

Forming Bonds and Molecular Orbitals

CHEM 361B: Introduction to Physical Chemistry

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Lecture 15

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Learning Objectives:

- Analyse the solutions to the Schrödinger Equation to predict bonding and antibonding orbitals
- Use bonding and antibonding orbitals to construct molecular orbital diagrams to predict the strength of chemical bonds

References:

- McQuarrie §10.1 to §10.4 and §11.1 to §11.2

Real Observables

We required that all quantum mechanical operators correspond to real observables (eigenvalues):

$$\hat{A}\psi = a\psi \quad (1)$$

In Equation 1, \hat{A} and ψ might be complex, but a must be real. To find out what this means, let's multiply on the left ψ^* and integrate

$$\int \psi^* \hat{A}\psi \, dx = a \int \psi^* \psi \, dx = a$$

Now, taking the complex conjugate of Equation 1

$$\hat{A}^*\psi^* = a^*\psi^* = a\psi^* \quad (2)$$

Note that the complex conjugates of a are equal to each other since a must be real. Taking Equation 2, multiply on the left by ψ and integrating gives:

$$\int \psi \hat{A}^* \psi^* \, dx = a \int \psi \psi^* \, dx = a$$

Hermetian Operators

This lets us re-write one of the postulates from earlier in the course

Theorem (Postulate 2)

*To every observable in classical mechanics there corresponds a linear, **Hermitian** operator in quantum mechanics*

An operator is Hermetian if

$$\int \psi_m^* \hat{A} \psi_n \, dx = \int \psi_n \hat{A}^* \psi_m^* \, dx$$

One significance of this is that if your operator is real, and Hermetian, then it is equivalent to apply the operator to the wavefunction or the complex conjugate of the wavefunction. For example, the Hamitonian is Hermetian and real, so:

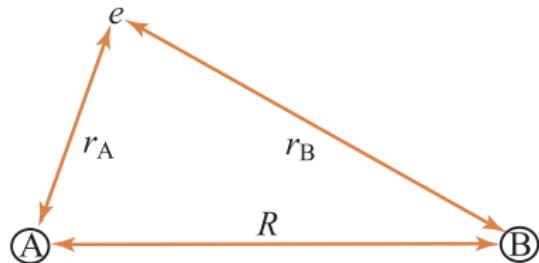
$$\int \psi_m^* \hat{H} \psi_n \, dx = \int \psi_n \hat{H}^* \psi_m^* \, dx$$

Hermitian Operators Example

Show that the momentum operator, $\hat{P}_x = -i\hbar \frac{d}{dx}$, is Hermetian.

Molecular Hamiltonians

H₂⁺ is the prototype diatomic molecule. It consists of two protons and one electron.

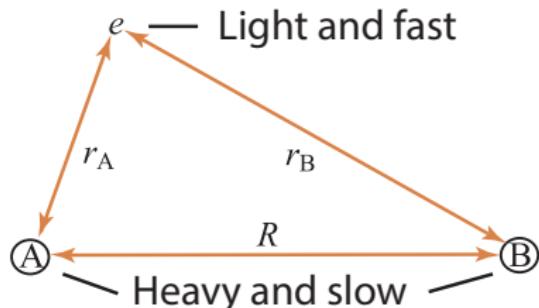


The Hamiltonian is expressed as:

$$\hat{H}_{mol} = \underbrace{-\frac{\hbar^2}{2M} (\nabla_A^2 + \nabla_B^2)}_{E_k \text{ of nuclei}} - \underbrace{\frac{\hbar^2}{2m_e} \nabla_e^2}_{E_p \text{ of } e^-} - \underbrace{\frac{e^2}{4\pi\epsilon_0 r_A} - \frac{e^2}{4\pi\epsilon_0 r_B}}_{E_p \text{ of nuclei}} + \underbrace{\frac{e^2}{4\pi\epsilon_0 R}}_{E_p \text{ of nuclei}}$$

Born-Oppenheimer Approximation

The nuclei are so much more massive than the electron and therefore move much more slowly.



