Chemical bonds

- **Molecules are identical and stable aggregates of atoms.**

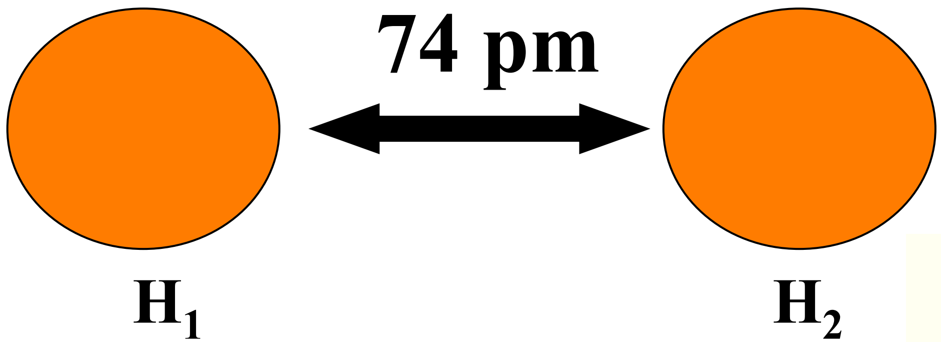
- **Their geometry does not change depending on their aggregation state.**

- **This is due to a form of interaction between atoms.**

The hydrogen molecule (H_2)

H_2 is the simplest molecule in nature:

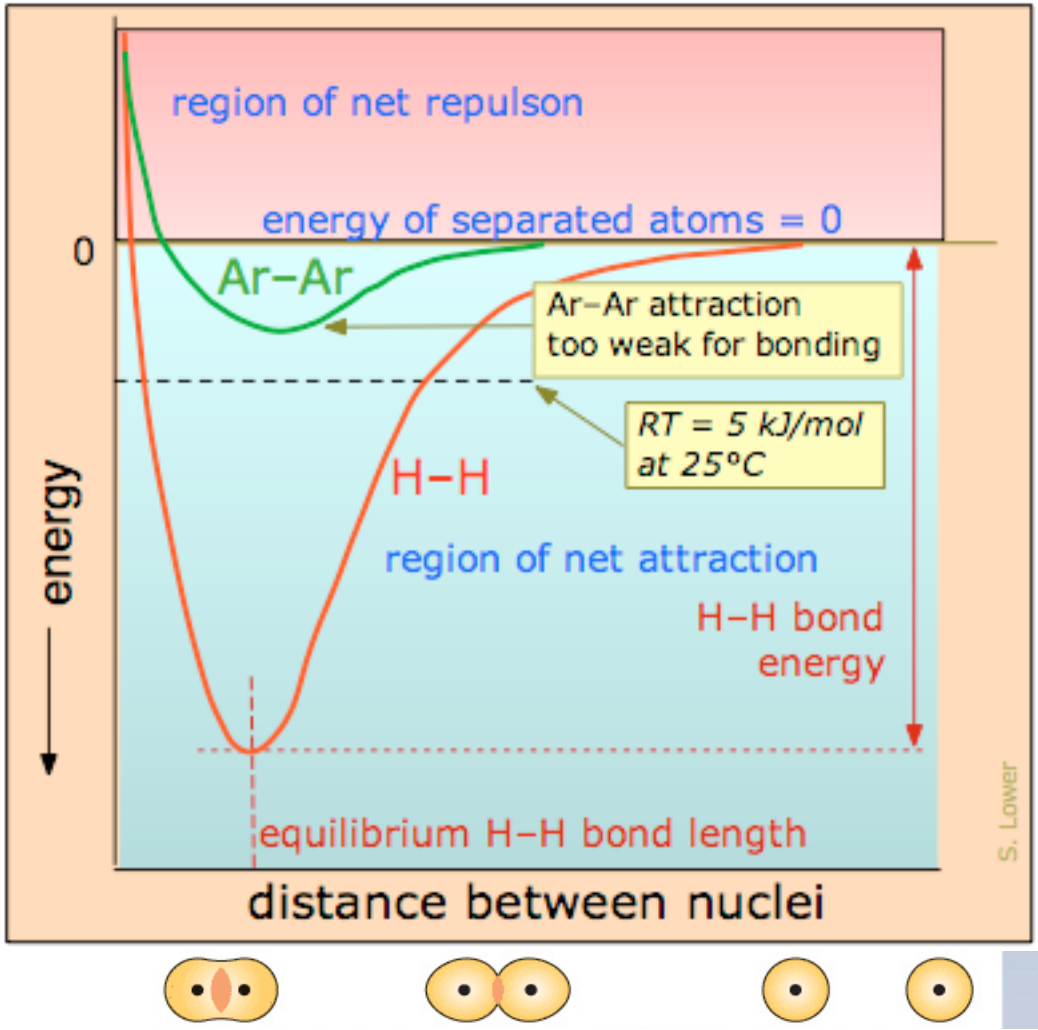
it is formed by two protons (the nuclei) and two electrons, from each H atom.



1 pm = 1 x10^{-12} metri

Potential energy

Potential energy as a function of bond formation.
A minimum is achieved at a distance of 74 pm, where s orbitals overlap.
Nuclei repulsion increases steeply at shorter distances.



Possible interactions

The interactions between atoms are electrostatic and they depend on distance.

Attractive interactions stabilize the system, reulsive ones destabilize it.

A covalent bond is a balance of attractive and repulsive forces.

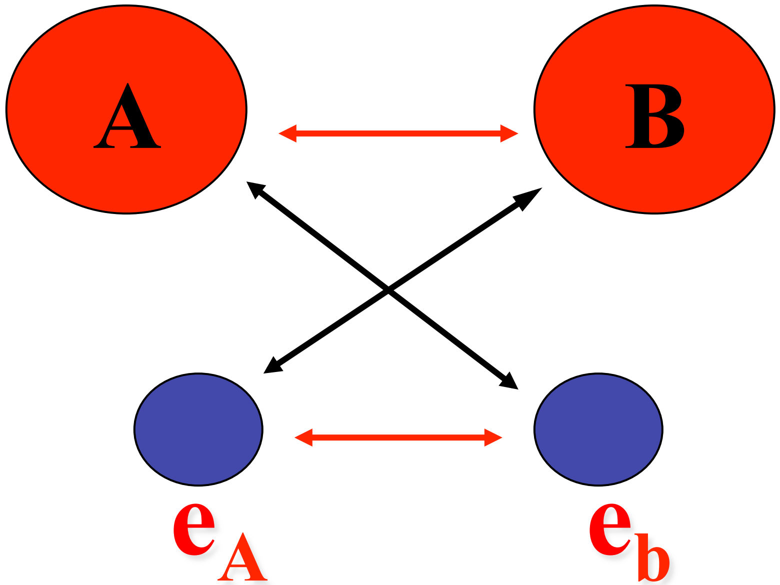
Interactions

If we define the nuclei as A and B and electrons as e_A and e_B we obtain:

ATTRACTION:

e_A - B

e_B - A



REPULSION:

e_A - e_B

A - B

Attractive and Repulsive forces

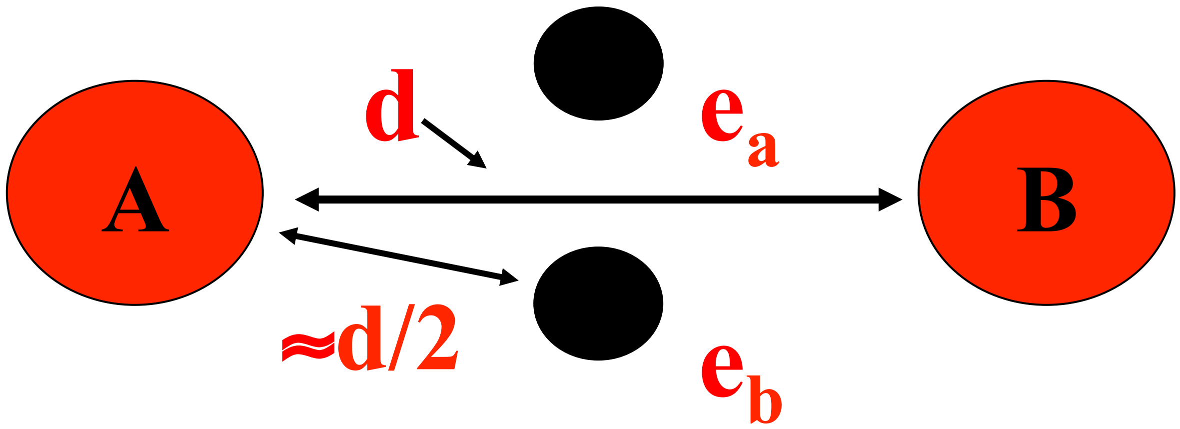
The intensity of the interactions follows Coulomb's low.

If in all conditions, repulsive and attractive forces were balanced, H_2 would not be more stable than isolated H atoms.

There is a position of the particles where attraction is maximized and repulsion is minimized.

Attractive and Repulsive forces

If the distance beween nuclei is fixed (d), we note that when the electrons are between them attractive forces are predominant.

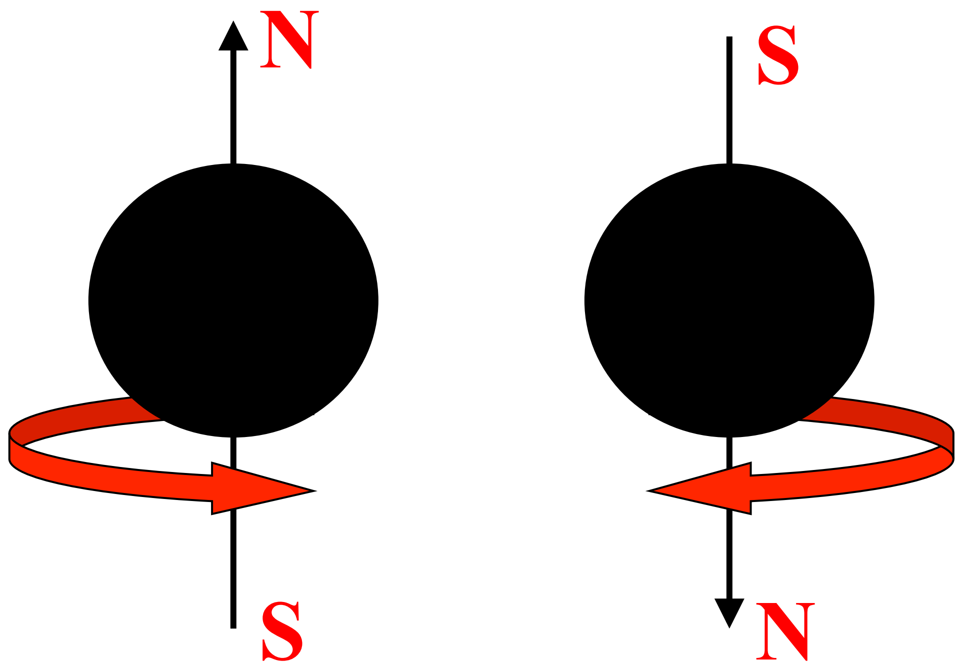


This arrangement maximizes the attractive interactions and minimize repulsive interactions (screen effect between the nuclei).

However, we have considerable repulsion between the electrons.

There is an interaction between electrons which balances this repulsion: a magnetic attraction due to their "**SPIN**".

Electons have been proven to "spin" around an axis, generating a weak magnetic field due to their intrinsic charge.



Electrons and bonds

To minimize repulsion between electrons their spin must be opposite.

In general, matter has no magnetic properties confirming that most of the electrons are magnetically coupled. **(diamagnetic compounds)**

If magnetic phenomena are observed, it implies that unpaired electrons are present **(paramagnetic compounds)**

Covalent bonding

A "covalent bond" can be defined as an interaction between two atoms due to a pair of electrons that spend most of their time in the internuclear region, with antiparallel spin.

The shared pair of electrons allows each H to have 2 electrons in the 1s orbital of the valence shell. H_2 has then the same electronic configuration of the noble gas helium (He).

The macroscopic properties of matter show that there is a strong tendency to form pairs of electrons with the criterion of opposite spins.

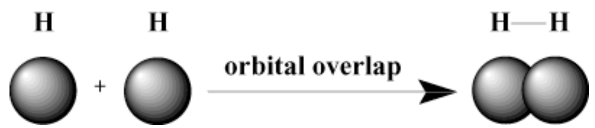
This does not apply only to electrons directly involved in bond formation, but also to the other valence electrons in an atom atom, that tend to form “nonbonding” pairs.

Valence shell electron pair repulsion theory (VSEPR) explains the shape of molecules, based on repulsion between electron pairs.

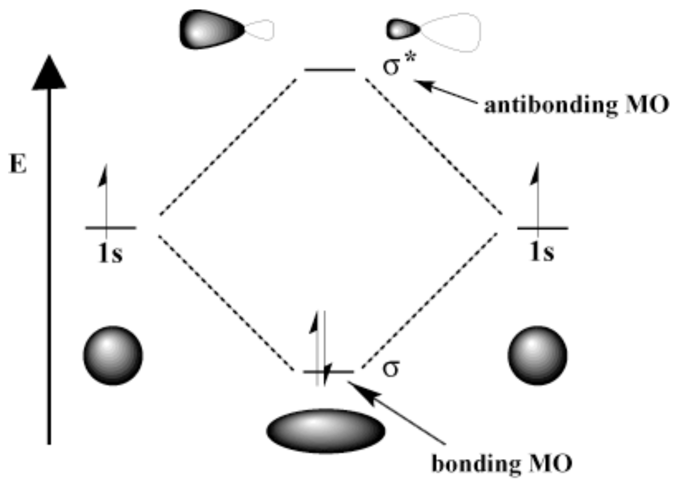
Theories of bonding: explanations for chemical bond, Lewis dot structures.

$$H\cdot + H\cdot \rightarrow H:H$$

Valence bond method considers the covalent bond as a result of overlap of atomic orbitals.



