VBT (Valence Bond Theory)

Lewis' theory considers bond as the lowering of energy that occurs during the approach of two atoms that share the individually unpaired electrons, which constitute the bond pair. The coovalent bond can be nonpolar (between two homologous atoms) or (hetero) polar (depending on the difference in electronegativity between two atoms involved).

Excerption

- Lewis found that he could account for the existence of a wide range of molecules by proposing the **octet rule**:
- *Each atom shares electrons with neighbouring atoms to achieve a total of eight valence electrons (an ‘octet’).*
- A closed-shell, noble-gas configuration is achieved when **eight** electrons occupy the s (1) and p (3) subshells of the valence shell. One exception is the hydrogen atom, which fills its valence shell, the 1s orbital, with two electrons (a ‘duplet’).
- The octet rule provides a simple way of constructing a **Lewis structure**, a diagram that shows the pattern of bonds and lone pairs in a molecule. In most cases we can construct a Lewis structure in three steps.
- NONPOLAR covalent bond
- POLAR covalent bond

Homo -Hetero polar bonds

- **Homopolar Bonds**
- **Definition**: Homopolar bonds occur between atoms that have similar electronegativities, resulting in an equal sharing of electrons.
- **Example**: The bond in molecular hydrogen (H_2) or oxygen (O_2) is homopolar since both atoms are the same and share electrons equally.
- **Heteropolar Bonds**
- **Definition**: Heteropolar bonds (also known as polar covalent bonds) occur between atoms with different electronegativities, leading to an unequal sharing of electrons.
- **Example**: The bond in water (H_2O) between hydrogen and oxygen is heteropolar because oxygen is more electronegative than hydrogen, resulting in a partial negative charge on the oxygen atom and partial positive charges on the hydrogen atoms.

Sigle-Multiple bonds

- **Single Bonds**
- **Definition**: A single bond is formed when two atoms share one pair of electrons.
- **Example**: The C-C bond in ethane (C_2H_6) is a single bond. Each carbon atom shares one electron with the other, forming a single covalent bond.
- **Multiple Bonds**
- **Definition**: Multiple bonds occur when two atoms share more than one pair of electrons. They can be double or triple bonds.
  - **Double Bonds**: Formed by the sharing of two pairs of electrons. Example: The C=C bond in ethylene (C_2H_4).
  - **Triple Bonds**: Formed by the sharing of three pairs of electrons. Example: The C≡C bond in acetylene (C_2H_2).
- **Summary**
- Homopolar = Equal sharing (e.g., H_2, O_2)
- Heteropolar = Unequal sharing (e.g., H_2O)
- Single bond = One pair of electrons shared (e.g., C-C)
- Double bond = Two pairs of electrons shared (e.g., C=C)
- Triple bond = Three pairs of electrons shared (e.g., C≡C)

Elementary

Single

H·

$1s^1$

2.1

3.0

$1\sigma^2$

σ

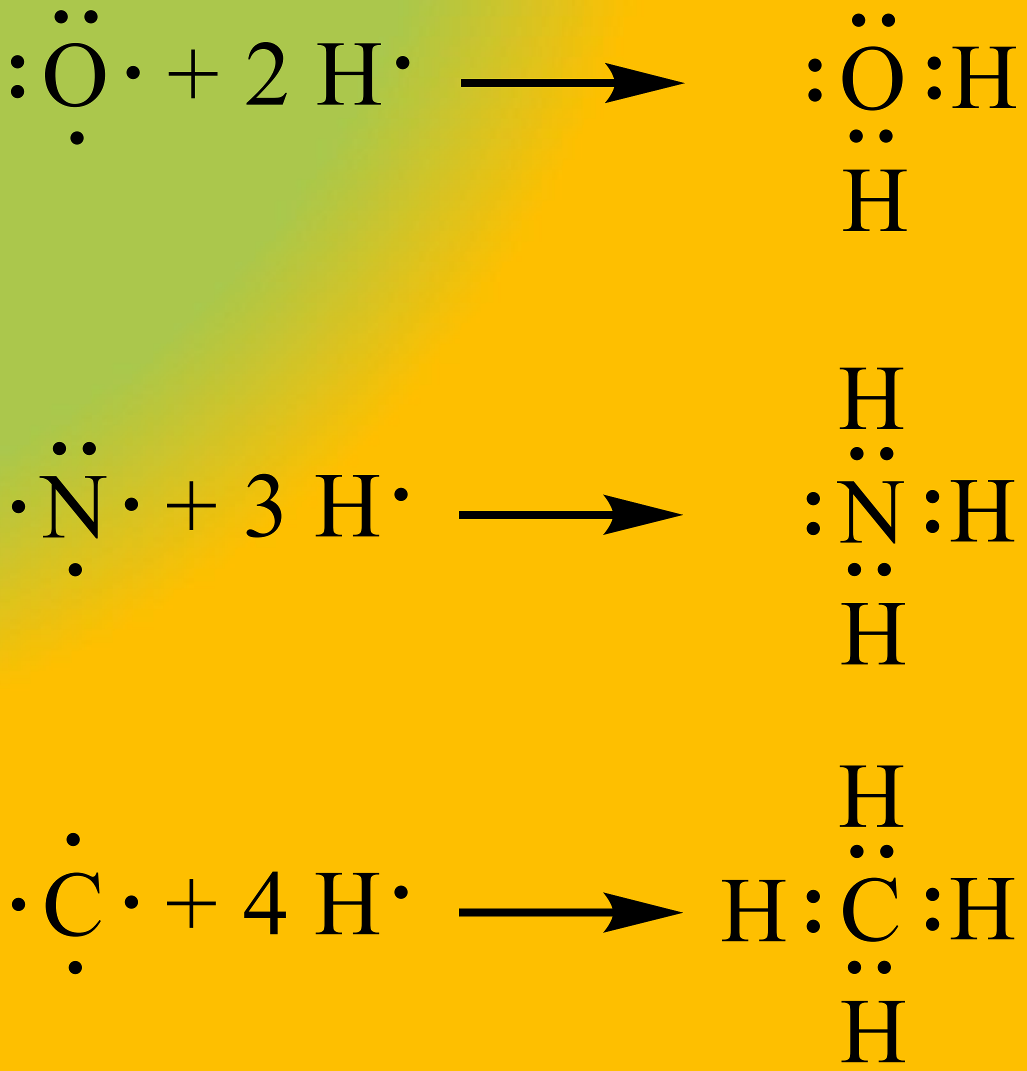
non polar

H — H

lone pair

bond

Simple Hydrogenated molecules



$$:\underset{\cdot}{\ddot{\mathrm{O}}}\cdot + 2\,\mathrm{H}\cdot \longrightarrow :\underset{\mathrm{H}}{\underset{\cdot\cdot}{\ddot{\mathrm{O}}}}:\mathrm{H}$$

$$\cdot\underset{\cdot}{\ddot{\mathrm{N}}}\cdot + 3\,\mathrm{H}\cdot \longrightarrow :\overset{\mathrm{H}}{\underset{\mathrm{H}}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{N}}}}}:\mathrm{H}$$

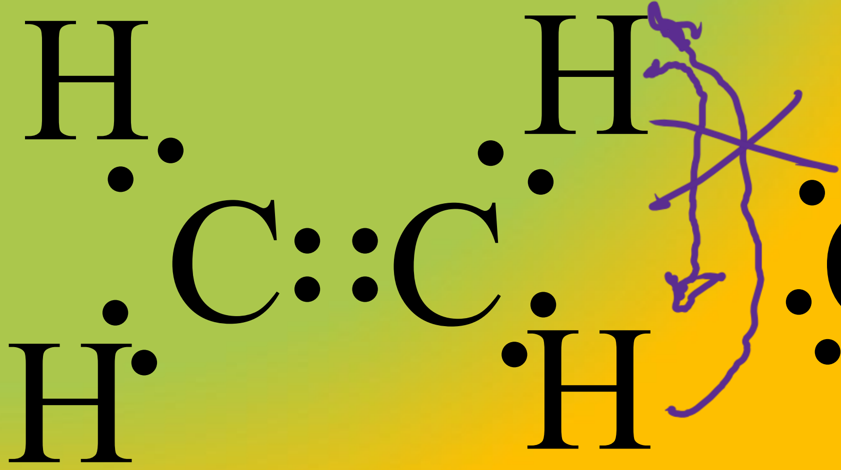
$$\cdot\overset{\cdot}{\underset{\cdot}{\mathrm{C}}}\cdot + 4\,\mathrm{H}\cdot \longrightarrow \mathrm{H}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{C}}}}}:\mathrm{H}$$

Single and Multiple bonds

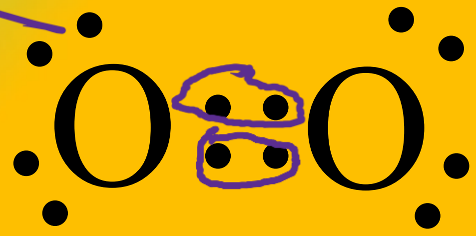
- *The sharing of two electrons between two atoms is known as a* **covalent bond**

The sharing of ***two*** *pairs of electrons between the same two atoms is known as a* **double bond**. *The sharing of three pairs is known as a* **triple bond**. A double bond is illustrated as '=' , and a triple bond is illustrated as '≡', . The use of a double bond to satisfy the octet rule is analogous to two people who wish to have access to $8 but only have a total of $6 each (12$ in total). In this case, each person could have $4 in a private account while sharing $4 in a joint account. A triple bond would be analogous to the two people having only $10 between them. Each could have only $2 in a private account while sharing $6 in the joint account.

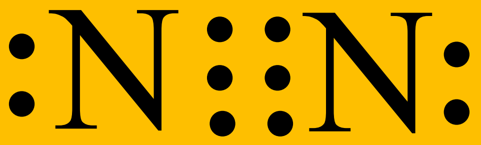
Multiple bonds



etene



diossigeno



diazoto

Valence and O.N.

The valence of an atom is given by the number of unpaired electrons available for the formation of a bond (plus any other electrons that are used for the same purpose such as doublets for dative bonds)

The oxidation number (O.N.) of an element is the formal number of electrons that, involved in POLAR chemical bonds, could be given (positive numbers) or acquired (negative numbers) by an element, according to its electronegativity compared to that of the atoms bound to it

From Atkins…

The **oxidation number**, N_{ox}, is a parameter obtained by exaggerating the *ionic* character of a bond. It can be regarded as the charge that an atom would have if the more electronegative atom in a bond acquired the two electrons of the bond completely. The **oxidation state** is the physical state of the element corresponding to its oxidation number. Thus, an atom may *be assigned* an oxidation number and be *in* the corresponding oxidation state. The alkali metals are the most electropositive elements in the periodic table, so we can assume they will always be present as M^+ and are assigned an oxidation number of 1. Because oxygen's electronegativity is exceeded only by that of F, we can regard it as O^{2-} in combination with any element other than F, and hence it is ascribed an oxidation number of -2. Likewise, the exaggerated ionic structure of NO_3^- is N[+5](O[-2])3, so the oxidation number of nitrogen in this compound is 5, which is denoted either N(V) or N(5). These conventions may be used even if the oxidation number is negative, so oxygen has oxidation number -2, denoted O(-2) or more rarely O(-II), in most of its compounds.

General rules

a) *Atoms, in their elemental forms, are given oxidation numbers equal to zero. For example, in H_2 , O_2 , O_3 , P_4 , Mg, Ne, etc., the n.o. of each individual element is 0 (zero). (no polar bonds – just nonpolar bonds)*

b) *The n.o. of oxygen in compounds is almost always equal to -2. Exceptions are peroxides and in general those compounds in which there is an O-O bond in the molecule, in these cases the n.o. of O is -1. Oxygen fluoride OF2 is also an exception; Only in this compound, the N.O. of oxygen is equal to +2 due to the bonds with the single most electronegative element*

c) *The n.o. of hydrogen is generally +1. Exceptions are hydrogen atoms present in those rare compounds in which they are directly bound to a metal (hydrides), in which the n.o. is 1.*

d) *Alkali metals, alkaline earth metals, and earth metals have n.o. +1, +2, and +3, respectively. All other metals, including transition elements, and non-metals, have variable oxidation numbers, even with regard to sign.*

e) *The algebraic sum of the oxidation numbers of all the atoms present in a neutral molecule must be zero; while, in an ion, it assumes the value of the electric charge it possesses.*

HALOGE

$Na^{+}Cl^{-}$

BINARY XY

oxides X Y-ides

$MgCl_2$

$\overset{+II}{Mg}\overset{-I}{Cl}$

$Na\overset{-I}{I}$

$\overset{+1}{Na}\overset{-1}{Cl}$

NaCl

$\overset{+3}{Al}\overset{-1}{Cl_3}$

$\overset{+3}{B}\overset{-3}{N}$

$\overset{+I}{Na_2}\overset{-II}{S}$

sufidos

H

He

O

$Na_3\overset{-III}{N}$

Na_2S

$\overset{-III}{B_2}\overset{-II}{S_3}$

$\overset{+II}{Ca_2}\overset{-II}{S_2}$

CaS

Li_2O

K_2O

Na_2O

$Mg\overset{-II}{O}$

$\overset{+I}{Na_2}\overset{-II}{O}$

METAL BASE
OXIDES

NON
METAL
OXIDES

$O^{=}$ M^{+}_{I} H

+I -II
$M_{I\,2}O$

M^{2+}_{II} H_2O

+IV -II
CO_2

+II
CO

+2 -II
$M_{II\,2}O_2$

B_2O_3

M^{3+}_{III} GeO_2

$M_{II}O$ CaO MgO
SrO

+3 -II
$M_{III\,2}O_3$

Al_2O_3

SnO_2 IC

stannic + higher ON

+IV GeO_2 O_3
SnO_2 Pb

SnO stannose

OSE lower ON

C

Si

$\boxed{SiO_2}$

Life chem

CO_2

IV

C +4 ON

+2

+NG

+NG-2

–

NGroup-8

+VI even

S +6

+4

+2

S_8 0

S -II

N $1s^2 2s^2 p^3$

$\overset{+5}{N_2}\overset{-2}{O_5}$ -ic

+5 →

+4

+3 →

N_2O_3 ←

+2

+1 → ipo-NITROSE

} P

P_2O_5

P_2O_3

NITR-IC

-OSE

+7 N°c Cl_2O_7 [per-chloric

+5 2 - Cl_2O_5 chlor-ic oxid

+3 - Cl_2O_3 chlor-OSE oxid

+1 - Cl_2O ipo chlorose

Cl
Br
I

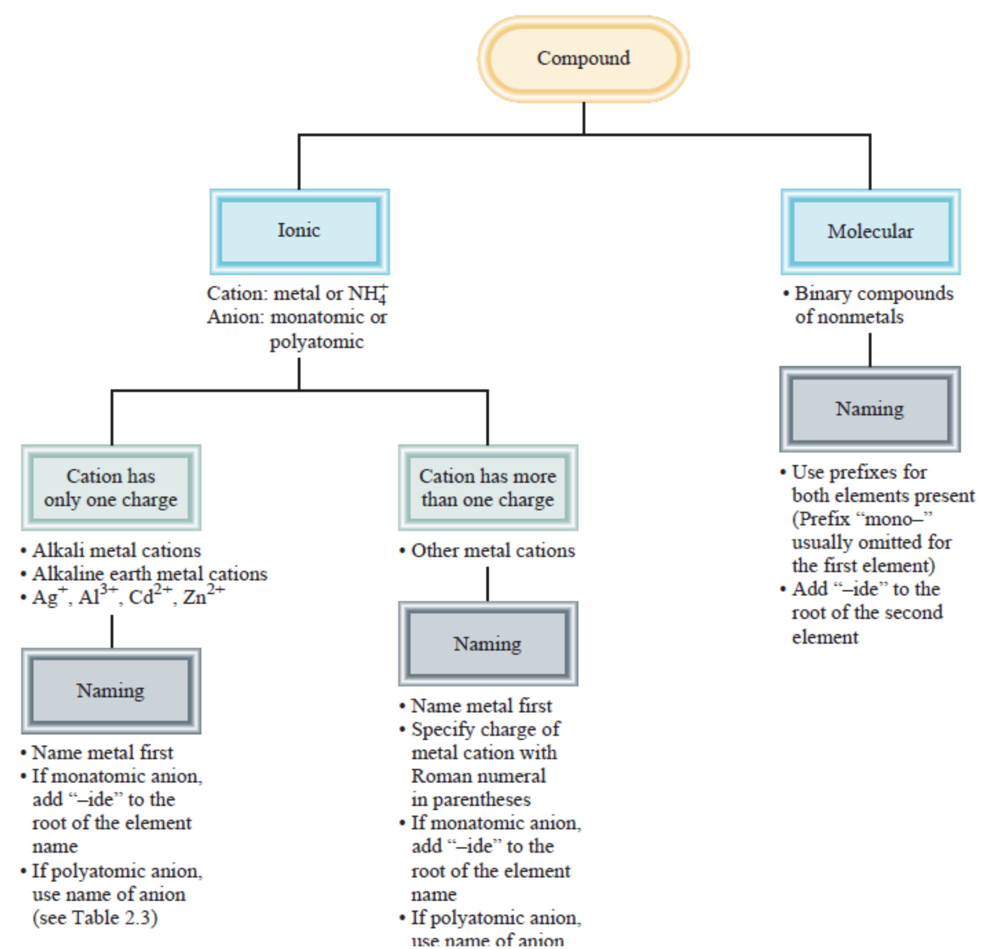
0 $\underline{Cl_2}$

<u>N°c -8</u> - ides

Names of binary compounds

X_nY_m where Y is the most electronegative element. If Y = O then “X oxides”
The name is “X Y-ide”
n is the |o.n.| of Y and m is the |o.n.| of X.
For inorganic compounds n and m are reduced if they share a common divider.
Very often X is a metal and Y is a non-metal which is leading to ionic compounds (solids), sometimes it leads to polar molecules (HCl, NH_3, BH_3)
Oxygen Fluoride is the only binary compound where O bears a positive o.n. (+2)

General Scheme



Compound

Ionic

Cation: metal or NH_4^+
Anion: monatomic or polyatomic

Cation has only one charge

- Alkali metal cations
- Alkaline earth metal cations
- Ag^+, Al^{3+}, Cd^{2+}, Zn^{2+}

Naming

- Name metal first
- If monatomic anion, add "–ide" to the root of the element name
- If polyatomic anion, use name of anion (see Table 2.3)

Cation has more than one charge

- Other metal cations

Naming

- Name metal first
- Specify charge of metal cation with Roman numeral in parentheses
- If monatomic anion, add "–ide" to the root of the element name
- If polyatomic anion, use name of anion

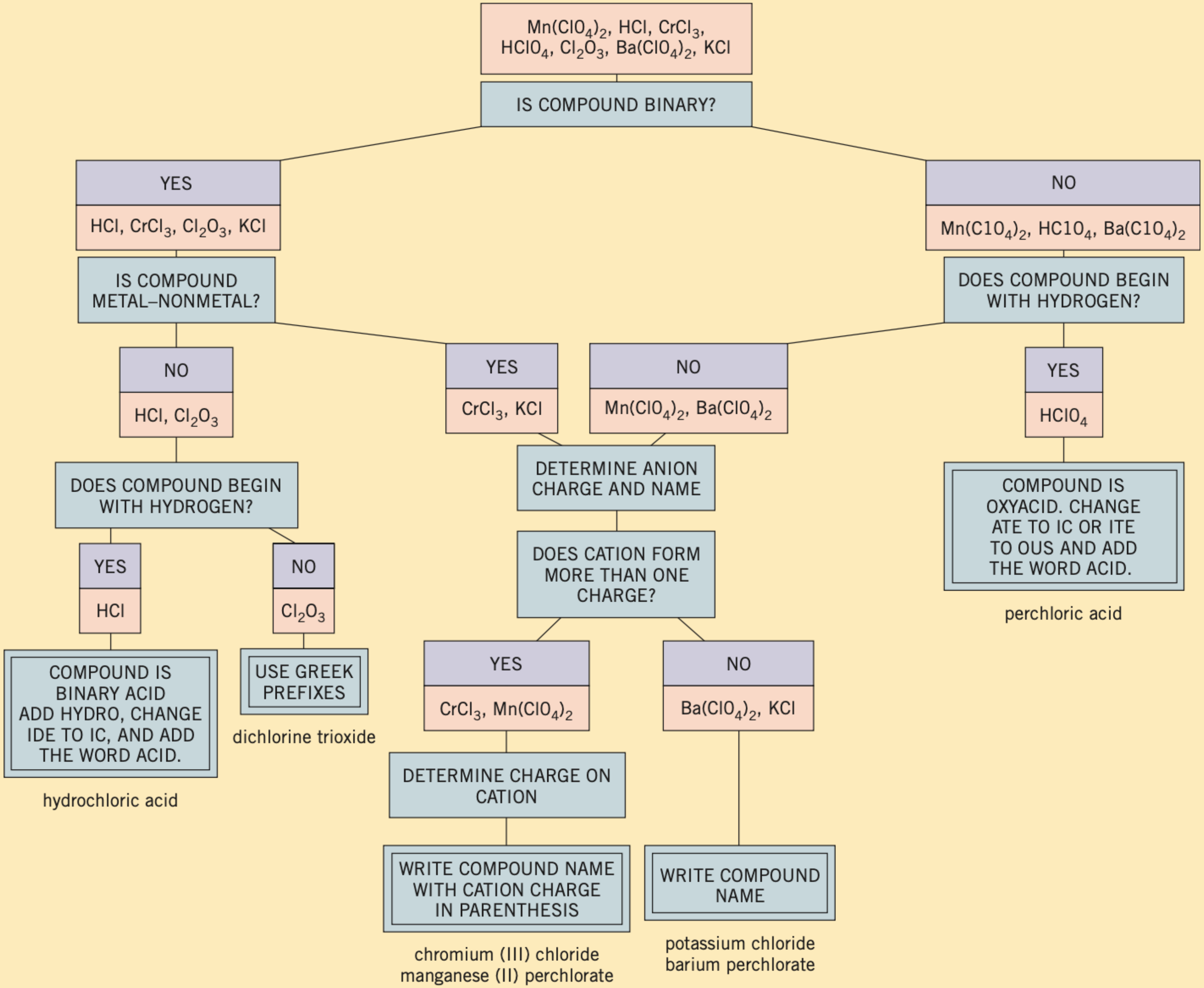
Molecular

- Binary compounds of nonmetals

Naming

- Use prefixes for both elements present (Prefix "mono–" usually omitted for the first element)
- Add "–ide" to the root of the second element

General scheme



$Mn(ClO_4)_2$, HCl, $CrCl_3$, $HClO_4$, Cl_2O_3, $Ba(ClO_4)_2$, KCl

IS COMPOUND BINARY?

YES

HCl, $CrCl_3$, Cl_2O_3, KCl

IS COMPOUND METAL–NONMETAL?

NO

HCl, Cl_2O_3

DOES COMPOUND BEGIN WITH HYDROGEN?

YES

HCl

COMPOUND IS BINARY ACID ADD HYDRO, CHANGE IDE TO IC, AND ADD THE WORD ACID.

hydrochloric acid

NO

Cl_2O_3

USE GREEK PREFIXES

dichlorine trioxide

YES

$CrCl_3$, KCl

NO

$Mn(C10_4)_2$, $HC10_4$, $Ba(C10_4)_2$

DOES COMPOUND BEGIN WITH HYDROGEN?

NO

$Mn(ClO_4)_2$, $Ba(ClO_4)_2$

DETERMINE ANION CHARGE AND NAME

DOES CATION FORM MORE THAN ONE CHARGE?