The electron can adjust instantaneously to any atomic motions.
Using this we can assume:

$$\psi_{mol}(\mathbf{r}_e, \mathbf{R}_A, \mathbf{R}_B) \approx \underbrace{\psi_{el}(\mathbf{r}_e, R)}_{\text{Bonding}} \underbrace{\psi_{nucl}(\mathbf{R}_A, \mathbf{R}_B)}_{\text{Vibrational/Rotational}}$$

Defining Electronic Schrödinger Equation

Since $\psi_{el}(\mathbf{r}_e, R)$ only depends on the position of the electron and the internuclear separation, R, which we will assume is fixed, the E_k of the nuclei terms in \hat{H}_{mol} evaluate to zero meaning:

$$\hat{H}_{el}\psi_{el}(\mathbf{r}_e, R) = E_{el}\psi_{el}(\mathbf{r}_e, R)$$

where

$$\hat{H}_{el} = \underbrace{-\frac{\hbar^2}{2m_e}\nabla_e^2}_{E_p \text{ of } e^-} - \underbrace{\frac{e^2}{4\pi\epsilon_0 r_A} - \frac{e^2}{4\pi\epsilon_0 r_B}}_{E_p \text{ of nuclei}} + \underbrace{\frac{e^2}{4\pi\epsilon_0 R}}_{E_k \text{ of } e^-}$$

Molecular Orbitals

Let us assume that ψ_{el} is a linear combination of 1s atomic orbitals

$$\psi_{el} = c_A \psi_{1sA} + c_B \psi_{1sB}$$

There are two ψ_{el} solutions that satisfy the Schrödinger Equation.
Each of these solutions is called a **molecular orbital (MO)**.

- Molecular orbitals can be made up of a linear combinations of atomic orbitals (LCAO)
- The individual atomic orbitals are called basis functions
- All of the atomic orbitals used are called a basis set

Apply the Variational Principle to Find MOs

Applying the Variational Principle to ψ_{el} we get a secular determinant:

$$\begin{vmatrix} H_{AA} - E & H_{AB} - ES \\ H_{BA} - ES & H_{BB} - E \end{vmatrix} = 0$$

where

$$H_{AA} = \int \psi_{1sA}^* \hat{H}_{el} \psi_{1sA} dV = \psi_{1sB}^* \hat{H}_{el} \psi_{1sB} dV = H_{BB}$$

$$H_{AB} = \int \psi_{1sA}^* \hat{H}_{el} \psi_{1sB} dV = \int \psi_{1sB}^* \hat{H}_{el} \psi_{1sA} dV = H_{BA}$$

$$S = S_{AB} = \int \psi_{1sA}^* \psi_{1sB} dV = \int \psi_{1sB}^* \psi_{1sA} dV = S_{BA}$$

Apply the Variational Principle to Find MOs

Solving this secular determinant we can solve for the energy:

$$E_{\pm} = \frac{H_{AA} \pm H_{AB}}{1 \pm S}$$

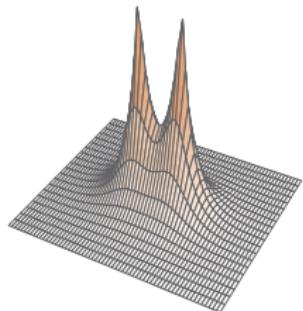
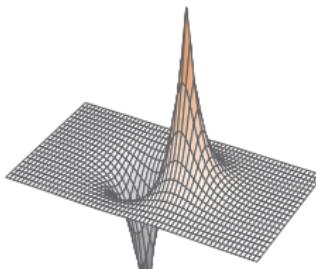
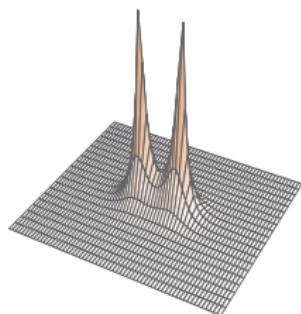
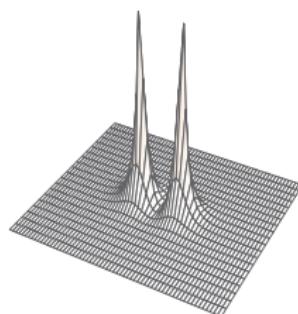
Note that there are two energies which means we will find two sets of c's. The first molecular orbital is:

$$\psi_+ = \frac{1}{\sqrt{2(1+S)}} (\psi_{1sA} + \psi_{1sB}) \quad \text{where } c_A = c_B$$

The second molecular orbital is:

$$\psi_- = \frac{1}{\sqrt{2(1-S)}} (\psi_{1sA} - \psi_{1sB}) \quad \text{where } c_A = -c_B$$