Molecular orbital theory states that atomic orbitals are not meaningful after atoms form molecules, molecular orbitals come into play.



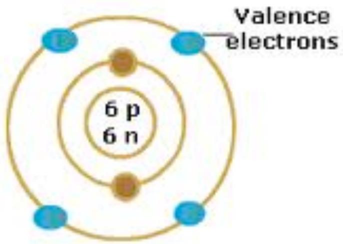
OCTET RULE

Atoms tend to lose or gain electrons to reach a configuration of the outer shell that contains eight electrons.

Exceptions to the octet rule

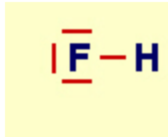
Atoms with external shell electrons in d and f orbitals.
Atoms before C in the periodic table.

Lewis structure

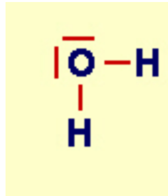


In the Lewis model the valence of an element (the number of valence electrons) is the number of its group of the periodic table.

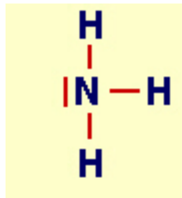
Fluorine F $1s^2 2s^2 2p^5$ Group 7 forms 1 covalent bond



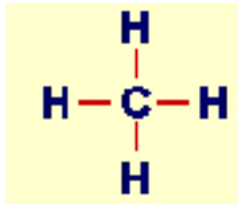
Oxygen O $1s^2 2s^2 2p^4$ “ 6 “ 2 “



Nitrogen $1s^2 2s^2 2p^3$ N “ 5 “ 3 “

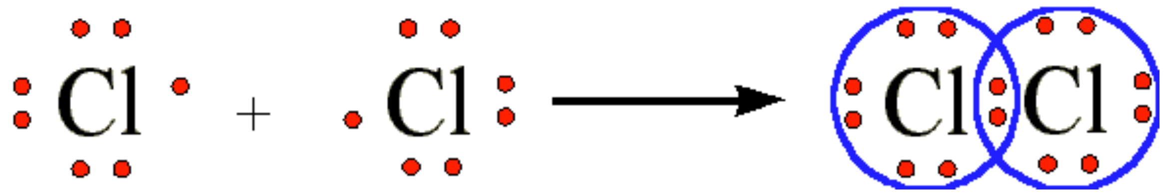


Carbon C $1s^2 2s 2p^3$ “ 4 “ 4 “

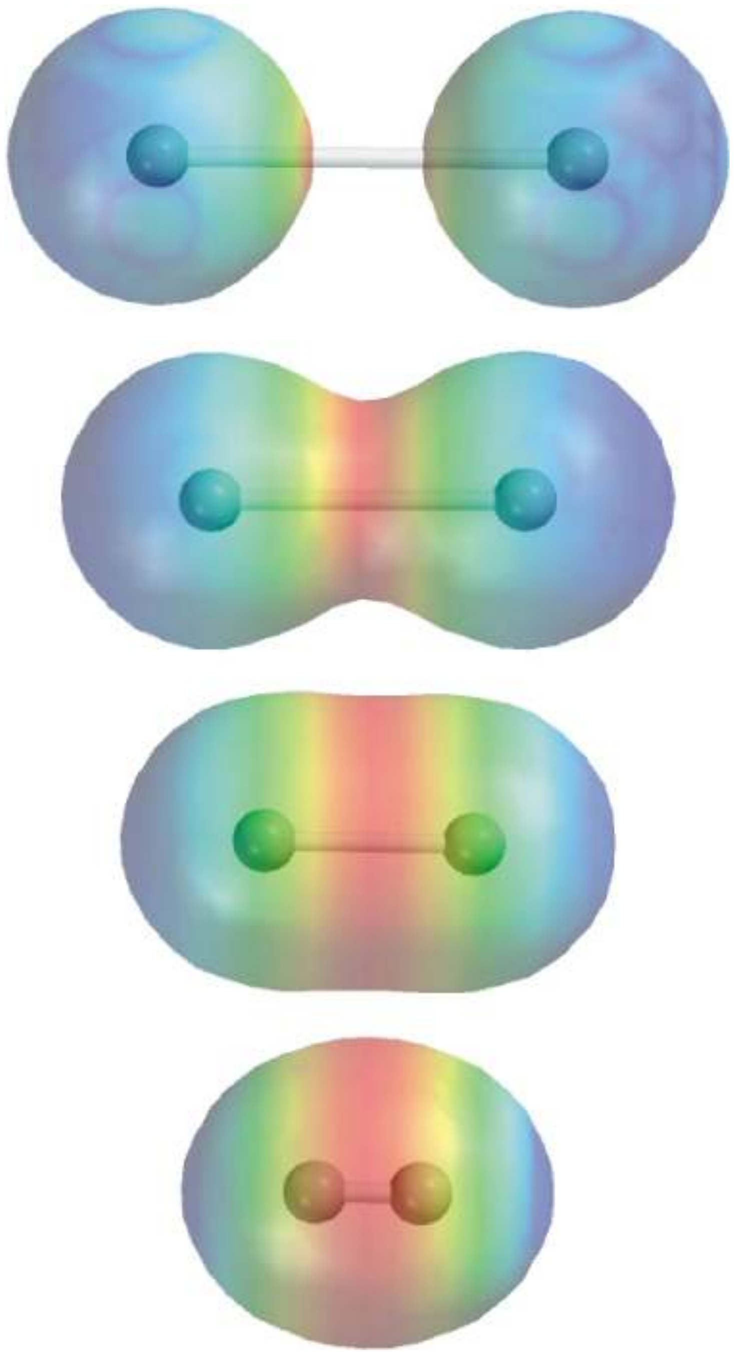


Homeopolar covalent bond

Electrons are equally shared

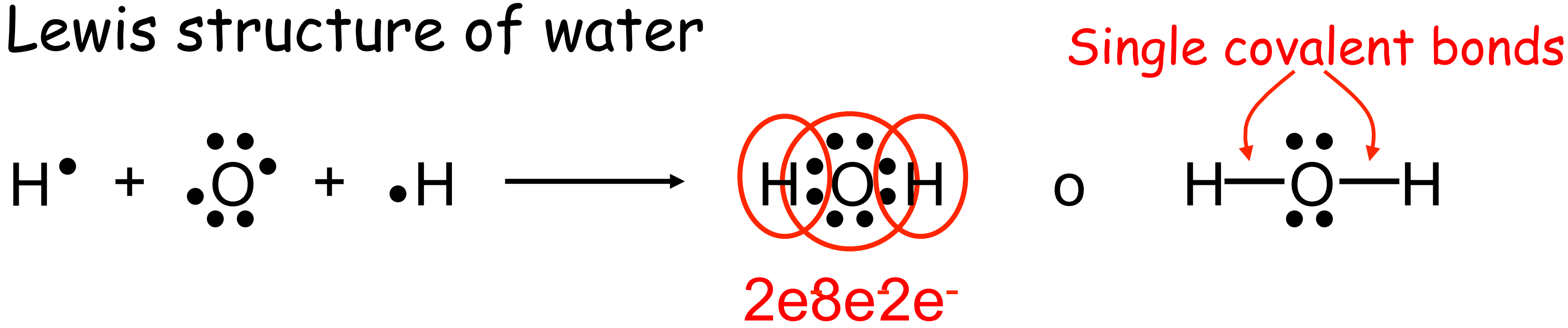


Covalent bond and octet rule:
atoms share electrons
completing their valence shell.

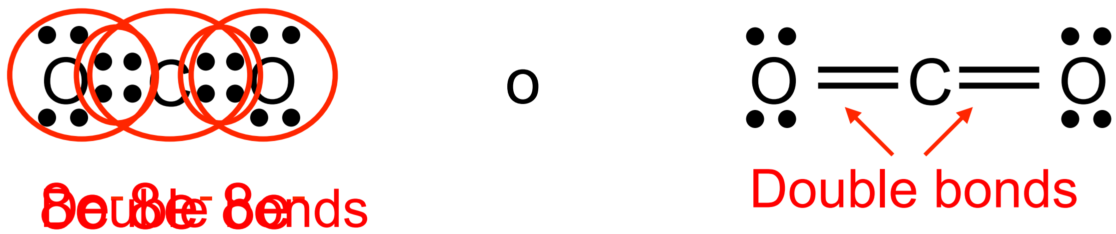


Changes in the electron density as two atoms approach.

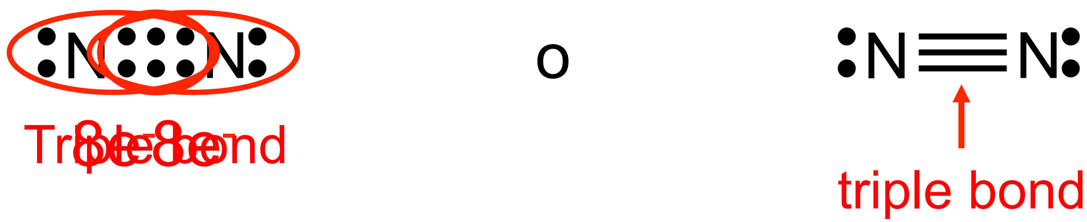
Lewis structure of water



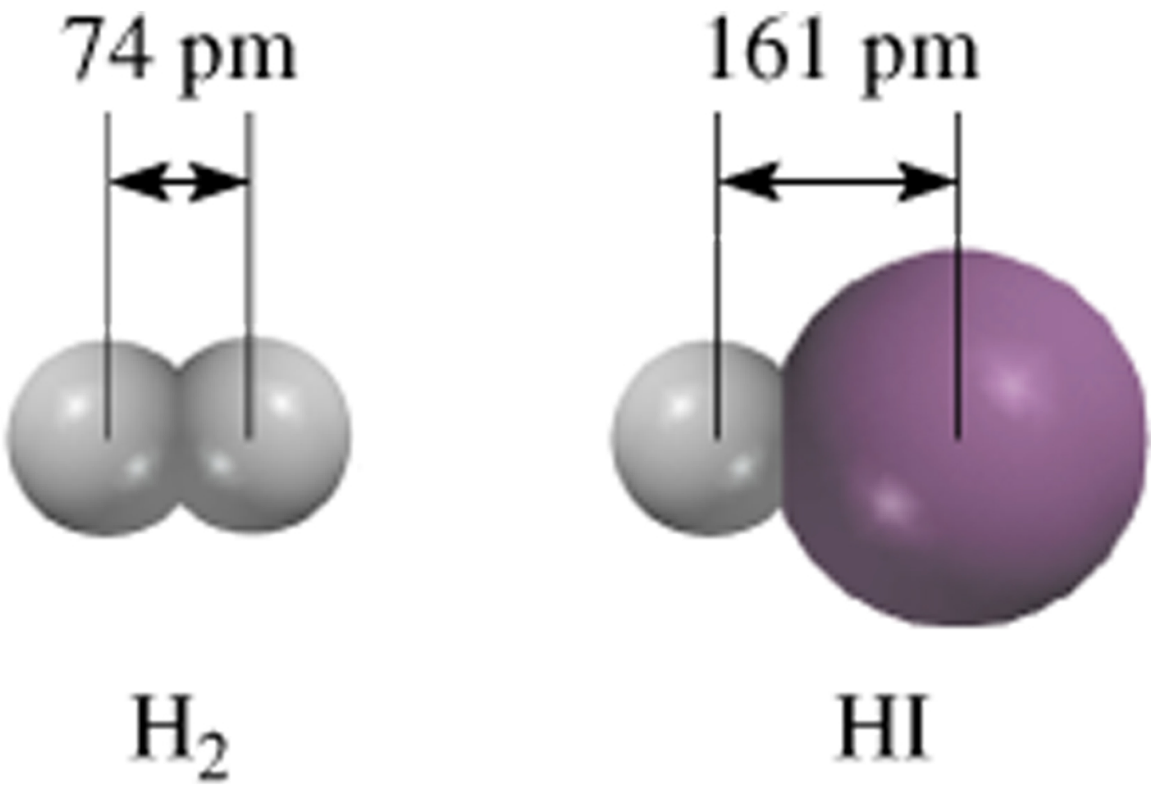
Double bond: *two atoms share two electron pairs*



Triple bond: *two atoms share three pairs of electrons*



Length of covalent bonds



Bond type	length (pm)
C-C	154
C=C	133
C≡C	120
C-N	143
C=N	138
C≡N	116

Bond length

Triple < Double < Single

Electronegativity

- Measures the tendency of atom in a molecule to attract electrons.