YES

$CrCl_3$, $Mn(ClO_4)_2$

DETERMINE CHARGE ON CATION

WRITE COMPOUND NAME WITH CATION CHARGE IN PARENTHESIS

chromium (III) chloride
manganese (II) perchlorate

NO

$Ba(ClO_4)_2$, KCl

WRITE COMPOUND NAME

potassium chloride
barium perchlorate

YES

$HClO_4$

COMPOUND IS OXYACID. CHANGE ATE TO IC OR ITE TO OUS AND ADD THE WORD ACID.

perchloric acid

Li^+

$$\overset{+I}{}\quad\overset{-I}{}$$

$\underline{Na_2O} + H_2O \longrightarrow 2Na(OH)$

$2Na + 2O + 2H$

$Na(OH)$

Cl^-

$S^=$

$O^=$

H^+

H^-

H_3O^+

$Ca(OH)_2$

$CaO + H_2O \longrightarrow Ca(OH)_2$

$Al(OH)_2 +$

TERNARY
COM

$Al_2O_3 + 3H_2O \longrightarrow 2Al(OH)_3$

CARBONIC ACID

$CO_2 + H_2O \rightarrow H_2CO_3$

H^+

(-ic) +4

$\overset{+I}{H_2}\overset{+IV}{C}\overset{-II}{O_3}$ O.N.

+4 - 6 = $\boxed{-2}$

H_sXO_m

H_2SO_4

H_2SO_3

$(CO_3^{=})$

CARBONATE

$\overset{+6}{H_2S}\overset{-II}{O_4}$

SULFURIC ACID

$SO_4^{=}$ SULFATE

OXO ACIDS

$H_2\overset{IV}{S}O_3$ $SO_3^{=}$ ITE

OSE

H $N_2O_5 + H_2O \rightarrow H_2N_2O_6$

$\rightarrow 2HNO_3$

+V

HNO_3 ic

+1 +5 + 3(-2)

NO_3^- ATE

PO_4

+V

HPO_3

N_2O_3 +

ClO_4^- per ch ite

ClO_3^-

SiO_4^{4-} H_4SiO_4

HNO_2 ClO_2^- NO_2^- ITE

+V

H_3PO_4

NITRO-OSE

+III

$HClO_4$ per chlor

tri 3

pH →

$HClO_3$ $HClO_2$ $HClO$

per -ic

-ic

-ose

ipo -ose

PERchlor -ATE

-ATE

-ITE

ipo -ite

ACIDS	BASES
ELECTRON WITHDRAWING	ELECTRON GIVERS
ELECTRON POOR	ELECTR RICH
CATIONS	ANIONS
ELECTROPHILES	NUCLEOPHILES
OXIDANTS	REDUCTANTS

Hydroxydes

FORMULA	TRADITIONAL NOMENCLATURE	NOTATION STOCK	IUPAC NOMENCLATURE
$NaOH$	sodium hydroxide	sodium hydroxide(I)	sodium hydroxide
$Fe(OH)_2$	ferrous hydroxide	iron(II) hydroxide	iron di-hydroxide
$Fe(OH)_3$	ferric hydroxide	iron(III) hydroxide	iron tri-hydroxide
$Cu(OH)$	Cuprous hydroxide	copper hydroxide(I)	copper hydroxide
$Cu(OH)_2$	Cupric hydroxide	copper(II) hydroxide	copper di-hydroxide
$Al(OH)_3$	Aluminum hydroxide	Aluminium hydroxide(III)	Aluminum tri-hydroxide
$Mg(OH)_2$	magnesium hydroxide	magnesium(II) hydroxide	magnesium di-hydroxide
KOH	potassium hydroxide	potassium(I) hydroxide	potassium hydroxide
$Ca(OH)_2$	calcium hydroxide	calcium(II) hydroxide	calcium di-hydroxide

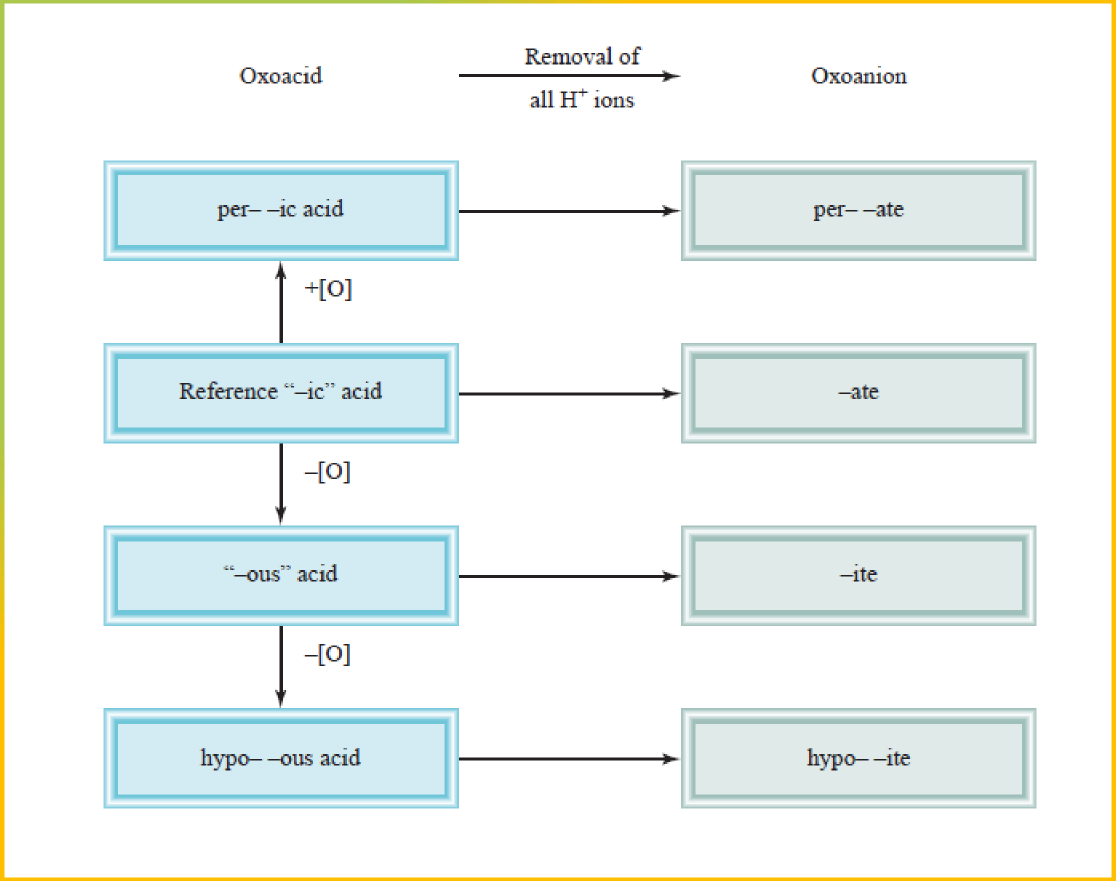
Oxacid

ACID	HALOGEN RESIDUE	SALT
H_2SO_3 = Sulphur-ous Acid	SO_3^{--} = sulphite ion	Na_2SO_3 = sodium sulfite
H_2SO_4 = sulphuric acid	SO_4^{--} = Sulfate Ion	Na_2SO_4 = sodium sulfate
H_2CO_3 = carbonic acid	CO_3^{--} = carbonate ion	Na_2SO_3 = sodium carbonate
H_3PO_4 = phosphoric acid	PO_4^{---} = Phosphate ion	Na_3PO_4 = sodium phosphate
$HClO_3$ = Chloric acid	ClO_3^- = Chlorate ion	$NaClO_3$ = sodium chlorate
HNO_3 = nitric acid	NO_3^- = nitrate ion	$NaNO_3$ = sodium nitrate

Nomenclature and molecular formulas

o.n. non metal	minimum number of O atom	Example of a ternary compound
+7	4 (4x2 = 8 >7; 8-7 = 1 di H)	$HClO_4$.
+6	4 (4x2 = 8 >6; 8-6 = 2 di H)	H_2SO_4.
+5	3 (3x2 = 6 >5; 6-5 = 1 di H)	HNO_3.
+4	3 (3x2 = 6 >4; 6-4 = 2 di H)	H_2CO_3, H_2SO_3
+3	2 (2x2 = 4 >3; 6-5 = 1 di H)	HNO_2, HNO_2
+2	2 (2x2 = 4 >2; 4-2 = 2 di H)	HCOOH, H_2SO_2
+1	1 (1x2 = 2 >1; 6-5 = 1 di H)	HClO.

Nomenclature



Oxoacid

Removal of all H^+ ions

Oxoanion

per– –ic acid → per– –ate

+[O]

Reference "–ic" acid → –ate

–[O]

"–ous" acid → –ite

–[O]

hypo– –ous acid → hypo– –ite

FORMULA	TRADITIONAL	IUPAC NOMENCLATURE
H_2CO_3	carbonic acid	di-hydrogen tri-oxo-carbonate.
HNO_3	nitric acid	hydrogen tri-oxo-nitrate
HNO_2	nitrous acid	hydrogen di-oxo-nitrate.
H_2SO_3	sulphurous acid	di-hydrogen tri-oxo-sulphate.
H_2SO_4	solfuric acid	di-hydrogen tetra-oxo-sulphate.
$HClO$	ipoclorous acid	mono-hydrogen di-oxo-chlorate.
$HClO_2$	chlorous acid	mono-hydrogen di-oxo-chlorate.
$HClO_3$	chloric acid	mono-hydrogen tri-oxo-chlorate.
$HClO_4$	per-chloric acid	hydrogen tetra-oxochlorate.
H_3PO_2	ipo-phosforous acid	di-oxophosphate tri-hydrogen.
H_3PO_4	orto-phosphoric acid	tetra-oxophosphate of tri-hydrogen.
H_3PO_3	orto-phosforous (phosphonic) acid	tri-oxophosphate tri-hydrogen.
H_2CrO_4	chromic acid	tetra-oxochromate of di-hydrogen.
$H_2Cr_2O_7$	dichromic acid	hepta-oxodi-chromate dihydrogen.

How to Write Structural Formulas

TEN =Total electrons needed to complete all the electronic configurations

TVE = Total valence electrons in the molecule/ion/fragment

TBN = Total number of covalent bonds

TLP = Total number of unshared electrons (lone pairs)

TBN = (TEN – TVE)/2

TLP = (TVE - TBN)/2

The non-H non-O atom is in the center and usually binds oxygens (if any). Hydrogens are almost always bound to O if there are any. Oxygen is bivalent with o.n. -2 and H mono-valent with o.n. +1

HNO_3

↑ ↑ ↑

2 8 8

TEN = 2 + 8 + (8×3)
= 34

TVE = 1 + 5 + (6×3) = 24

TEB = TEN - TVE
= 10

$B = \frac{10}{2} = \boxed{5}$

6 - 6 - 1 = -1

5 - 0 - 4 = +1

$FC = VE_x - LP_x \times 2 - B$

TANBE = TVE - TEB
= 24 - 10 = 14

SN = NBA + NLP

3 + 0

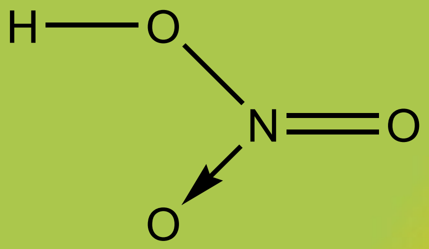
(n-1)

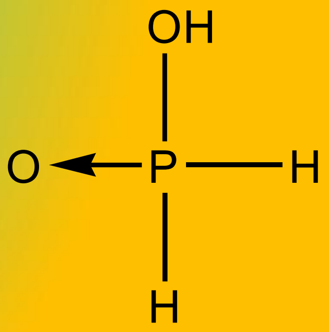
1.19

1.25Å

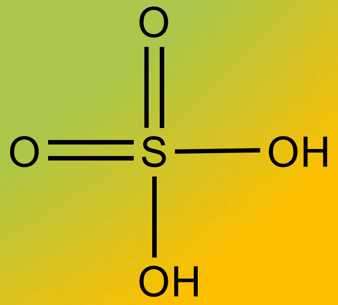
1.42Å

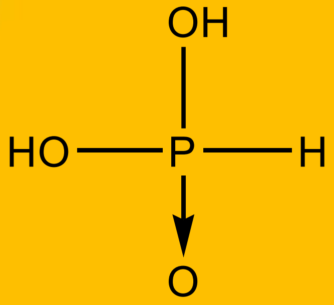
Oxoacids structures



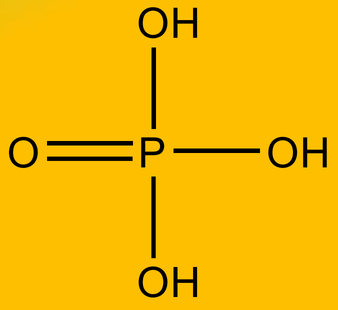


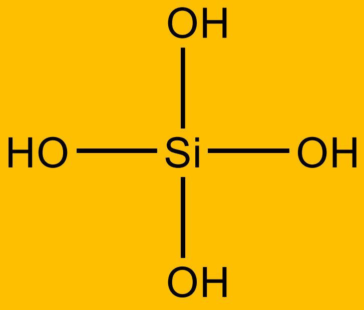
mono-protic





di-protic





triprotic

tetra-protic

Geometry

The molecular geometry is defined by VSEPR (valence shell electron pair repulsion) rationalized by the steric/coordination number (**SN**)

The steric number is the number of atoms bonded to a central atom of a molecule plus the number of lone pairs attached to the central atom. The steric number of a molecule is used in VSEPR (valence shell electron pair repulsion) theory to determine the molecular geometry of a molecule.

The geometry depends on the repulsion of these (bonded atoms and lone doublets) in the following order

lone pair/lone pair>lone pair/bonding region>bonding region/bonding region

Coordination number is sometimes misunderstood as steric number but usuualy is meant as number of atoms/groups directly bonded to the core atom.

Sulfite steric number is 3+1= 4, whereas the coordination number is 3 which is leading to a trigonal pyramidal geometry with bond angles to S of around 108°

Steric number

NBA = number of bonded atoms, X

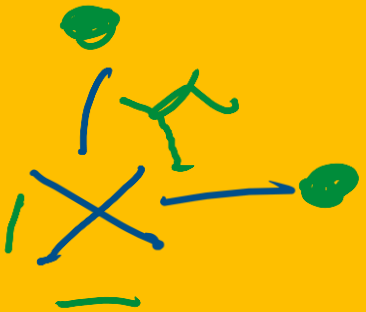
LP = lone pairs on the considered atom, L

steric number SN = X+ L

Steric Number	**Geometry**	**Bond angle**	**reference geometry**	**LP angles**	**Examples**
2, AX_2L_0	Linear	180°	180°	-	CO_2, $HC\equiv CH$, nitriles
3, AX_3L_0	Planar, Trigonal	120°	120°	-	H_2CO_3, HNO_3
3, AX_2L_1	Bent	118°	<120°	>120°	HNO_2, SO_2
4, AX_4L_0	Tetrahedral	109.5°	109.5°	-	CH_4, $HClO_4$, H_2SO_4, H_3PO_4
4, AX_3L_1	trigonal pyramidal	108°	<109°, 1LP	>109°	NH_3, $HClO_3$, H_2SO_3
4, AX_2L_2	bent	105°	<109°, 2LP	>109°	H_2O, HClO2

VESEPR

LP B



SN = BA + LP

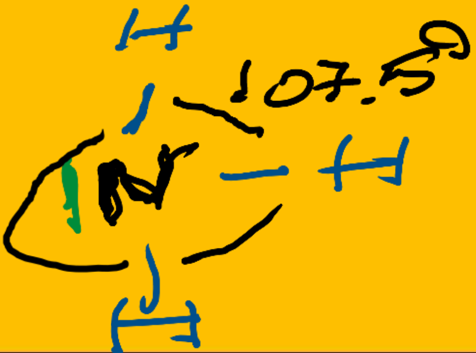
 = $\frac{2+2}{}$

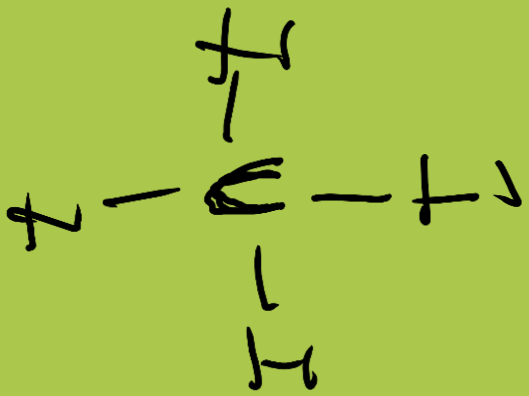
109.5°

bent

105°

SN = 3 + 1





SN = NBA+LP

108°.5

4 + 0

TRIGON. PYRAMID

108°

4 = SN = 3 + 1

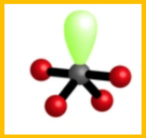
105°

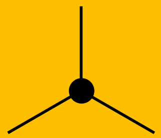
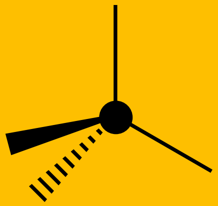
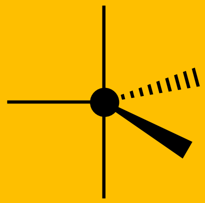
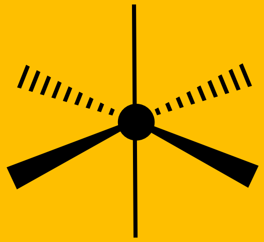
4 = SN = 2 + 2 −

BENT

SN=5

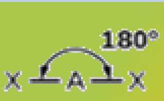
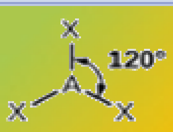
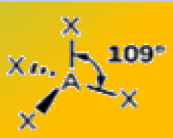
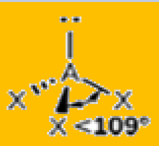
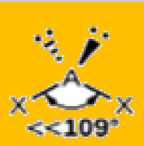
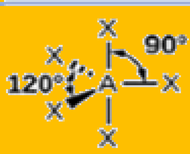
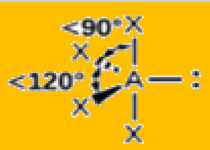
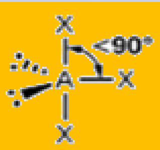
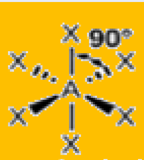
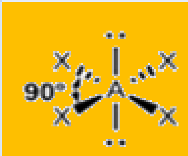
d

Steric Number	Geometry	Bond angle	reference geometry	Molecules	Draw
5, AX_5L_0	Bi-pyramidal trigonal	90°,180°	BPT	PF_5	
5, AX_4L_1	skewed	109°,117°	120°	SF_4	
5, AX_3L_2	T-shaped	<90°	T	IF_3	
5, AX_4L_2	**Linear**	**180°**	**linear**	**XeF2**	

Coordination Number	*Geometry*	*Bond angles*	*Configuration*
2	***linear***	*180°*	
3	***Trigonal planar***	*120°*	
4	***Tetrahedral***	*109°*	
5	***Bipyramidal trigonal***	*120° e 90°*	
6	***Octahedral***	*90°*	

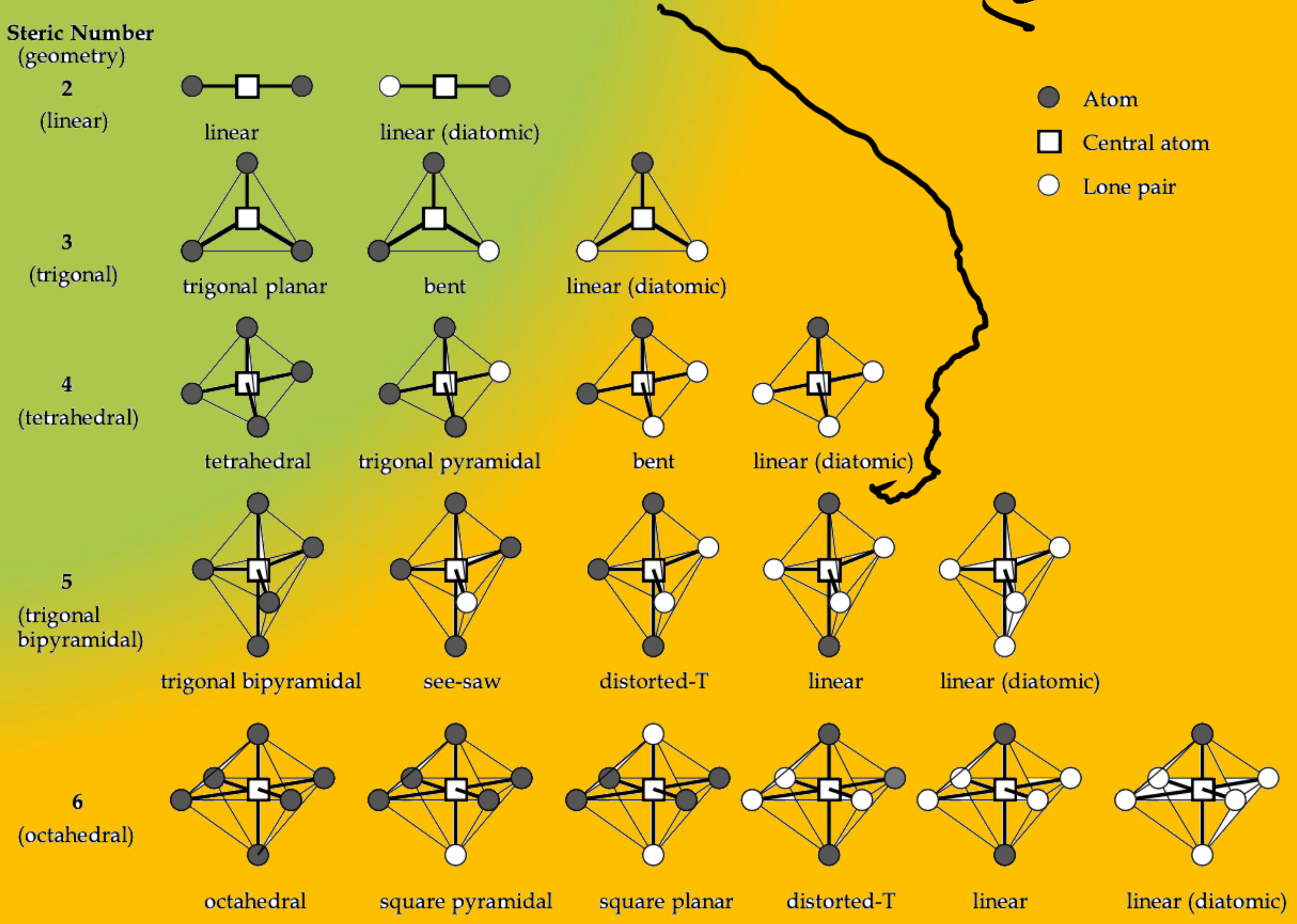
VSEPR

Molecular geometries based on VSEPR

Steric Number/ Electron Domains	Hybridization	Electronic geometries 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	sp	 linear				
3	sp^2	 trigonal planar	 bent			
4	sp^3	 tetrahedral	 trigonal pyramidal	 bent		
5	sp^3d	 trigonal bipyramidal	 seesaw	 T-shaped	 linear	
6	sp^3d^2	 octahedral	 square pyramidal	 square planar	 T-shaped	 linear