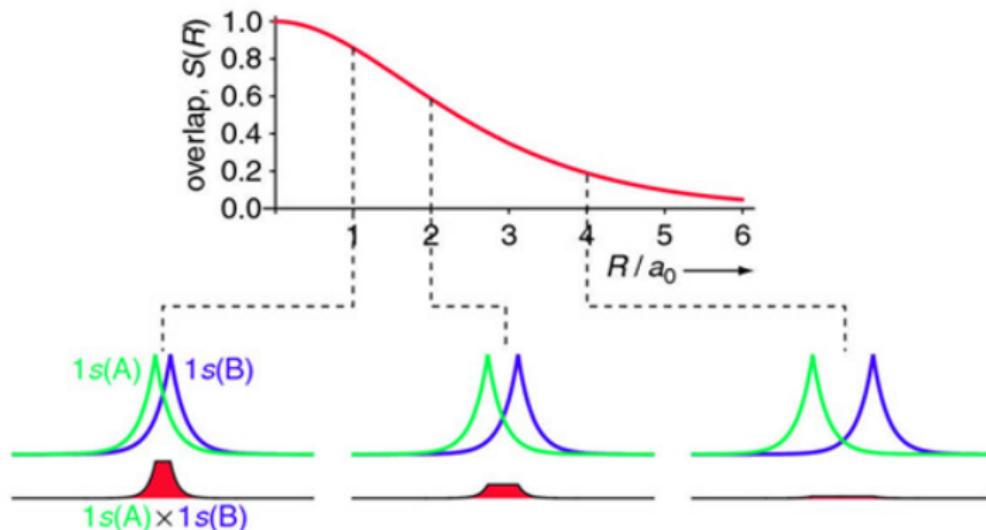
Bonding and Anti-Bonding Molecular Orbitals

 ψ_+  ψ_-  ψ_+^2  ψ_-^2

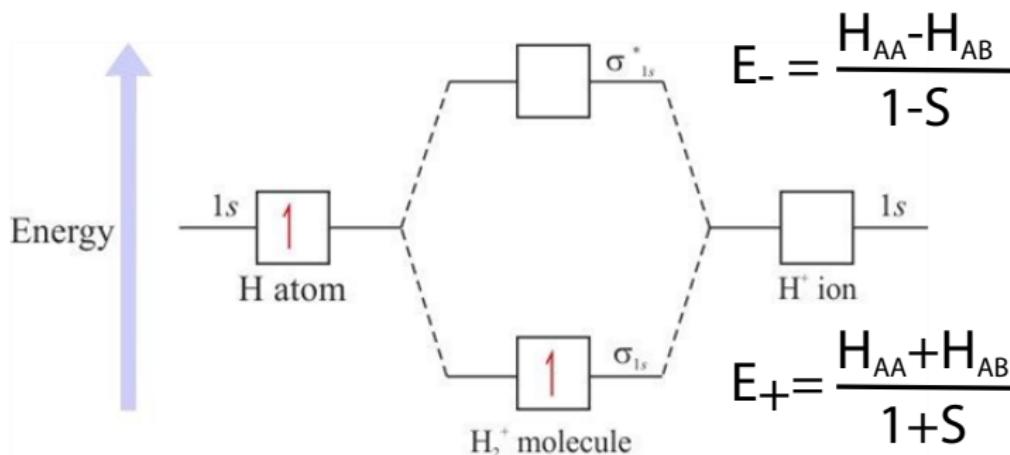
The Overlap Integral

Recall the S Integral:

$$S = S_{AB} = \int \psi_{1sA}^* \psi_{1sB} \, dV = \int \psi_{1sB}^* \psi_{1sA} \, dV = S_{BA}$$



The overlap integral provides a good indication of bond strength.

Molecular Orbital Diagram for H₂⁺

- H_{AA} and H_{AB} are negative
- $0 \leq S \leq 1$
- Therefore $E_+ < E_-$

Multielectron Molecular Orbitals

Multielectron molecules must be solved numerically. Their molecular orbitals can be used to describe bonding. Molecular orbitals

- can be constructed as a linear combination of atomic orbitals
- populated with electrons using the Pauli Exclusion Principle and Hund's Rules

