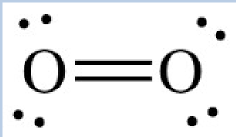
1. Valence Bond Theory

Valence Bond theory – Limitations

- Assumes electrons are highly localized between the nuclei (sometimes requires resonance structures).
- Doesn't easily deal with unpaired electrons (incorrectly predicts physical properties in some cases).
- Doesn't provide direct information about bond energies.

Example: O_2

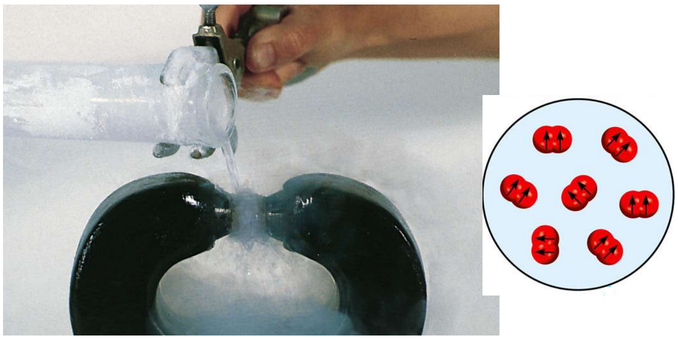
- O atoms with sp^2 hybridization
- 1 σ bond and 1 π bond
- Lone pairs in sp^2 orbitals
- No unpaired electrons!



All electrons are paired $\longrightarrow$ Contradicts experiment!

1. Valence Bond Theory

Valence Bond theory – Limitations



Experiments show O_2 is *paramagnetic*

A quick note on magnetism…

Paramagnetic
The molecule contains **unpaired electrons** and is attracted to (has a positive susceptibility to) an applied magnetic field

Diamagnetic
The molecule contains only **paired electrons** and is ***not*** attracted to (has a negative susceptibility to) an applied magnetic field

2. Molecular Orbitals

When atomic orbitals interact to form a bond, the result is the formation of new MOLECULAR ORBITALS, that in principle spread all over the molecule.

$$\mathrm{H}\Psi = \mathrm{E}\Psi$$

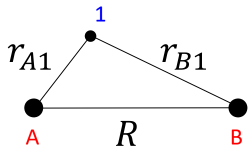
Ψ is called **MOLECULAR ORBITAL**

Important features of molecular orbitals:

1. The molecular orbitals are the solutions of the same Schrödinger equation applied to the molecule.
2. All the atomic orbitals of appropriate symmetry contribute to a molecular orbital.
3. Each molecular orbitals can hold 2 electrons with opposite spins.
4. The electron probability for the molecular orbital is given by $|\Psi|^2$.
5. Orbitals are conserved: in bringing together 2 atomic orbitals, we have to end up with 2 molecular orbitals!

2. Molecular Orbitals

Molecule H_2^+



$$H\Psi = E\Psi$$

$$H = \underbrace{-\frac{\hbar^2}{2m_e}\nabla_1^2}_{\text{Related to kinetic energy of electron}} \underbrace{- \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{A1}} + \frac{1}{r_{B1}} - \frac{1}{R}\right)}_{\text{Related to electrostatic interaction between electron and nuclei}}$$

Ψ is called **MOLECULAR ORBITAL**

The Schrödinger equation can be solved for H_2^+ but the wavefunctions are very complicated functions and cannot be extended to polyatomic molecules.

2. Molecular Orbitals

A simpler procedure shall be adopted that, while more approximated, can be extended to other molecules.

If an electron can be found in an atomic orbital belonging to atom A and also in an atomic orbital belonging to atom B, the overall wavefunction is a superimposition of the two orbitals:

$$\boxed{\Psi_{\pm} = c_A\Psi_A \pm c_B\Psi_B}$$ Linear Combination of Atomic Orbitals – LCAO

For H_2^+:

$$\Psi_{\pm} = N_{\pm}\,(\Psi_{H1sA} \pm \Psi_{H1sB})$$

$$\Psi_{+} = N_{+}(\Psi_{H1sA} + \Psi_{H1sB})$$

Bonding orbital

$$\Psi_{-} = N_{-}(\Psi_{H1sA} - \Psi_{H1sB})$$

Anti-bonding orbital

2. Molecular Orbitals

Bonding orbital

$$\Psi_+ = N_+(\Psi_{H1sA} + \Psi_{H1sB})$$

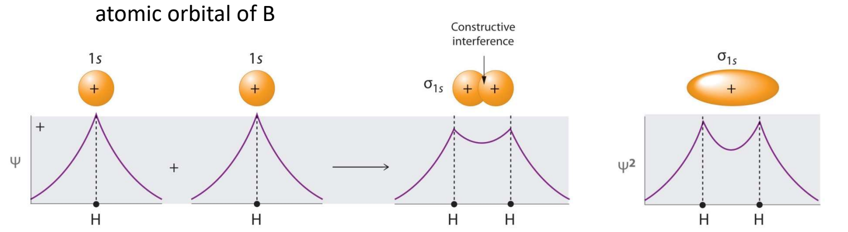
The probability density is:

$$\Psi_+^2 = N_+^2\left(\Psi_{H1sA}^2 + \Psi_{H1sB}^2 + \underbrace{2\Psi_{H1sA} * \Psi_{H1sB}}\right)$$

Probability density if electron is confined in the atomic orbital of A

Probability density if electron is confined in the atomic orbital of B

Constructive interference: enhancement of probability in the internuclear region



(a) Wave functions combined for σ_{1s} (b) Bonding probability density

2. Molecular Orbitals

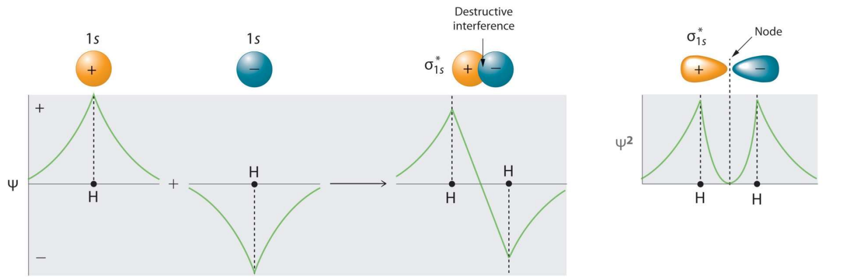
Anti-bonding orbital

$$\Psi_- = N_-(\Psi_{H1sA} - \Psi_{H1sB})$$

The probability density is:

$$\Psi_-^2 = N_-^2\left(\Psi_{H1sA}^2 + \Psi_{H1sB}^2 - \underbrace{2\Psi_{H1sA} * \Psi_{H1sB}}\right)$$

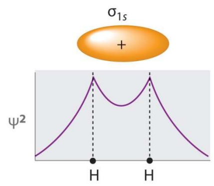
Destructive interference : reduction of probability in the internuclear region



(c) Wave functions combined for σ^*_{1s} (d) Antibonding probability density

2. Molecular Orbitals

Molecule H_2^+



(b) Bonding probability density

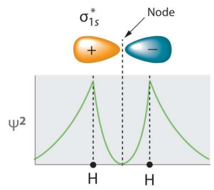
Cylindrical symmetry around the internuclear axis:

σ orbital

Bonding orbital

- Improved electron density in the space between the atoms.

σ_{1s}



Anti-bonding orbital

- Improved electron density in the region outside the atoms and with a nodal plane in the middle.

