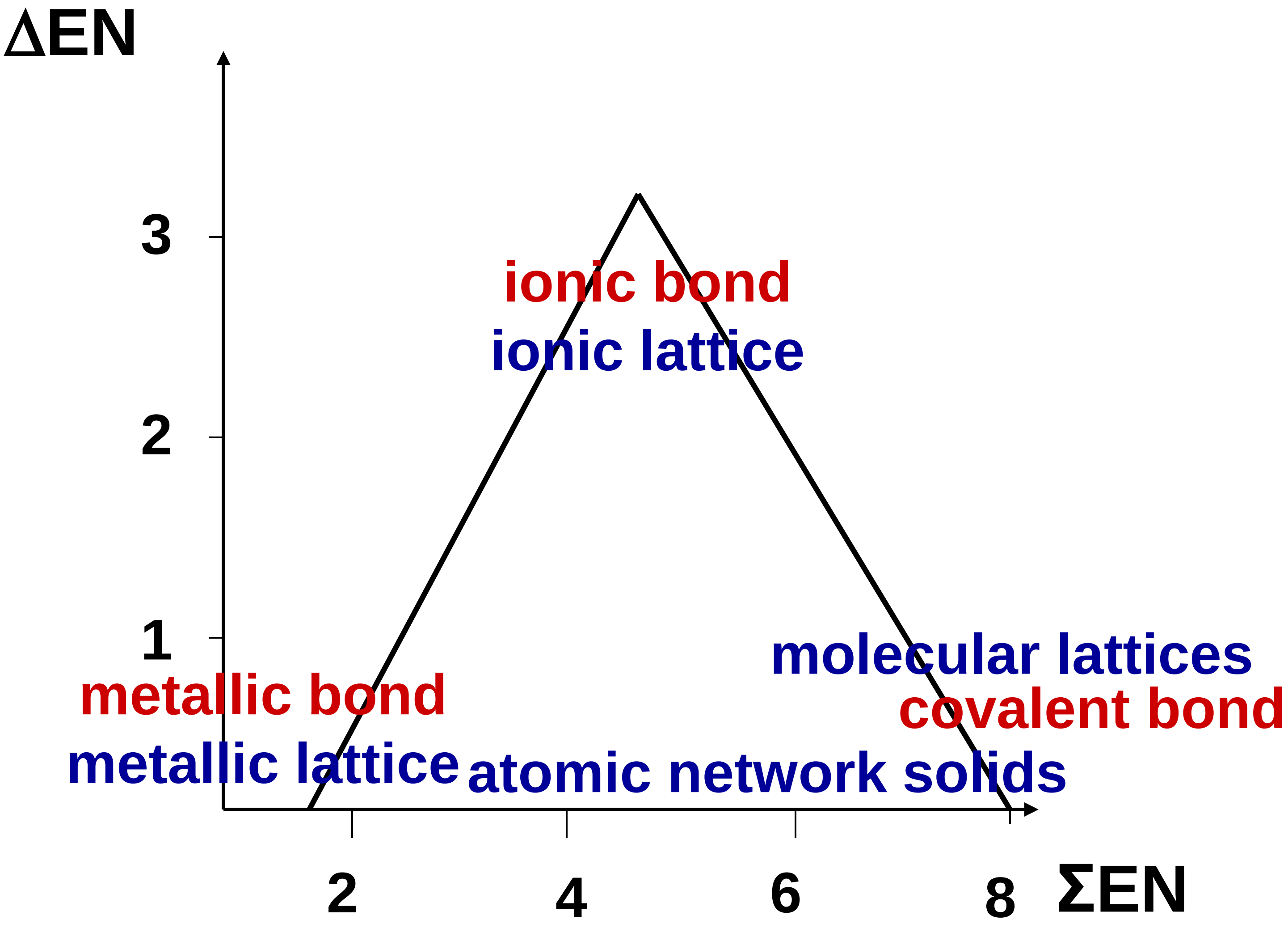
CHEMICAL BONDING

1. Primary chemical bonding forces (ΔE > 100 kJ/mol)
   - a/ Ionic bonding (Kossel – 1916)
     - Δx > 2 occurrence: ionic solids
   - b/ Covalent bonding *(Lewis – 1916)*
     - Δx < 0.5 occurrence:
       - molecules
       - covalent network solids
   - c/ Metallic bonding
     - Δx ~ 0 occurrence: metallic solids

2. Secondary chemical bonding forces (ΔE < 100 kJ/mol)
   - dispersion forces
   - dipole–dipole (induced dipole) interaction
   - hydrogen bonding