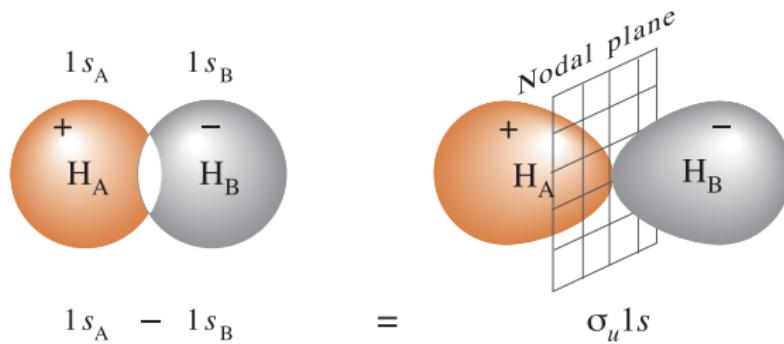
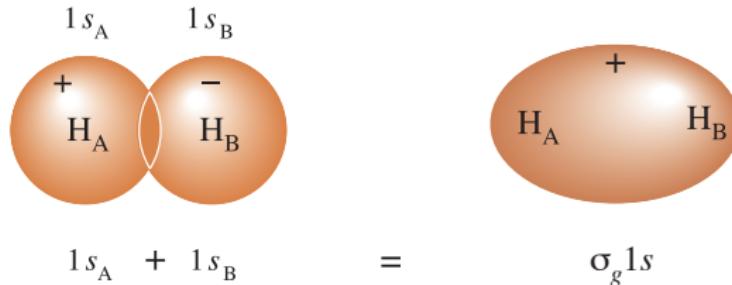
We can do a lot of analysis qualitatively. For example, H₂ in the ground state will have a molecular orbital of the form

$$\psi_{\pm} = 1s_A \pm 1s_B$$

- ψ_+ concentrates electron density between the two protons
 - is a bonding orbital
- ψ_- excludes electron density between the two protons
 - is an antibonding orbital

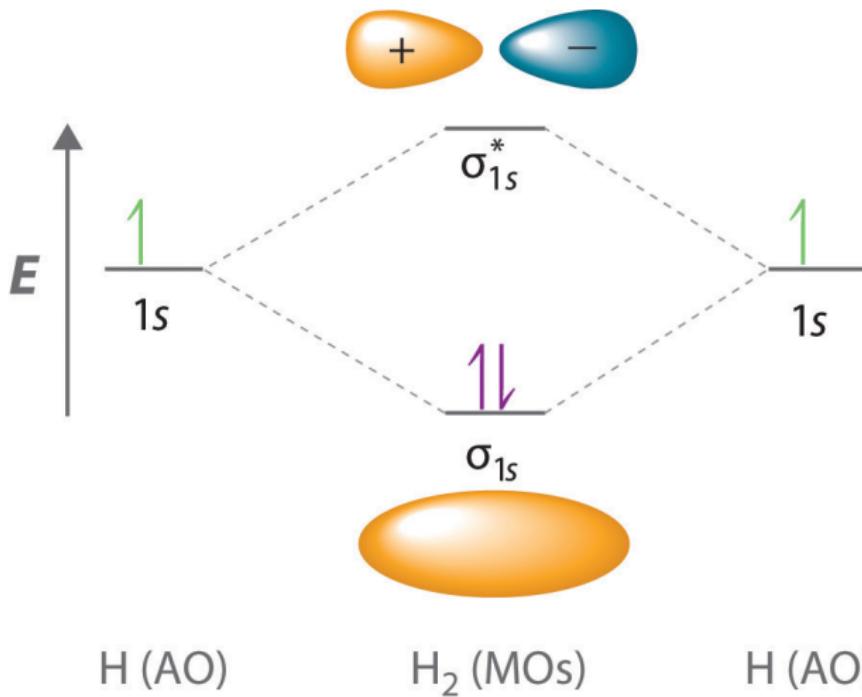
Sigma Orbitals in H₂

Since the electron density is symmetric about the internuclear axis, both are called σ orbitals.