σ^*_{1s}

(d) Antibonding probability density

2. Molecular Orbitals

$$H\Psi = E\Psi$$

What about energy of the molecular orbitals?

$$E_{\pm} = E_{H1s} + \frac{e^2}{4\pi\varepsilon_0 R} - \frac{j \pm k}{1 \pm S}$$

Energy of 1s orbital of H atom

Potential energy deriving from repulsion between nuclei

+ for σ_{1s}
- for σ^*_{1s}

2. Molecular Orbitals

$$\mathrm{H\Psi = E\Psi}$$

What about energy of the molecular orbitals?

$$\mathrm{E_{\pm} = E_{H1s} + \frac{e^2}{4\pi\varepsilon_0 R} - \frac{j \pm k}{1 \pm S}}$$

$$S = \int \Psi_{H1sA}\Psi_{H1sB}d\tau = \left\{1 + \frac{R}{a_0} + \frac{1}{3}\left(\frac{R}{a_0}\right)^2\right\}e^{-R/a_0}$$

Overlap integral: extent of overlap of the two atomic wavefuntions

$$j = \frac{e^2}{4\pi\varepsilon_0 R}\int \frac{\Psi^2_{H1sA}}{r_B}d\tau = \frac{e^2}{4\pi\varepsilon_0 R}\left\{1 - \left(1 + \frac{R}{a_0}\right)e^{-2R/a_0}\right\}$$

Interaction of a nucleus with the electron density centered on the other nucleus

$$k = \frac{e^2}{4\pi\varepsilon_0 R}\int \frac{\Psi_{H1sA}\Psi_{H1sB}}{r_A}d\tau = \frac{e^2}{4\pi\varepsilon_0 a_0}\left(1 + \frac{R}{a_0}\right)e^{-R/a_0}$$

Interaction of a nucleus with the excess electron density deriving from overlap

All integrals are positive values!

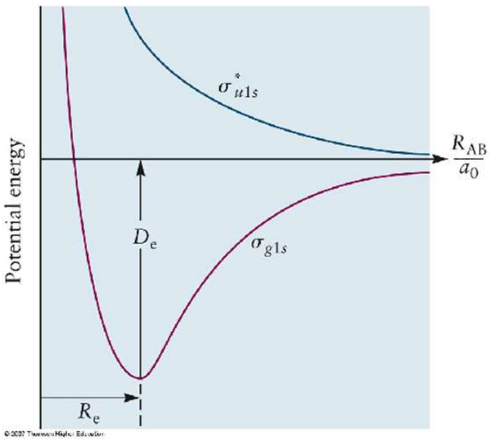
2. Molecular Orbitals

$$\mathrm{H\Psi = E\Psi}$$

What about energy of the molecular orbitals?

$$E_{\pm} = E_{H1s} + \frac{e^2}{4\pi\varepsilon_0 R} - \frac{j \pm k}{1 \pm S}$$

Plotting versus R



2. Molecular Orbitals

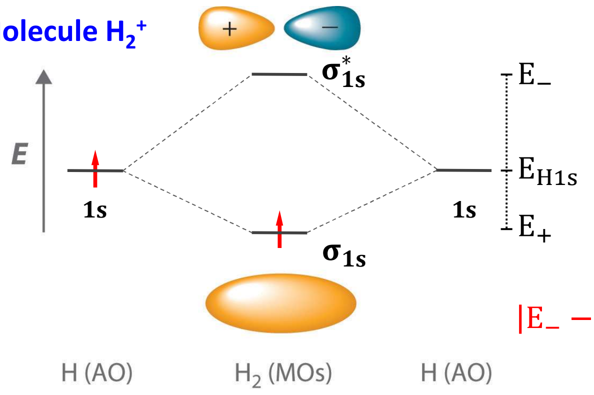
$$H\Psi = E\Psi$$

What about energy of the molecular orbitals?

$$E_{\pm} = E_{H1s} + \frac{e^2}{4\pi\varepsilon_0 R} - \frac{j \pm k}{1 \pm S}$$

<u>At the equilibrium distance:</u>

Molecule H_2^+

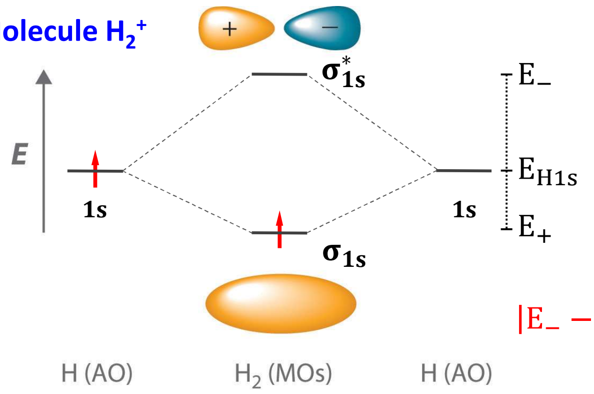


Because of electrostatic repulsion between nuclei:

$$|E_- - E_{H1s}| > |E_+ - E_{H1s}|$$

2. Molecular Orbitals

Molecule H_2^+



Because of electrostatic repulsion between nuclei:

$$|E_- - E_{H1s}| > |E_+ - E_{H1s}|$$

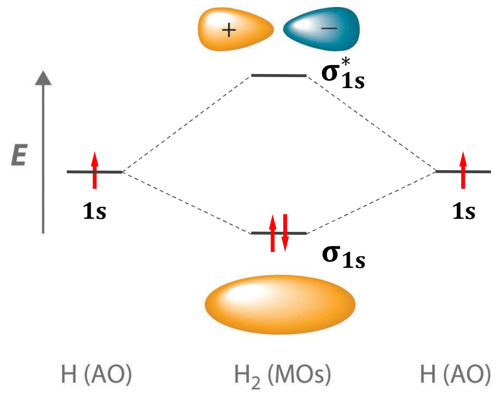
When we draw a molecular orbitals energy diagram:

- as the overlap between two atomic orbitals increases, the difference in energy between the resulting bonding and antibonding molecular orbitals increases;
- the interaction (overlapping) between atomic orbitals is greatest when they have the same energy.

2. Molecular Orbitals

Molecule H_2

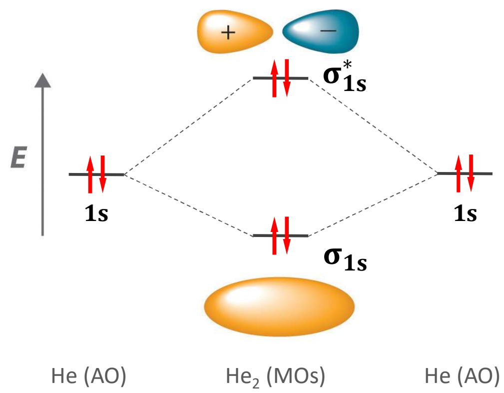
The same procedure is adopted, but the electron-electron repulsion must be taken into account. Although an exact solution cannot be obtained, the MO model allows to obtain qualitatively the same energy diagram for bonding and anti-bonding orbitals:



2. Molecular Orbitals

Molecule He_2

The same procedure than H_2:



2. Molecular Orbitals

Bond order $\boxed{b = \frac{1}{2}(n - n^*)}$

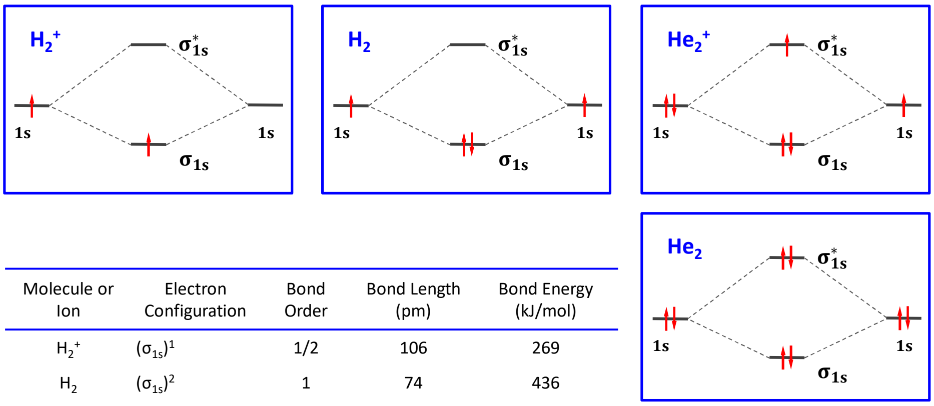
n Number of electrons in bonding orbitals

n^* Number of electrons in anti-bonding orbitals

- The greater the bond order between two atoms of a given pair of elements, the shorter the bond.
- The greater the bond order, the higher the bond strength.