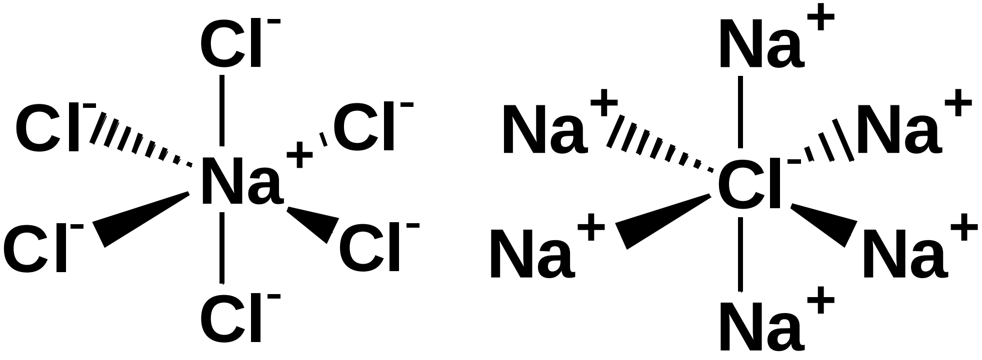
ELECTRONEGATIVITY AND LATTICE



IONIC SOLIDS

Ionic compounds:

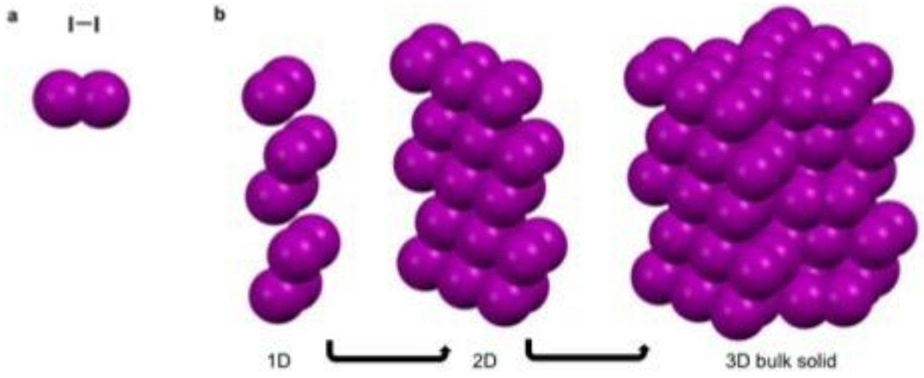
- composed of oppositely charged ions (the sites are occupied by cations and anions)



- crystal lattice is held together by electrostatic forces
- generally have very high melting and boiling points and a low vapour pressure
- high brittleness (they cannot deform malleably, instead they fracture)
- high solubility in polar solvents (e.g. water)
- in the solid state: poor conductors
    - their aqueous solutions and ionic compounds in melted form conduct electricity

MOLECULAR SOLIDS

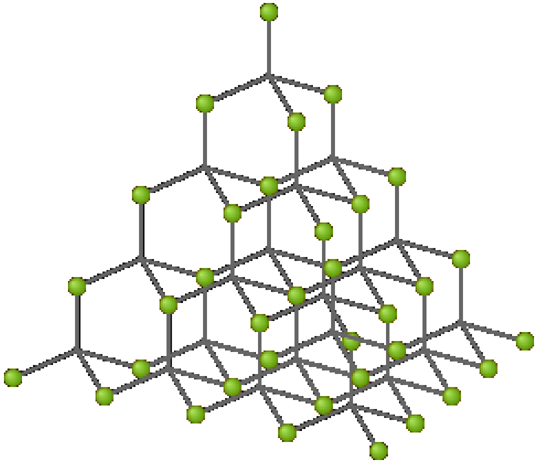
- the sites are occupied by molecules

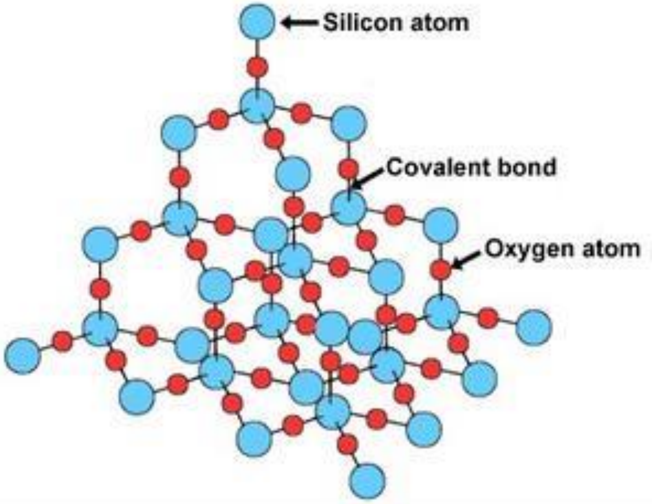


- crystal lattice is held together by secondary forces
- generally have lower melting and boiling points and a higher vapour pressure
- low mechanical strength
- like dissolves like (e.g. polar molecules are soluble in polar solvents; nonpolar molecules are soluble in nonpolar solvents)
- poor thermal and electrical conductors
- examples: He, H_2, O_2, S_8, H_2O, CO_2, hydrocarbons, carbohydrates etc.