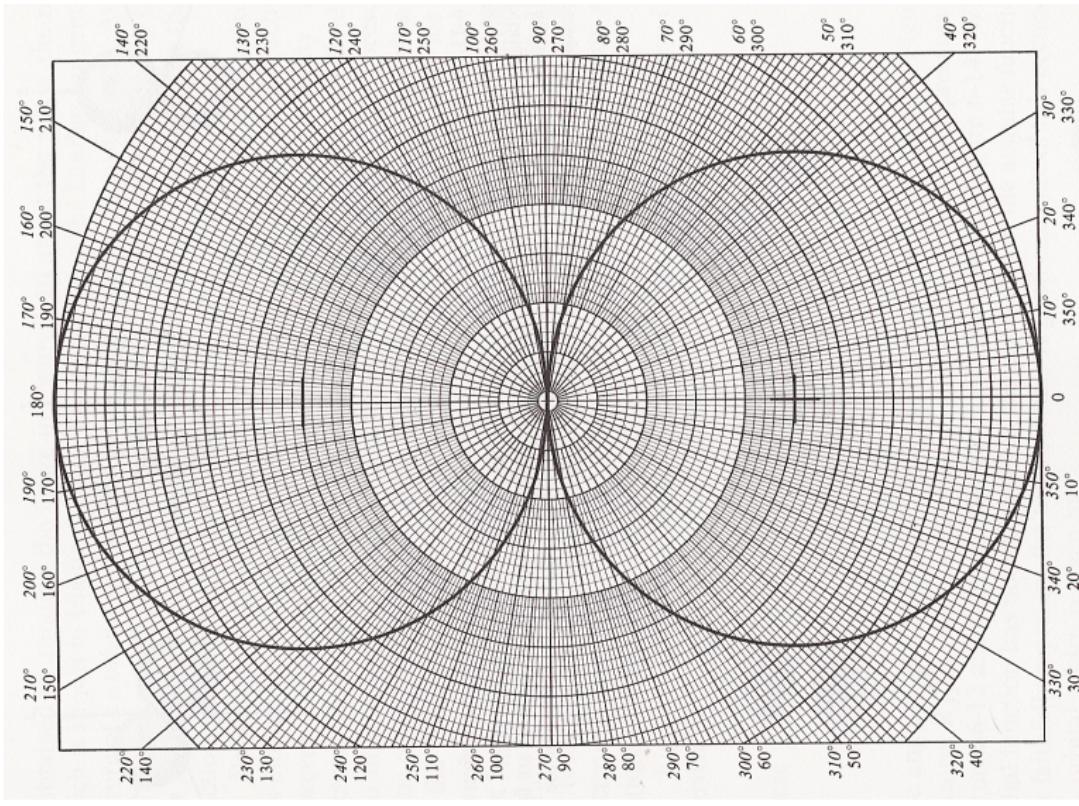


Molecular Orbital Diagram

Bonding orbitals will have a lower energy than antibonding orbitals
 $(E_{\sigma 1s} < E_{\sigma^* 1s})$

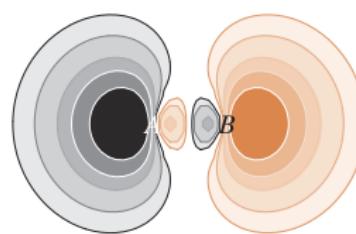
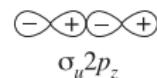
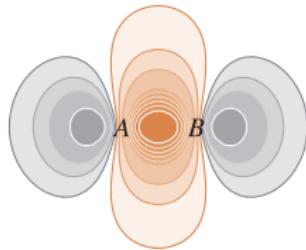
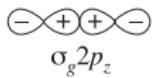


p Orbital Diagram



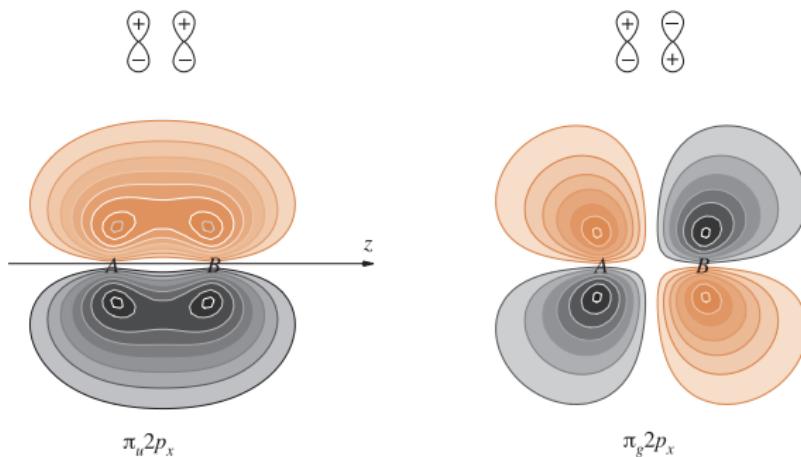
p Orbital Through the Internuclear Axis

- In general, p orbitals will have a higher energy than s orbitals.
- Given their orientation, two types of molecular orbitals formed from p orbitals exist. Assume the z-axis to be the internuclear axis. Then
 - The p_z orbital forms a σ orbital