2. Molecular Orbitals

Period 1 molecules



Molecule or Ion	Electron Configuration	Bond Order	Bond Length (pm)	Bond Energy (kJ/mol)
H_2^+	$(\sigma_{1s})^1$	1/2	106	269
H_2	$(\sigma_{1s})^2$	1	74	436
He_2^+	$(\sigma_{1s})^2(\sigma_{1s}^*)^1$	1/2	108	251
He_2	$(\sigma_{1s})^2(\sigma_{1s}^*)^2$	0	not observed	not observed

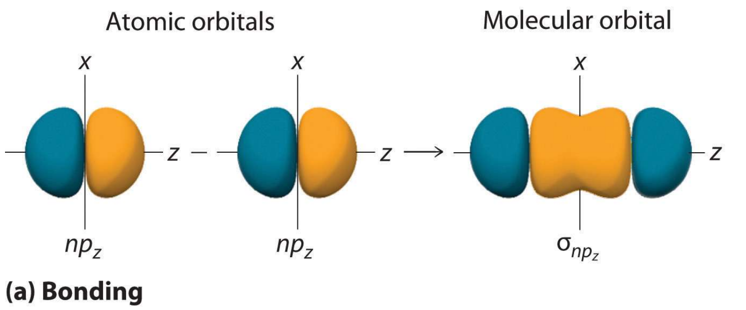
2. Molecular Orbitals

Period 2 homonuclear diatomic molecules

Valence atomic orbitals:

2s 2p$_x$ 2p$_y$ 2p$_z$

Cylindrical symmetry around the internuclear axis:



σ_{2p_z}

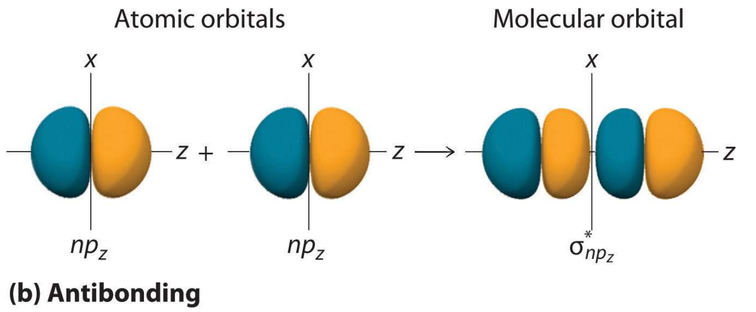
2. Molecular Orbitals

Period 2 homonuclear diatomic molecules

Valence atomic orbitals:

2s 2p$_x$ 2p$_y$ 2p$_z$

Cylindrical symmetry around the internuclear axis:



$\sigma^*_{2p_z}$

2. Molecular Orbitals

Period 2 homonuclear diatomic molecules

Valence atomic orbitals:

2s $2p_x$ $2p_y$ $2p_z$

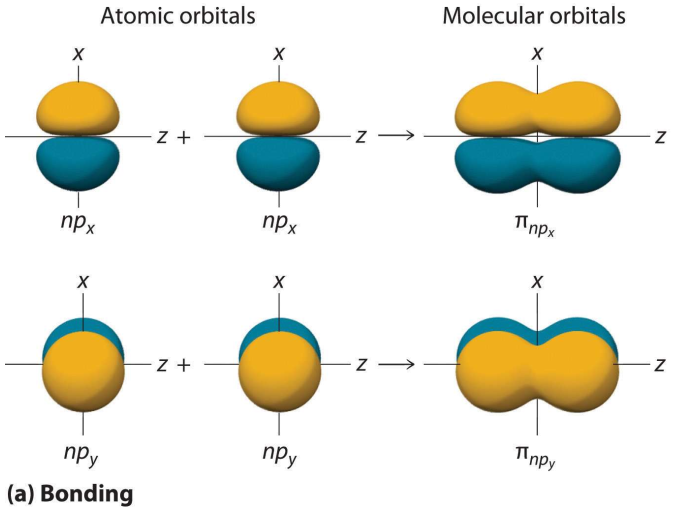
Orthogonal to the internuclear axis

π orbitals

2. Molecular Orbitals

Period 2 homonuclear diatomic molecules

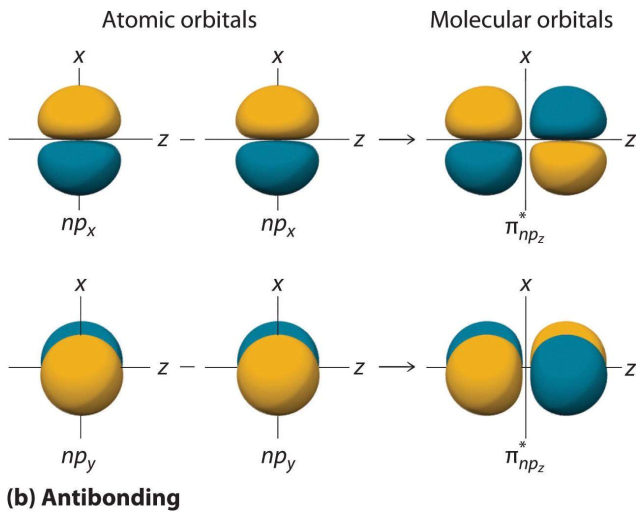
π orbitals



2. Molecular Orbitals

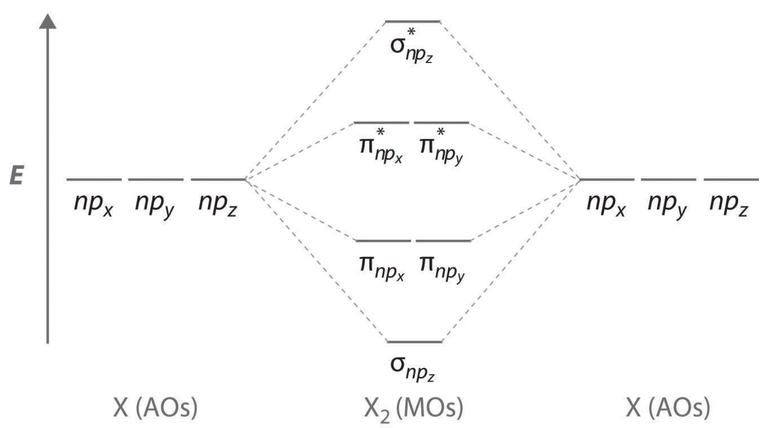
Period 2 homonuclear diatomic molecules

π^* orbitals



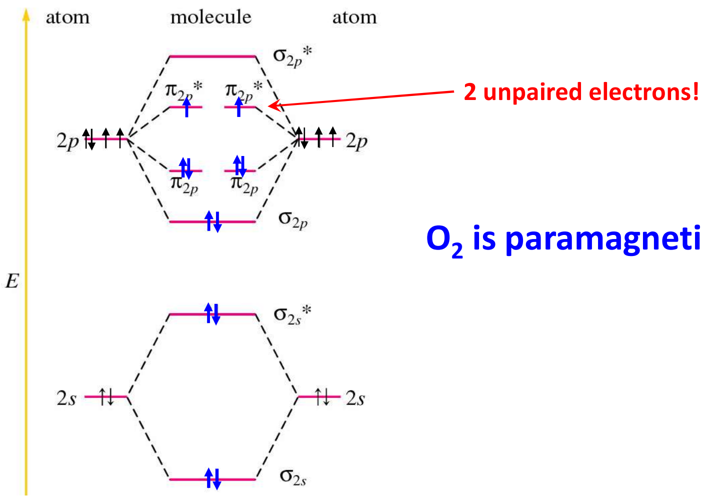
2. Molecular Orbitals

Expected energy diagram



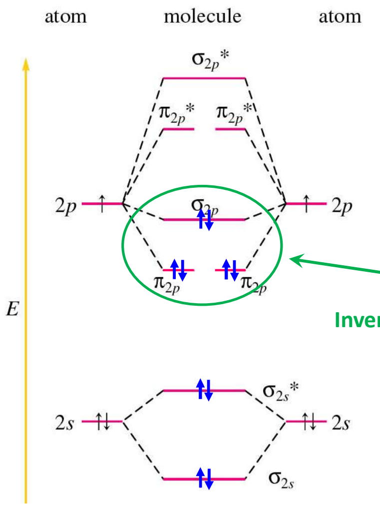
2. Molecular Orbitals

M.O. Diagram for O_2 (similar for F_2 and Ne_2)