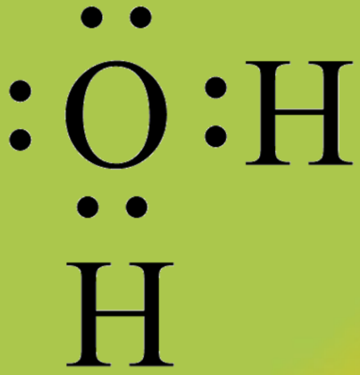
Geometry

$O=C=O$



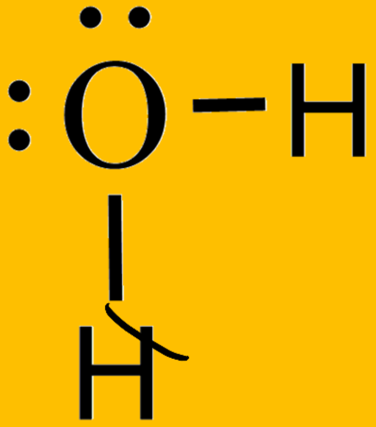
Steric Numbers, Geometries and the Shapes of Molecules

Lewis

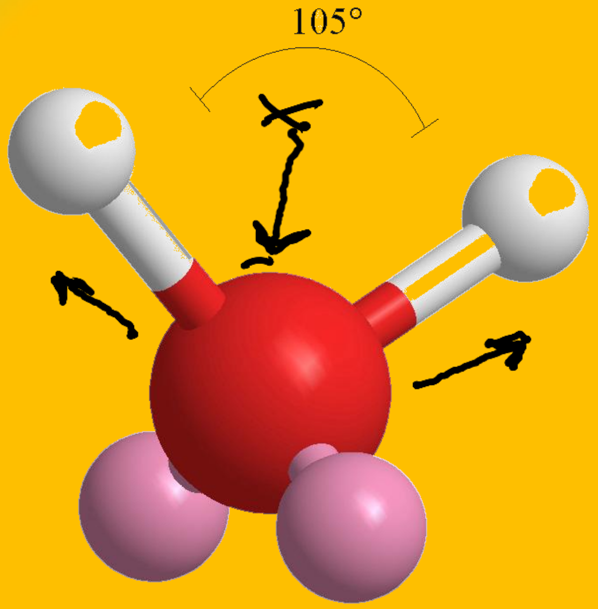


$$:\overset{\cdot\cdot}{\underset{\underset{\displaystyle H}{\cdot\cdot}}{O}}:H$$

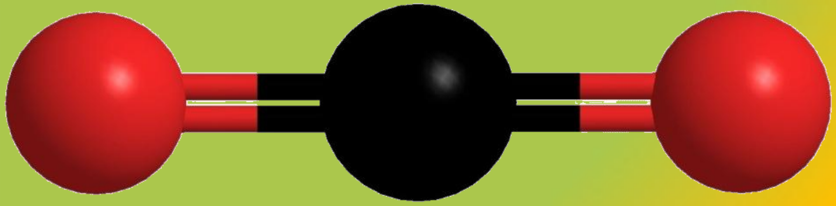
oppure

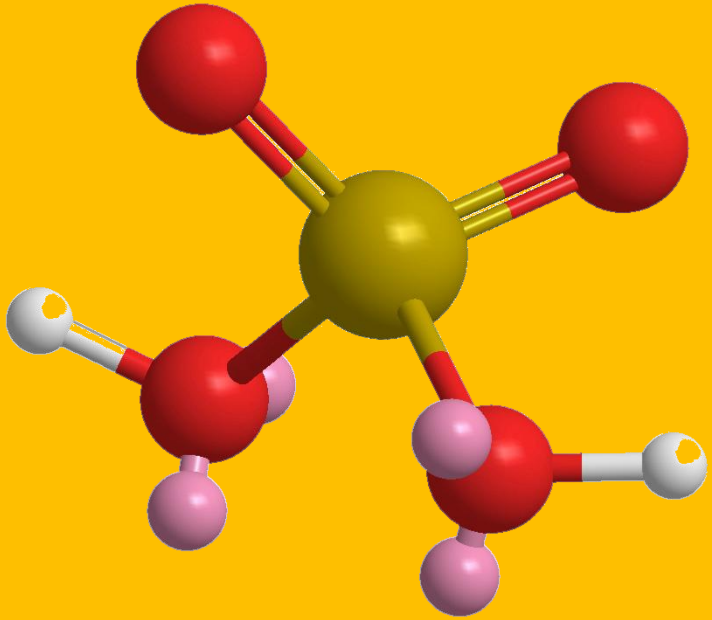


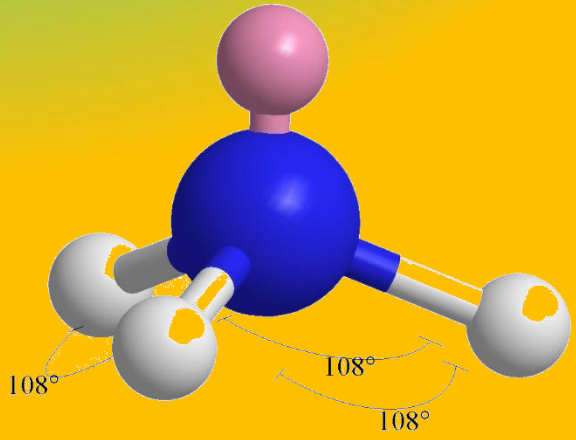
$$:\overset{\cdot\cdot}{\underset{\underset{\displaystyle H}{|}}{O}}-H$$

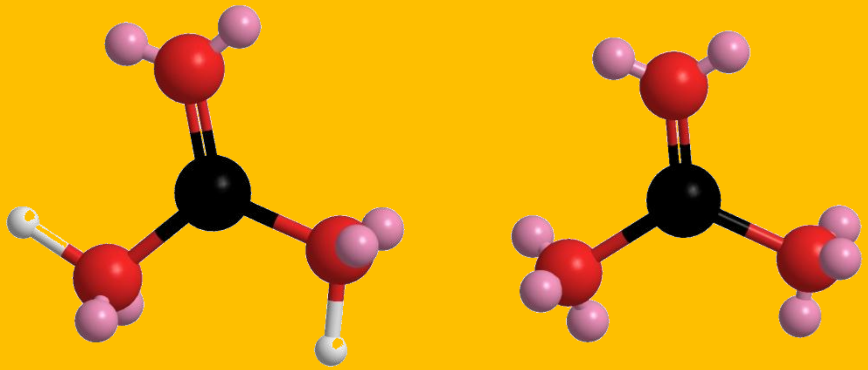


Molecular models









$\underline{HNO_2}$

$\underline{\overset{+I}{H}\overset{+3}{N}\overset{-II}{O}_2}$ → $\boxed{NO_2^-}$ -ATE -ITE

SN = NBA + LP

(1+2)