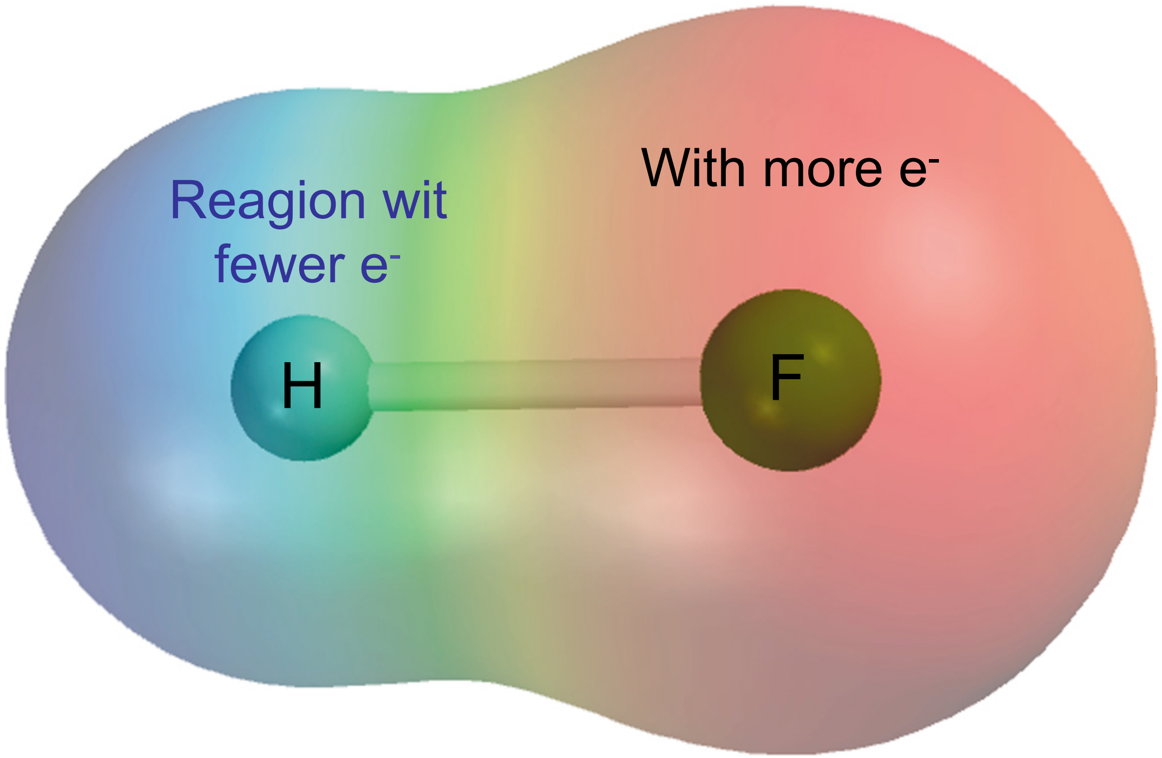
- It is related to the energy associated to the addition of an electron to an atom or an ion.

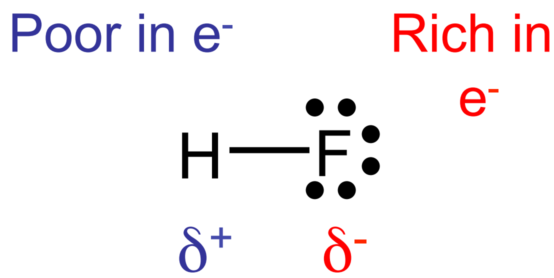
- $X + e^- \rightarrow X^-$

- $X^+ + e^- \rightarrow X$

- For most of the atoms and for all the positive ions the addition of an electron results in a release of energy (E has a negative sign).

The polar covalent bond yields different densities of electrons on atoms.





Electronegativity

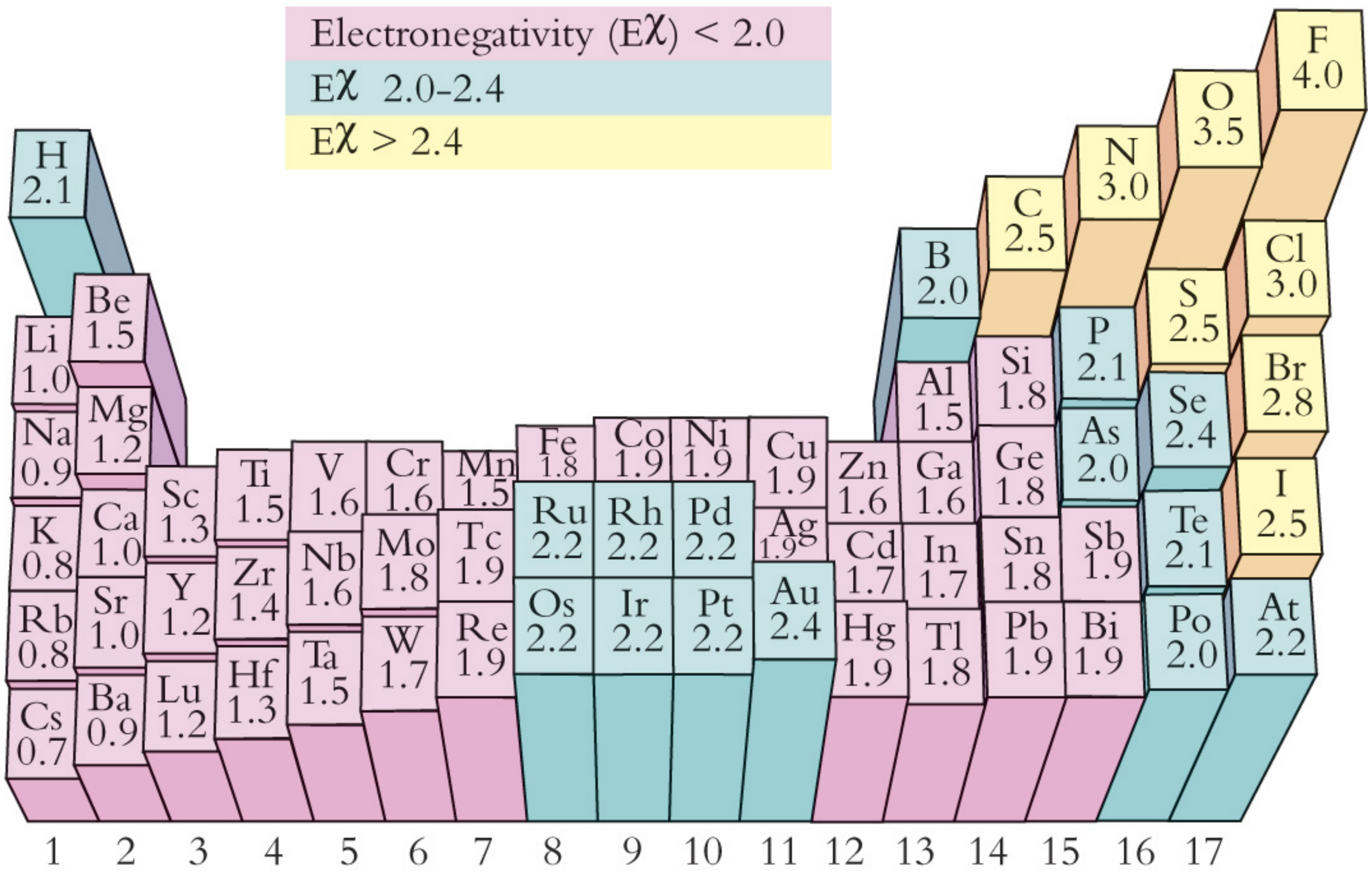
- Since we do not have electron affinity values for all elements E.N. can be evaluated empirically.

- A widely used method uses a relative scale with a value of 4 for fluorine as a reference.

- Electronegativity decreases in the Periodic Table from top to bottom and from right to left.

Electronegativity

The tendency of an atom to attract electrons when it forms a bond.



- If two atoms forming a bond have different electronegativity, bond electrons are not shared equally shared between them.

- There is a higher probability of finding them close to the more electronegative atom.

Bonds can be classified using electronegativity

Difference	Bond type
0	Covalent
≥ 2	Ionic
$0 < e < 2$	Polar covalent

Increase of the difference in E.N. →

Covalent	→	Polar Covalent	→	Ionic
Shared e^-		Partial e^- transfer		Transferred E^-

Covalent
$\Delta E = 0$

Polar
$0 < \Delta E < 2.0$

Ionic
$\Delta E > 2.0$

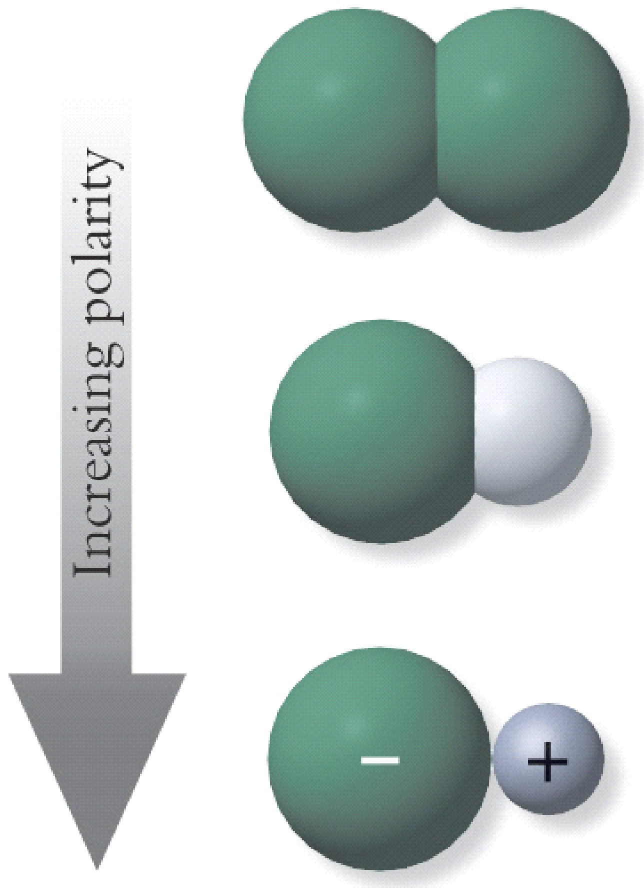
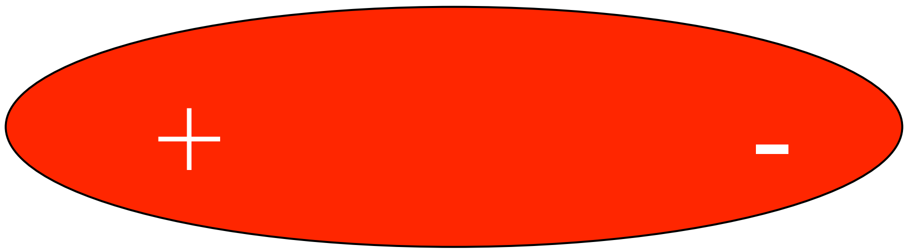


Table 8-1
Representative Electronegativity Differences

Pg 335

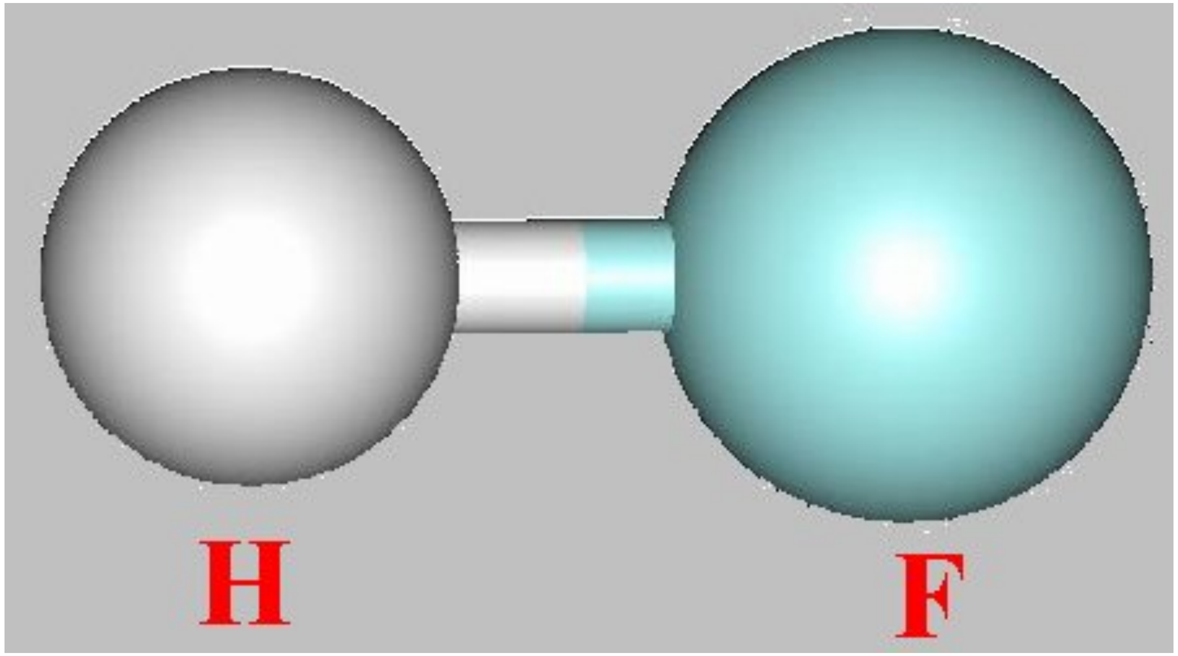
Permanent dipoles

- **The centre of mass (nuclei) is no longer the same as the electrical one (bonding and non bonding e^-): an electric dipole is formed.**

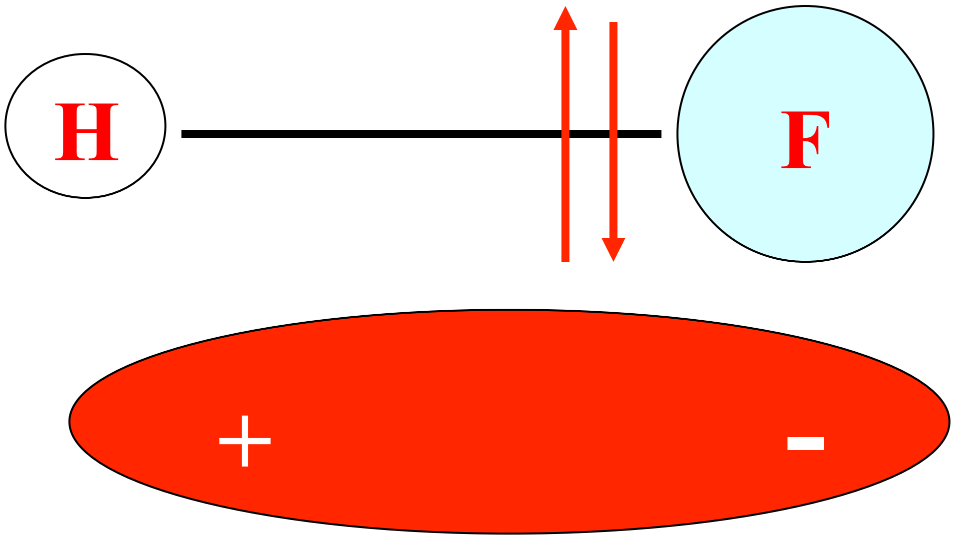


A permanent electric dipole is a system consisting of two electric charges of equal magnitude but opposite sign placed at a fixed distance.