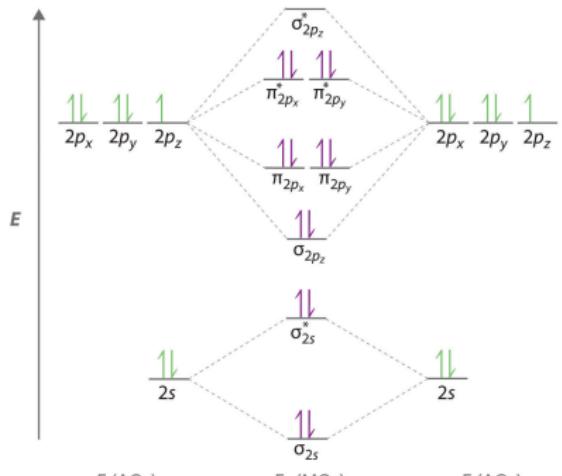


p Orbitals Not Symmetric About the Internuclear Axis

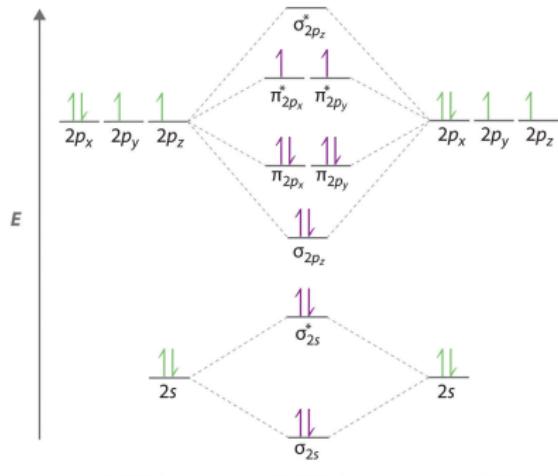
- In this case p_x and p_y are not symmetric about the internuclear axis
- They have a node through a plane which includes the internuclear axis
- As a result, they are called π orbitals



Molecular Orbital Diagrams



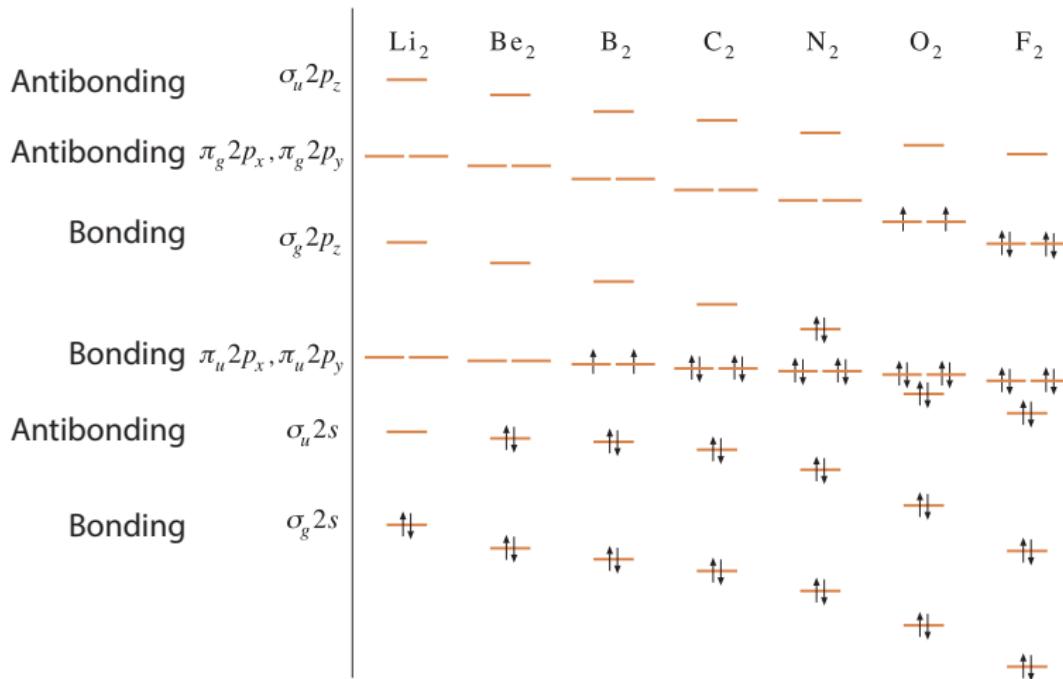
(a)



(b)

2nd Row Molecular Orbital Energy Level Diagrams

The relative energies (not to scale) of the molecular orbitals for the homonuclear diatomic molecules Li₂ through F₂.