COVALENT NETWORK SOLIDS

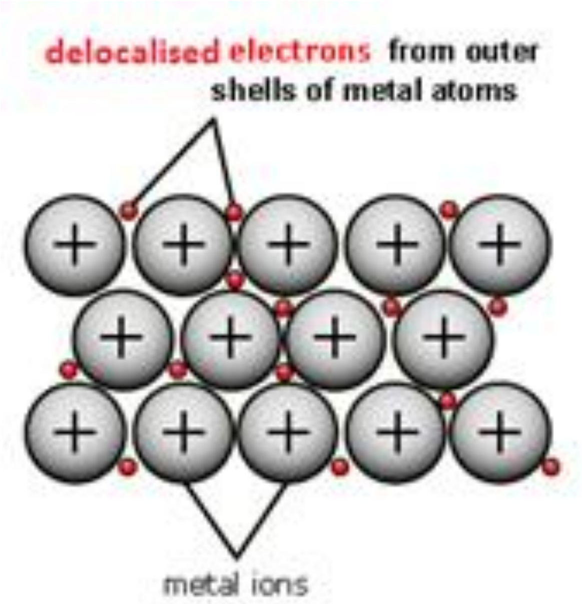
- the atoms are bonded by covalent bonds in a continuous network extending throughout the material
- there are no individual molecules, and the entire crystal may be considered a macromolecule
- crystal lattice is held together by covalent bond
- very high melting and boiling points and low vapour pressure
- they are very hard
- low solubility in any solvent
- poor conductors
- examples: diamond, silicon, boron, SiO_2, SiC





METALLIC SOLIDS

- metals readily lose their outer shell electrons, resulting in a free flowing cloud of electrons within the solid.
- the sites are occupied by metal cations
- crystal lattice is held together by metallic bond: electrostatic interaction between each atom and the electron cloud (delocalized electrons)
- wide variation in melting and boiling points and densities
- hardness varies, but generally good malleability
- low solubility in polar and nonpolar solvents, however they may dissolve in an other liquid metal
- good thermal and electrical conductivity both in solid and liquid (melted) states



LATTICE ENERGY

$\mathrm{MX\ (s) \rightarrow M^{+}\ (g) + X^{-}\ (g)}$ ***U*, kJ/mol**

the energy required to break up an ionic solid into individual gaseous ions

always high positive value

e.g. LiF 1036 kJ/mol, CaO 3401 kJ/mol

Depends on:

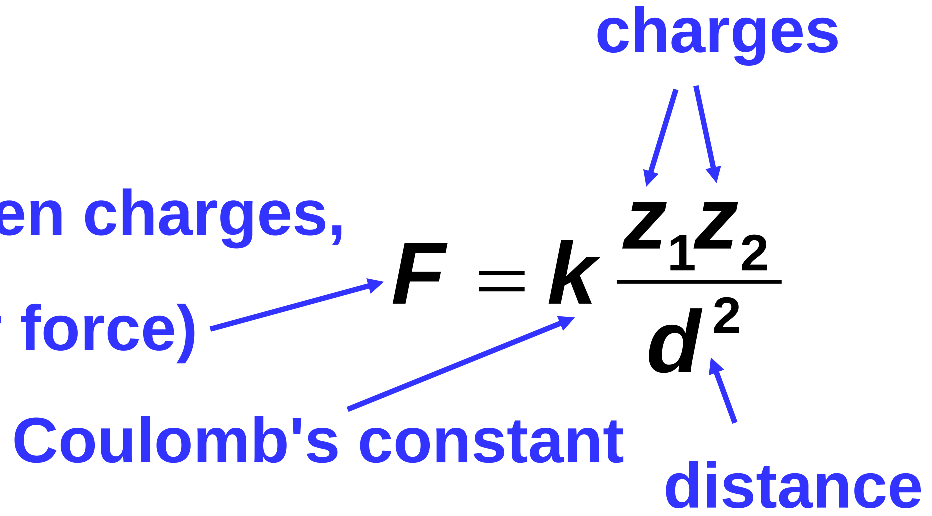
lattice geometry (distance and number of close neighbor ions)

charge of ions in the lattice

LATTICE ENERGY

Origin: interaction between charges,

Coulomb's law (for force)



$$F = k\frac{z_1 z_2}{d^2}$$

charges

Coulomb's constant

distance

Like charges: repulsion (positive)