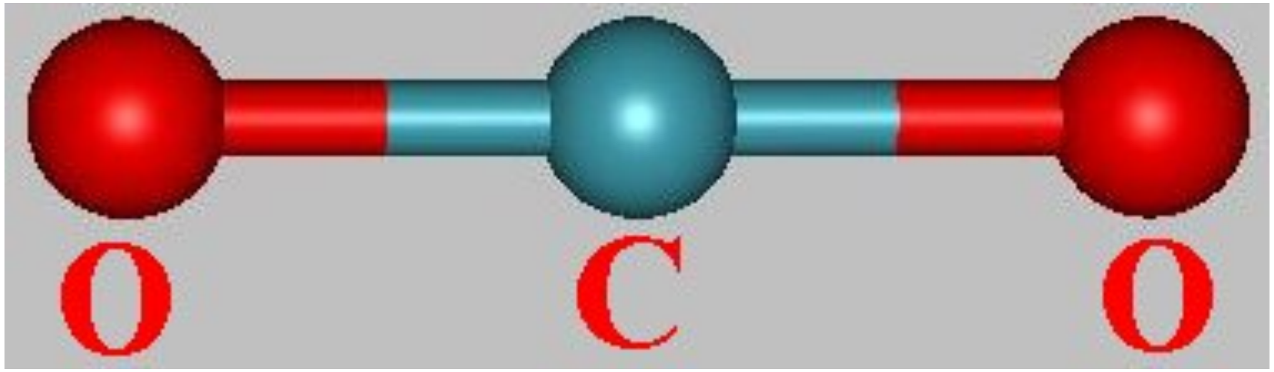
Polar molecules



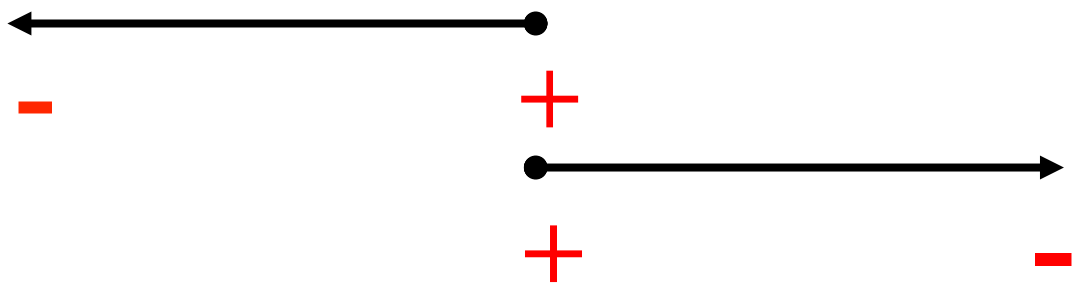
Electronegativity: 2.1 4.0



Polar and apolar molecules



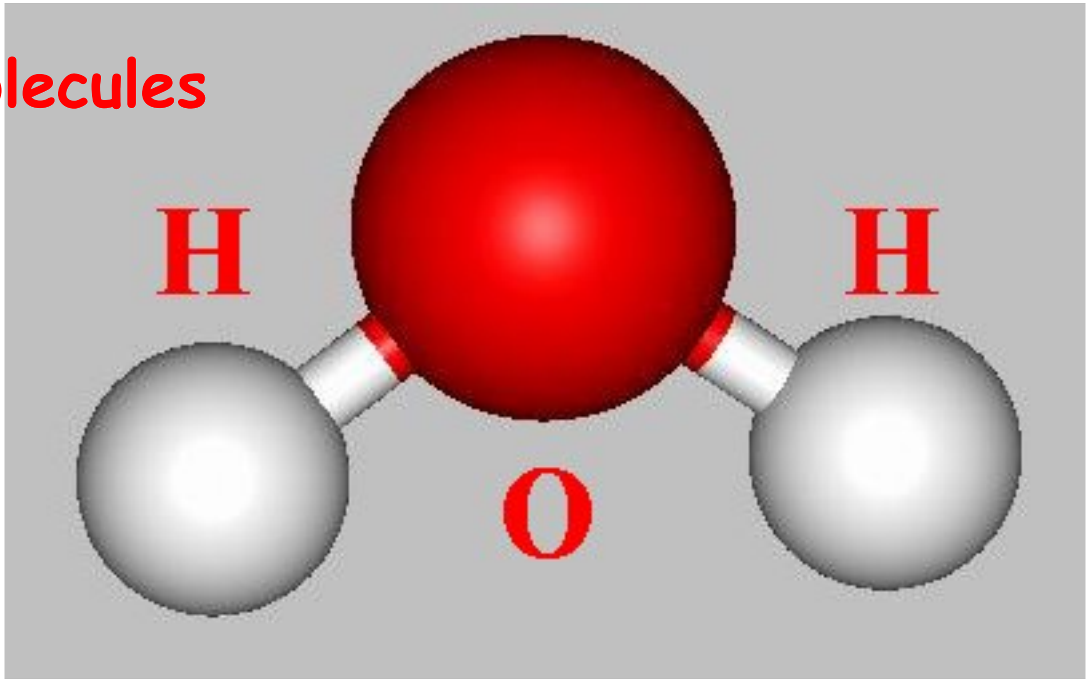
Eletcronegativity: 3.5 2.1 3.5



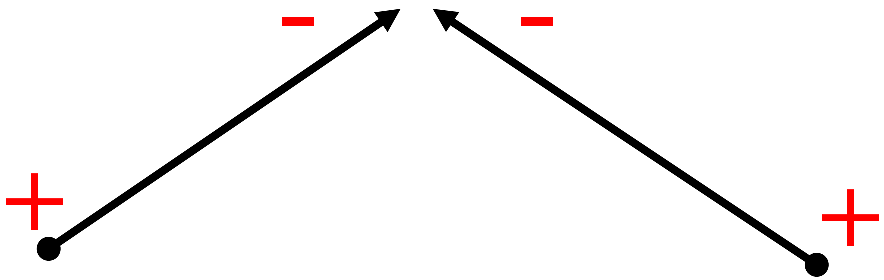
The sum vector is equal to zero.

Bonds are polarized, but the molecule is not.

Polar and apolar molecules



Electronegativity: 2.1 3.5 2.1

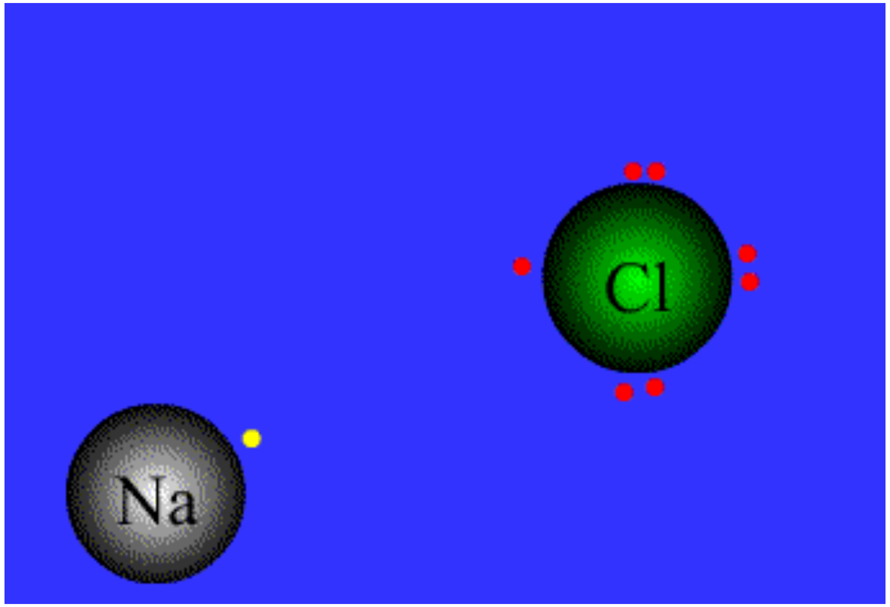


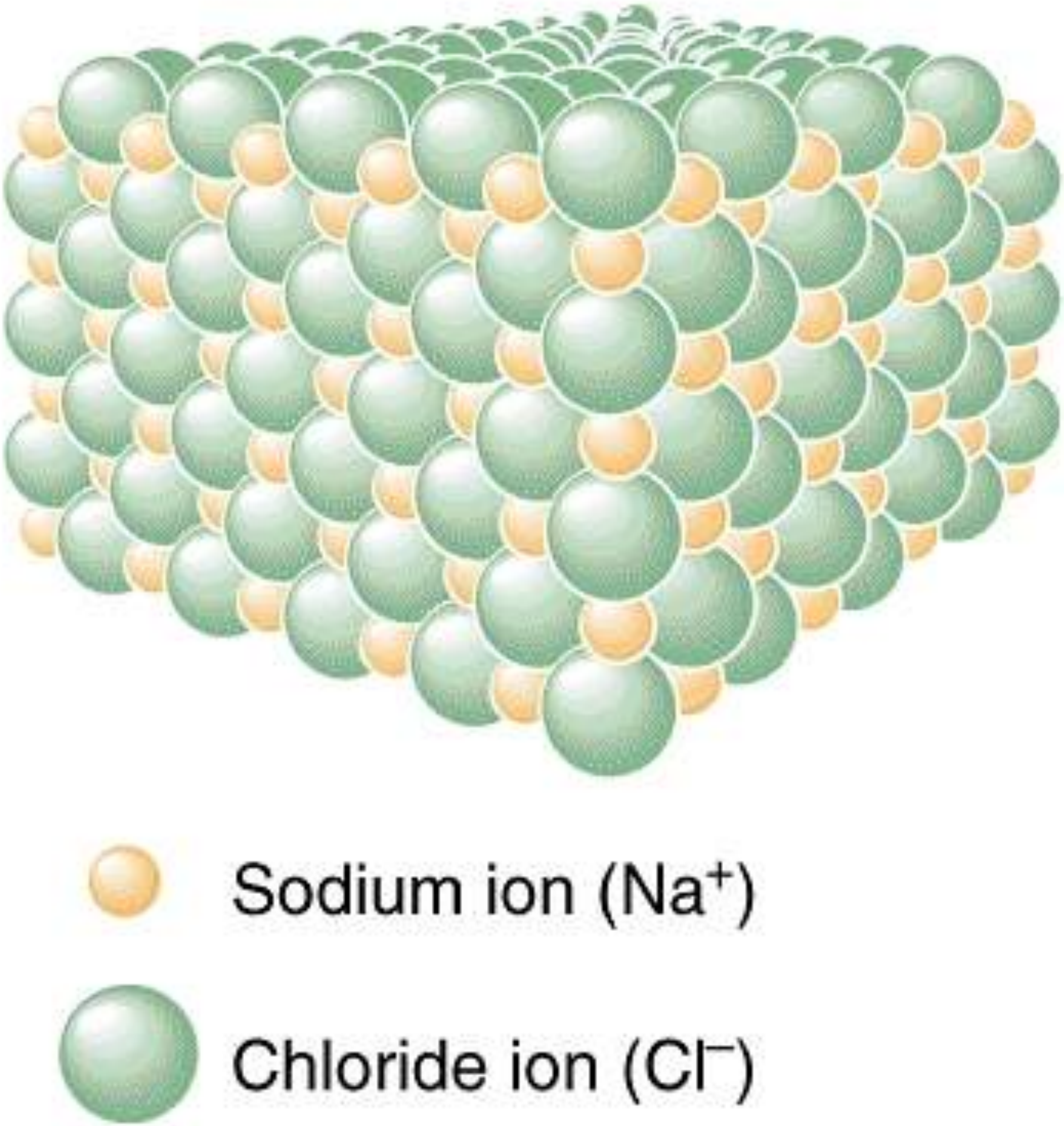
he vector sum is not =zero

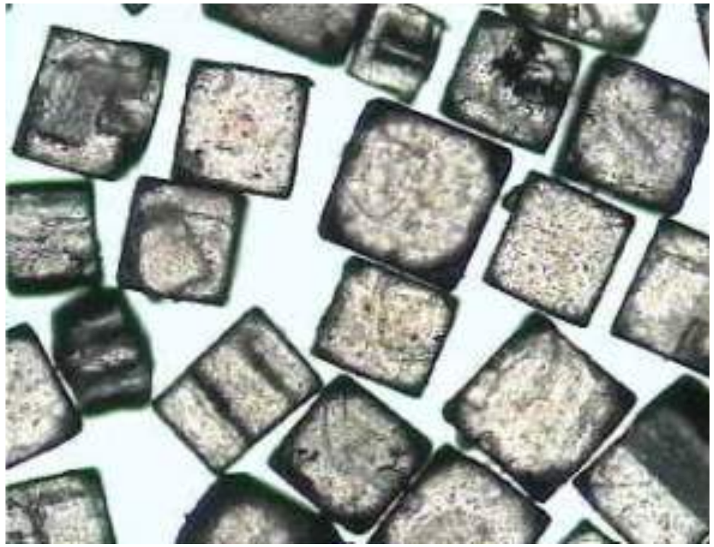
Bonds are polar and the molecule is polar.