TEN = 2 + 8 + 8 × 2 = 26

TVE = 1 + 5 + (6 × 2) = $\boxed{18}$

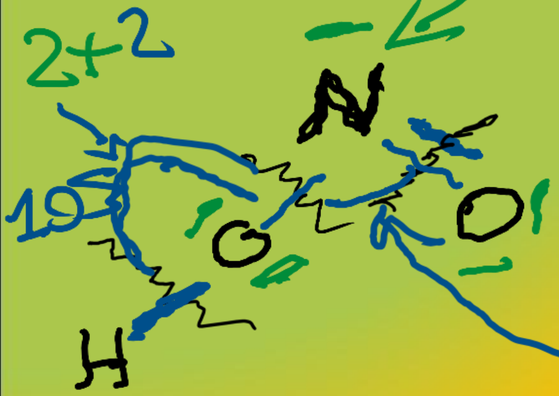
NBE = TEN − TVE = 8

4 BONDS

LPE = TVE − NBE = 10

LP = 5

BE0VF



BENT 118°

F.C. = NVE$_x$ − LPE$_x$ − NB

5 − 3 − 2 = 0

+I H_2SO_4

$(-2) \times 4 + 6 = -2$

1O OH + S

SO_4^{2-} ATE

$F.C._S = 6 - 0 - 4 = 2$

~~TEE~~ TEN = (2×2) + 8 + 8×4

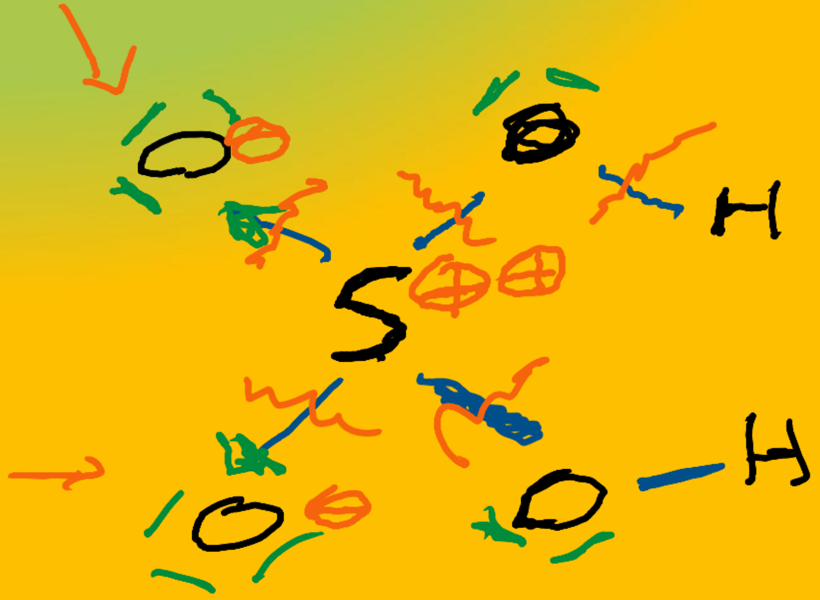
44

TVE = (1×2) + 6 + 6×4 = 32

TEN - TVE = NBE = $\boxed{12}$ → 6b

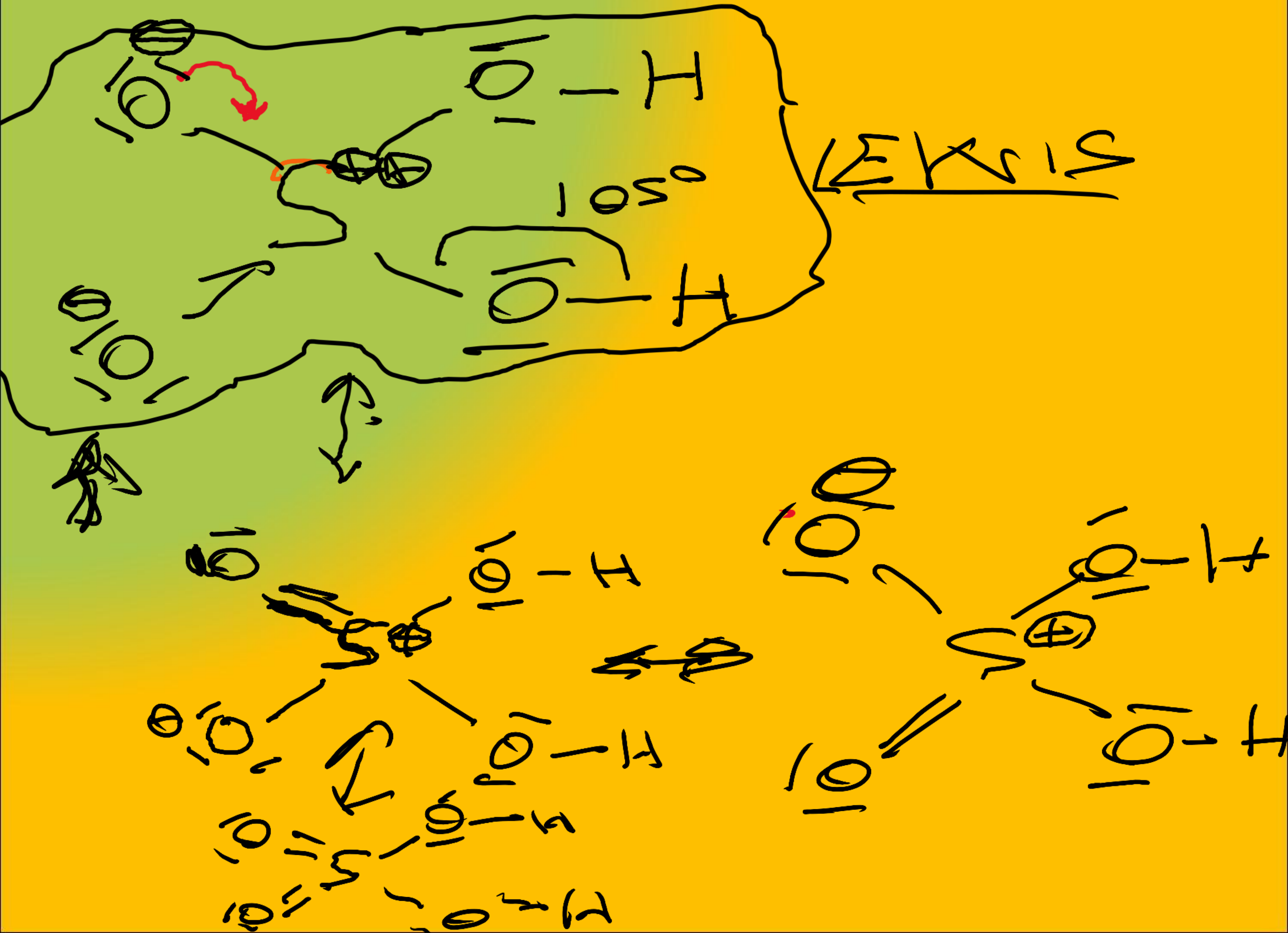
LPE = TVE - NBE = 20

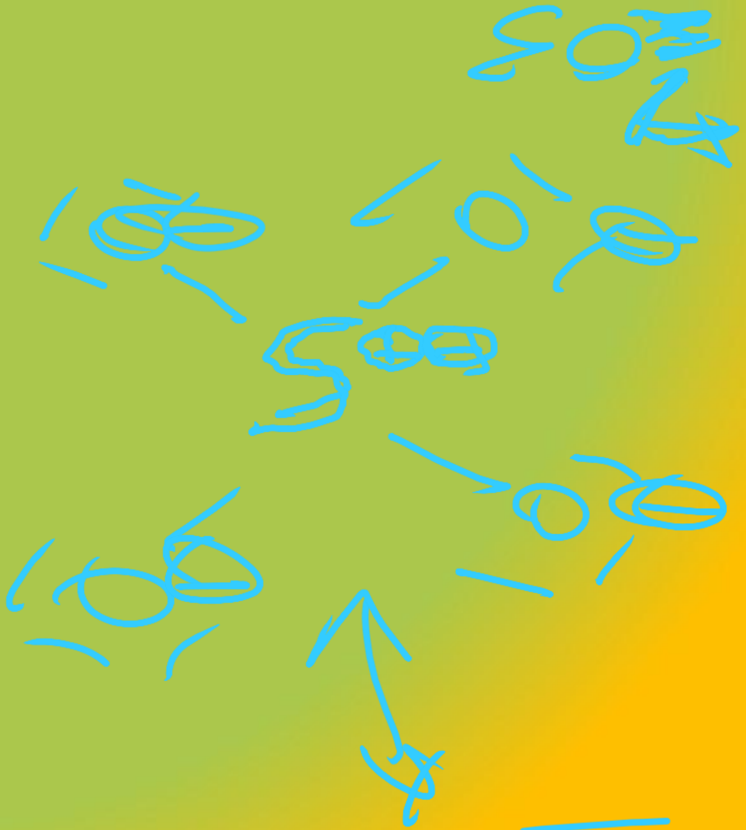
10 LP



$F.C._{SH} = 0$

$F.C._{TO} = 6 - 6 - 1 = -1$


LEWIS
105°



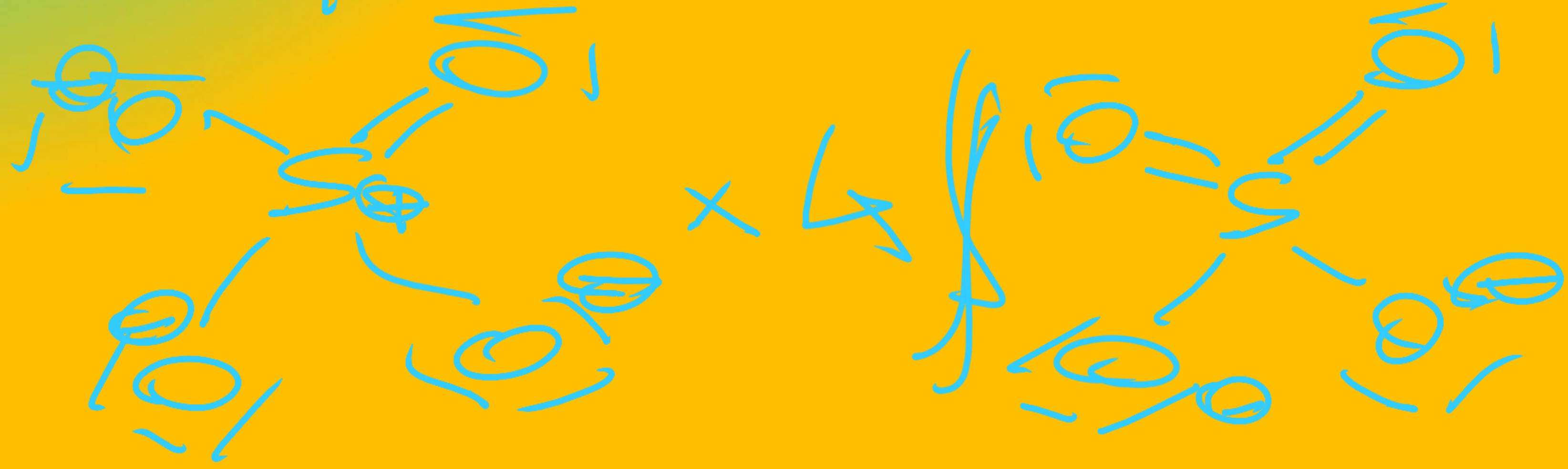
TEN = 40

TVE = 32

TBE = 8

TLPE = 24

$\boxed{\Sigma S = 4}$



EXPANDED OCTETS

THEY INVOLVE ELEMENTS THAT HAVE VALENCE ELECTRONS IN THE THIRD LAYER OR HIGHER

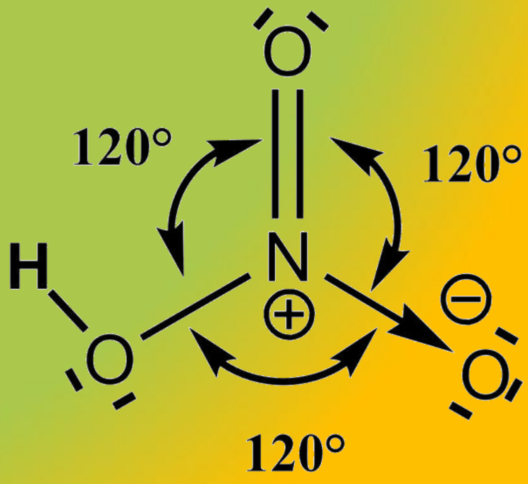
IN THESE CASES, SUB-SHELS d (NOT CONSIDERED BY THE OCTET RULE) MAY PLAY A ROLE

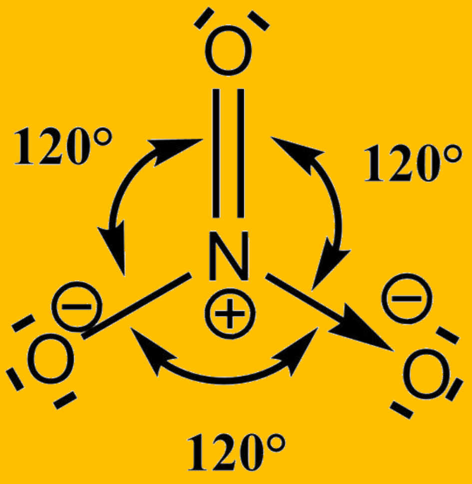
INCOMPLETE OCTETS

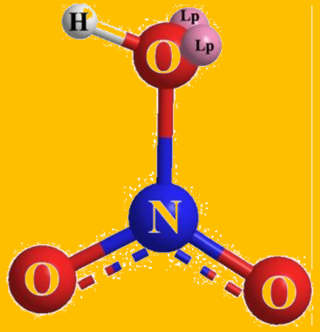
- THEY ARE TYPICAL OF ELECTRON-POOR ELEMENTS IN THE LAST LAYER

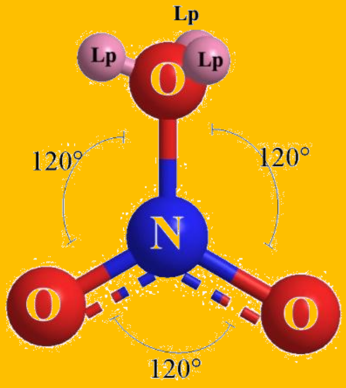
- THESE ELEMENTS (FOUND IN MANY LEWIS ACIDS) HAVE ELECTRONIC VACANCIES

Representations, Comparisons, and Geometries

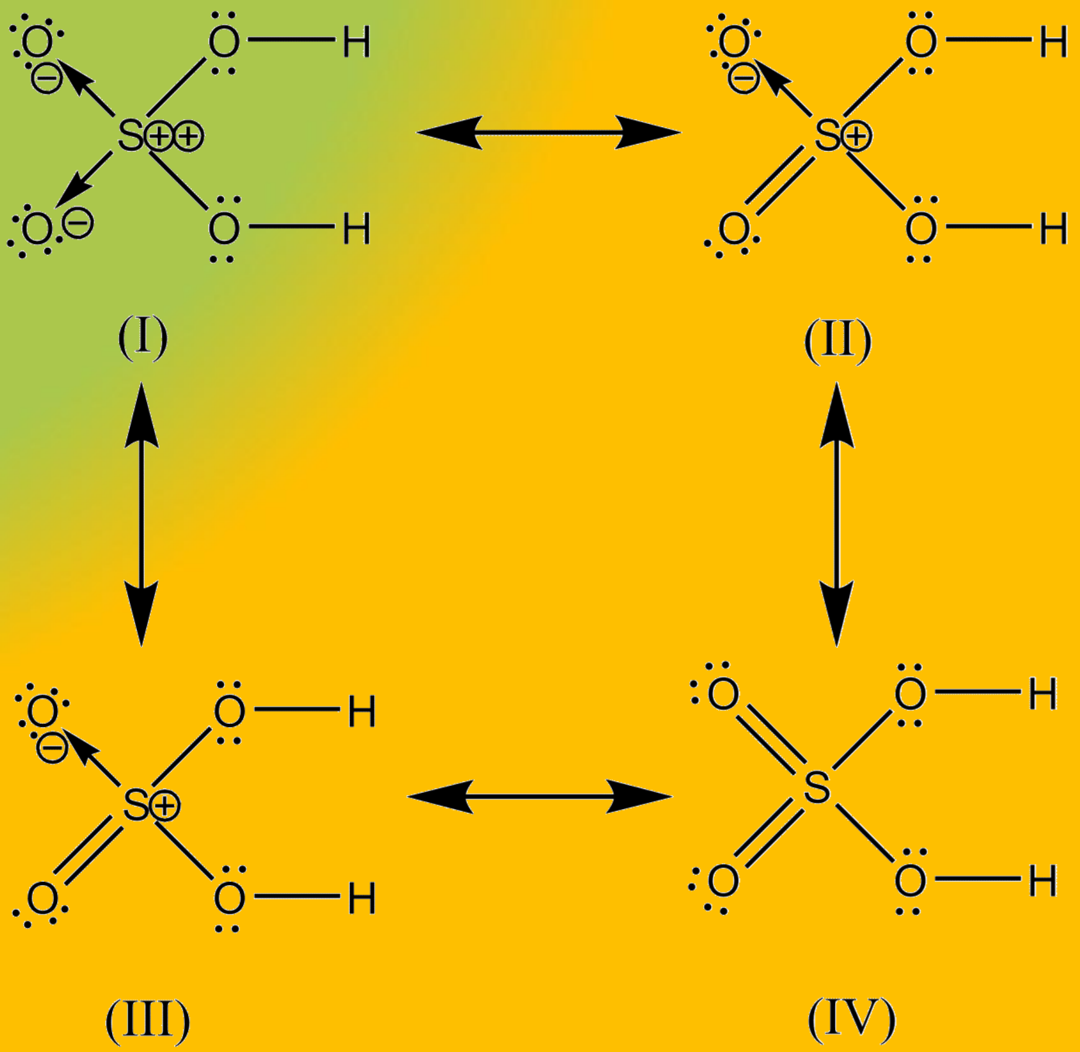




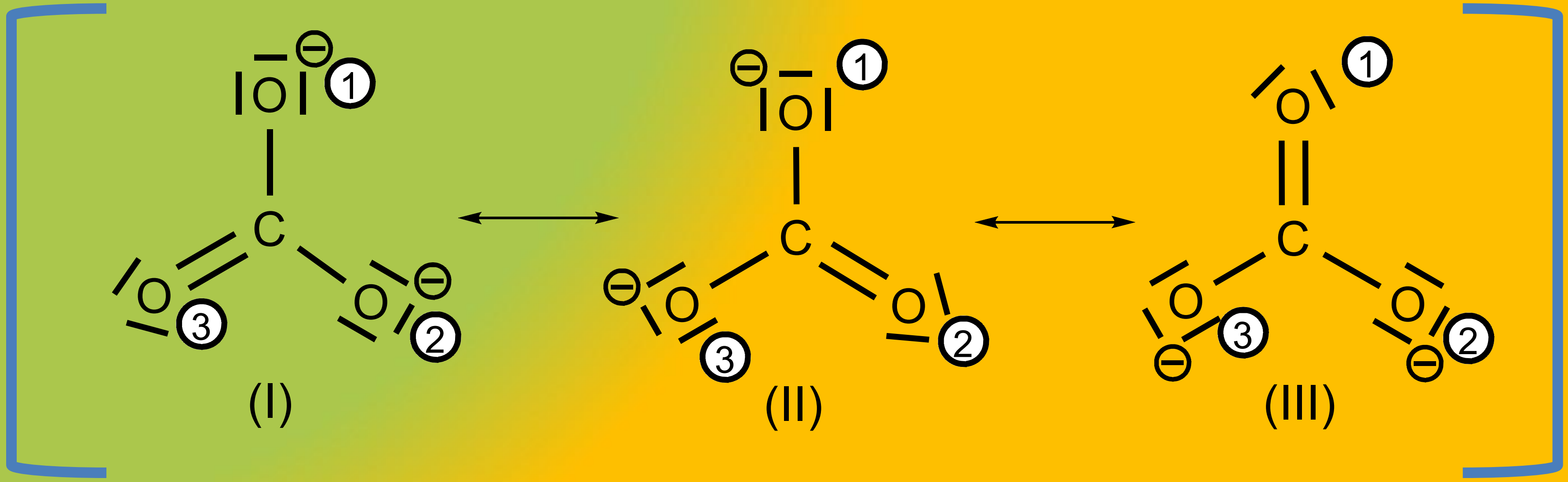




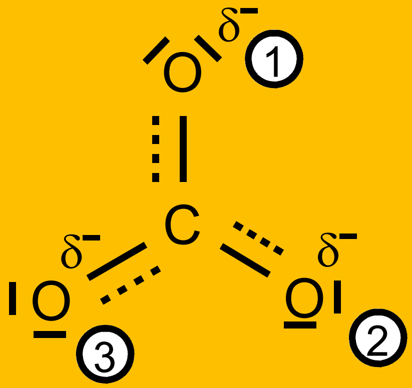
Resonance I



Resonance II

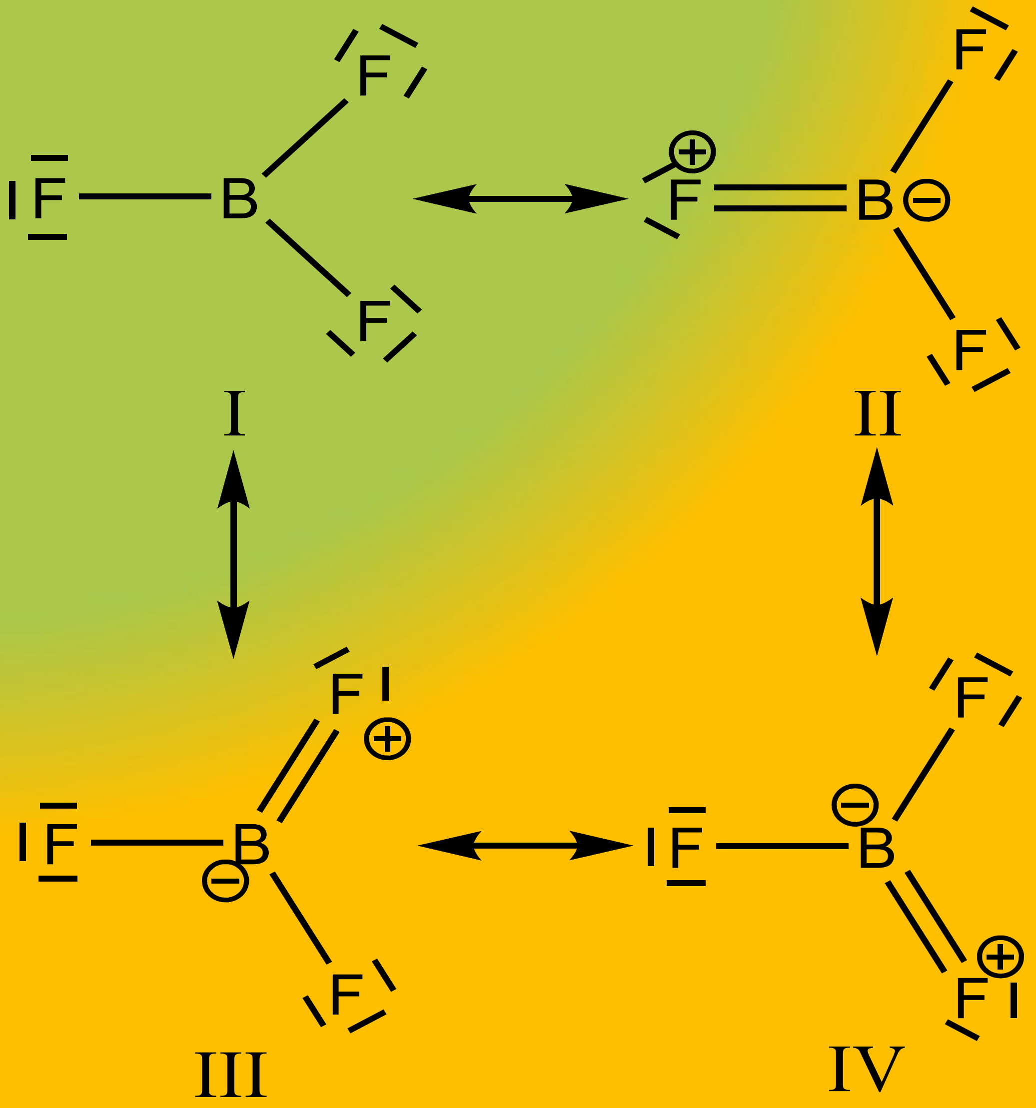


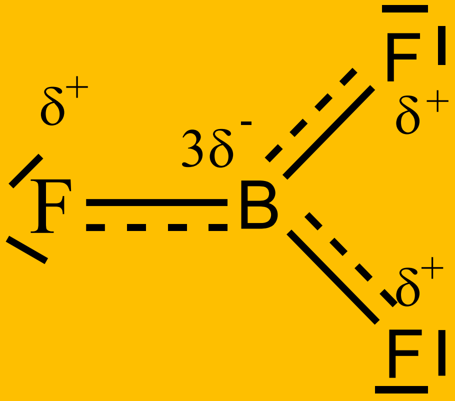
(I) (II) (III)



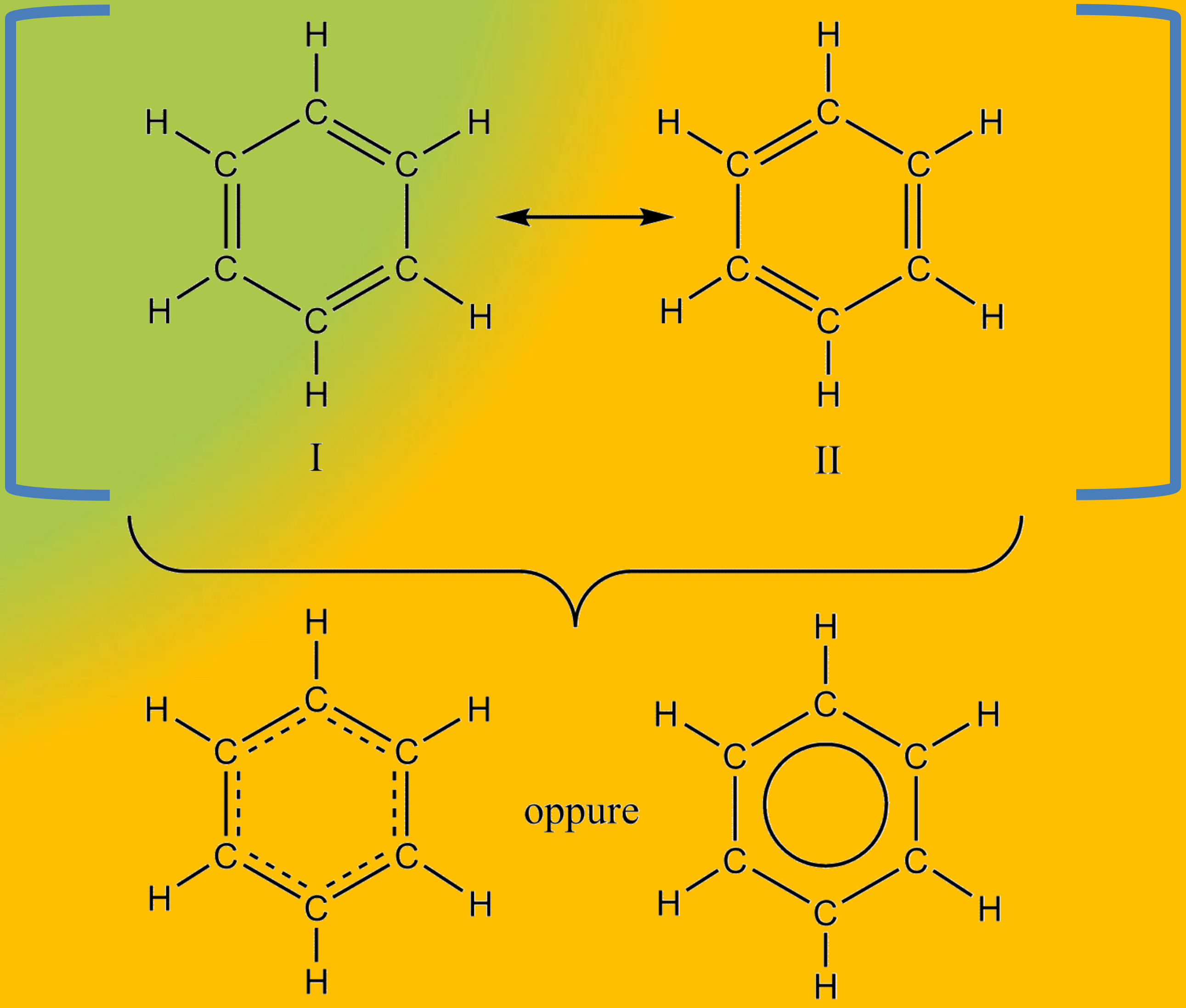
(IV)

Resonance III





Resonance IV



I

II

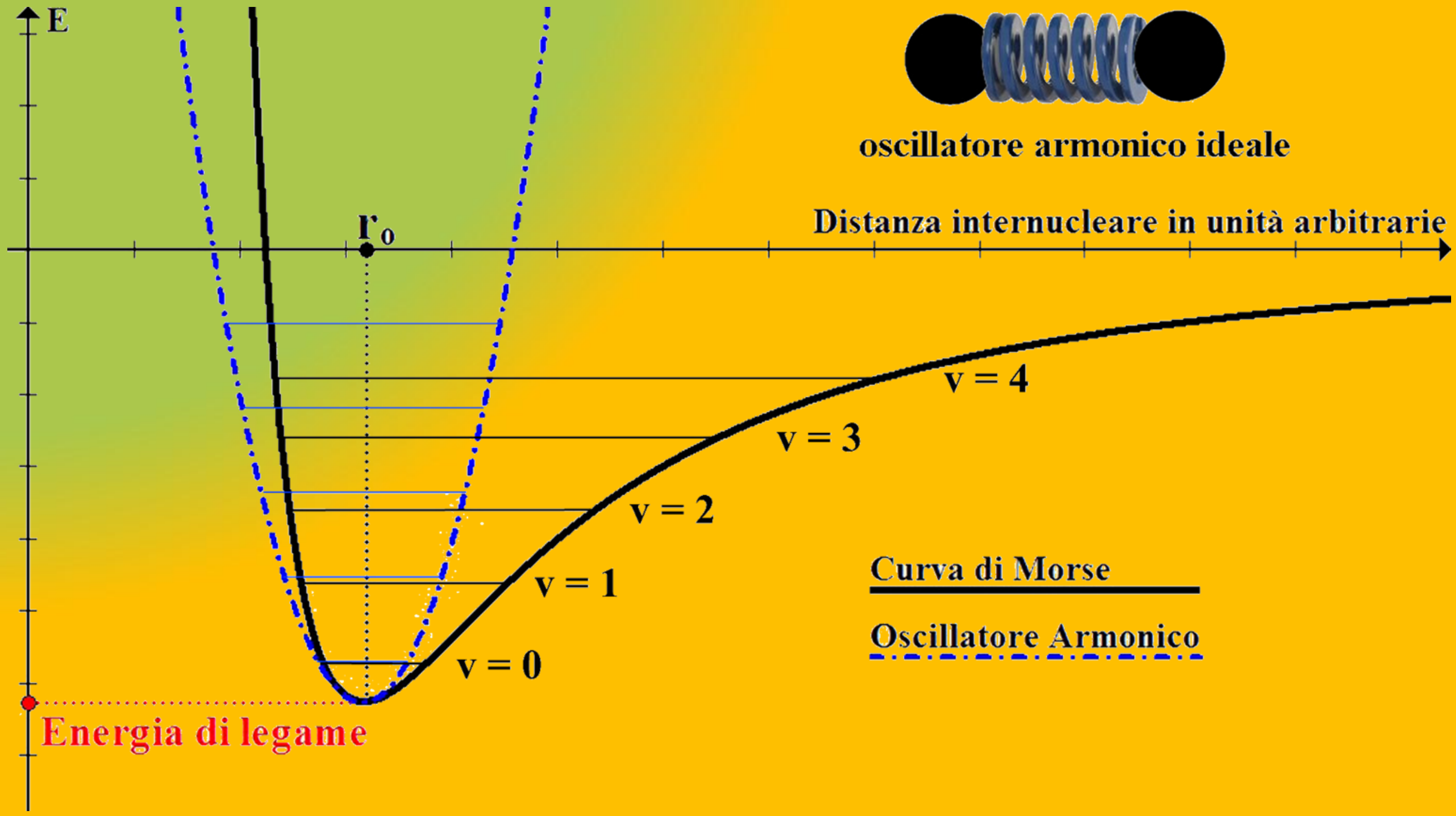
oppure

III

Bonding parameters

Bond and Bond order	Length (pm)	Bonding Energy (kJ/mol)
H-H, 1	74	436
H-O, 1	96	366
H-Cl, 1	127	432
H-C, 1	109	413
C-C, 1	154	348
C=C, 2	134	614
C≡C, 3	120	839
C-N, 1	147	308
C-O, 1	143	360
N-H, 1	101	391
N-N, 1	145	170
N≡N, 3	110	945
O-O, 1	148	145
O=O, 2	121	498
I-I, 1	267	151

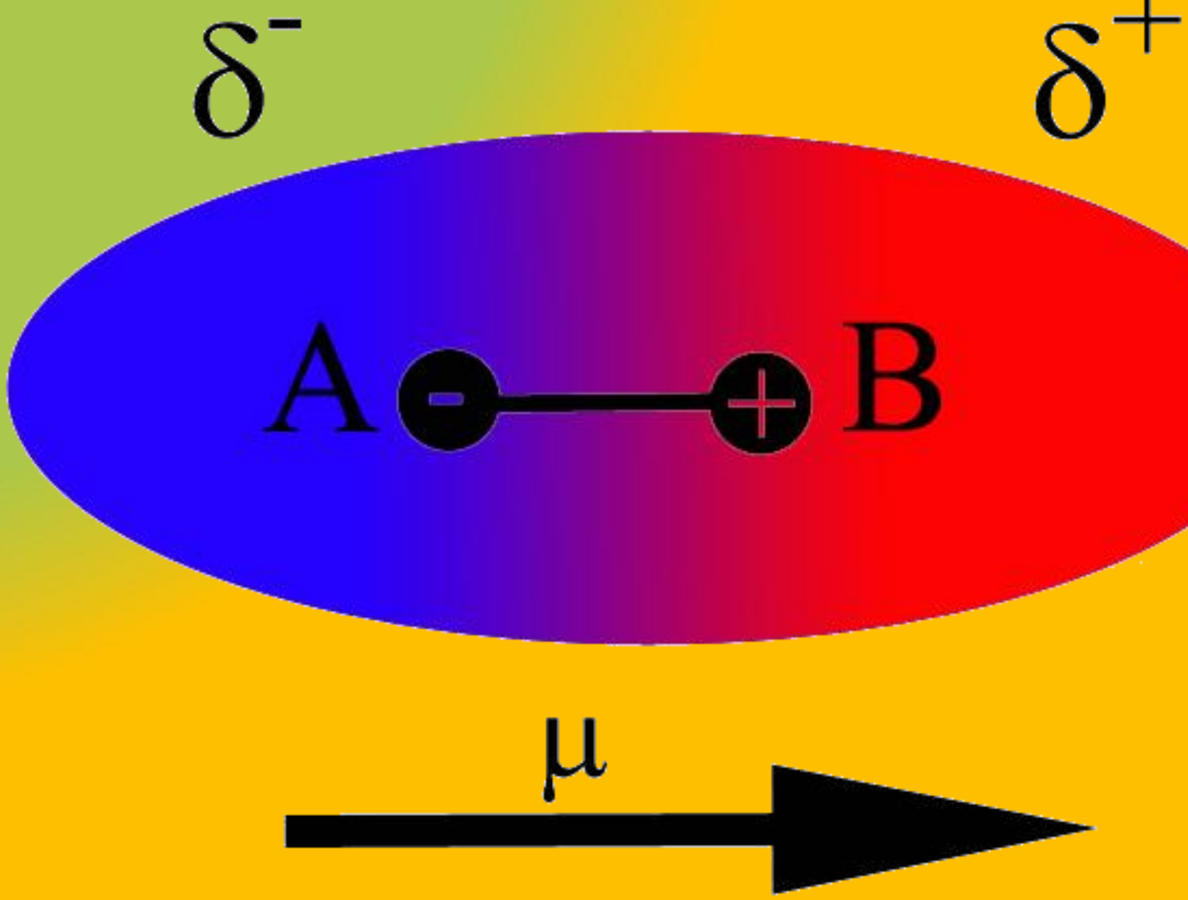
Morse graph "oscillators" IR



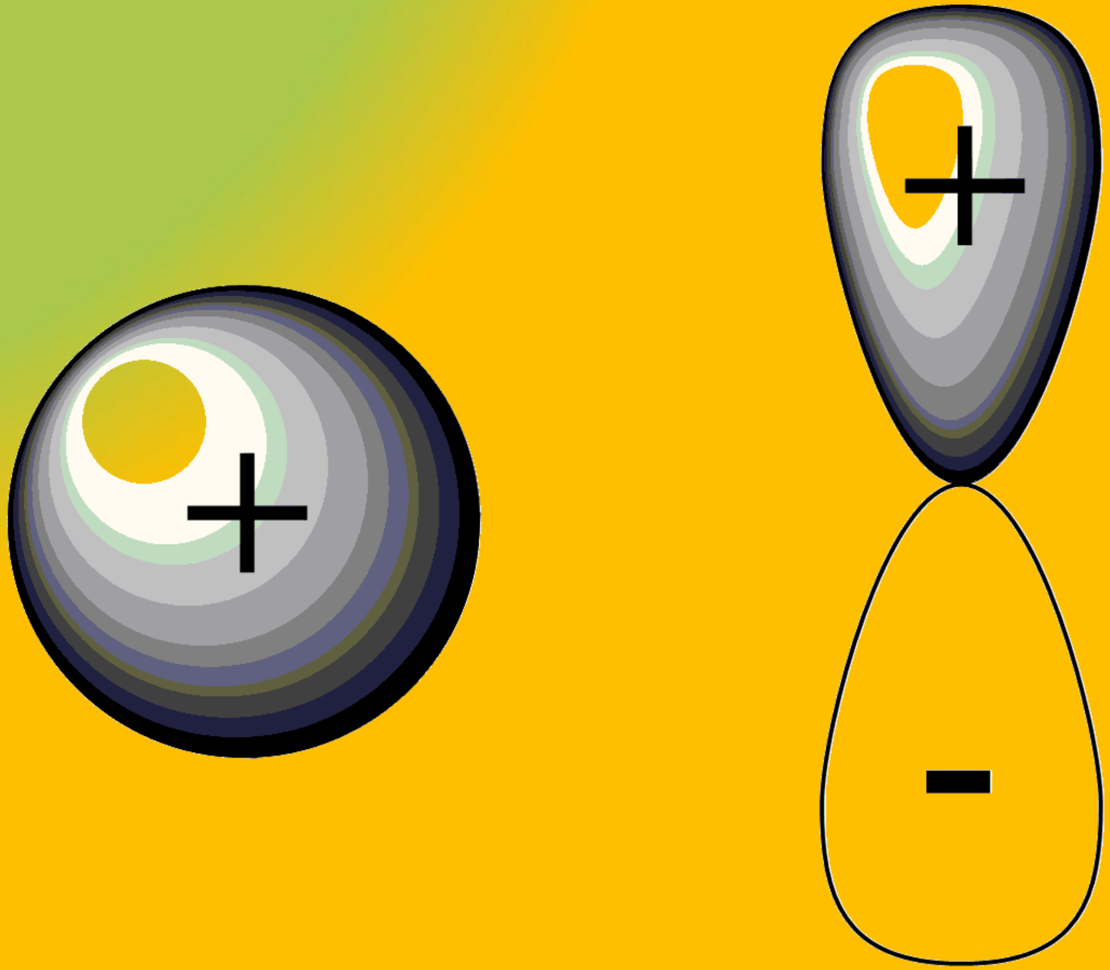
Homopolar and heteropolar covalents

Covalente puro Omopolare	Covalente polare
H---H	$H^{\delta+}$---$Cl^{\delta-}$
F---F	$H^{\delta+}$---$F^{\delta-}$
Cl---Cl	$O^{\delta-}$---$C^{\delta+}$---$O^{\delta-}$
N---N	$H_2N^{\delta-}$---$H^{\delta+}$
O---O	$HO^{\delta-}$---$H^{\delta+}$