Unlike charges: attraction (negative)

Lattice energy:

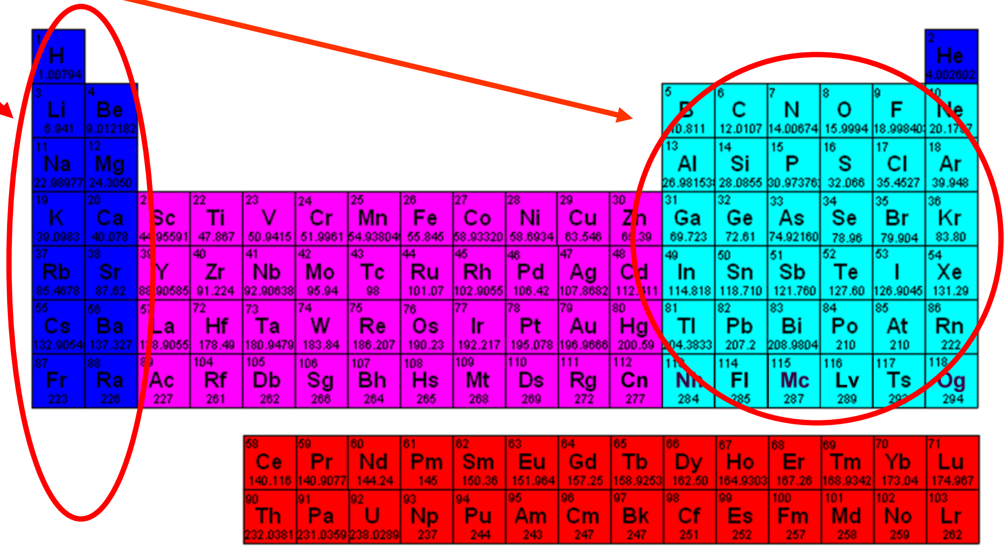
$$U = -Mk\frac{z_1 z_2}{d}$$

need to be summed for every possible pairs of ions in a lattice

M: Madelung constant (depends on lattice type)

Octet rule

A simple *rule* (not *law*) useful for interpreting and predicting electronic structure of main group elements in compounds:



Main-group elements tend to undergo reactions that leave them with eight outer-shell electrons.

or

Main group elements react so that they attain a noble gas electron configuration with filled s and p sublevels in their valence electron shell.

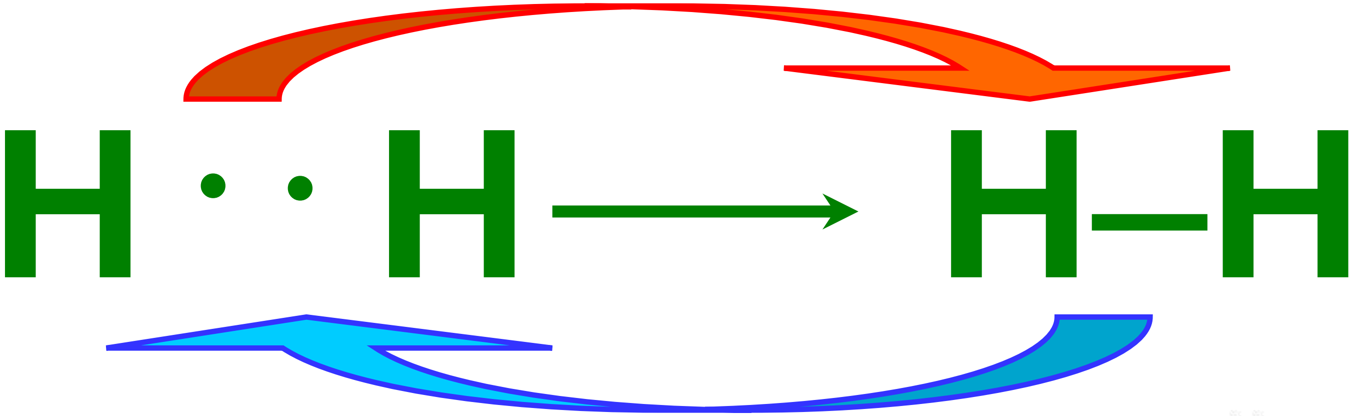
Octet rule
Examples

- Alkali metals tend to lose their ns^1 valence-shell electron, thereby adopting the electron configuration of the noble gas element in the previous row of the periodic table; M^+
- Alkali earth metals: loss of both ns^2 valence-shell electrons; M^{2+}
- Boron group: loss of all three ns^2np^1 electrons; M^{3+}
- Oxygen group: gain of two electrons, $ns^2np^4 \rightarrow ns^2np^6$, X^{2-}
- Halogens: gain of one electron, $ns^2np^5 \rightarrow ns^2np^6$, X^-
- Noble gas elements are essentially inert; they rarely gain or lose electrons.