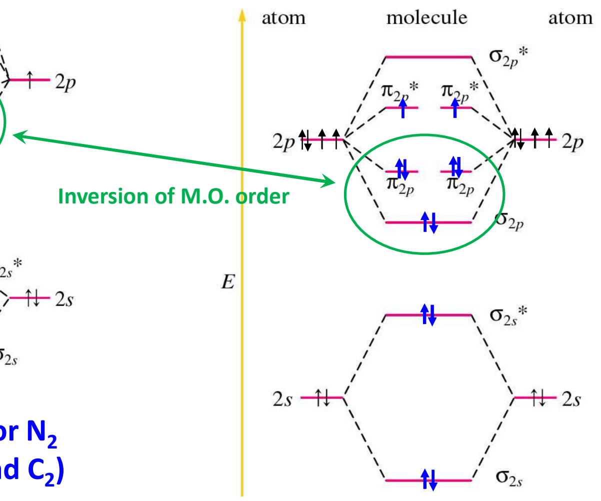
O_2 is paramagnetic

2. Molecular Orbitals

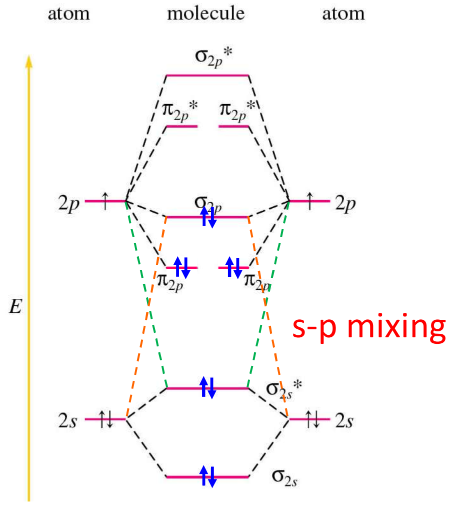


M.O. Diagram for N_2 (similar for B_2 and C_2)

M.O. Diagram for O_2 (similar for F_2 and Ne_2)

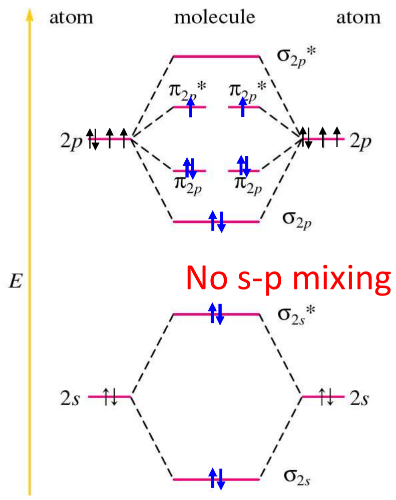


2. Molecular Orbitals



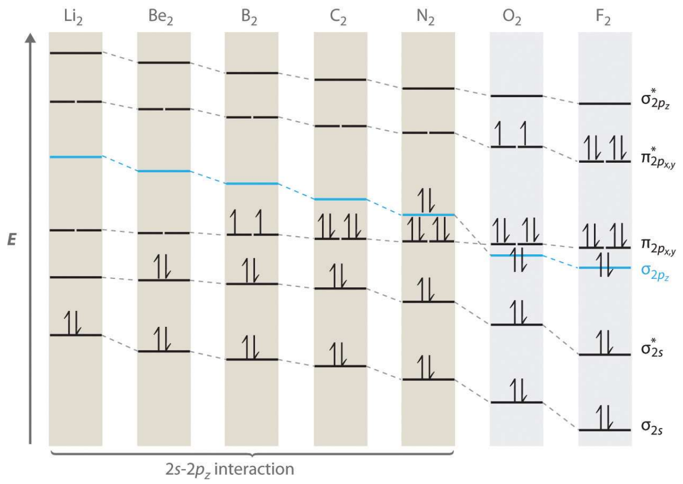
M.O. Diagram for N_2 (similar for B_2 and C_2)

M.O. Diagram for O_2 (similar for F_2 and Ne_2)



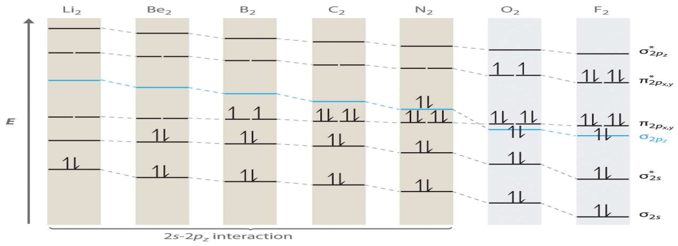
2. Molecular Orbitals

Period 2 homonuclear diatomic molecules



2. Molecular Orbitals

Period 2 homonuclear diatomic molecules



Bond order	1	0	1	2	3	2	1
Bond dissociation energy (kJ mol^{-1})			290	620	942	495	154
Bond length (pm)			159	131	110	121	143

2. Molecular Orbitals

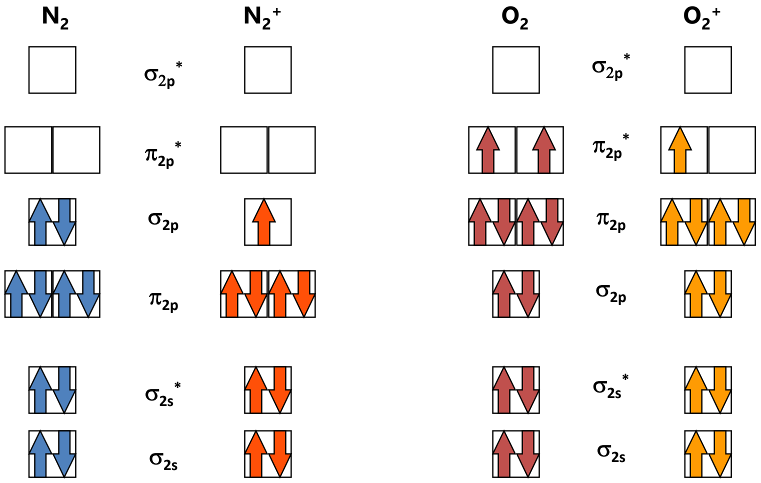
Problem: Justify the following data for these homonuclear diatomic species:

	N_2	N_2^+	O_2	O_2^+
Bond energy (kJ/mol)	945	841	498	623
Bond length (pm)	110	112	121	112

Plan: We first draw the MO energy levels for the four species, recalling that they differ for N_2 and O_2. Then we determine the bond orders and compare them with the data: bond order is related directly to bond energy and inversely to bond length.

2. Molecular Orbitals

Problem: Justify the following data for these homonuclear diatomic species:



Bond Orders:

(8-2)/2 = **3** (7-2)/2 = **2.5** (8-4)/2 = **2** (8-3)/2 = **2.5**

2. Molecular Orbitals

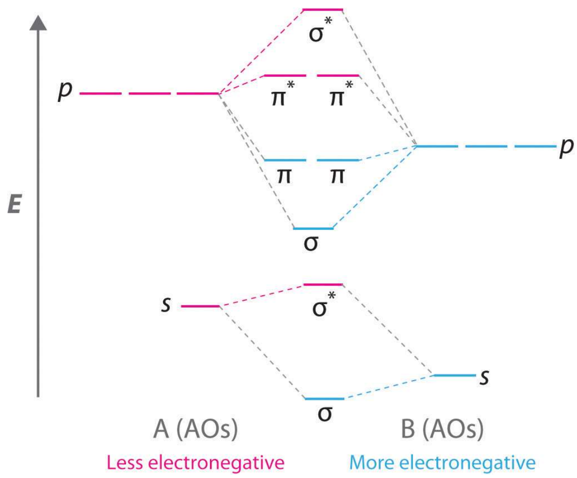
Problem: Justify the following data for these homonuclear diatomic species:

	N_2	N_2^+	O_2	O_2^+
Bond energy (kJ/mol)	945	841	498	623
Bond length (pm)	110	112	121	112
Bond order	3	2.5	2	2.5

Answer ???

