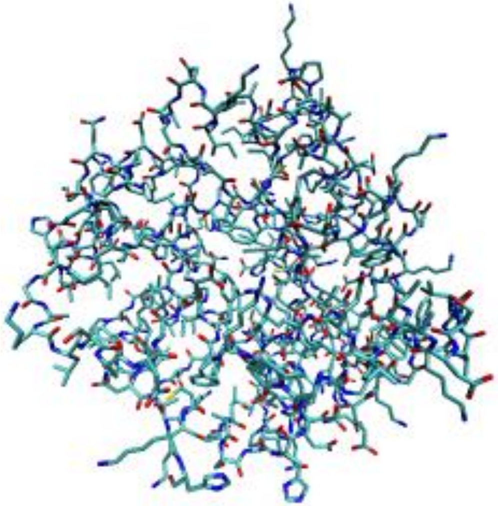
Intermolecular hydrogen bonding is responsible for the high boiling point of water (100 °C) compared to the other group 16 hydridesthat have no hydrogen bonds.

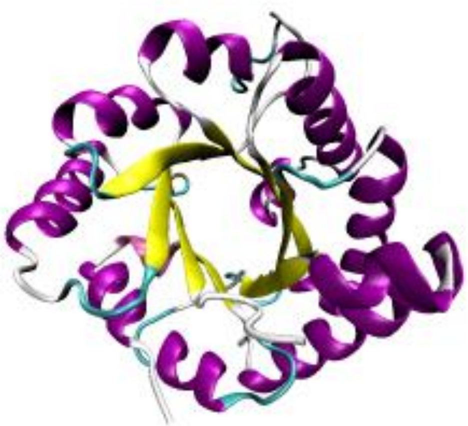


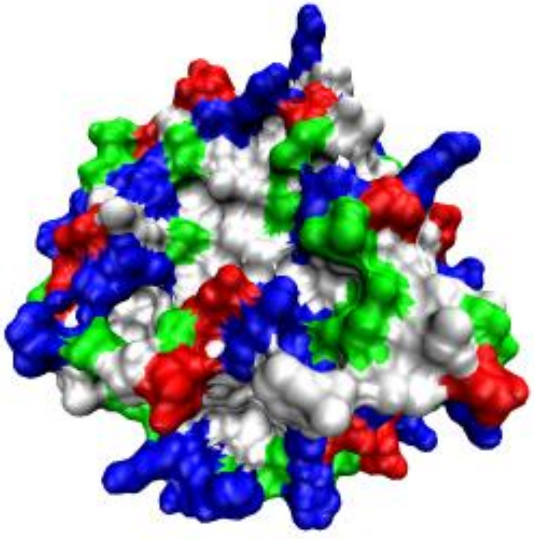


Hydrogen bond can occur in inorganic molecules such as water and in organic molecules like DNA and proteins.

Intramolecular hydrogen bonding is partly responsible for the secondary and tertiary structures of proteins and nucleic acids.
It also plays an important role in the structure of polymers, both synthetic and natural.

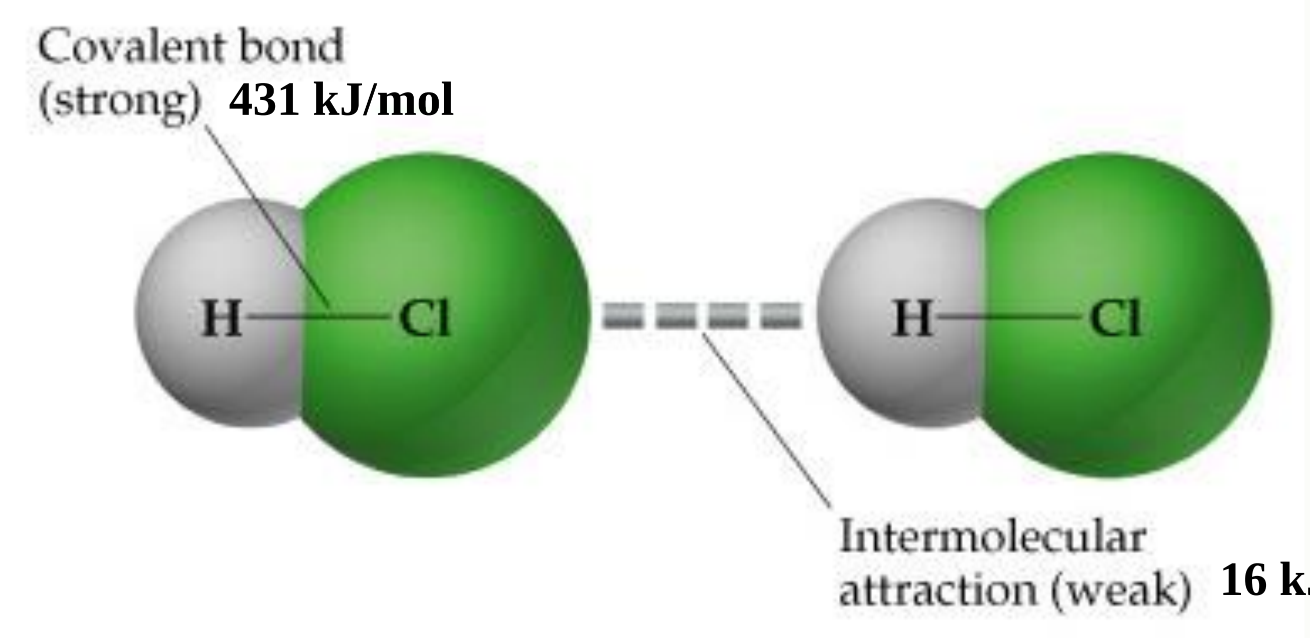






Intermolecular Forces

The attraction between molecules is an ***intermolecular force* - *Van der Waals forces***



Intermolecular forces are much weaker than ***ionic*** or ***covalent*** bonds

Van der Waals forces are weak electrostatic interactions

(~15% as strong as a covalent or ionic bond)

Orientation (dipole-dipole) interaction

between polar molecules HCl

Induction (polarization) interaction

between the polar HCl and non-polar molecules Cl_2

Dispersion interaction

between non-polar molecules Cl_2