COVALENT BONDS

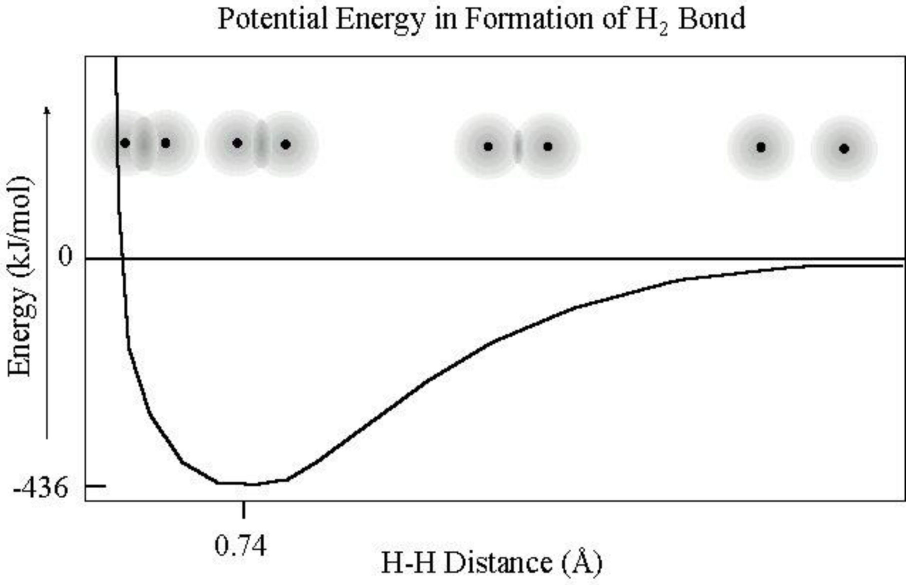
bonds formed through sharing an electron pair

436 kJ/mol energy released



$$H \cdot \cdot H \longrightarrow H{-}H$$

436 kJ/mol energy absorbed



ELECTRON-DOT STRUCTURES

Lewis structures:

♦ **represent every atom's valence electrons by dots**

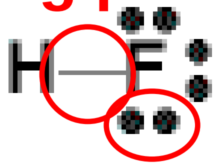
♦ **the placement of the dots indicate how the valence electrons are distributed in the molecule**

♦ **non-valence electrons (core electrons) are never involved in bond-making**

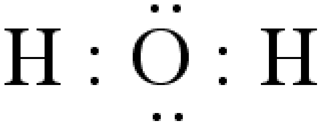
♦ ***OCTET RULE*: an atom in a molecule is happy with eight electrons in the valence shell (exception: H ⇒ 2)**

hydrogen molecule H:H H–H

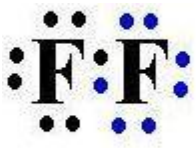
bonding pair



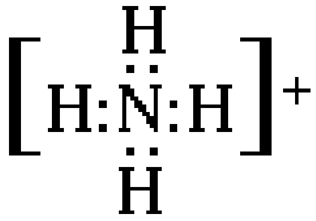
lone pair



2 bonding pairs
2 lone pairs

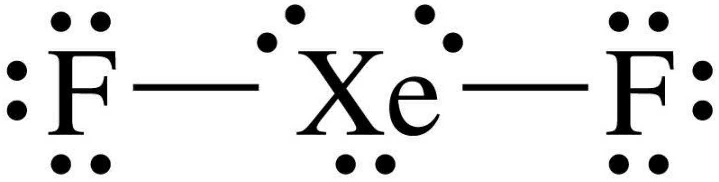


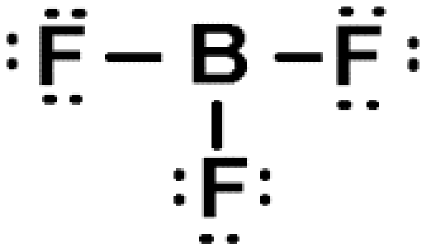
1 bonding pair
3 + 3 lone pairs



4 bonding pairs

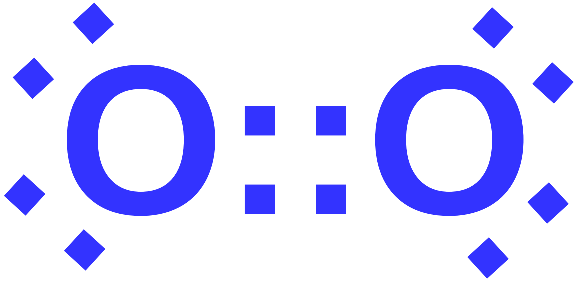
Octet rule violation





MULTIPLE BONDS

oxygen molecule



double bond

nitrogen molecule :N:::N:

triple bond

$|N\equiv N|$

QUANTUM MECHANICAL DESCRIPTION OF COVALENT BONDS

VB: Valence bond method

some of the orbitals in the valence shells of atoms interact with orbitals in neighboring atoms to form bonds

MO: molecular orbital method

All electrons originally in separate atoms are on new molecular orbitals (σ or π, bonding, nonbonding, and antibonding)

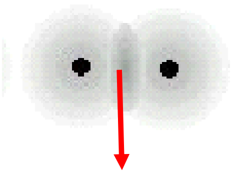
Conclusions from the two different methods are often very similar.

VALENCE BOND METHOD

Quantum mechanical basis of Lewis dot structures

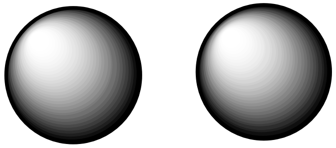
KEY IDEAS:

1. Covalent bonds are formed by overlap of singly occupied atomic orbitals.
2. Bonded atoms maintain their atomic orbitals, but overlapping orbitals are shared.
3. The greater the overlap, the stronger the bond.

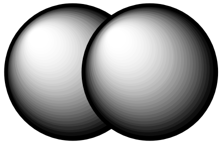


H_2 molecule

overlap

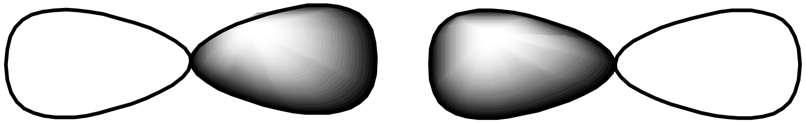


H: $1s^1$ H: $1s^1$



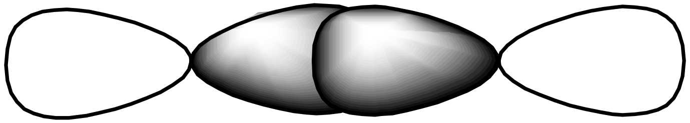
s–s overlap

H_2



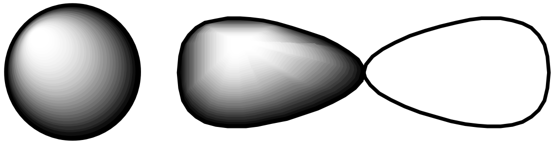
$2p_z^1$ $2p_z^1$

F: $1s^22s^22p^5$



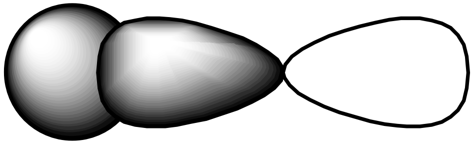
p–p overlap

F_2



$1s^1$ $2p_z^1$

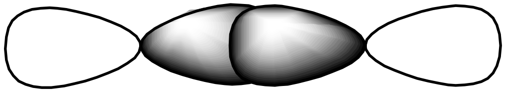
H: $1s^1$ F: $1s^22s^22p^5$



s–p overlap

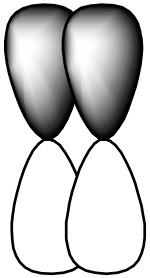
HF

O_2



first bond

$2p_z^1$ $2p_z^1$



second bond

$2p_y^1$ $2p_y^1$

MOLECULAR ORBITAL THEORY

Electrons in a molecule: belong to the whole molecule and not to individual atoms or pair of atoms

1. All electrons in a molecule are on molecular orbitals (MOs)

2. Molecular orbitals are formed by the combination of original atomic orbitals (LCAO method = linear combination of atomic orbitals)

3. MOs lower in energy than combined atomic orbitals ⇒ BONDING ORBITALS

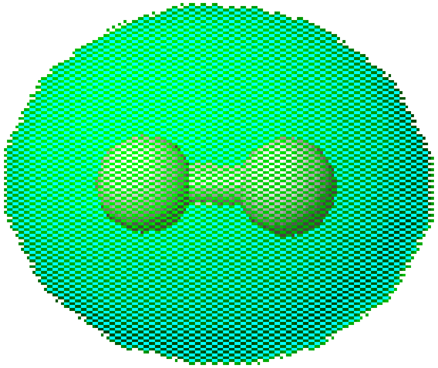
MOs higher in energy than combined atomic orbitals ⇒ ANTIBONDING ORBITALS