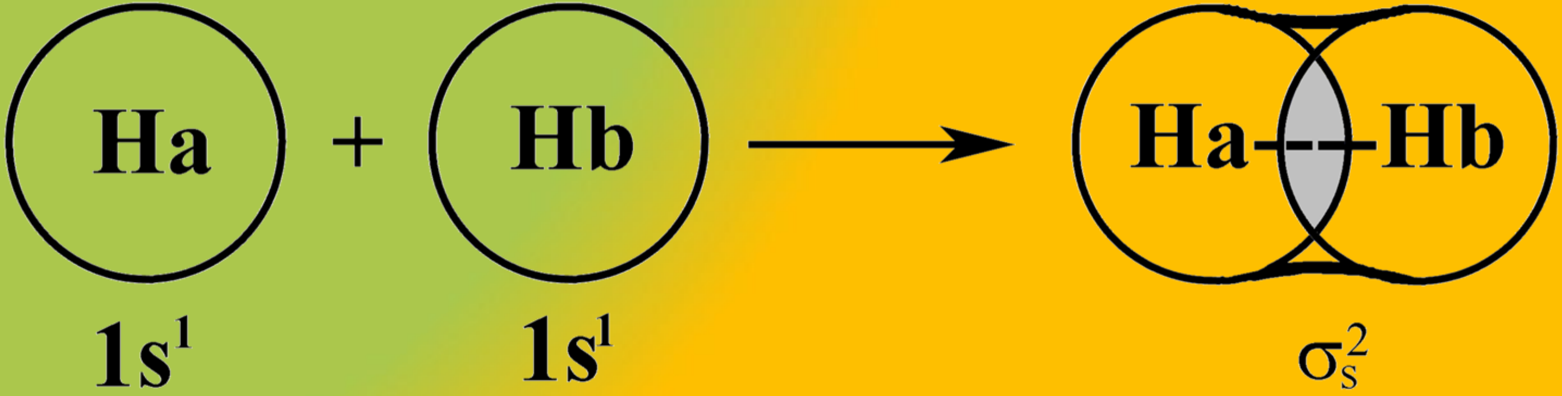
Dipole

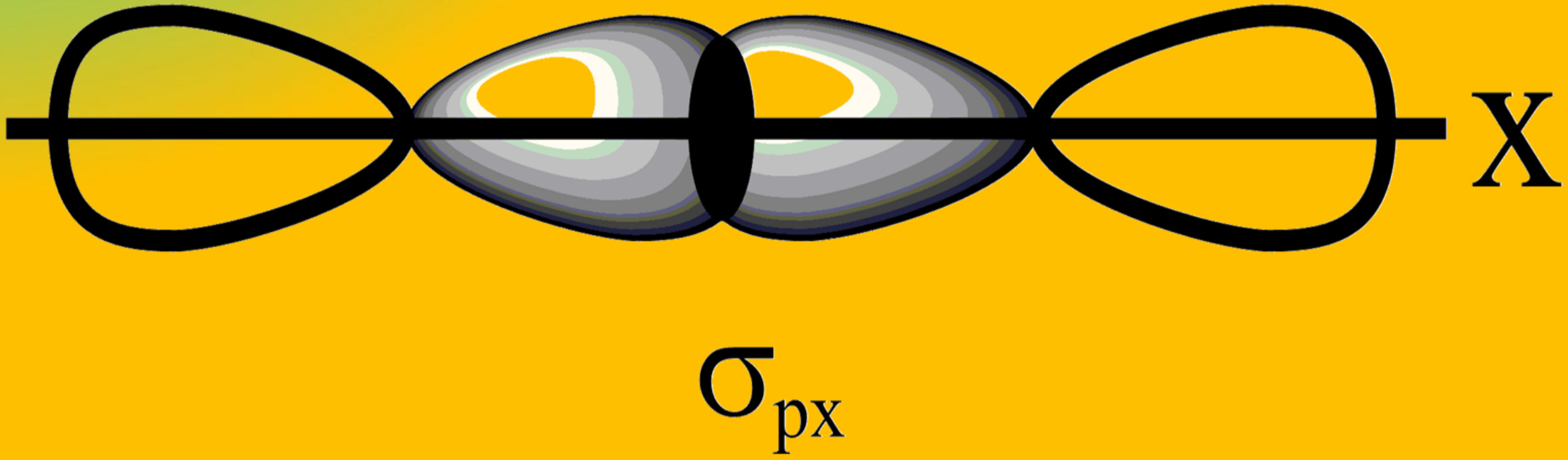


Atomic orbitals AO that then combine to give rise to molecular orbitals MO

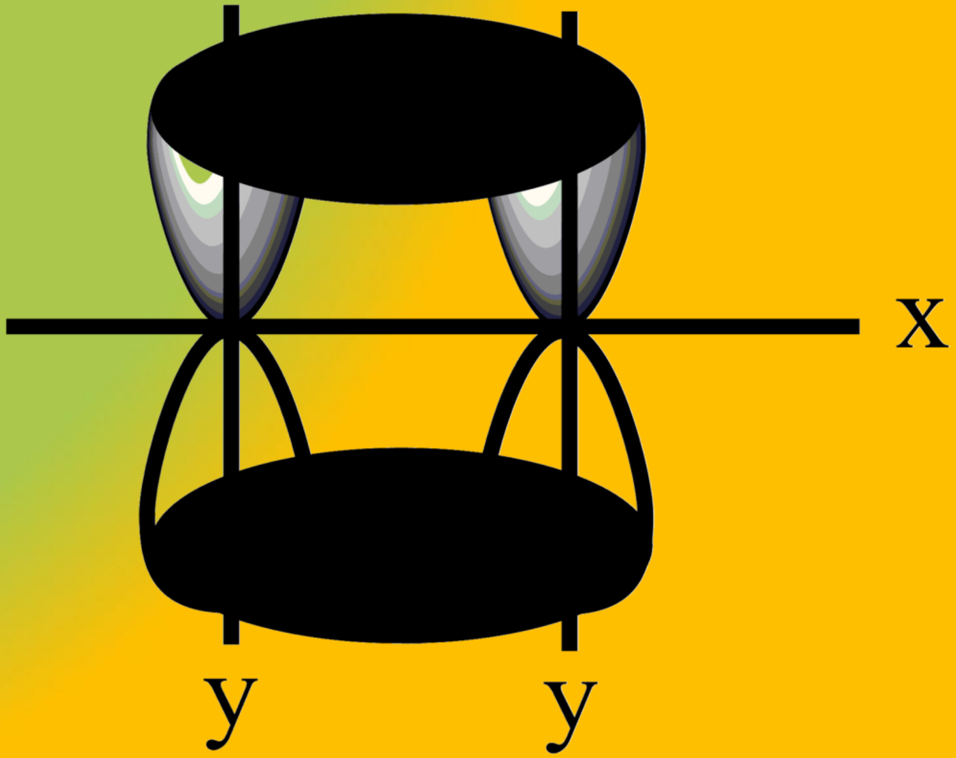


Sigma bond (density and AO overlap along the internuclear axes)





π-bond



π_{py}

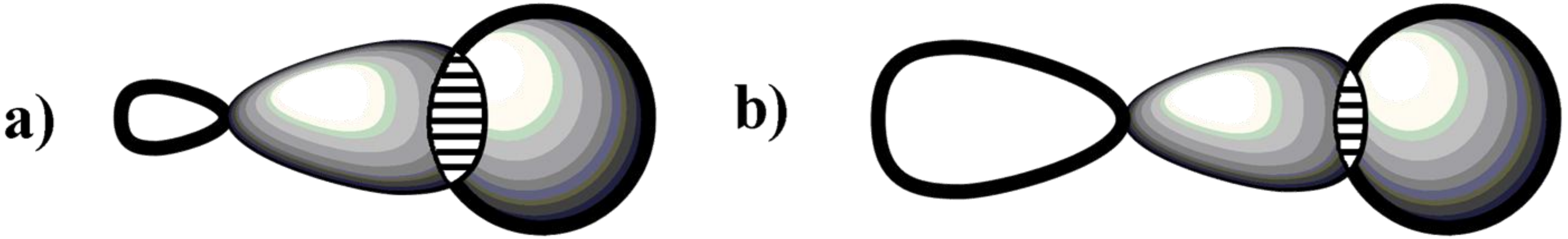
The binding energy is proportional to the overlap of the orbitals.

<u>The greater the overlap, the stronger the bond</u>

Hybridization

Combination of atomic orbitals with each other on the same atom

The total energy keeps unchanged, but it favours stabilization in view of the formation of bonds

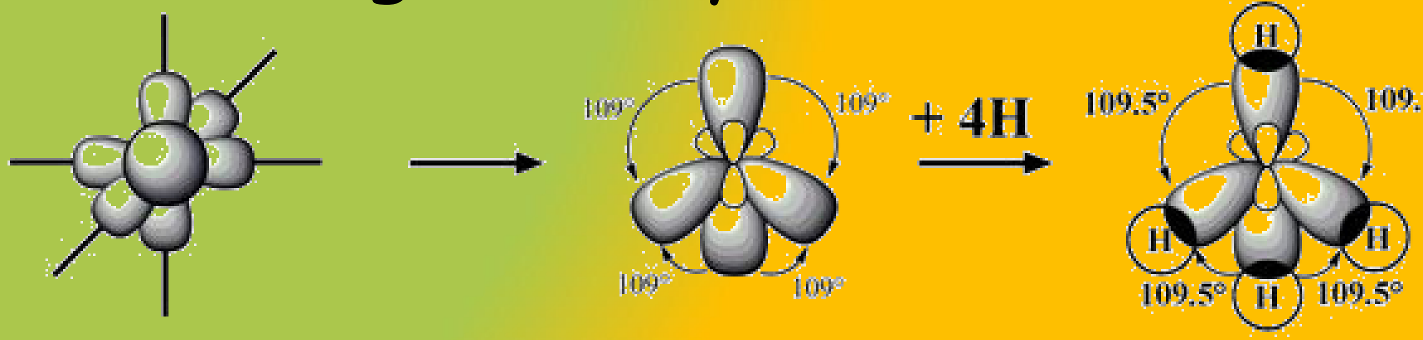


CH4 sp^3 →4 σ bonds, tetrahedral geometry, 109.5°

NH_3

4

O-H



ORBITALI
2s E 2p
PURI

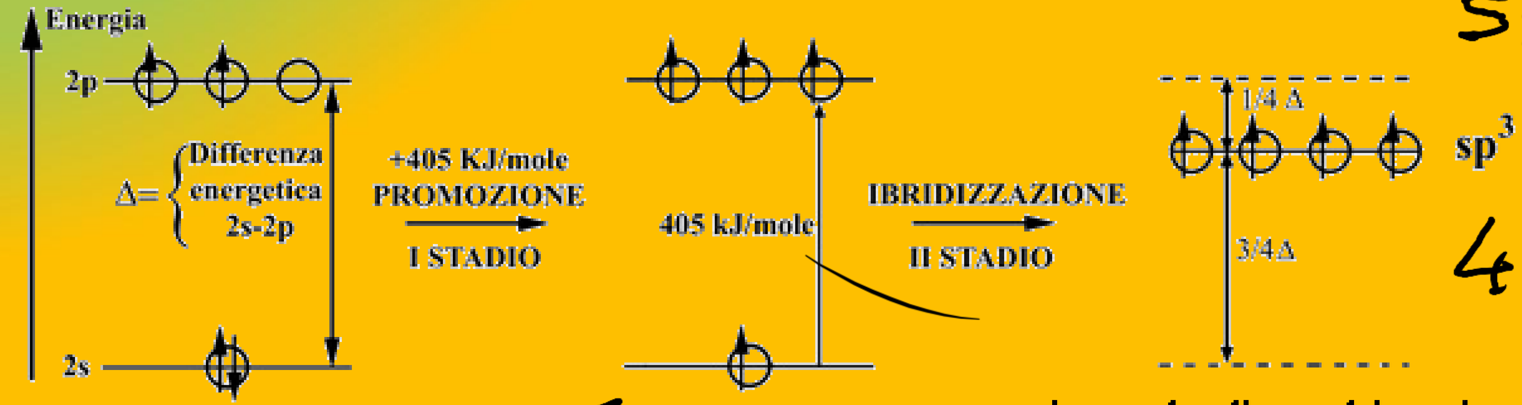
IBRIDI
2 sp^3

CH_4
TETRAEDRICO
SOVRAPPOSIZIONE
$2sp^3$(C)-1s(H)