Ionic bond

Indicates the ionic nature of electrostatic forces acting between particles of opposite electric charge. In general, ionic compounds are formed by the interaction of metals (left side of the periodic table) with non-metals (right side of the table) excluding the noble gases, group. 8A.

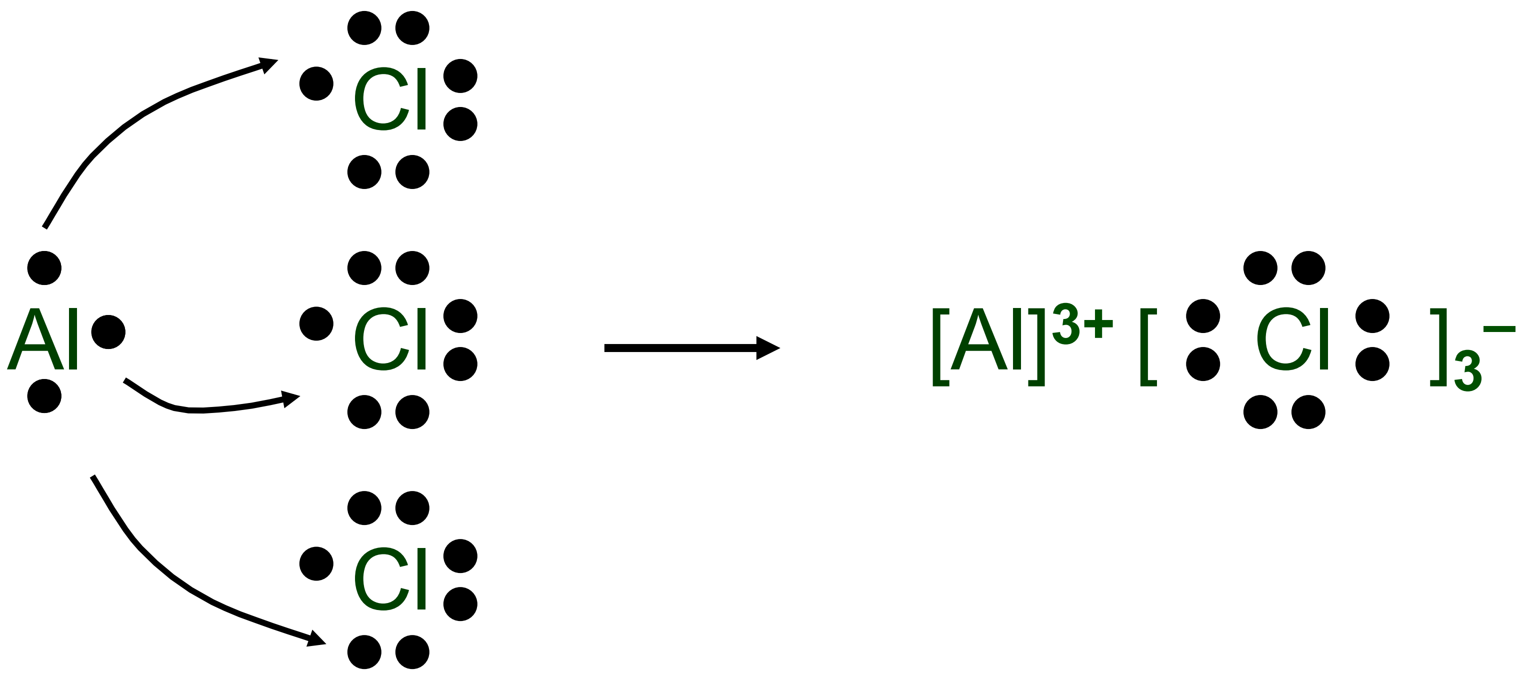



Sodium ion (Na^+)
Chloride ion (Cl^-)