4. Electrons fill the orbitals according to the *Aufbau* principles (same as for atoms)

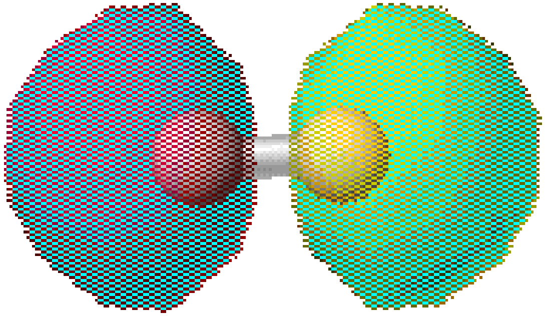
5. Symmetry considerations are important in selecting which atomic orbitals can be combined

MOLECULAR ORBITALS

σ (small Greek sigma) and σ* molecular orbitals

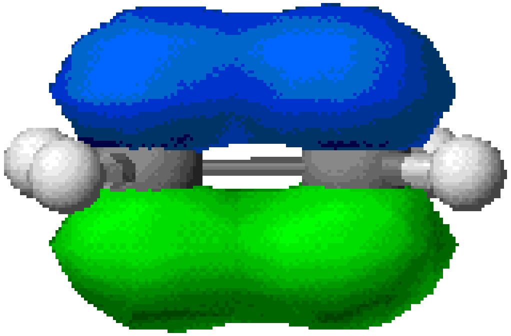


Bonding

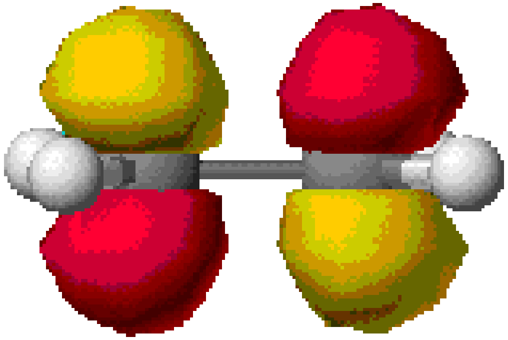


Antibonding

π (small Greek pi) and π* molecular orbitals



Bonding



Antibonding

POLAR COVALENT BOND

Basic requirement:

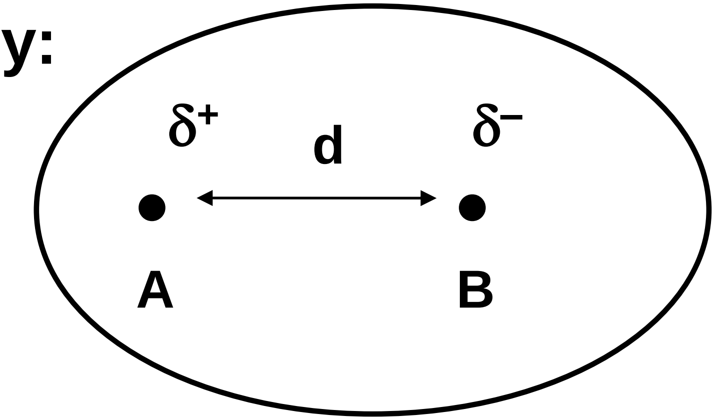
difference in electronegativity $\Delta x > 0$ e.g. $x_B > x_A$

Characteristic physical property:

dipole moment (μ)

$$\mu = q \times d$$

q: partial charge, d: distance



Polarity of multiatomic molecules:

- polar covalent bond - asymmetric geometry

molecule	polar	non-polar
AB	HCl	H_2
AB_2	H_2O	CO_2
AB_3	NH_3	BF_3
AB_4 (AB_3X)	- ($CHCl_3$)	CH_4

SECONDARY CHEMICAL BONDING FORCES

Intermolecular forces which mediate interaction between molecules

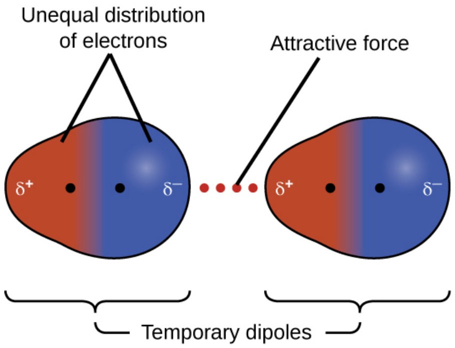
1. Dispersion (London) forces:

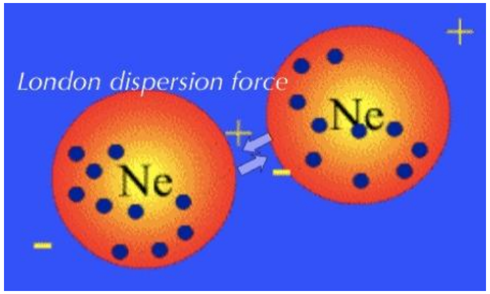
Occurrence: between non-polar molecules

Origin: relative oscillation of the atomic nuclei and the electron clouds

Energy: 0.1 - 1 kJ/mol

Depends on: size, polarizability





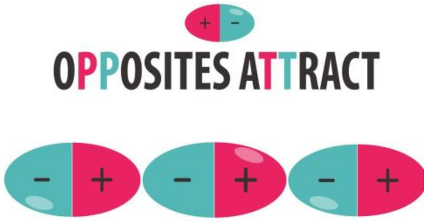
2. Dipole-dipole interaction

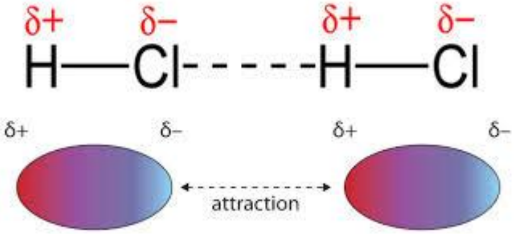
Occurence: between polar molecules

Origin: electrostatic interactions between molecules which have permanent dipole, these interactions align the molecules

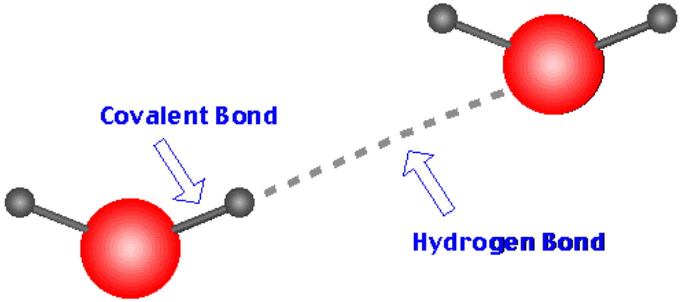
Energy: 1 - 10 kJ/mol

Depends on: μ, size, *T*





SECONDARY CHEMICAL BONDING FORCES



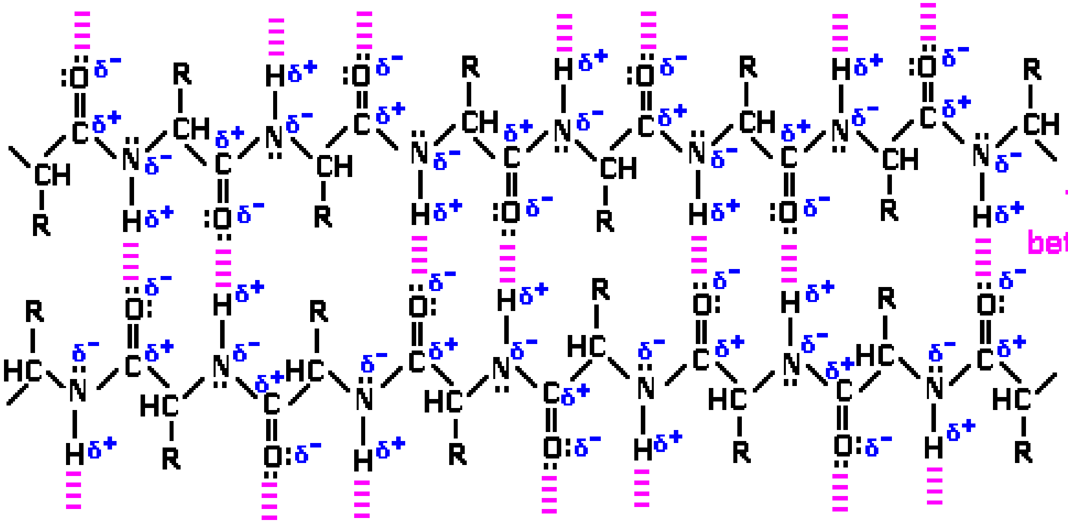
3. Hydrogen bonding

Requirements: - polar HX bond

- non-bonding electron pair on X

Energy: 10 - 50 kJ/mol

Occurence: F-, O- and N-containing inorganic (HF, H_2O, NH_3) and organic compounds (carboxylic acids, amino acids, proteins, nucleic acids, etc.)



hydrogen bonding ≡ holding together beta-sheeting in protein structure

(c) doc b