CARBENES

$sp^3 - 2\sigma$

$4sp^2$



in grado di combinarsi
per formare 4 legami σ

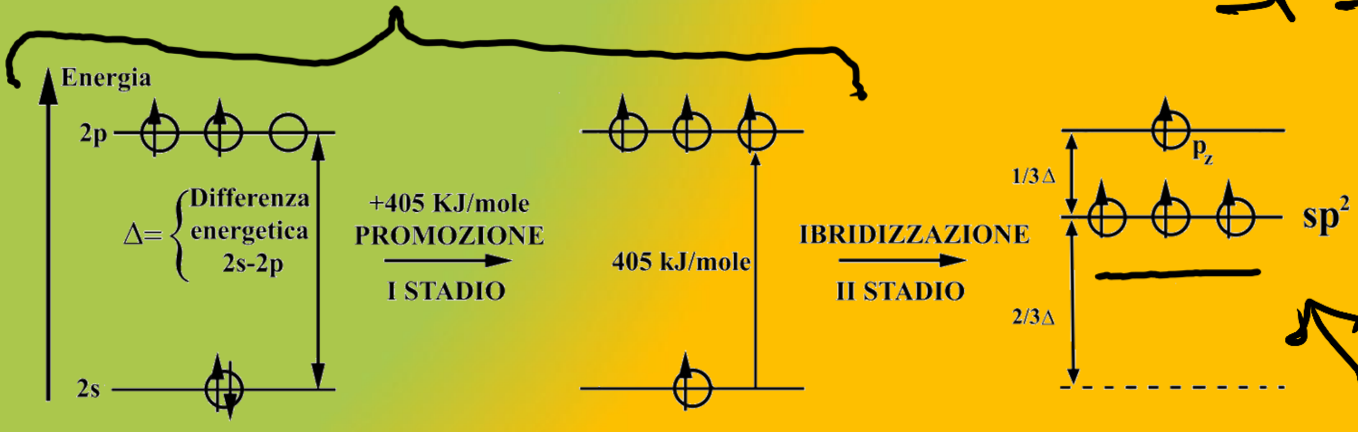
$2s^2p^2$

$2s^1p^3$ ④

no → nO

Ethene (ethylene), sp^2 → 3 σ bonds, trigonal planar geometry

sp^2 3 # σ



Energia

2p

2s

Δ= Differenza energetica 2s-2p

+405 KJ/mole
PROMOZIONE
I STADIO

405 kJ/mole

IBRIDIZZAZIONE
II STADIO

1/3Δ

2/3Δ

p_z

sp^2

s+2p

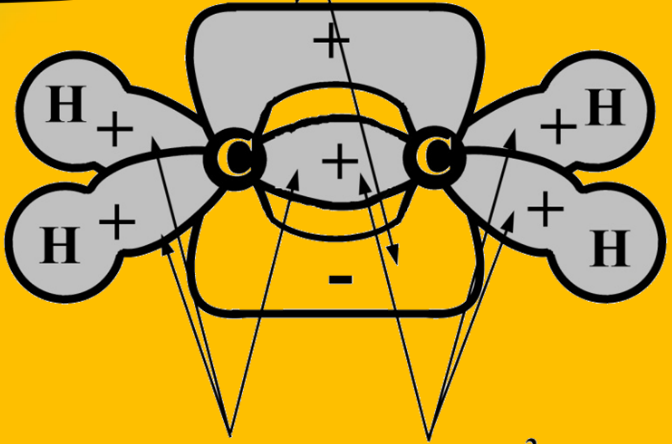
3σ

405kJ/mol

TRIGONAL PLANAR

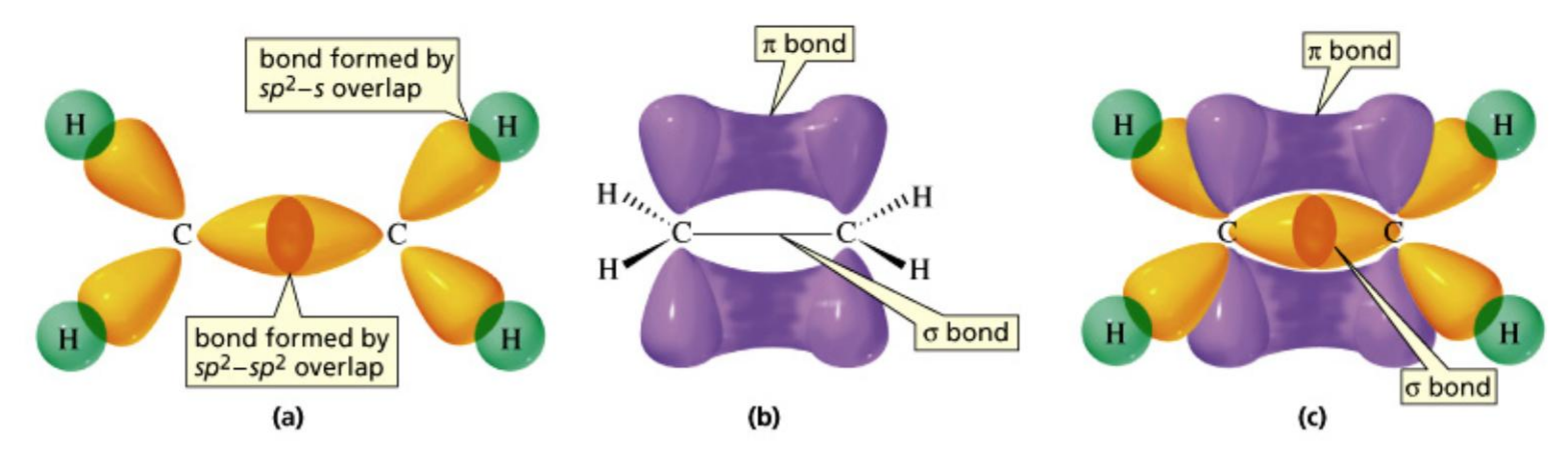
∠ 120°

combinazione dei due orbitali p_z che originano il legame π

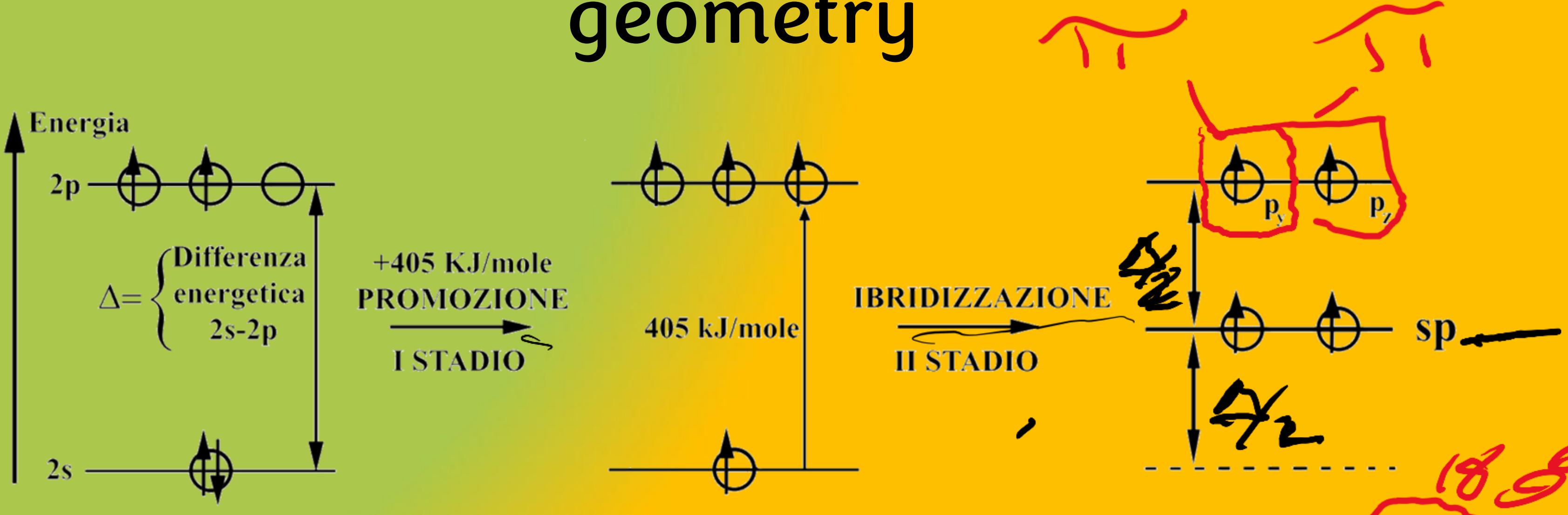


varie combinazioni degli orbitali sp^2 originano per ogni C 3 legami σ

Better Picrture

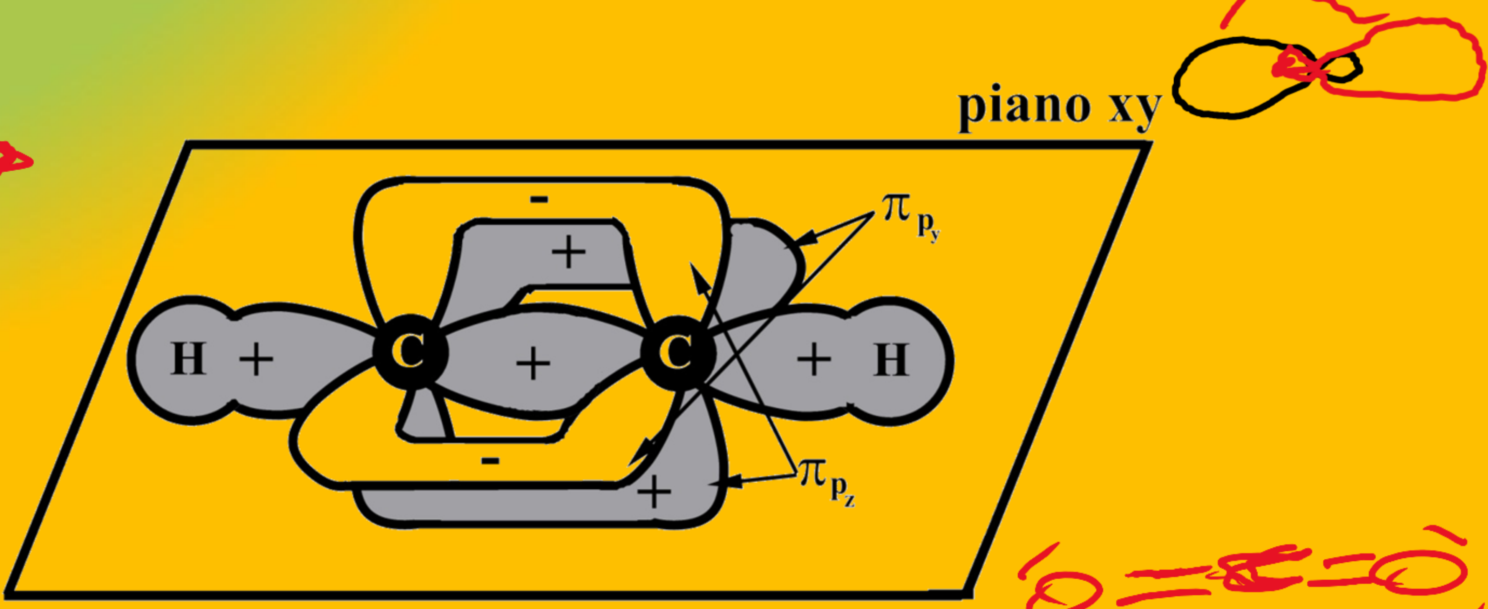


Ethine (acethylene), sp → 2 σ bonds, linear geometry



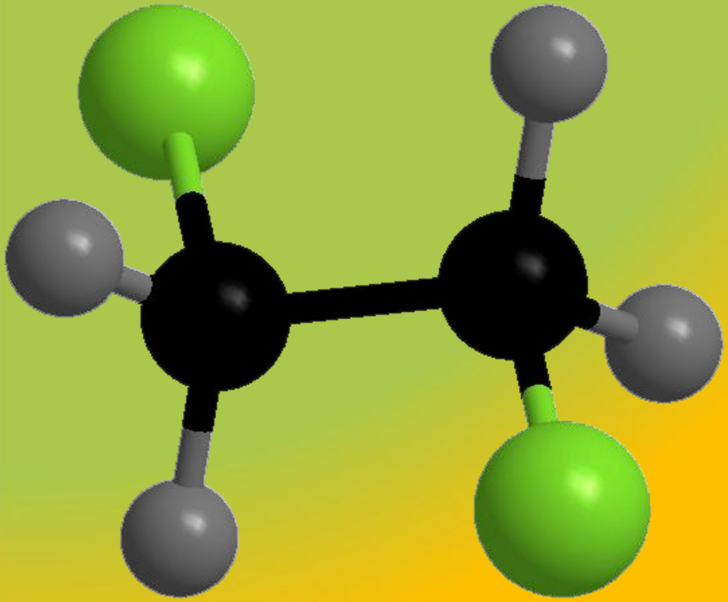
180°

N≡N →

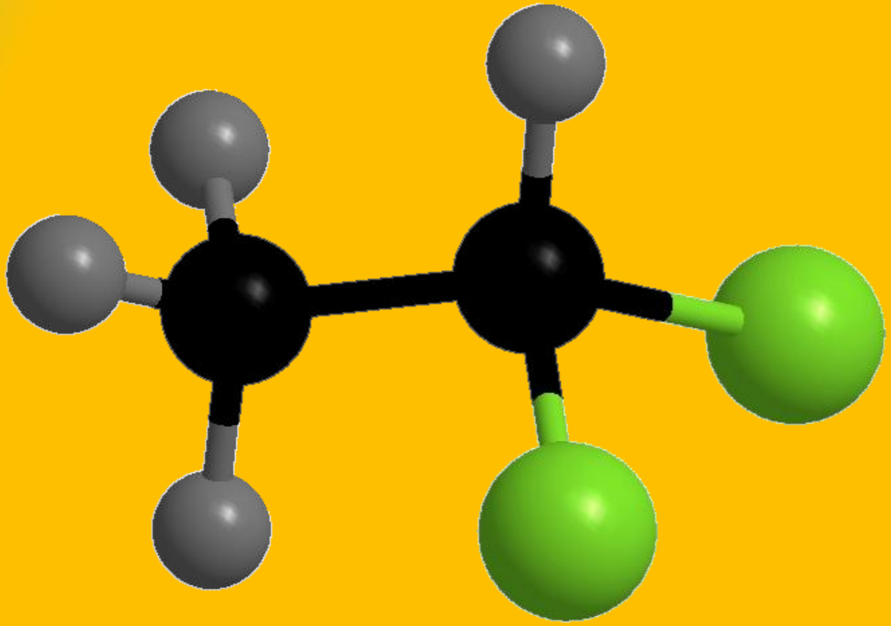


(O=C=O)

Functional isomers

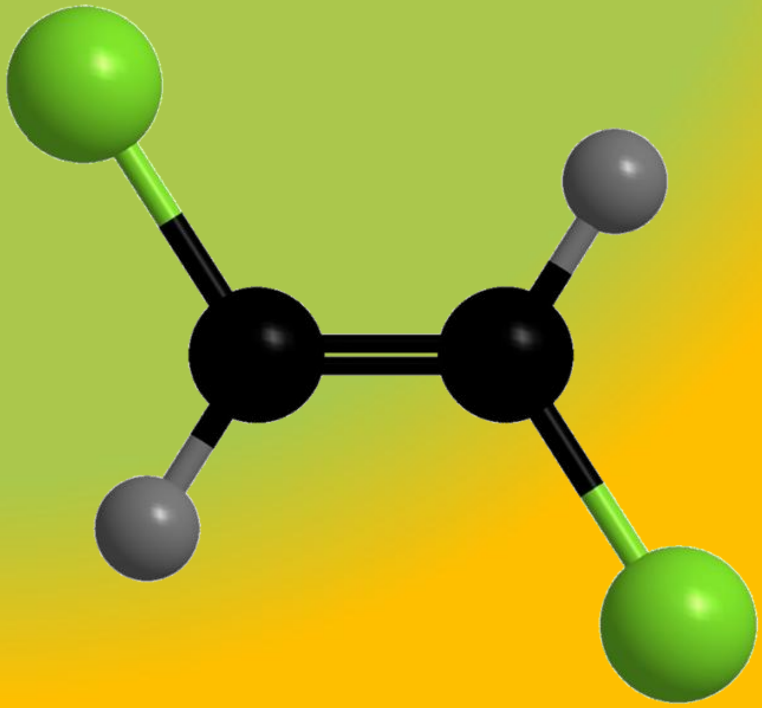


1,2-dicloroetano

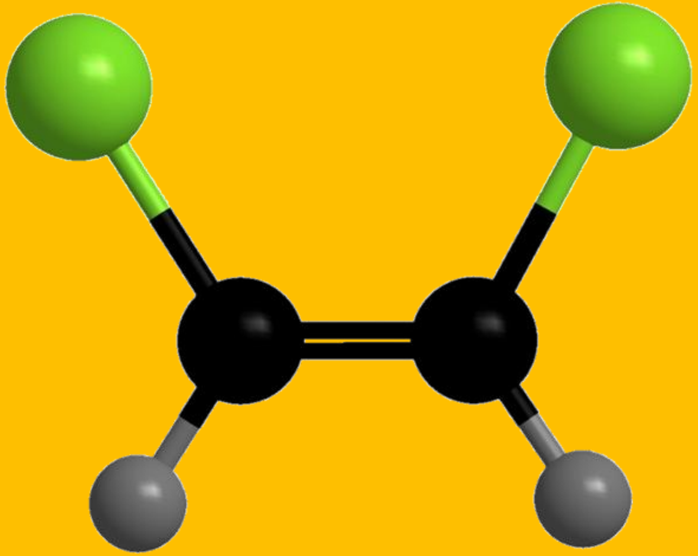


1,1-dicloroetano

Geometric isomers

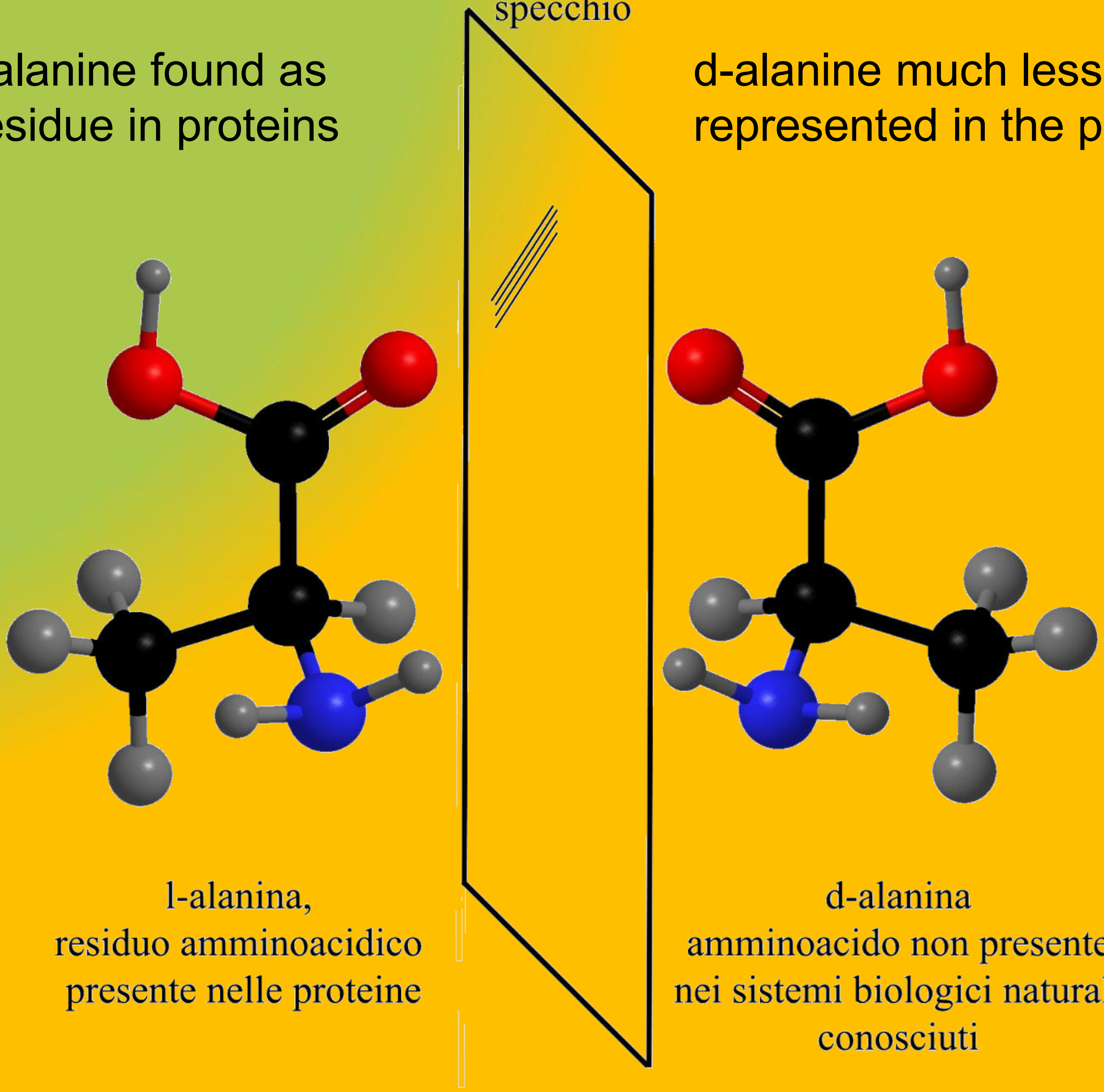


trans-dicloroetilene



cis-dicloroetilene

Optical isomers



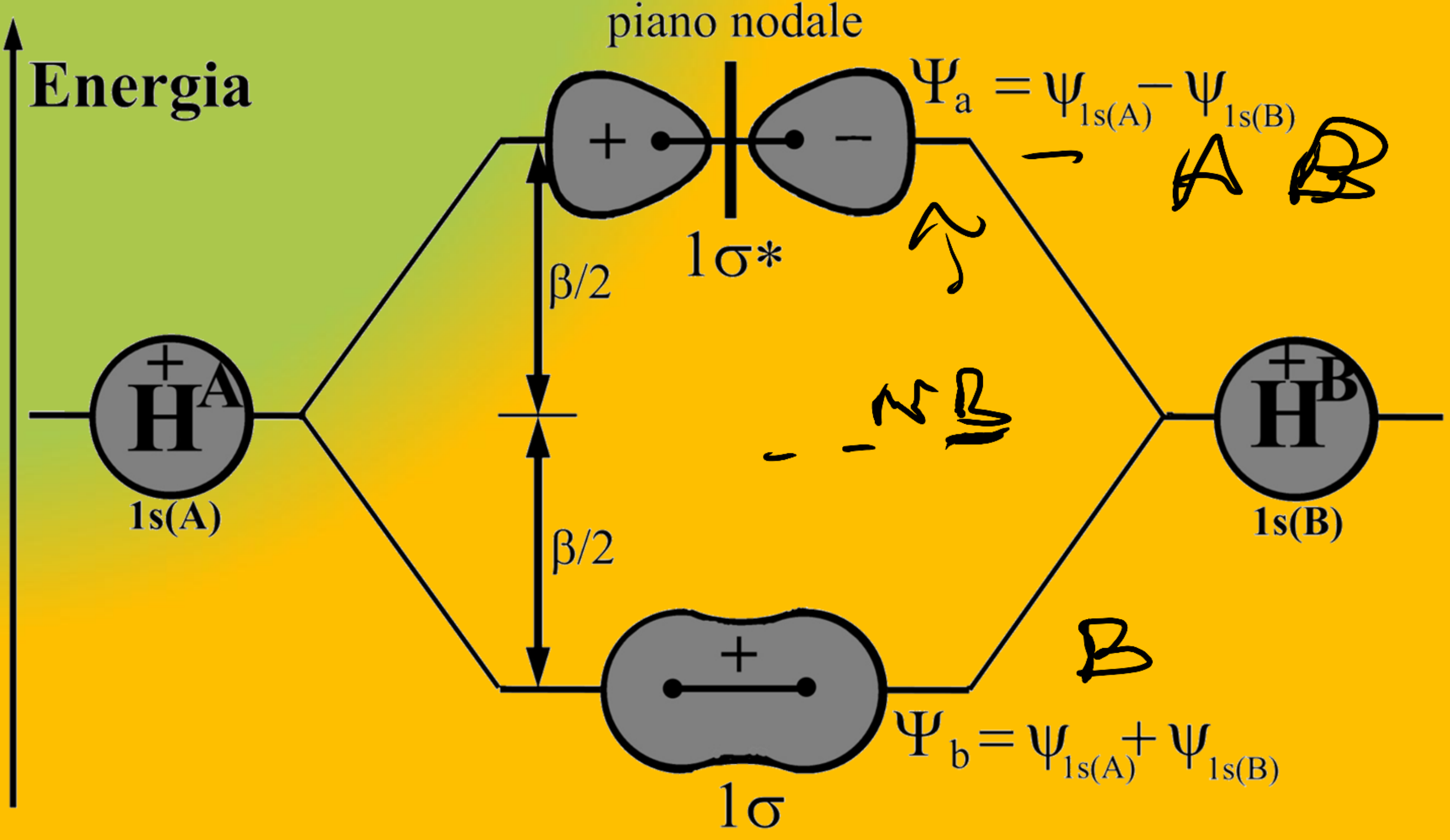
l-alanine found as
residue in proteins

d-alanine much less
represented in the planet

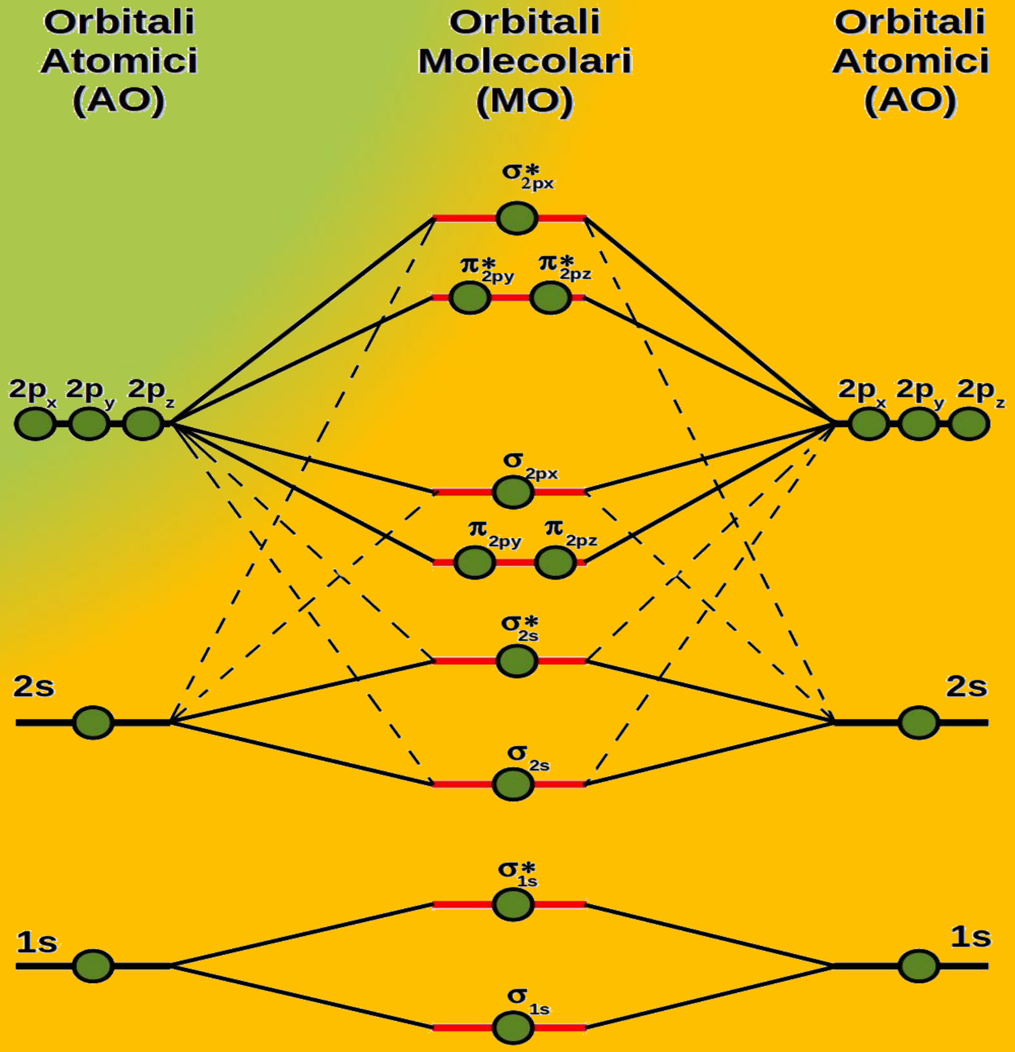
l-alanina,
residuo amminoacidico
presente nelle proteine

d-alanina
amminoacido non presente
nei sistemi biologici naturali
conosciuti

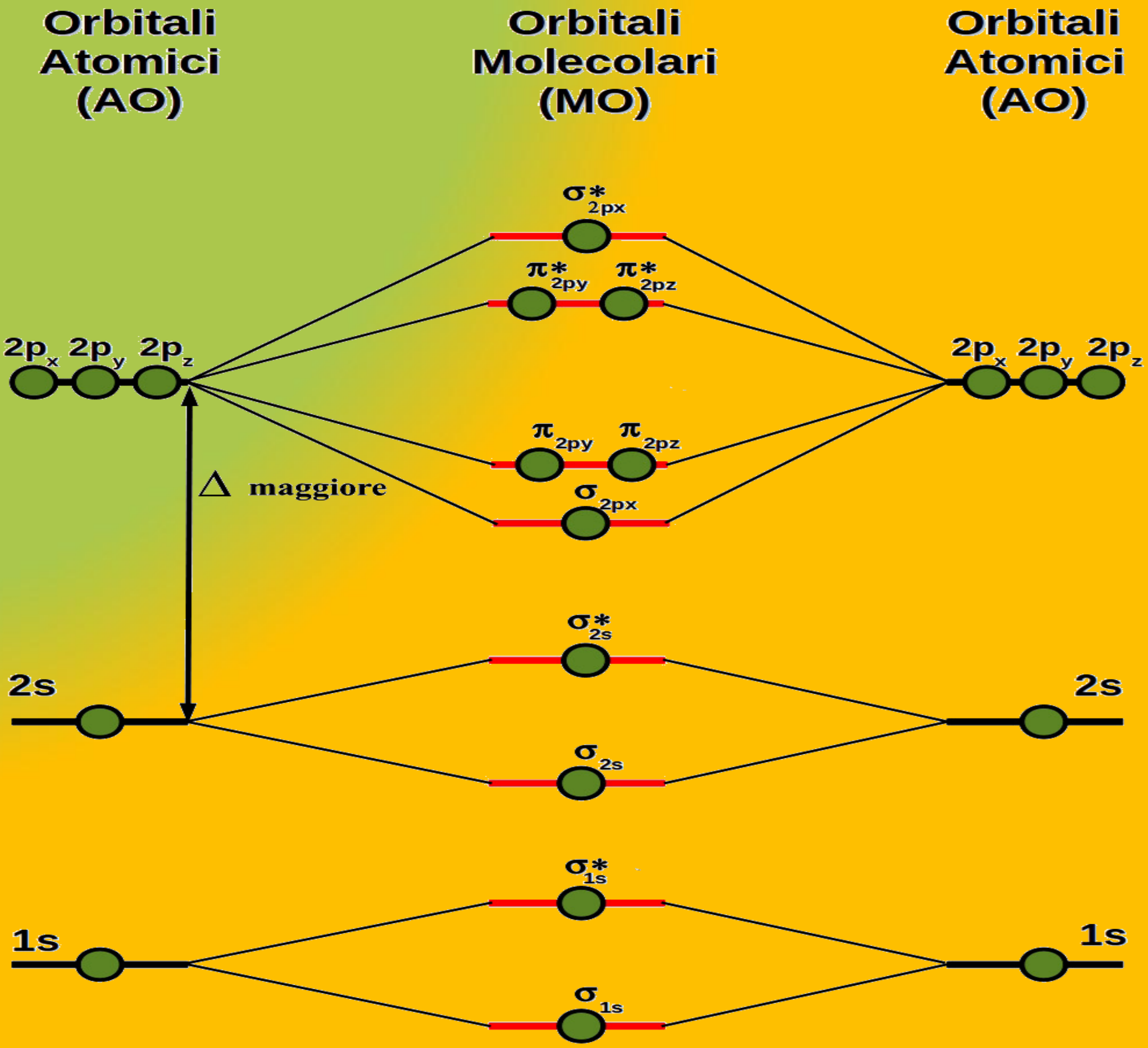
MOT
molecular orbital theory



MOT diatomic molecules up to nitrogen



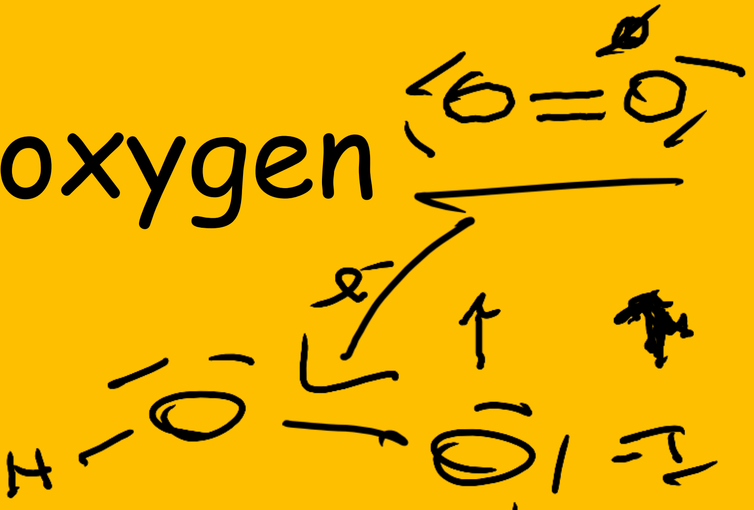
O_2 e F_2

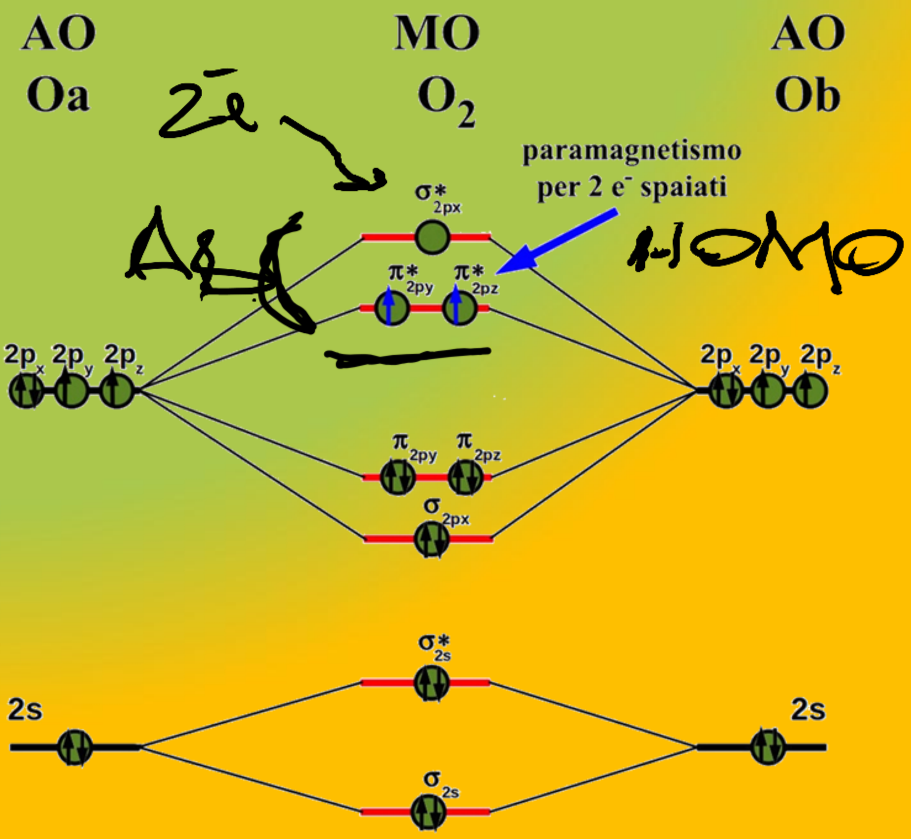

Orbitali Atomici (AO)
Orbitali Molecolari (MO)
Orbitali Atomici (AO)
σ^*_{2px}
π^*_{2py}
π^*_{2pz}
$2p_x$ $2p_y$ $2p_z$
$2p_x$ $2p_y$ $2p_z$
π_{2py}
π_{2pz}
Δ maggiore
σ_{2px}
σ^*_{2s}
2s
2s
σ_{2s}
σ^*_{1s}
1s
1s
σ_{1s}