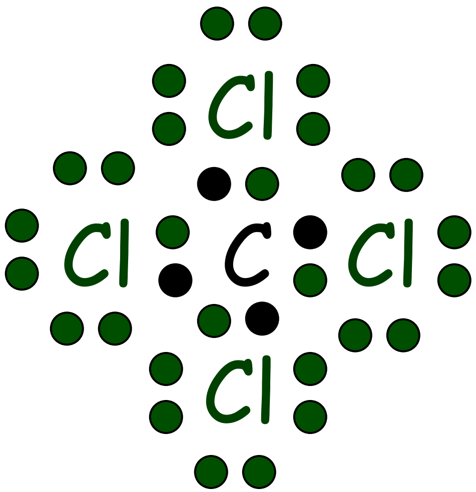
Ionic bond: Al + Cl

$Al + 3Cl \rightarrow [Al]^{3+}[Cl]_3^{-}$

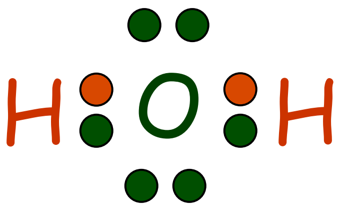


Covalent and ionic bonds

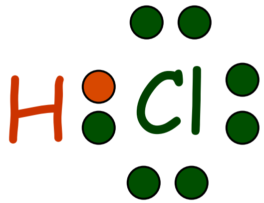
CCl_4 Covalent



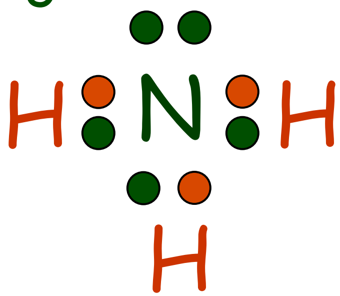
H_2O Covalent



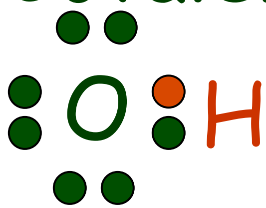
HCl Covalent



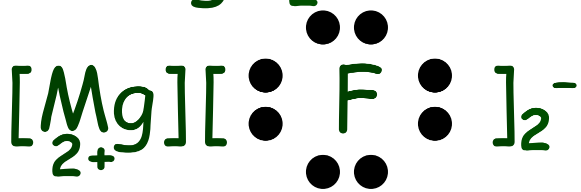
NH_3 Covalent



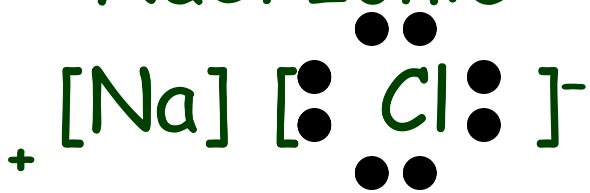
OH^- Covalent



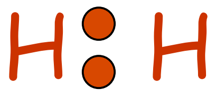
MgF_2 Ionic



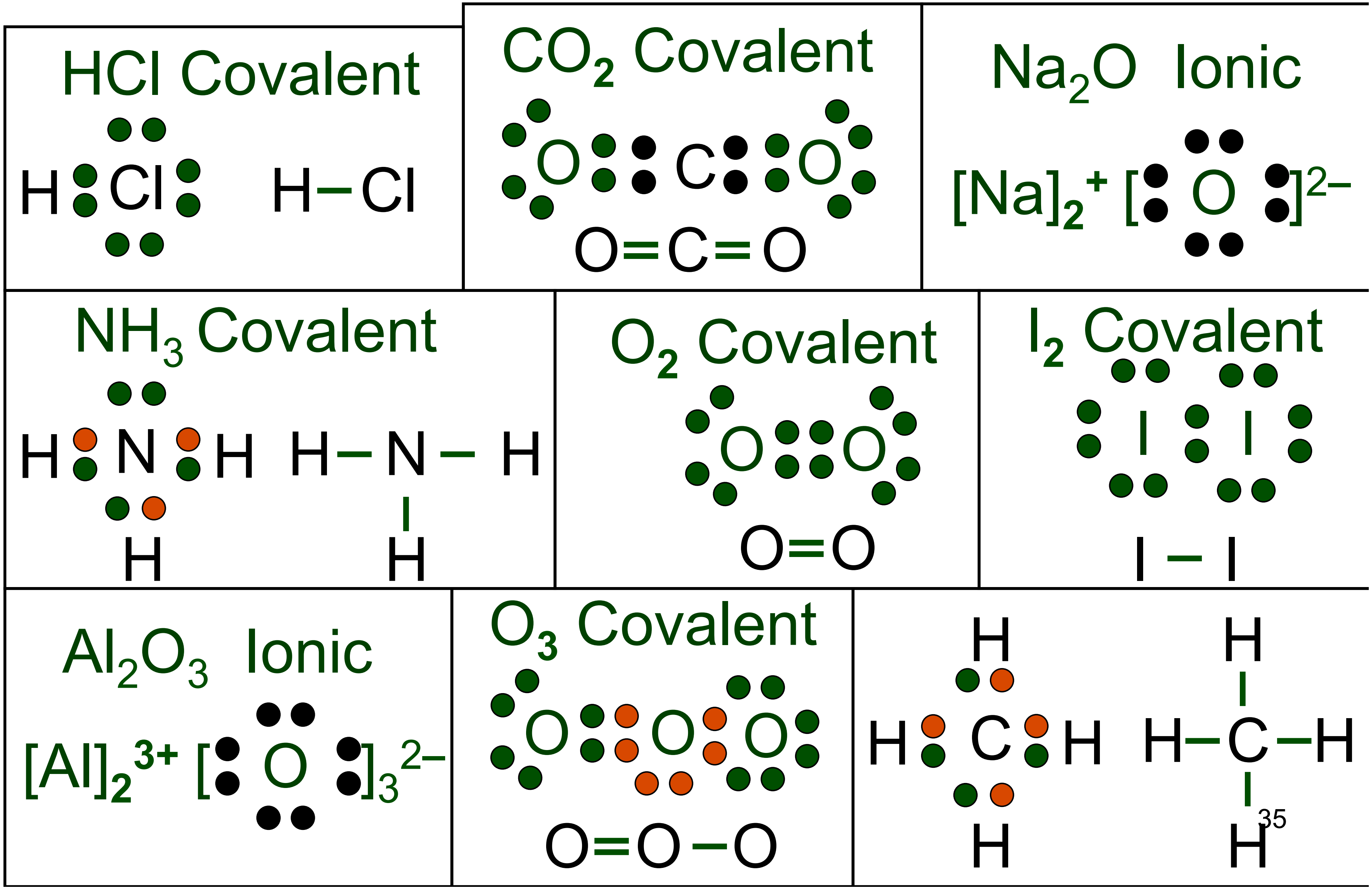
NaCl Ionic



H_2 Covalent

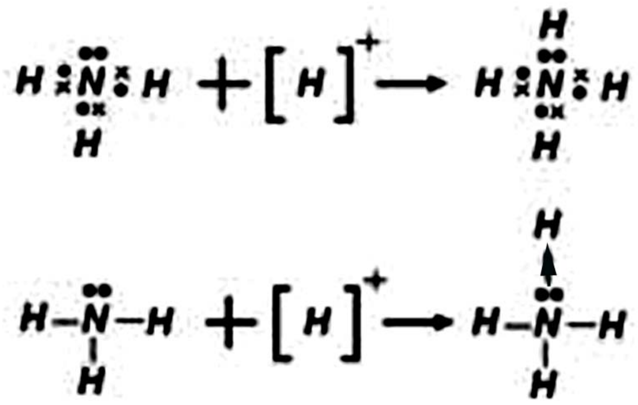


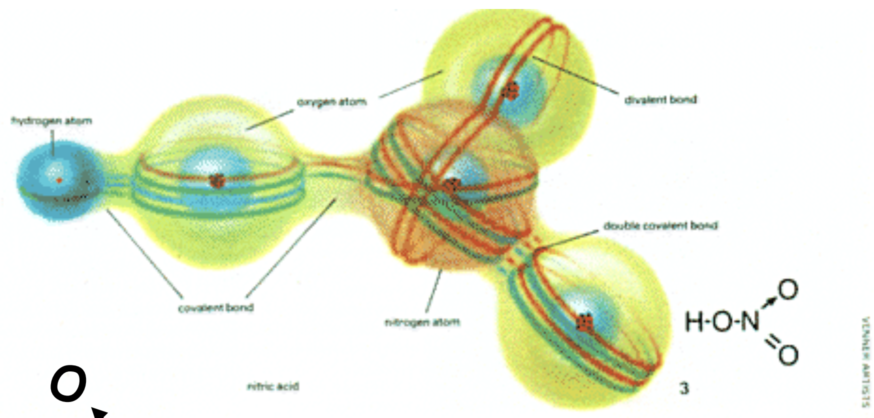
Multiple bonds

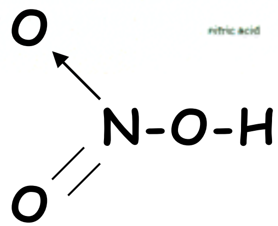


COORDINATION BOND

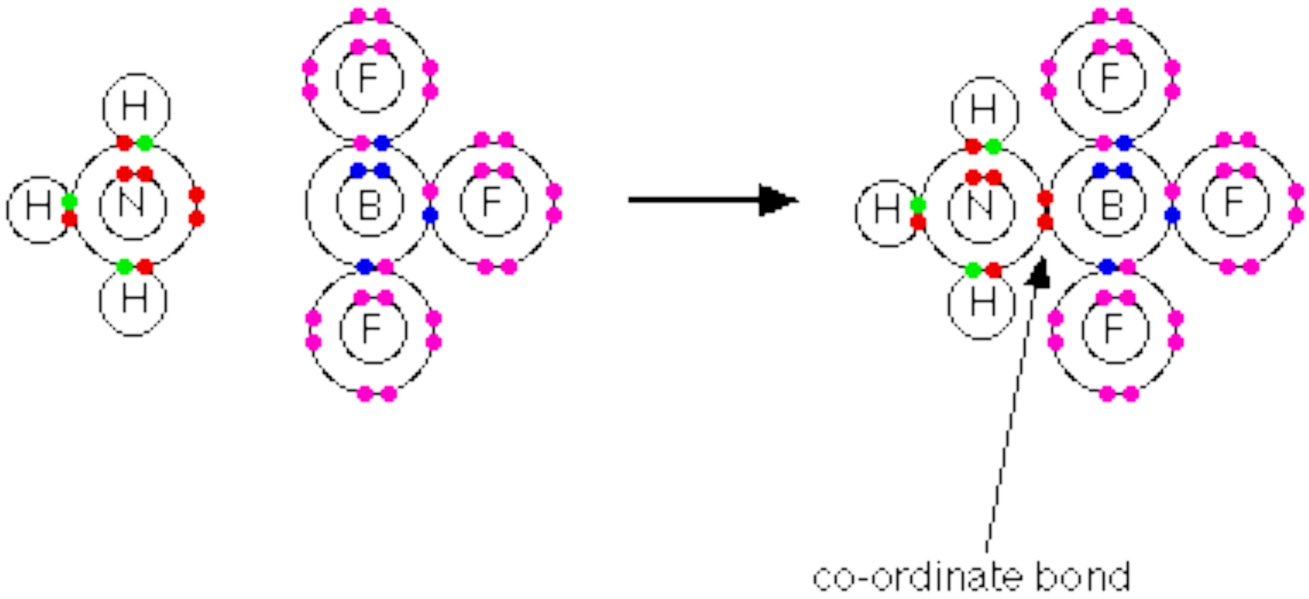
An atom shares an electron “lone pair” with another atom which has an “empty” orbital available.

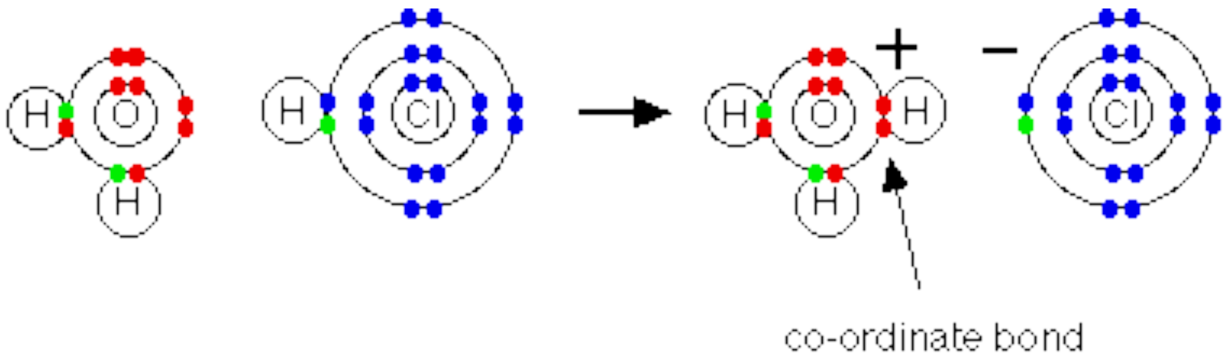




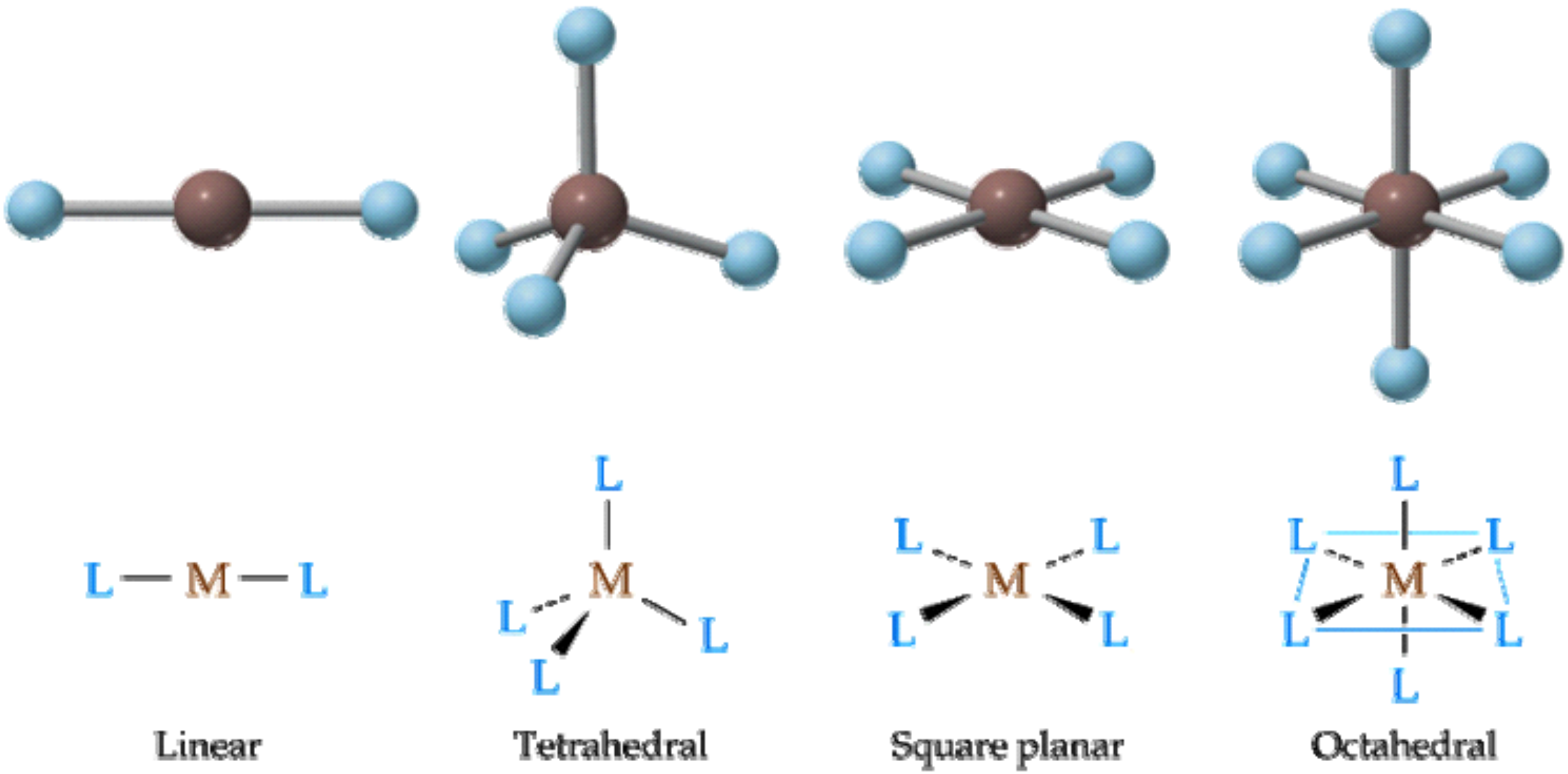


Nitric acid


co-ordinate bond

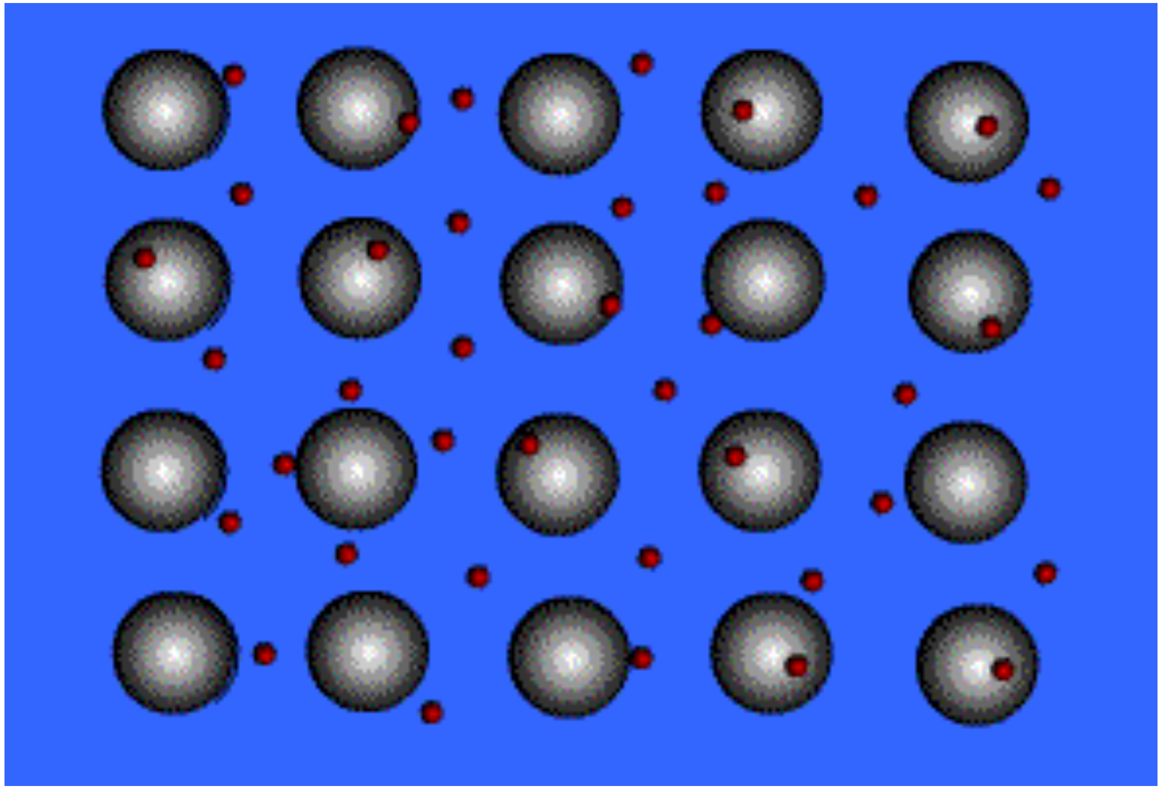

+
−
co-ordinate bond

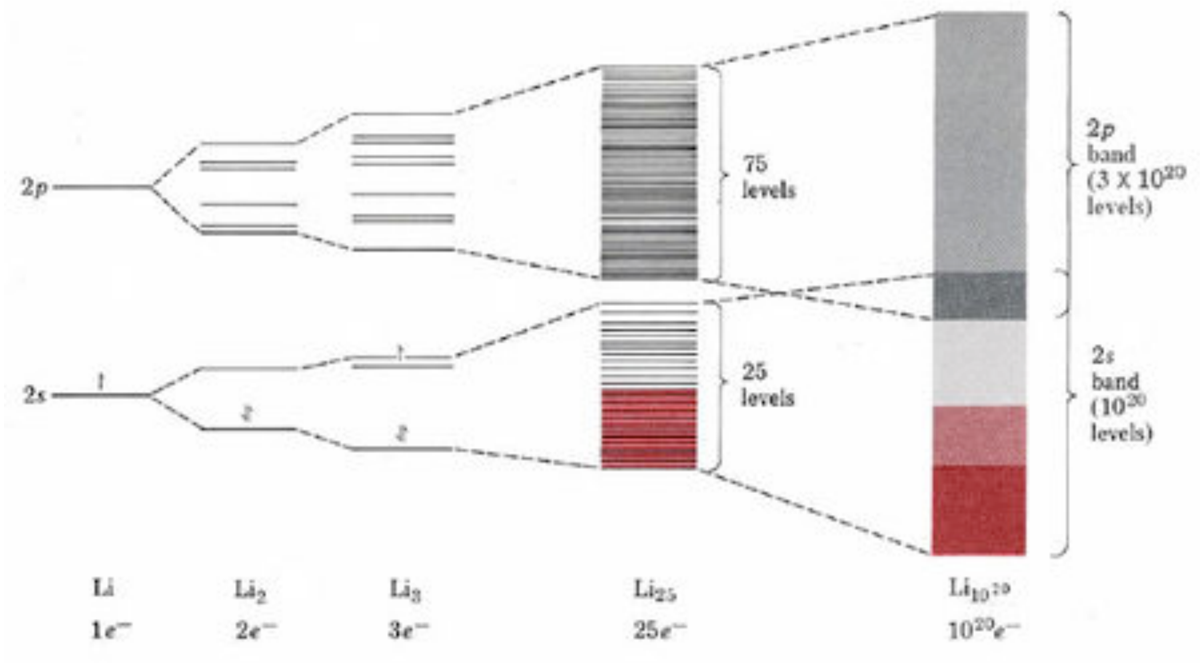
Transition metals which have empty d orbitals can form coordination compounds using up to 6 pairs of electrons.