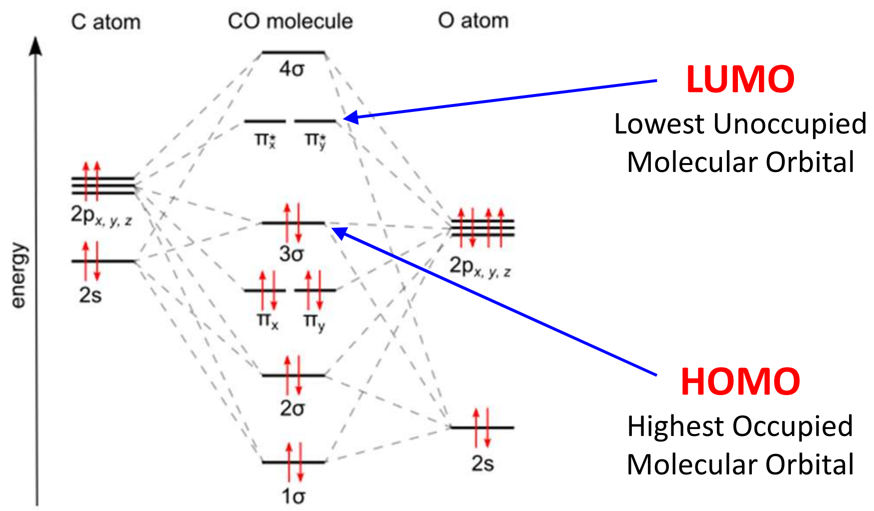
2. Molecular Orbitals

Period 2 heteronuclear diagonal molecules



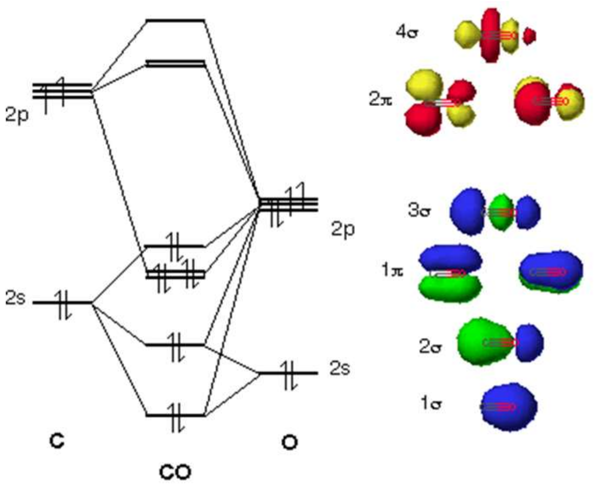
2. Molecular Orbitals

Carbon monoxide – CO



2. Molecular Orbitals

Carbon monoxide – CO

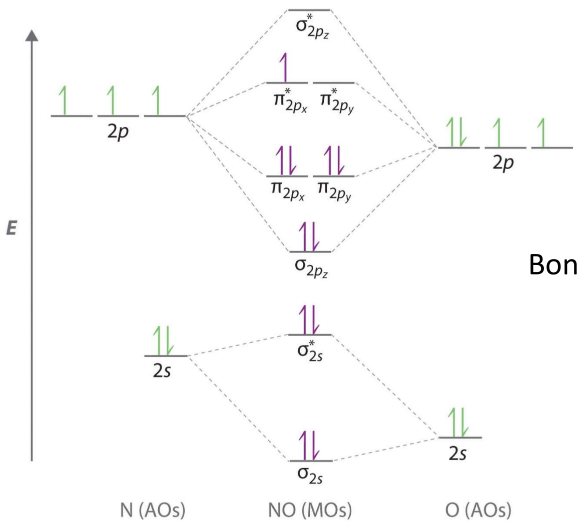


LUMO

HOMO

2. Molecular Orbitals

Nitrogen monoxide – NO

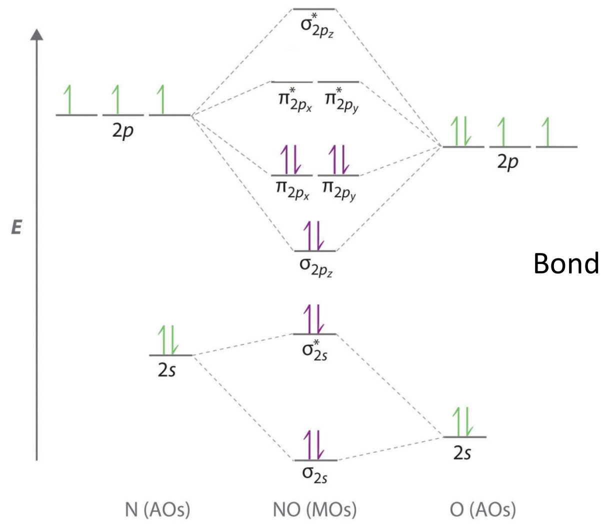


Bond order = (8-3)/2 = 2.5

Easily forms …

2. Molecular Orbitals

NO⁺



Bond order = (8-2)/2 = 3

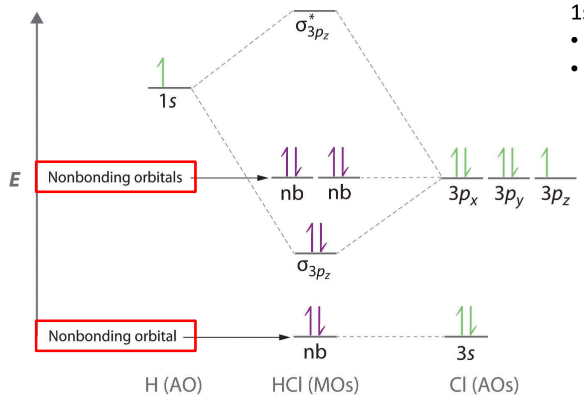
2. Molecular Orbitals

Non-bonding molecular orbitals

Hydrogen chloride - HCl

$$\Psi_{\pm} = c_H \Psi_H \pm c_{Cl} \Psi_{Cl} \qquad \boxed{c_H \neq c_{Cl}}$$

1s of H mixes with $3p_z$ of Cl:
- same symmetry
- closer in energy than 3s



2. Molecular Orbitals

Non-bonding molecular orbitals

Hydrogen chloride - HCl

$$\Psi_{\pm} = c_H\Psi_H \pm c_{Cl}\Psi_{Cl} \qquad \boxed{c_H \neq c_{Cl}}$$

1s of H mixes with $3p_z$ of Cl:
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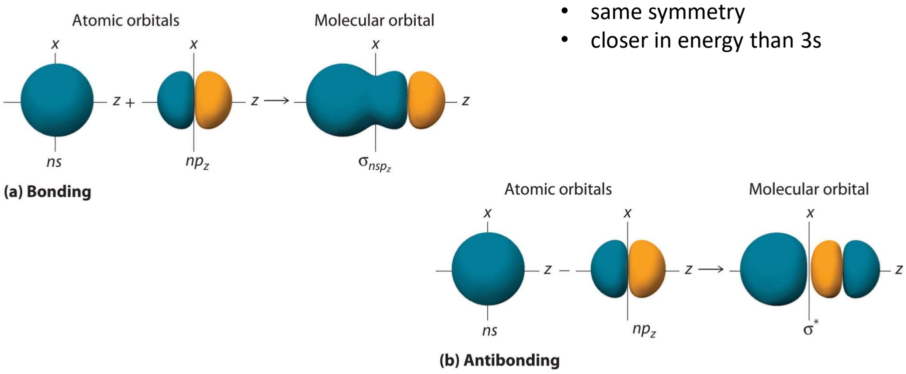
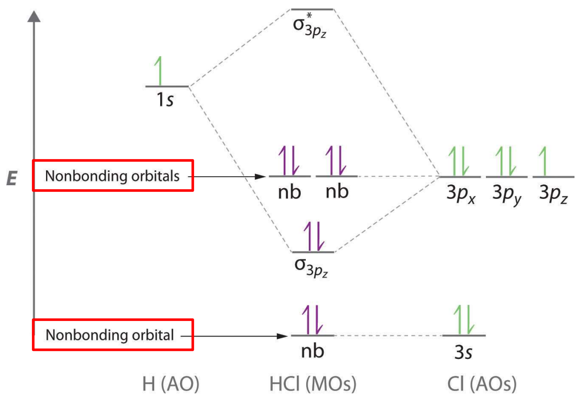