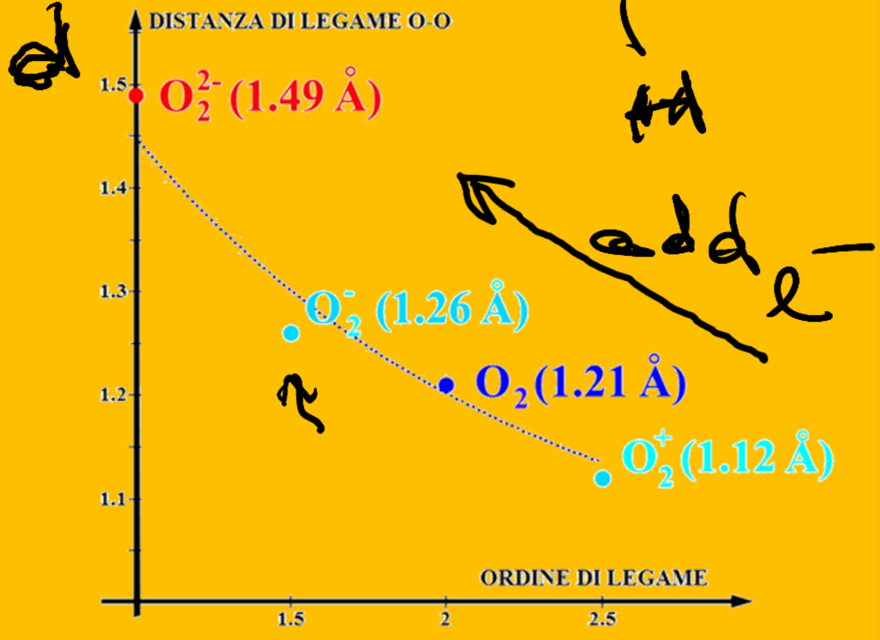
Electronic configuration of diatomic molecules

Molecola	Configurazione elettronica	Elettroni spaiati	Ordine di legame
Li_2	$(kk),(\sigma_s)^2$	0	1
Be_2	$(kk),(\sigma_s)^2,(\sigma_s*)^2$	0	0
B_2	$(kk),(\sigma_s)^2,(\sigma_s*)^2,(\pi_{py})^1,(\pi_{pz})^1$	2	1
C_2	$(kk),(\sigma_s)^2,(\sigma_s*)^2,(\pi_{py})^2,(\pi_{pz})^2$	0	2
N_2	$(kk),(\sigma_s)^2,(\sigma_s*)^2,(\pi_{py})^2,(\pi_{pz})^2,(\sigma_{px})^2$	0	3
O_2	$(kk),(\sigma_s)^2,(\sigma_s*)^2,(\sigma_{px})^2,(\pi_{py})^2,(\pi_{pz})^2,(\pi_{py}*)^1,(\pi_{pz}*)^1$	2	2
F_2	$(kk),(\sigma_s)^2,(\sigma_s*)^2,(\sigma_{px})^2,(\pi_{py})^2,(\pi_{pz})^2,(\pi_{py}*)^2,(\pi_{pz}*)^2$	0	1

The case for oxygen





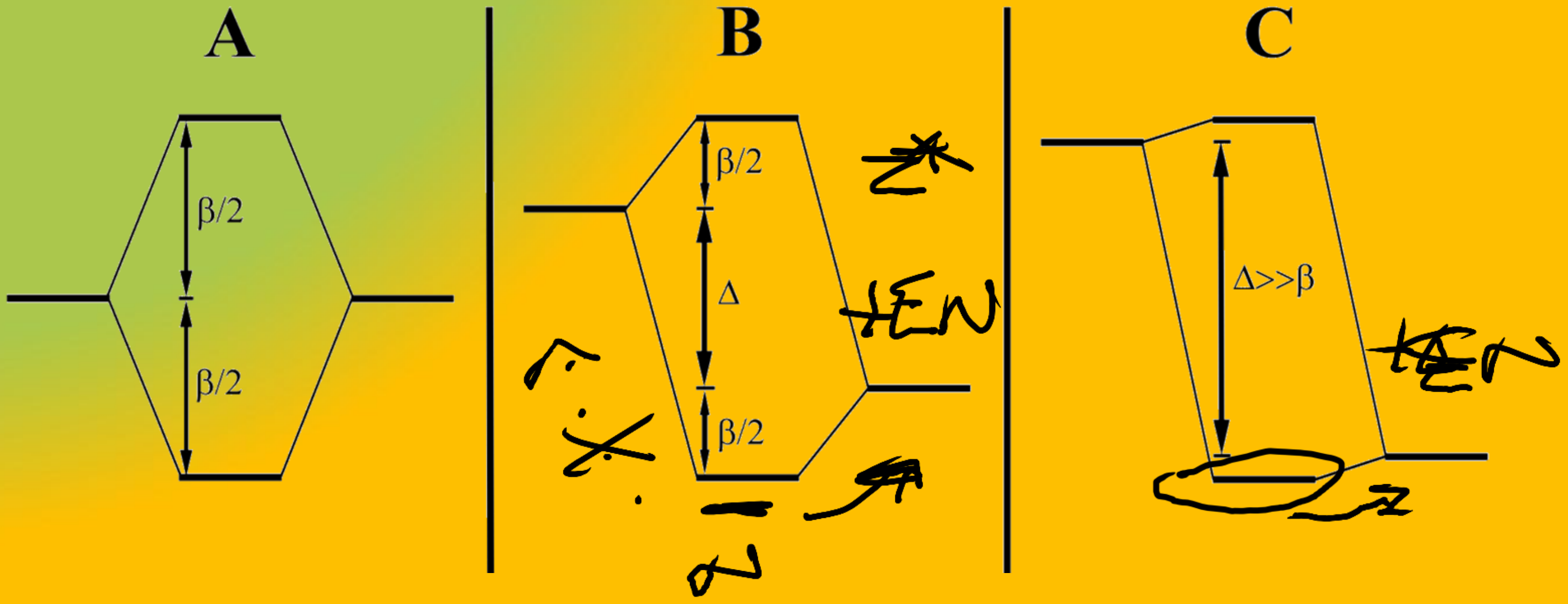


SOD

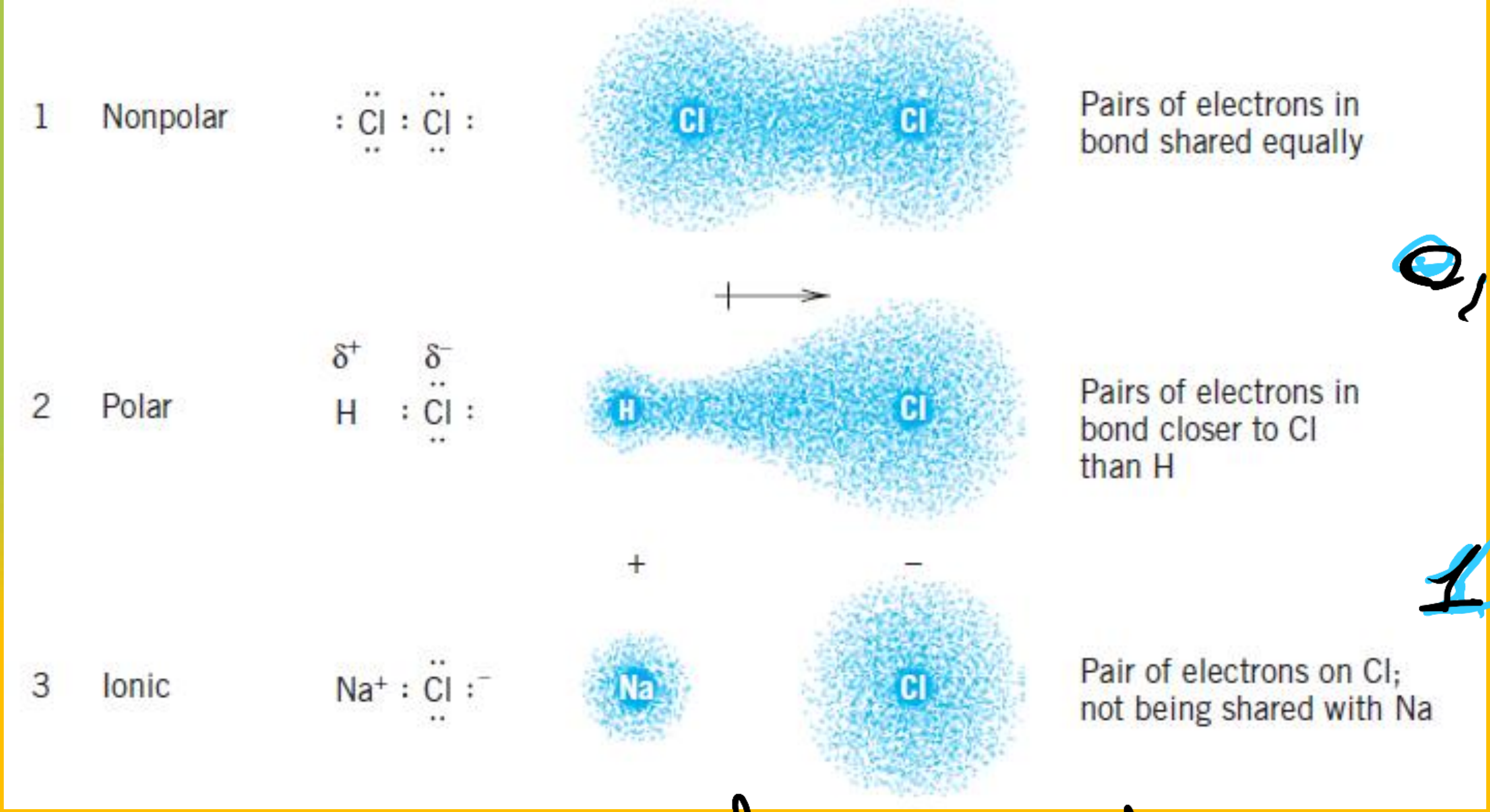
O^{2-}

BOND ORDER

Omopolare, eteropolare e ionico



Pictorial terms



1	Nonpolar	:Cl:Cl:	Pairs of electrons in bond shared equally
2	Polar	δ^+ H :Cl: δ^-	Pairs of electrons in bond closer to Cl than H
3	Ionic	Na^+ :Cl:$^-$	Pair of electrons on Cl; not being shared with Na

ΔEN

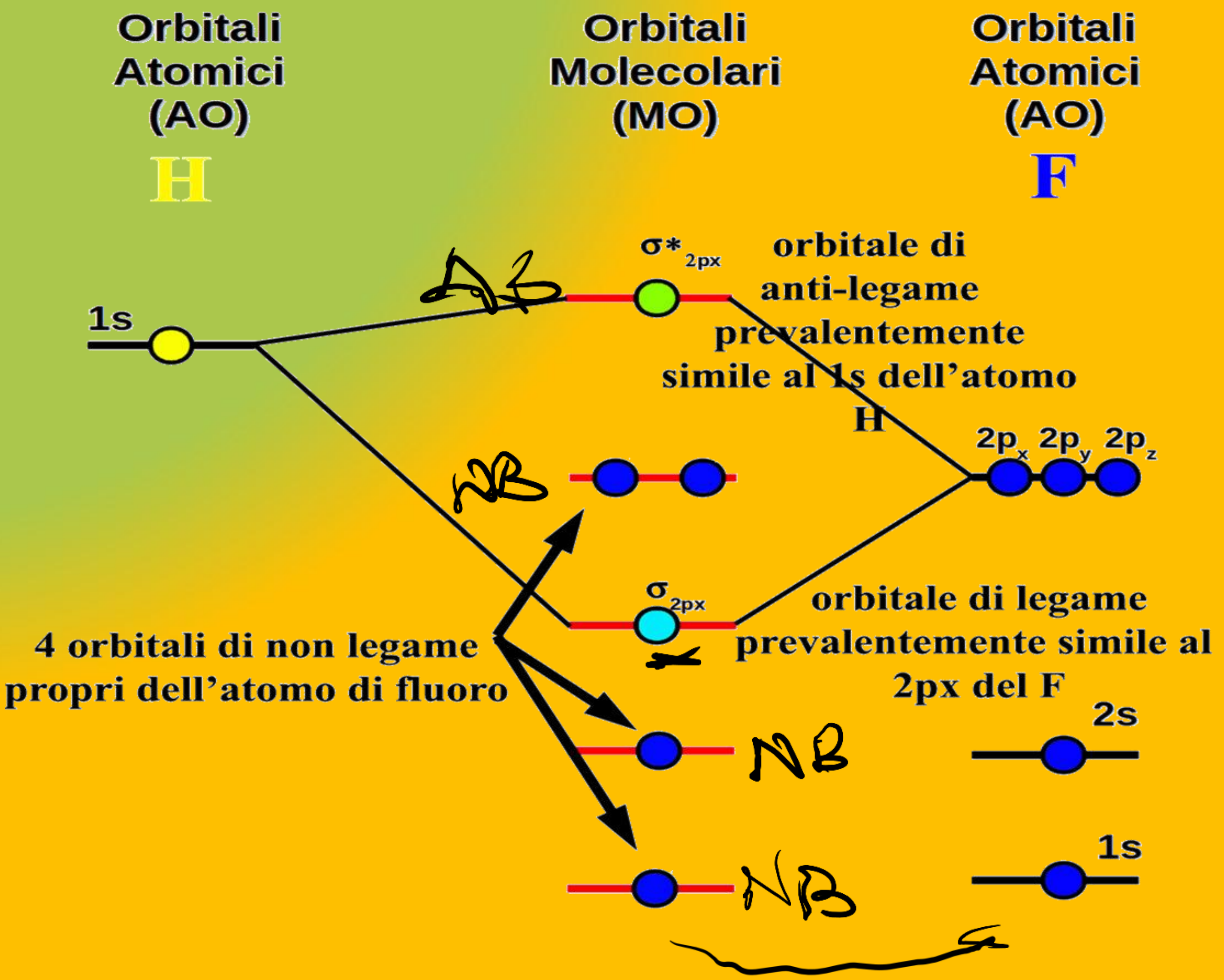
0,4

1,8

CATION ANION

HF eteropolare

H—F



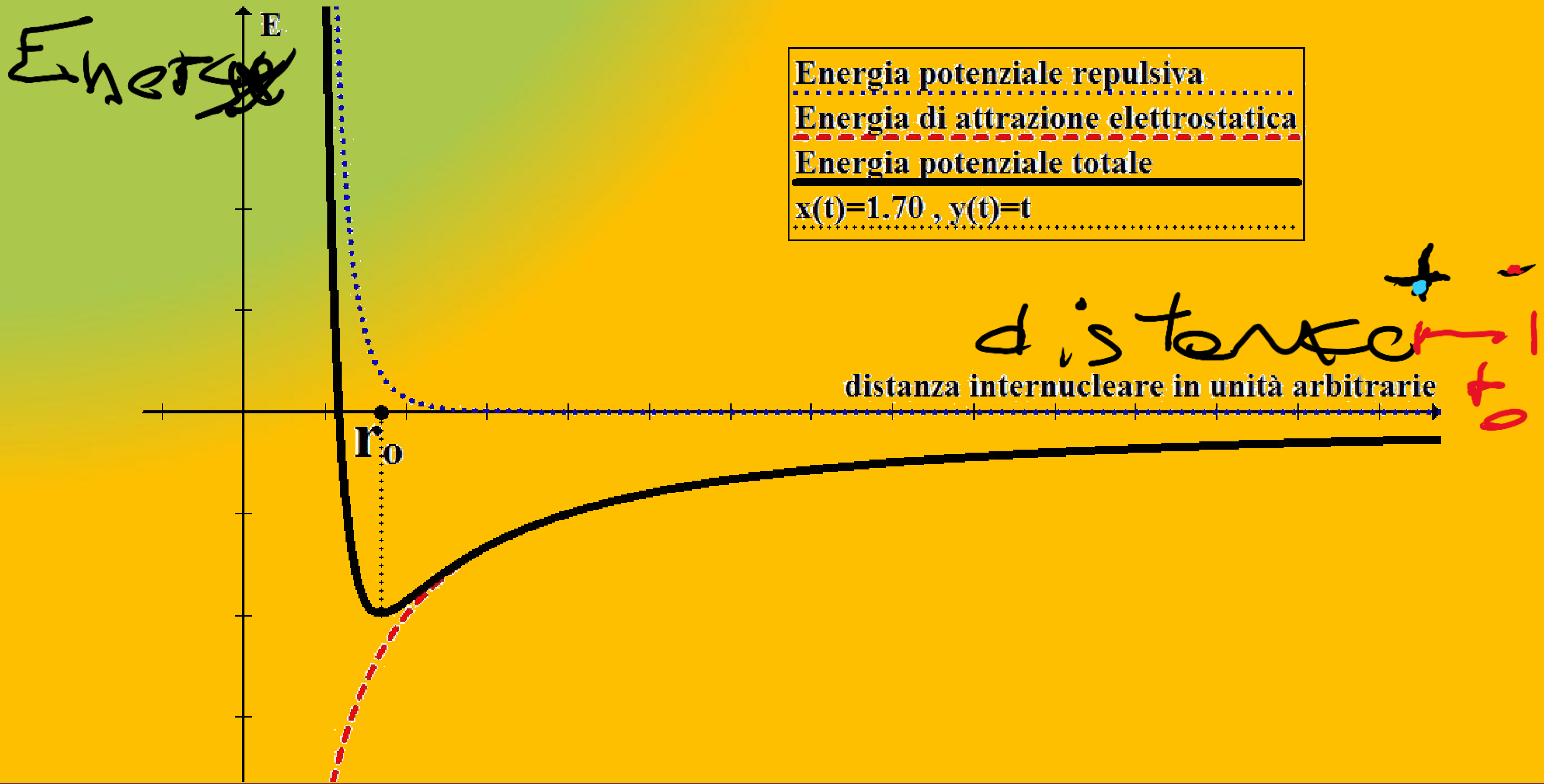
orbitale di anti-legame prevalentemente simile al 1s dell'atomo H

orbitale di legame prevalentemente simile al 2px del F

4 orbitali di non legame propri dell'atomo di fluoro

Ionic bond

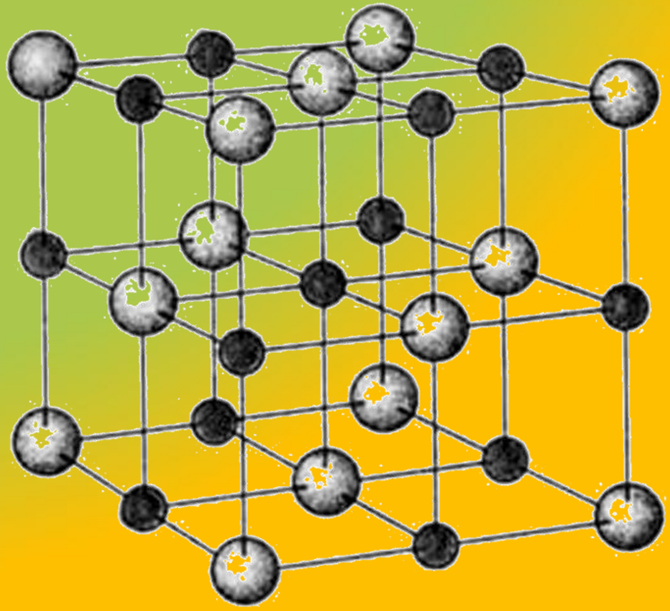
It is the extreme case of polar bonding envisagable as the total transfer of the pair of bonding electrons to the most electronegative center. The cohesion between the nuclei is therefore totally dependent on the pure electrostatic attraction between charged particles of opposite sign