Metallic bonding

Accounts for many physical properties of metals (plasticity, thermal and electrical conductivity). **Outer shell electrons are weakly bound and delocalized on degenerate orbitals (Na, Fe, Al, Cu, Ag).**





Molecular-orbital energies corresponding to delocalization of valence electrons over increasing numbers of Li atoms. A 1 mg sample of Li would contain nearly 10^{20} atoms. The corresponding orbital energies are so closely spaced that they constitute essentially continuous bands.

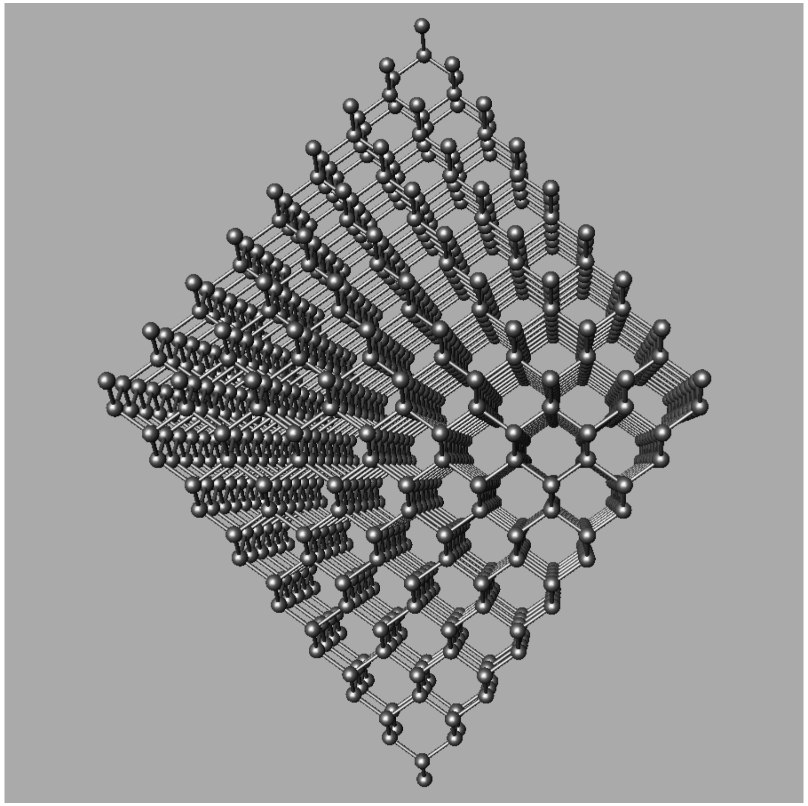
Molecular interactions

-Why some compounds are solid, liquid or gaseous?

- Why must we provide heat to obtain less condensed states?

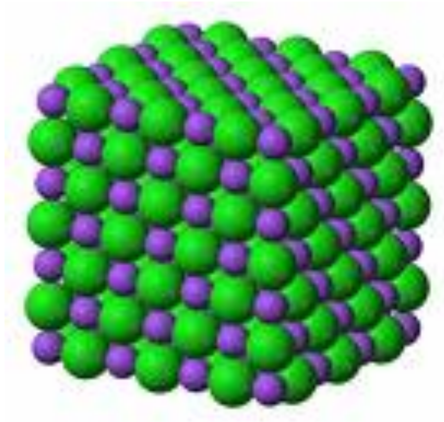
This is due to interactions between molecules (intermolecular).

Strong interactions -> reticular solids e.g..: Diamond



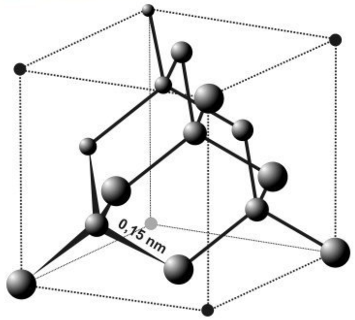
vaporization at 3500°C

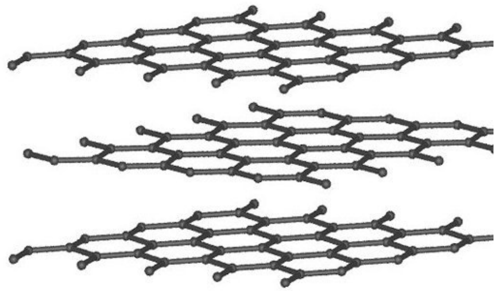
Ionic bond: salt crystals



NaCl melts at 801°C

Bond strength can be measured using the heat required to break it (kcal/mole, kjoul/mole).





- Diamond and graphite are two allotropes of carbon: pure forms of the same element that differ in structure.

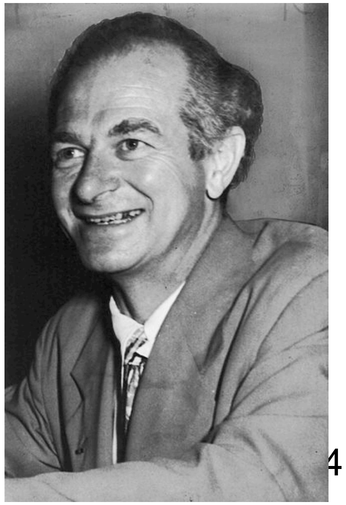
Weak intermolecular interactions

Electrostatic interactions.

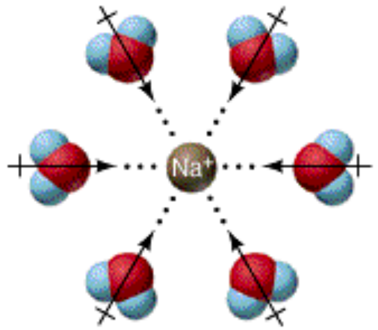
Interactions between dipoles (permanent and transient).

Hydrogen bond (Linus Pauling).

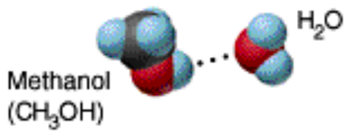
Linus C. Pauling 1901-1994



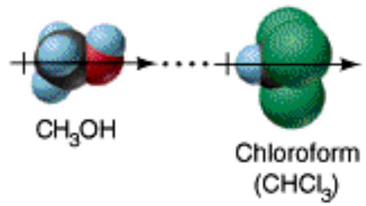
Ion-dipole
40-600 kJ/mol

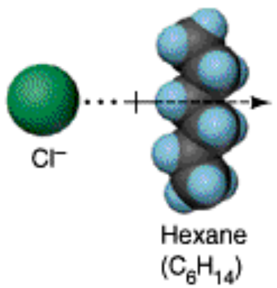


Hydrogen bond
10-40 kJ/mol

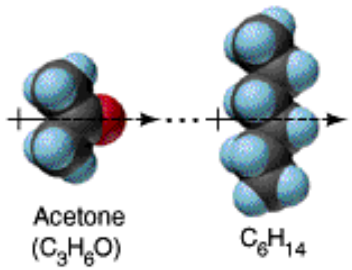


Dipole-dipole
5- 25 kJ/mol

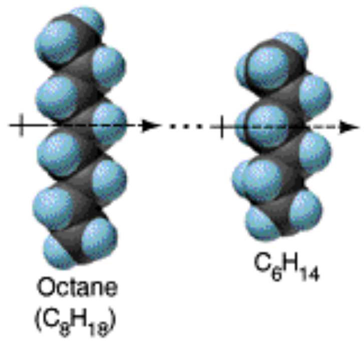




Ion-transient dipole
5-12 kJ/mol



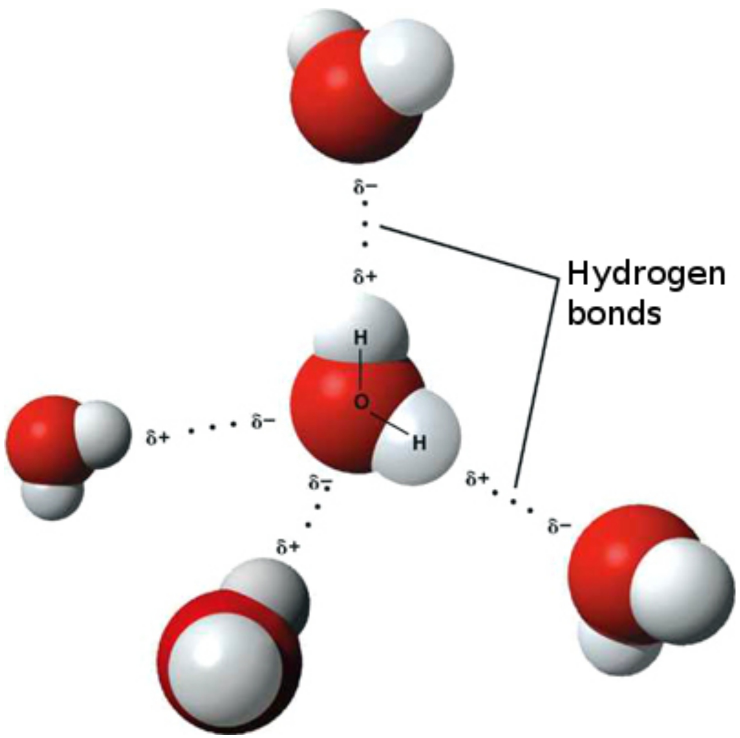
Dipole-transient dipole
2-10 kJ/mol



Transient dipole-transient dipole
London's dispersion force
0.05-40 kJ/mol

Hydrogen bonds play a key role in biology.

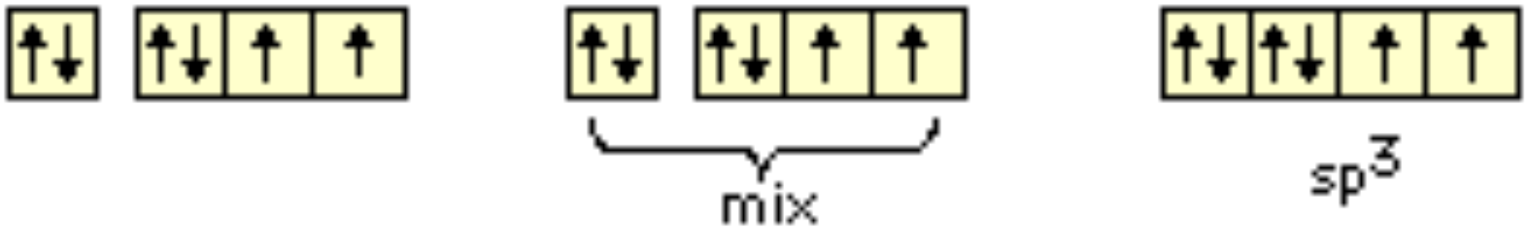
A hydrogen atom atom bound to S, O, N, F or Cl
AND
An electron pair from a highly electronegative atom