Bond Order

Electrons in

- bonding orbitals tend to draw nuclei together
- antibonding orbitals tend to push nuclei apart

As a result, electrons in antibonding orbitals cancel out the attractive effect of a bonding orbital. This can be formalized as

$$\text{Bond order} = \frac{\# \text{ of } e^- \text{ in bonding orbitals} - \# \text{ of } e^- \text{ in antibonding orbitals}}{2}$$

A bond order of

- One means a single bond
- Two means a double bond
- Three means a triple bond

Bond Order Examples

Determine the bond order of

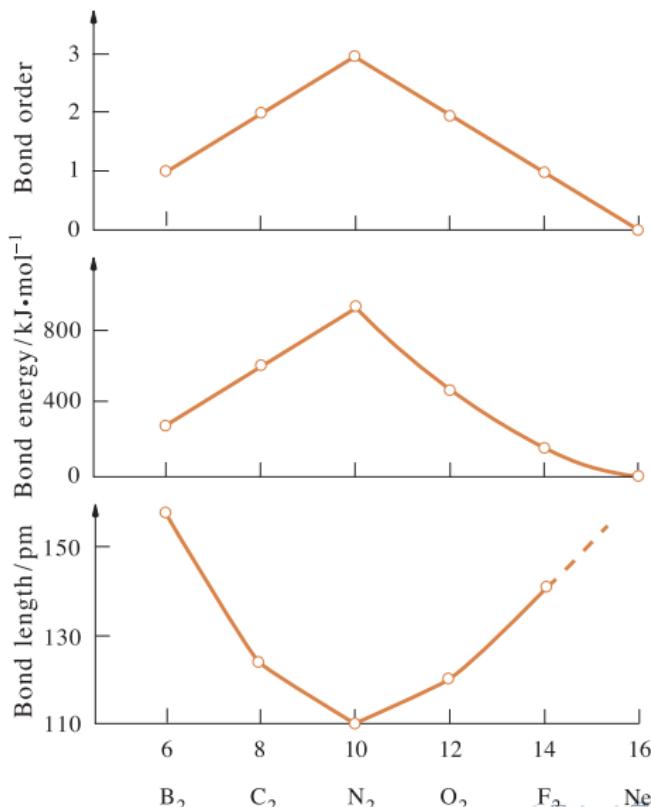
- ① H₂⁺
- ② H₂
- ③ He₂⁺
- ④ He₂

Properties of Diatomic Molecules

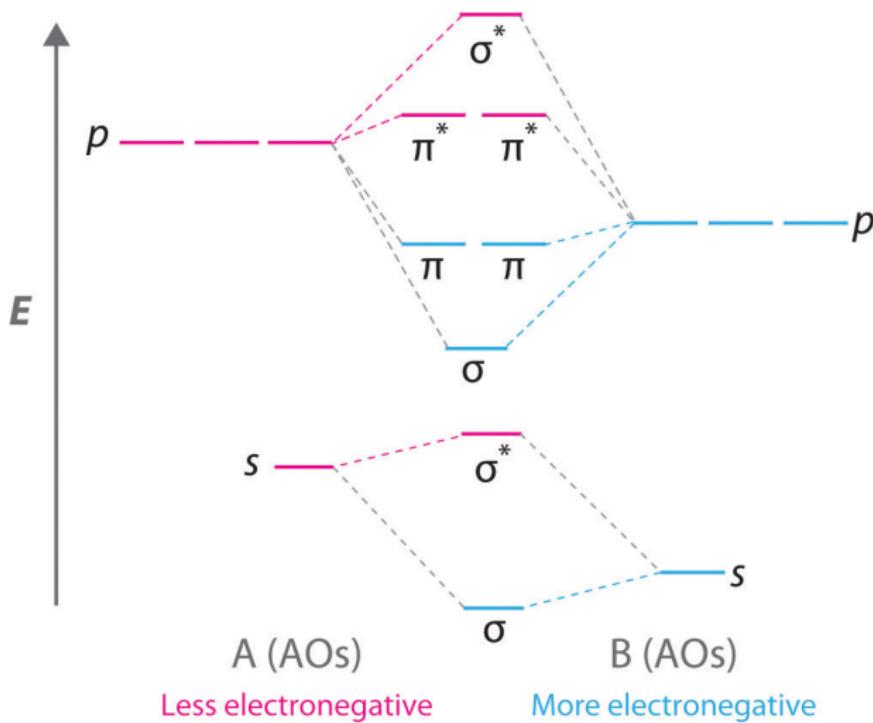
Species	Ground-State electron configuration	Bond order	Bond Length (pm)	Bond energy (kJ·mol ⁻¹)
H ₂ ⁺	(σ 1s) ¹	$\frac{1}{2}$	106	255
H ₂	(σ 1s) ²	1	74	431
He ₂ ⁺	(σ 1s) ² (σ^* 1s) ¹	$\frac{1}{2}$	108	251
He ₂	(σ 1s) ² (σ^* 1s) ²	0	Not observed	
Li ₂	KK(σ 2s) ²	1	267	105
Be ₂	KK(σ 2s) ² (σ^* 2s) ²	0	Not observed	
B ₂	KK(σ 2s) ² (σ^* 2s) ² (π 2p) ²	1	159	289
C ₂	KK(σ 2s) ² (σ^* 2s) ² (π 2p) ⁴	2	124	599
N ₂	KK(σ 2s) ² (σ^* 2s) ² (π 2p) ⁴ (σ 2p) ²	3	110	942
O ₂	KK(σ 2s) ² (σ^* 2s) ² (π 2p) ⁴ (σ 2p) ² (π^* 2p) ²	2	121	494
F ₂	KK(σ 2s) ² (σ^* 2s) ² (π 2p) ⁴ (σ 2p) ² (π^* 2p) ⁴	1	141	154
Ne ₂	KK(σ 2s) ² (σ^* 2s) ² (π 2p) ⁴ (σ 2p) ² (π^* 2p) ⁴ (σ^* 2p) ²	0	Not observed	