2. Molecular Orbitals

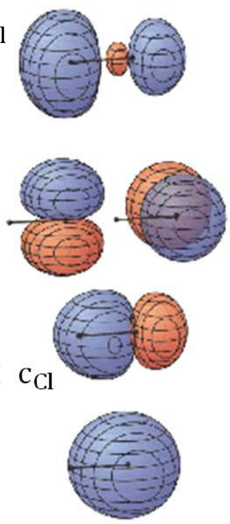
Non-bonding molecular orbitals

Hydrogen chloride - HCl

$$\Psi_{\pm} = c_H\Psi_H \pm c_{Cl}\Psi_{Cl}$$



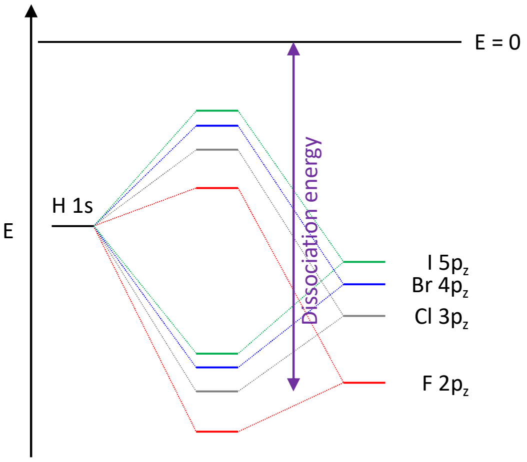
$c_H > c_{Cl}$



$c_H < c_{Cl}$

2. Molecular Orbitals

H-X molecules



The orbital employed by the halogen:

- increases in energy
- Increases in size

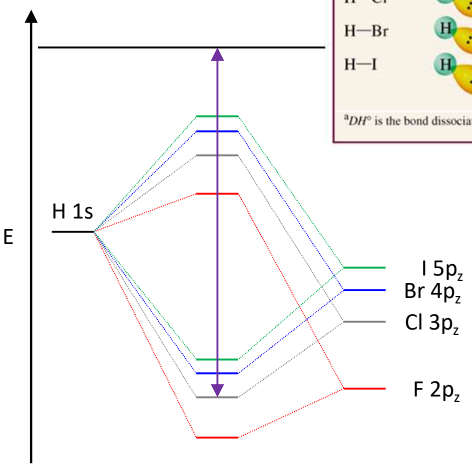
2. Molecular Orbitals

H-X molecules

TABLE 1.6 Hydrogen–Halogen Bond Lengths and Bond Strengths

Hydrogen halide	Bond length (Å)	Bond strength ($DH°$)[a] kcal/mol	kJ/mol
H—F	0.917	136	571
H—Cl	1.2746	103	432
H—Br	1.4145	87	366
H—I	1.6090	71	298

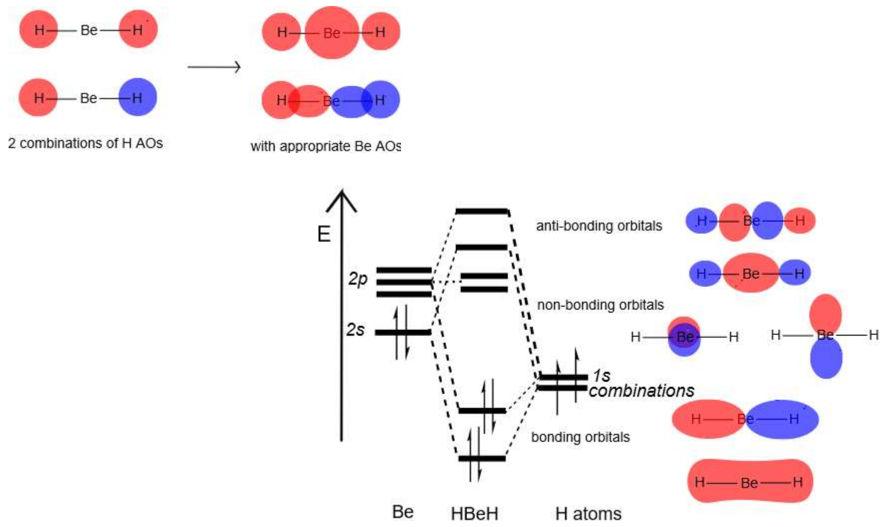
[a] $DH°$ is the bond dissociation energy.



Why HF is a weak acid?

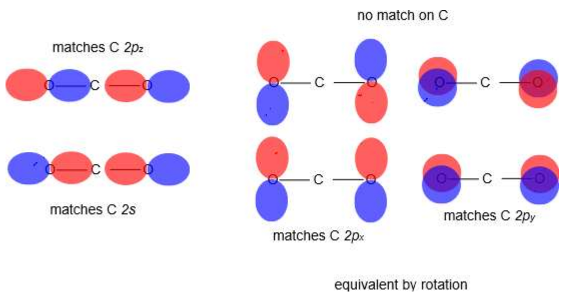
2. Molecular Orbitals

Triatomic molecules BeH_2



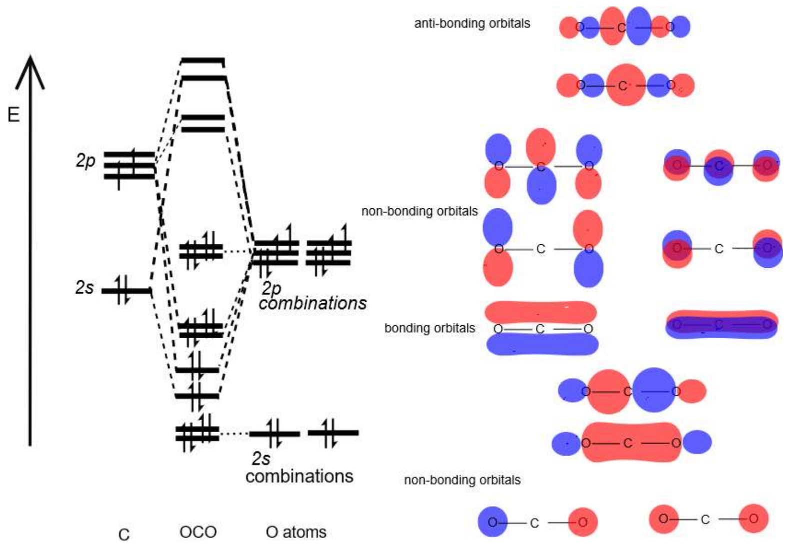
2. Molecular Orbitals

Triatomic molecules CO_2



2. Molecular Orbitals

Triatomic molecules CO_2



2. Molecular Orbitals

Hückel method

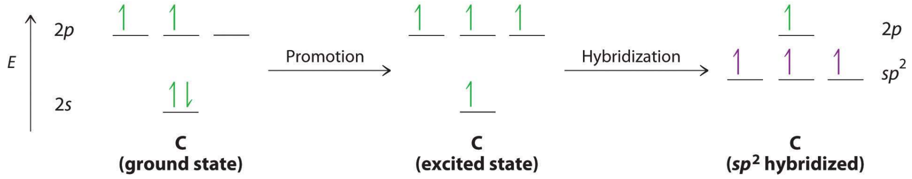
The description of polyatomic molecules with multiple bonds is very complicated using molecular orbitals.

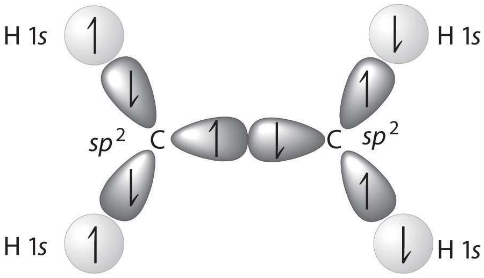
Molecular properties (physical parameters, spectroscopic characteristics and reactivity) can be explained adopting a simplified procedure:

- σ bonding using localized electron-pair bonds formed by hybrid atomic orbitals: describe mostly atomic arrangement and geometry.
- π bonding using molecular orbitals formed by unhybridized np atomic orbitals: describe fine details of atomic arrangement, spectroscopic and reactivity properties.

2. Molecular Orbitals

Ethylene





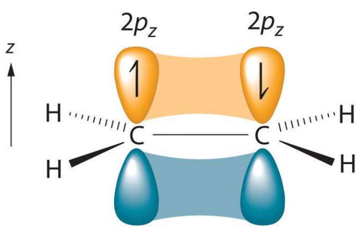
(a) C_2H_4 σ-bonded framework

The geometry of the molecule is described by the σ bonds network.

Bonds are formed by overlapping of semi-occupied sp^2 of C and 1s of H.