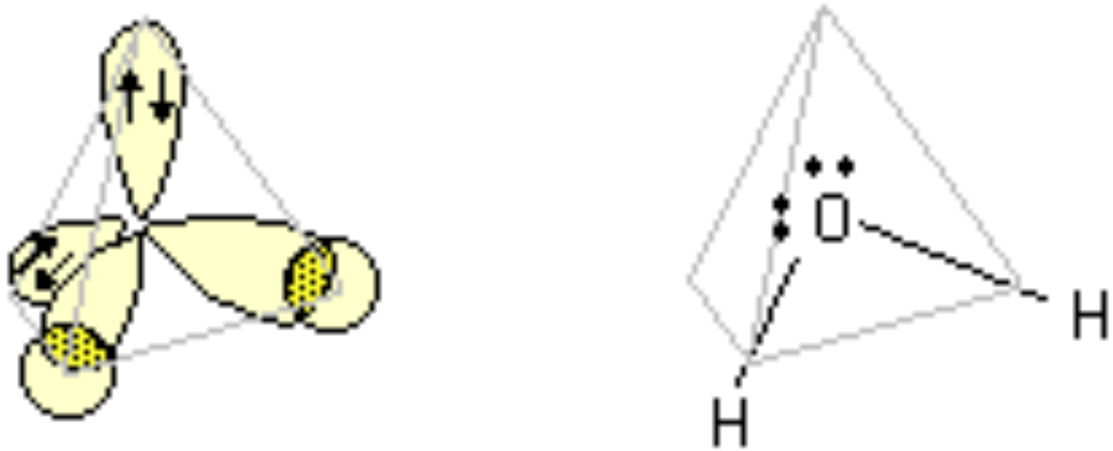


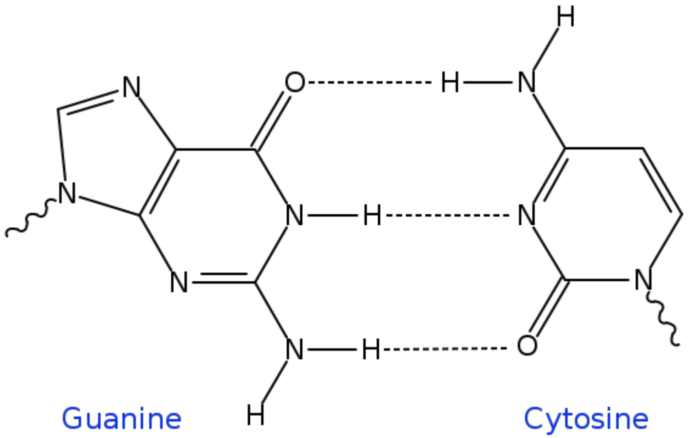
Hydrogen bonding in water

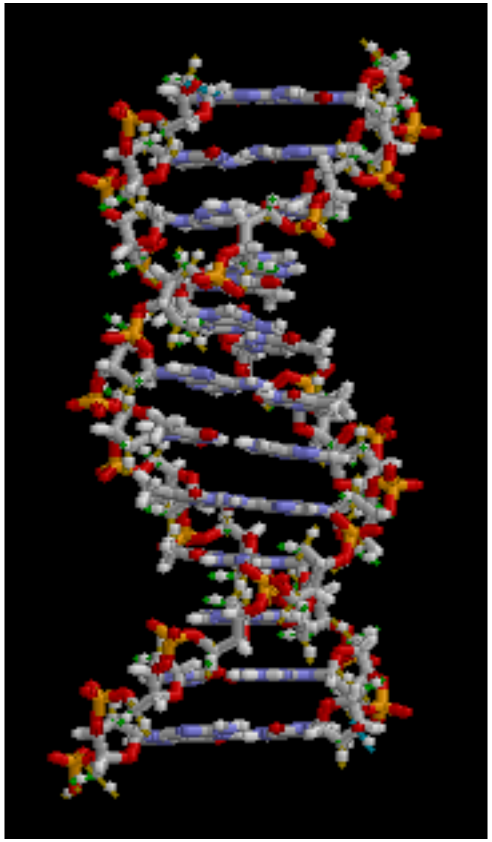
Water and Hydrogen bonds

Hybridization sp^3: 4 degenerate orbitals with tetraedric geometry and only unpaired electrons. The structure of water is bent.



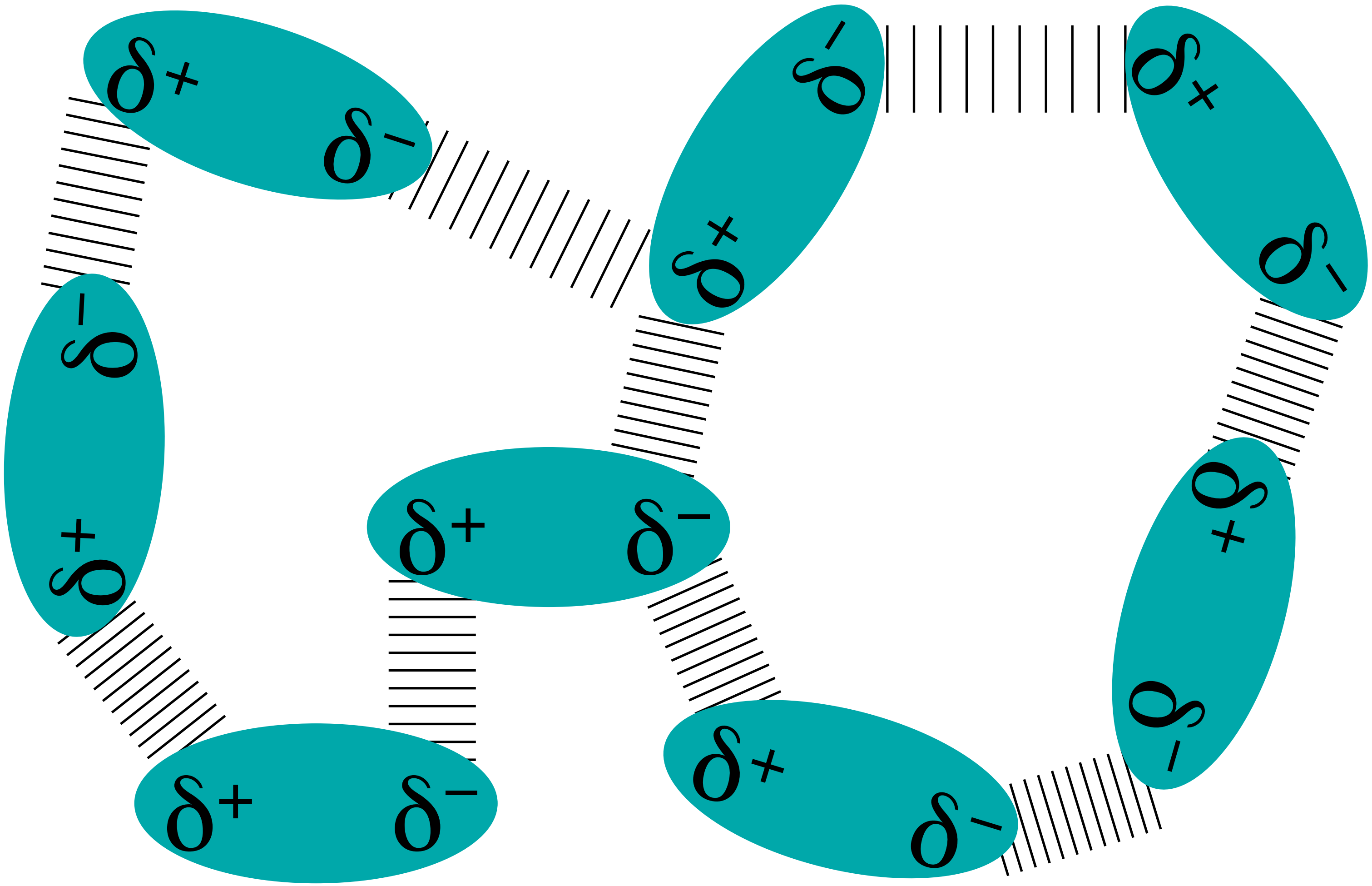






DNA base pair recognition
relies on hydrogen bond formation.

Dipole-dipole interaction

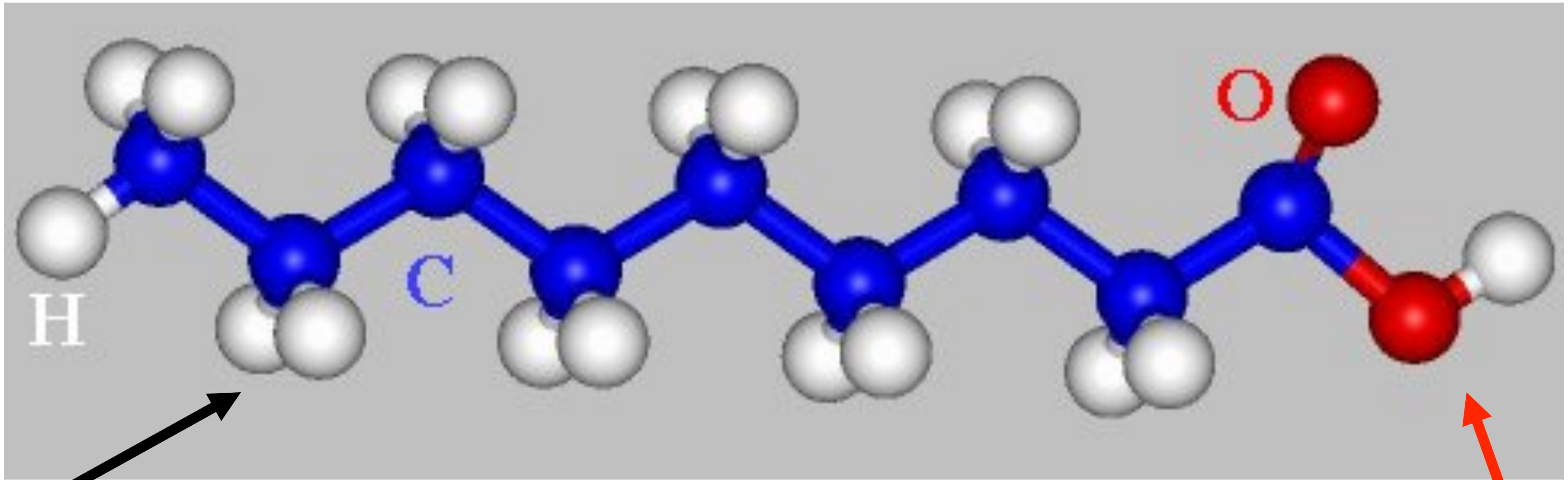


Transient dipoles

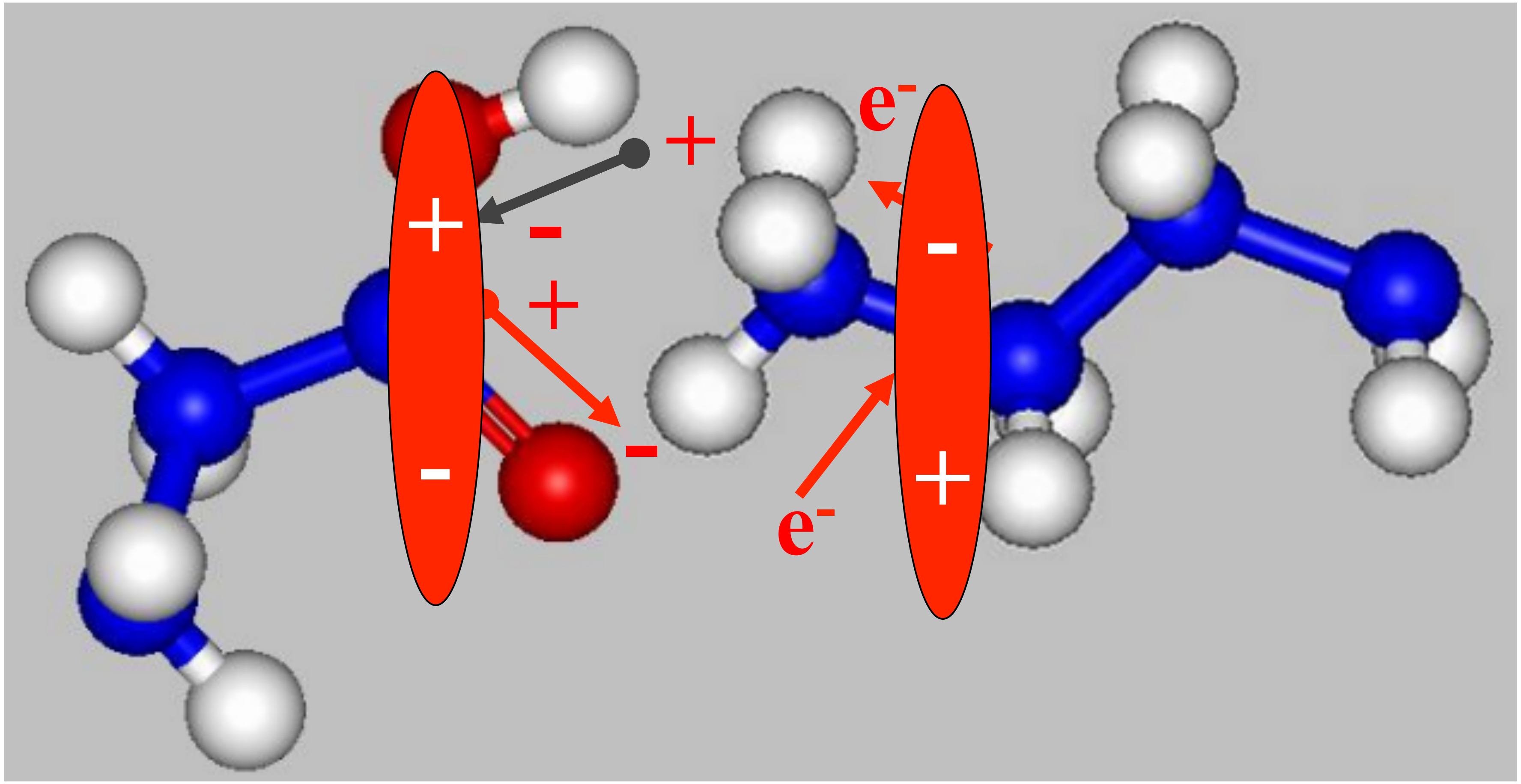
When a molecule endowed with a dipole is close to an apolar atom, it induces an asymmetry in its electronic structure.

A transient dipole is formed, and an attractive interaction with the permanent dipole is established.

Permanent and induced dipoles



Atoms with weaker (C e H: 2,1) and stronger (O : 3,5) electronegativity.
The molecule has polar and apolar regions.



The permanent dipole induces a transient one, resulting into attractive forces.
If the distance increases, the induced dipole disappears.