The KK represents a full shell ($n = 1$) for each core.

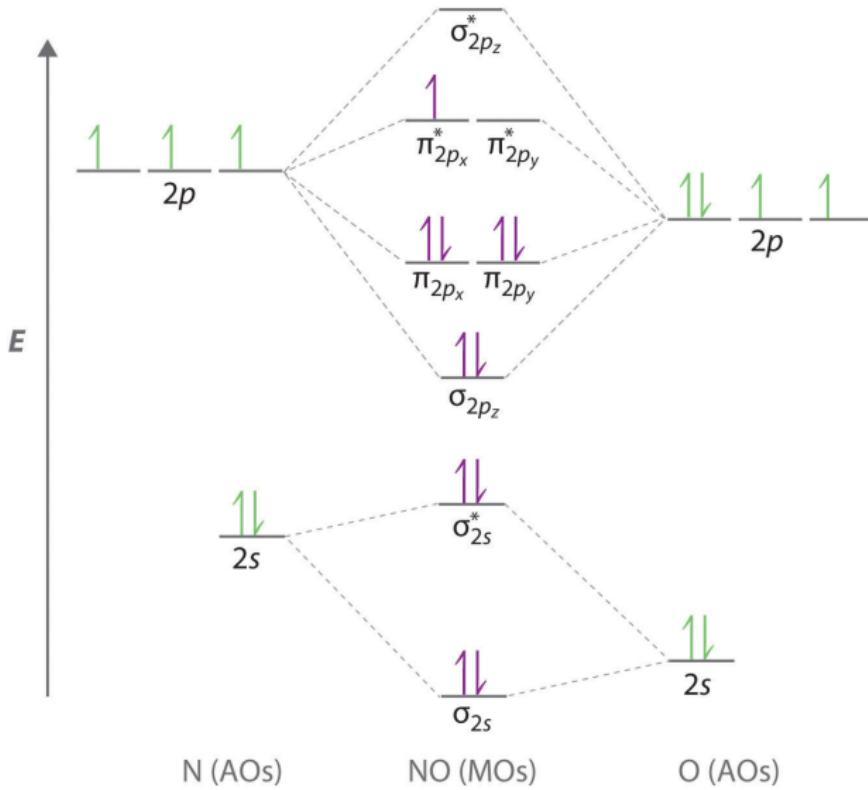
Properties of Diatomic Molecules Illustration



Heteronuclei Diatomic Molecular Orbitals



Heteronuclei Diatomic Molecular Orbitals - NO



Summary

- Molecular orbitals

- Formed from a linear combination of basis functions
- They are either
 - Bonding - Lower in energy
 - Antibonding - Higher in energy
- Molecular orbital diagrams can be constructed from molecular orbitals to qualitatively describe bond strength through bond order.