2. Molecular Orbitals

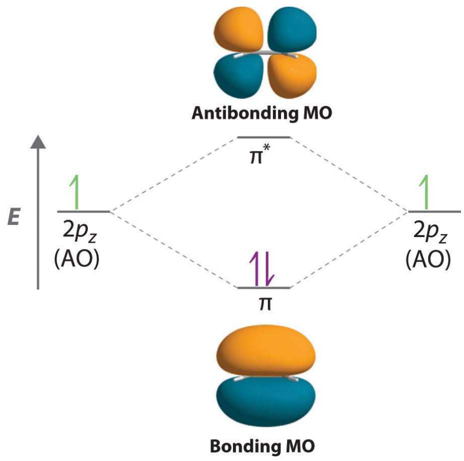
Ethylene



(b) C_2H_4 π bonding

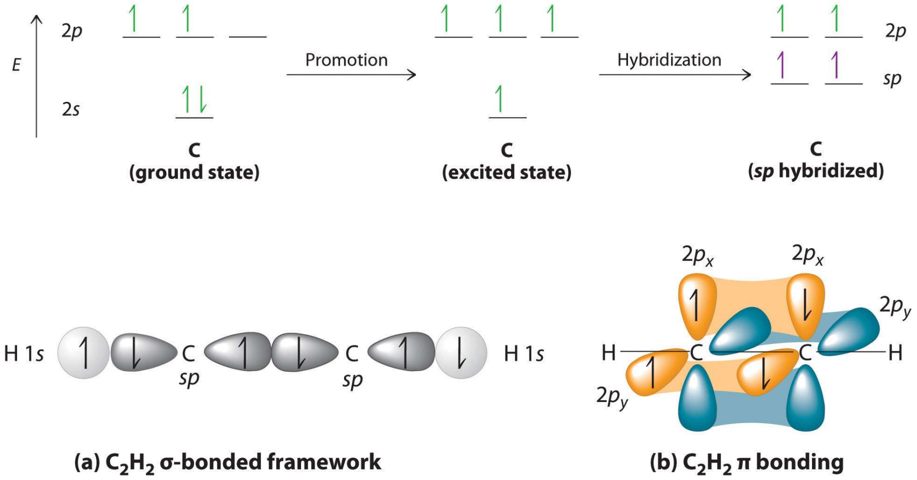
$\boxed{b = 2}$

π bonding is better described by MO



2. Molecular Orbitals

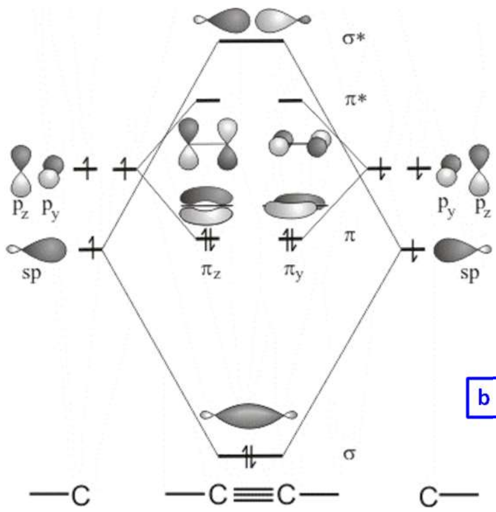
Acetylene



b = 3

2. Molecular Orbitals

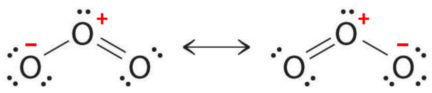
Acetylene



b = 3

2. Molecular Orbitals

Ozone



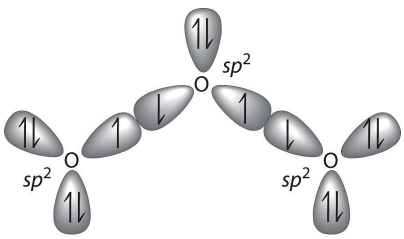
Experimental angle: 117.5°

VSEPR, Valence Bond theory and Resonance well predicts geometry

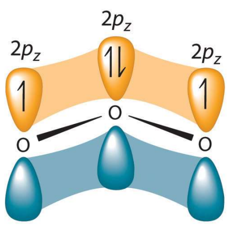
The net positive charge on the central atom is not acceptable.

2. Molecular Orbitals

Ozone



(a) O_3 σ-bond framework

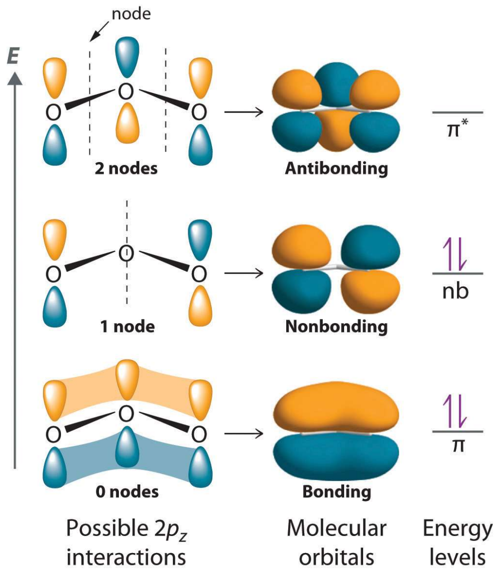


(b) O_3 π bonding

π bonding is better described by MO

2. Molecular Orbitals

Ozone

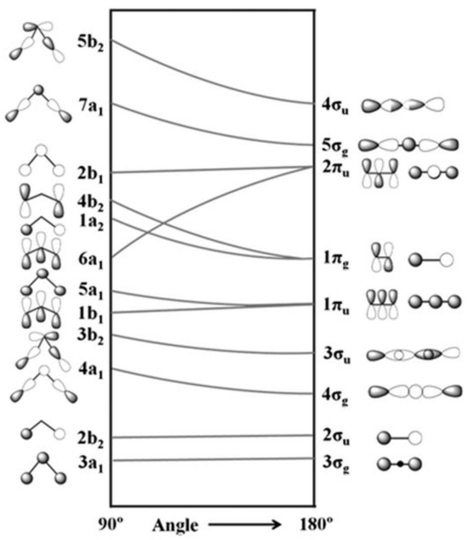


b_{O-O} =
1 (σ) + 0.5 (π) = 1.5

Higher electron density on the terminal O atoms.

2. Molecular Orbitals

Ozone

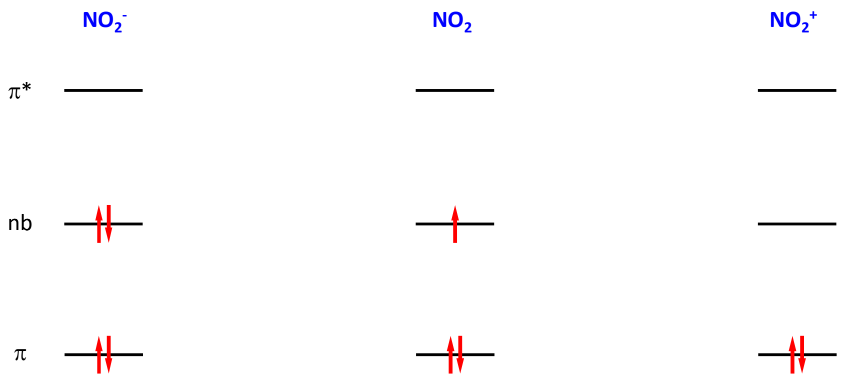


Why O_3 is not linear?

2. Molecular Orbitals

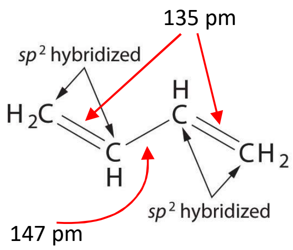
Problem: On the basis of MO theory, describe the electronic configuration of NO_2^-, NO_2 and NO_2^+. Which one is paramagnetic?

NO_2^- has the same electron configuration than O_3.