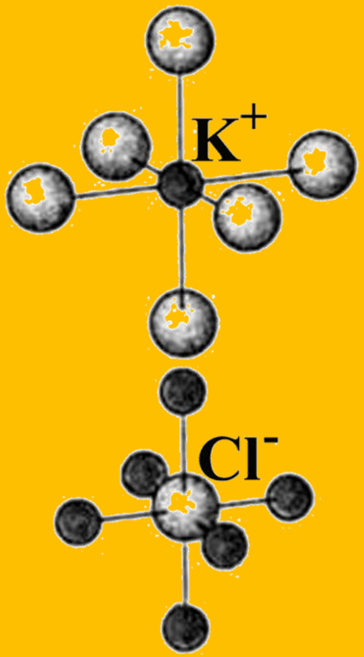


Crystal lattices (ionic solids)

ionic com

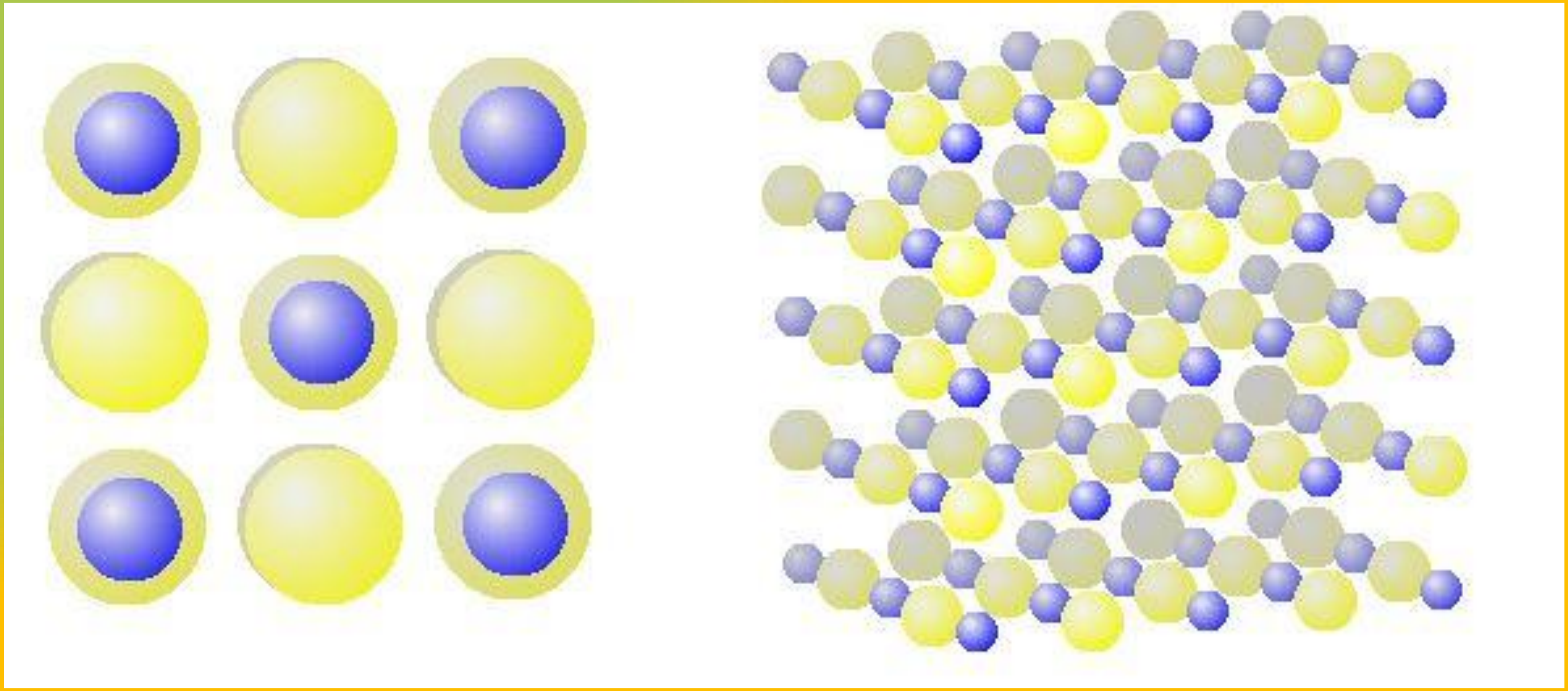
K^+ -ve Cl^-



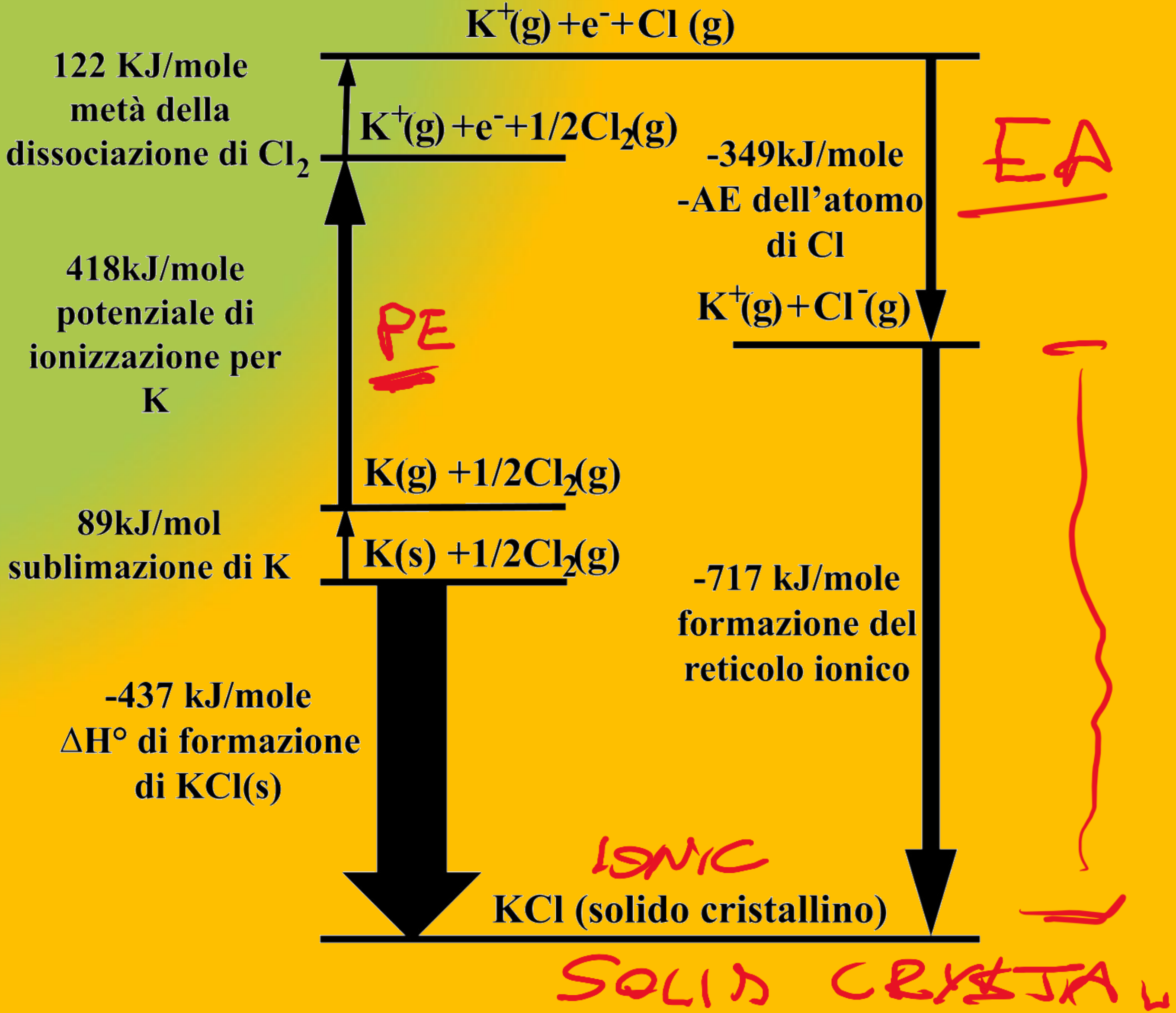


LATTICE ENERGY

Lattices II



Born-Haber cycle



$K^+(g) + e^- + Cl\ (g)$

122 KJ/mole
metà della
dissociazione di Cl_2

$K^+(g) + e^- + 1/2Cl_2(g)$

-349kJ/mole
-AE dell'atomo
di Cl

EA

418kJ/mole
potenziale di
ionizzazione per
K

PE

$K^+(g) + Cl^-(g)$

$K(g) + 1/2Cl_2(g)$

89kJ/mol
sublimazione di K

$K(s) + 1/2Cl_2(g)$

-717 kJ/mole
formazione del
reticolo ionico

-437 kJ/mole
ΔH° di formazione
di KCl(s)

IONIC

KCl (solido cristallino)

SOLID CRYSTAL

Madelung lattice and constant energy

$\Delta H^\circ_{ret} = - 6\ ke^2N/\ r_o + 12\ ke^2N/(r_o \cdot \sqrt{2}) - 8\ ke^2N/(r_o \cdot \sqrt{3}) + 6ke^2N/2r_o + \dots$

Mettendo in evidenza - $ke^2N/\ r_o$

$\Delta H^\circ_{ret} = - ke^2N/\ r_o\ (6 - 12/\sqrt{2} + 8/\sqrt{3} - 6/2 + \dots)$

M is approximately 1.747..... For KCl and NaCl then it is different for different types of pakings

Theory and practice....

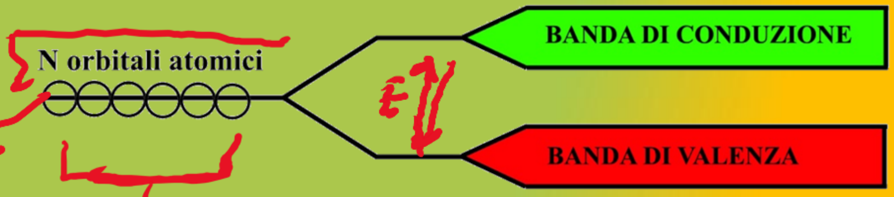
By substituting the value of r_o and the appropriate Madelung constant, the lattice energies are also obtained theoretically: with the same M the most compact lattices have the highest lattice enthalpy in absolute value (NaCl = 864; KCl = 773 Kj/mol)

$\Delta H^\circ_{ret} = - ke^2N/ r_o (6 - 12/ + 8/ - 6/2 +....) =$
$= (M) - ke^2N/ r_o$

Metals

E = hν

conduction band



N/2 orbitali molecolari di antilegame

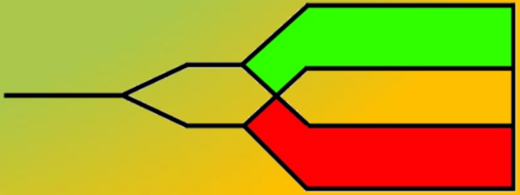
N/2 antibonding molecular orbitals

N/2 orbitali molecolari di legame

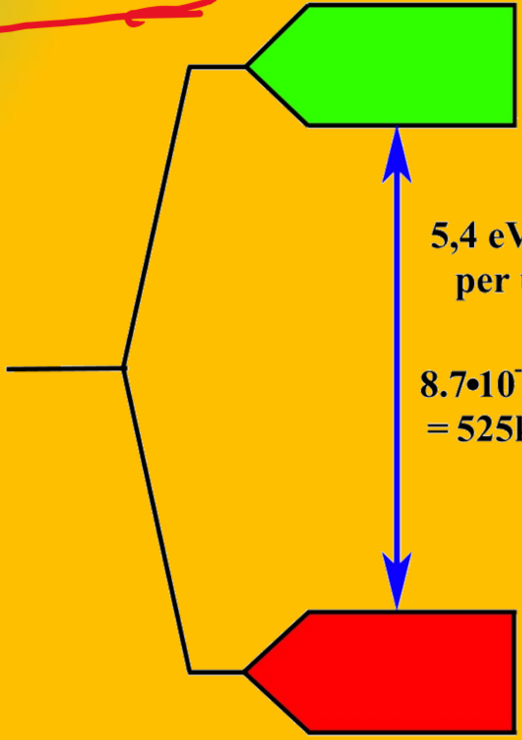
N/2 bonding molecular orbitals

valence band

N = Ma



Conduttori (Metalli):
Le bande sono sovrapposte



Diamante (isolante):
Le bande sono ben distanziate

Metals display very close or overlaped bands.

Insulators have a large Energy gap between the valence band and the conduction band.

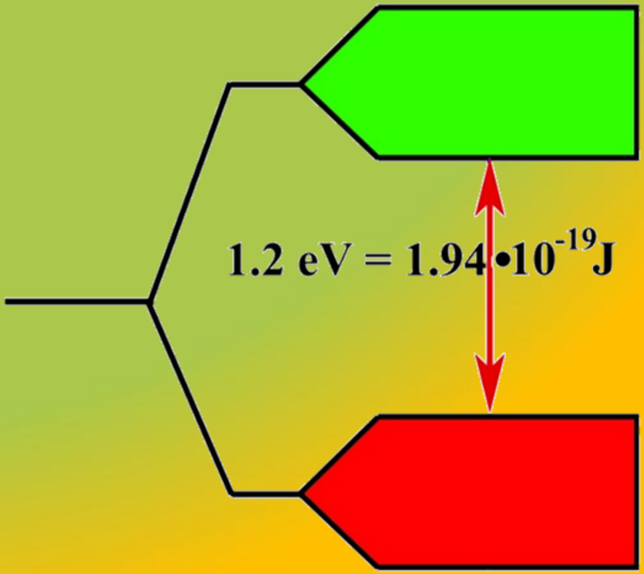
Metallic bond

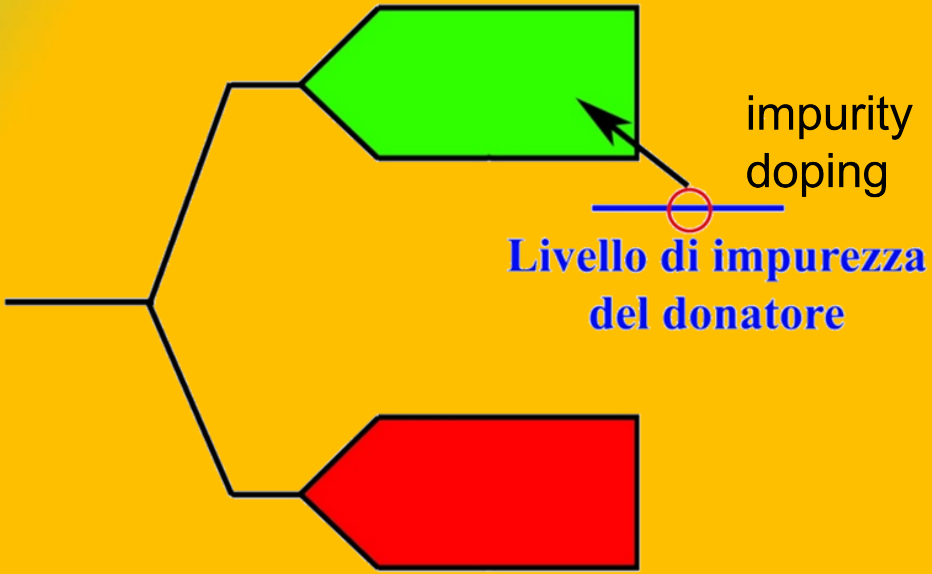
- **Metallic Bond**
- A metallic bond is the type of chemical bond found in metals, where atoms are bonded in a structure that allows for the delocalization of electrons. In metallic bonding, atoms in a metal release some of their electrons to form a "sea" of free-moving, delocalized electrons. These electrons are not bound to any particular atom and can move throughout the metal structure, which explains many of the unique properties of metals, such as conductivity, malleability, and ductility.
- Here's a summary of the key aspects of metallic bonding:

1. **Electron Sea Model:** In metals, atoms release some of their outer (valence) electrons, which move freely throughout the entire structure. This "sea" of electrons acts as a glue, holding positively charged metal ions in place.
2. **Conductivity:** The free electrons in a metal's structure allow it to conduct electricity easily because electrons can move in response to an electric field. Similarly, this mobility makes metals good conductors of heat.
3. **Malleability and Ductility:** Since the electrons are not attached to any specific atom, metal atoms can slide past each other without breaking the bond. This explains why metals can be hammered into sheets (malleability) and drawn into wires (ductility).


e⁻
e⁻

Semiconductors





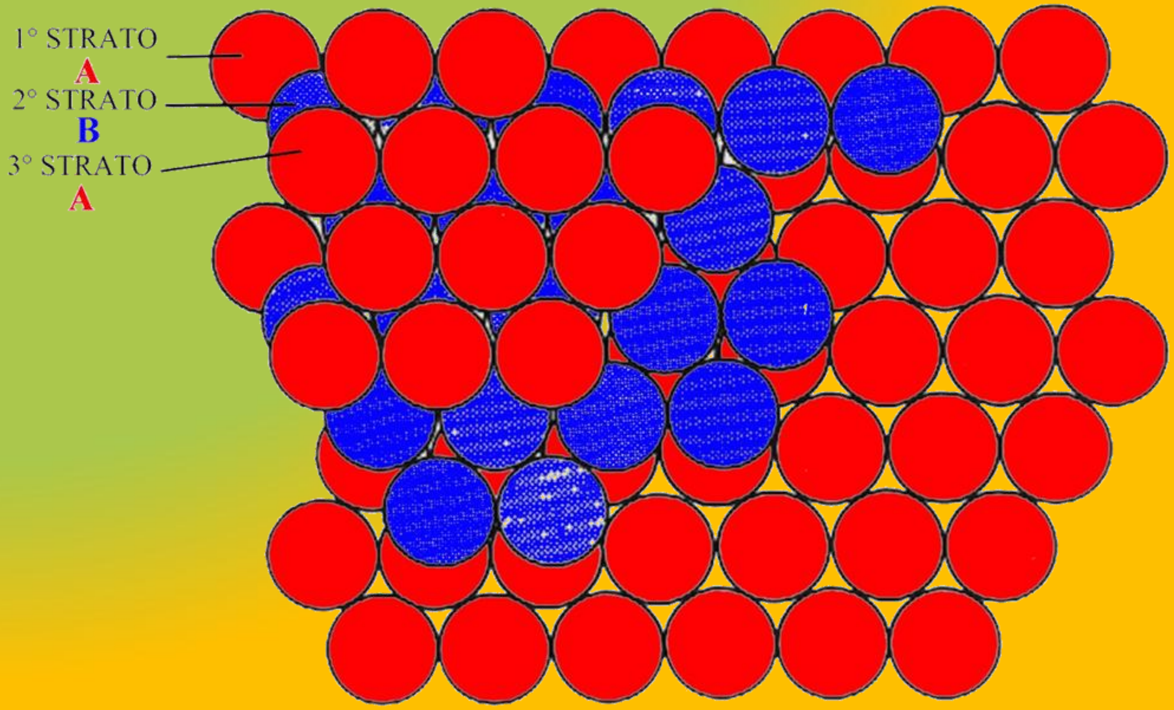
Silicio (semiconduttore)

Si

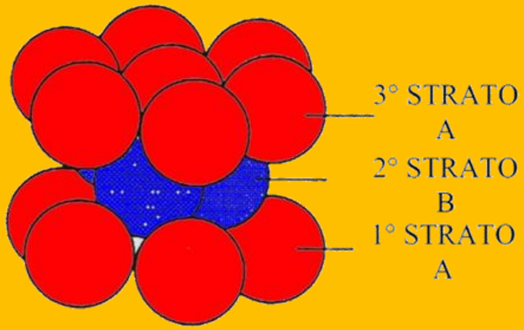
**Silicio "drogato" con
un elemento del V gruppo
(semiconduttore "n")**

hcp (HEXAGONAL CLOSE PACKED)

PROIEZIONE VERTICALE



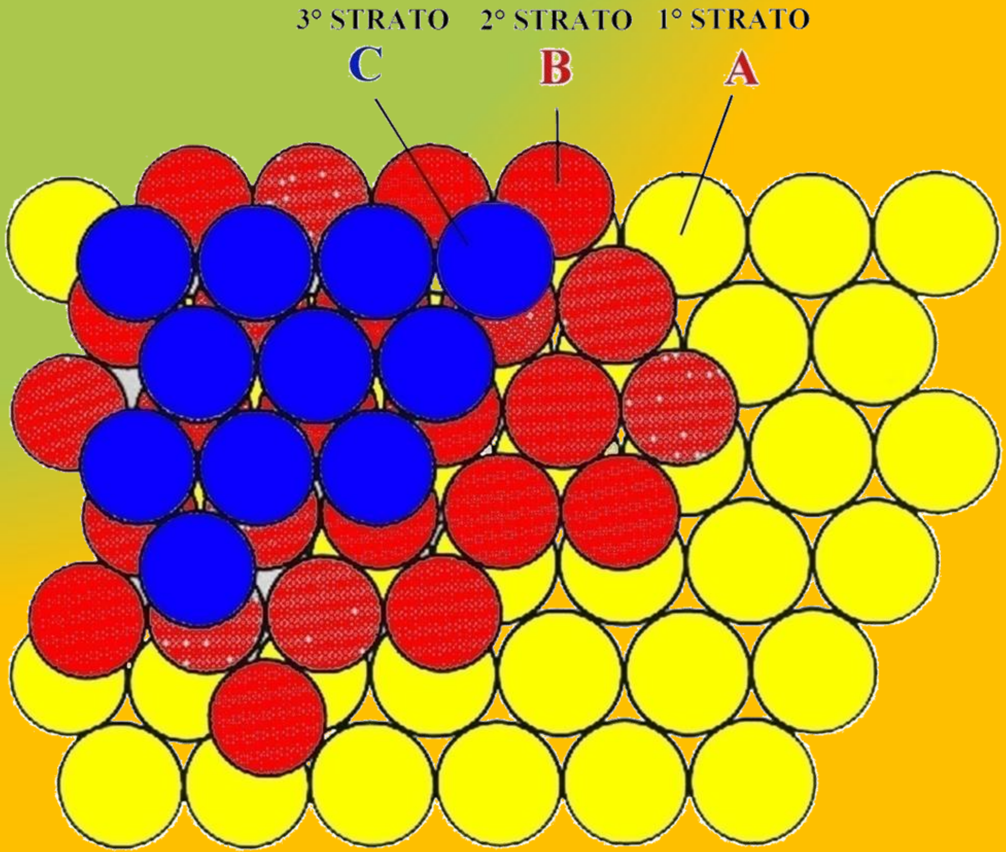
PROIEZIONE TRASVERSALE



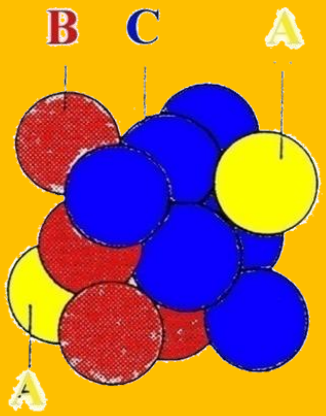
CCP

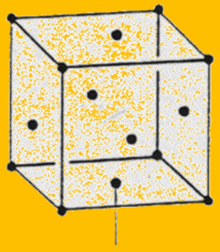
ccp (cubic-close packed) o fcc (face-centered cubic)

PROIEZIONE VERTICALE



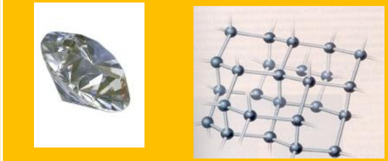
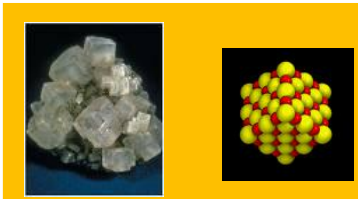
PROIEZIONE TRASVERSALE





CHEMICAL BONDS

TYPES OF CRYSTALLINE SOLIDS

Cohesive forces	Type of Solid	Examples	Images
Continuous Covalent bonds	Covalent network Solids. Also polymeric covalent solids	C(diamond), SiO_2(quartz)	
Ionic Bond	Ionic solids	NaCl, $CaSO_4$, MgO, $NaHCO_3$	
Metal Bond	Metals	Cu, Al, Fe, Au	
Intermolecular interactions	Molecular solids	sugars, urea, ice, solid CO_2, solid I_2, solid biological molecules