2. Molecular Orbitals

1,3-butadiene



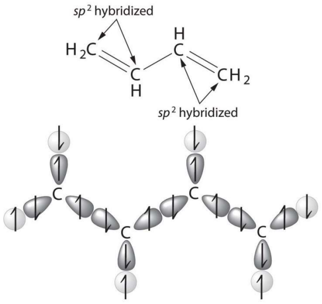
The molecule is planar:
no rotation around C2-C3 bond

C – C single bond:
154 pm

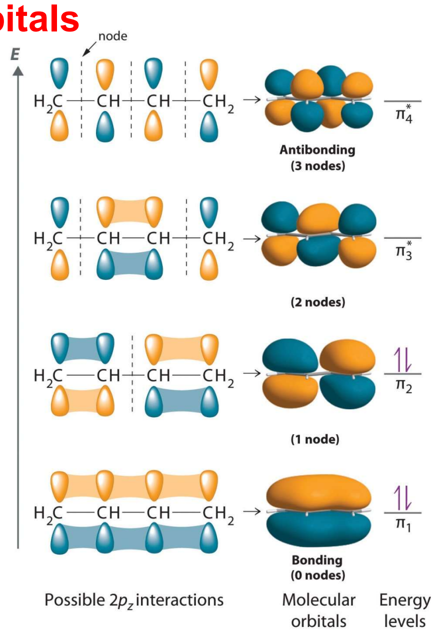
C = C double bond:
133 pm

2. Molecular Orbitals

1,3-butadiene



(a) 1,3-Butadiene σ-bonded framework



(b) 1,3-Butadiene π bonding

2. Molecular Orbitals

1,3-butadiene

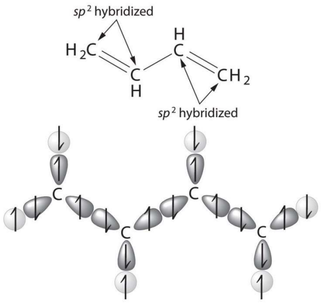
$b_{C1-C2} = b_{C3-C4} =$

$$\frac{2\,(\sigma)+0.67\,(\pi_1)+1\,(\pi_2)}{2} = 1.835$$

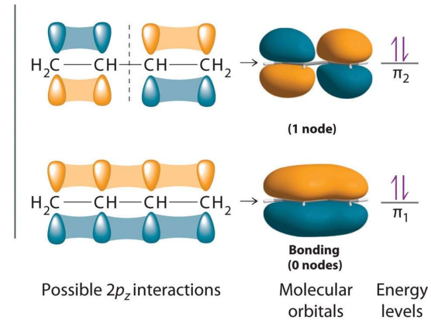
$b_{C2-C3} =$

$$\frac{2\,(\sigma)+0.67\,(\pi_1)}{2} = 1.335$$

Rotation is impossible !!!



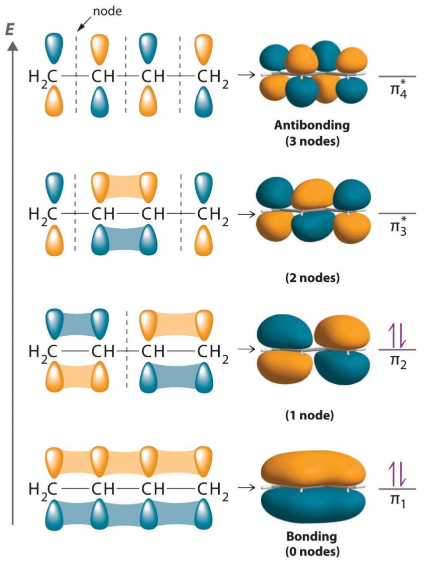
(a) 1,3-Butadiene σ-bonded framework



(b) 1,3-Butadiene π bonding

2. Molecular Orbitals

1,3-butadiene



$E = \alpha + 1.62\beta$

$E = \alpha + 0.62\beta$

$E = \alpha - 0.62\beta$

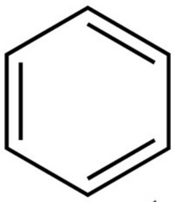
$E = \alpha - 1.62\beta$

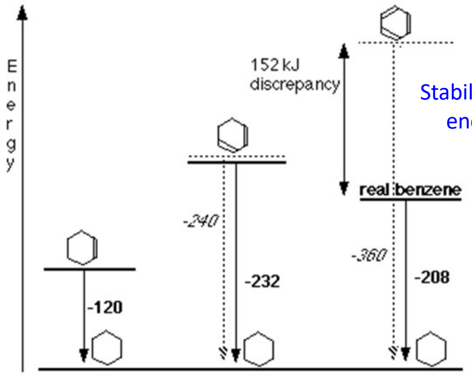
α: energy of one electron in a 2p orbital.

β: interaction energy between two p orbitals; independent from the type of molecule.

2. Molecular Orbitals

Benzene





Stabilization energy

It is not made by 3 double bond!

2. Molecular Orbitals

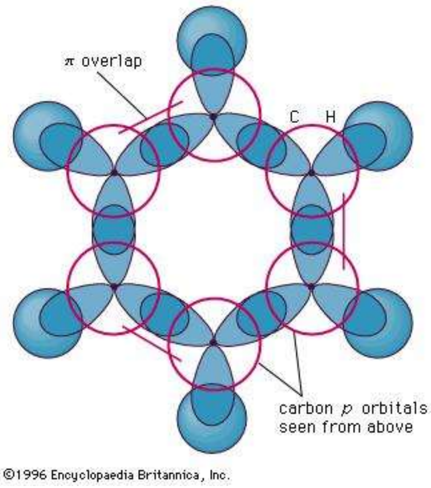
Benzene

Resonance hybrid model of benzene.

Do not describe properly the reactivity of benzene!!!

2. Molecular Orbitals

Benzene



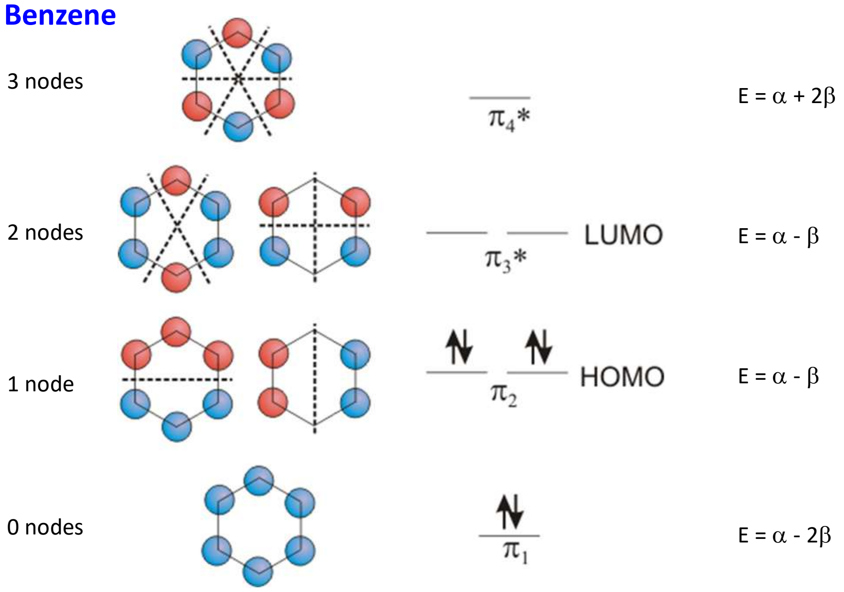
Molecular skeleton by overlapping of hybridized C $2sp^2$ and H 1s.

6 C 2p orbitals are orthogonal to the molecular plane.

They are combined by MO theory.

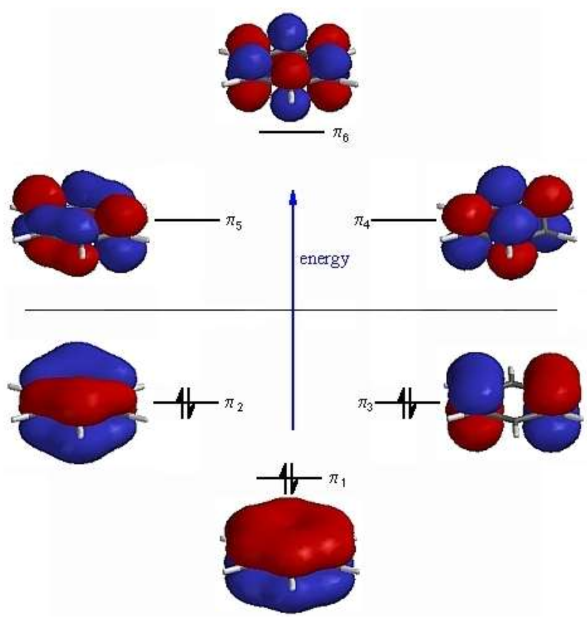
2. Molecular Orbitals

Benzene



2. Molecular Orbitals

Benzene



2. Molecular Orbitals

Polymers