

## GENERAL CHEMISTRY

CHEM-110



## CHEMICAL BONDING M.O. Theory

## CHEMICAL BONDING

Lewis Theory: 10.1 – 10.6

V.S.E.P.R.: 10.7 – 10.8

Valence Bond Theory: 11.1-11.2

Hybridization: 11.3 -11.4

M.O. Theory: 11.5-11.6

Metallic Bonding: 11.7

### Valence Bond Theory (Hybridization)

Bonding	✓
Geometry	✓
Magnetism	✗

### Atomic Theory

1. Derive a set of atomic orbitals
2. Arrange the atomic orbitals in order of increasing energy
3. Distribute the electrons among the available atomic orbitals obeying Hund's rule and Pauli's exclusion principle

### M.O. Theory

1. Derive a set of **molecular** orbitals
2. Arrange the **molecular** orbitals in order of increasing energy
3. Distribute the electrons among the available **molecular** orbitals obeying Hund's rule and Pauli's exclusion principle

### Diatomeric Molecules

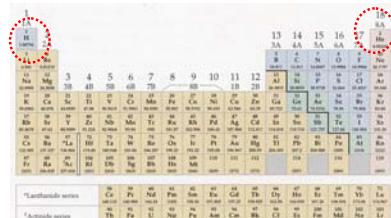
Hydrogen       $H_2$

Oxygen       $O_2$

Nitrogen       $N_2$

etc...

## Diatom Molecules



1<sup>st</sup> period elements

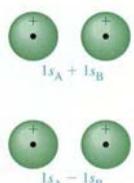
Hydrogen  
Helium

## M.O. Theory

1. Derive a set of molecular orbitals

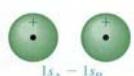
Linear combination of atomic orbitals  
(L.C.A.O. method)

Molecular orbitals



$$\Psi_A + \Psi_B = \Psi_{M.O.}$$

bonding



$$\Psi_A - \Psi_B = \Psi^*_{M.O.}$$

Antibonding

Atomic orbitals

$$\Psi_A + \Psi_B = \Psi_{M.O.}$$

$$\Psi_A - \Psi_B = \Psi^*_{M.O.}$$

Calculate probability density ( $\Psi^2$ )

$$\Psi^2_{M.O.} = \Psi_A^2 + \Psi_B^2 + 2\Psi_A\Psi_B$$

$$\Psi^{*2}_{M.O.} = \Psi_A^2 + \Psi_B^2 - 2\Psi_A\Psi_B$$

Bonding orbital

$$\Psi^2_{M.O.} = \Psi_A^2 + \Psi_B^2 + 2\Psi_A\Psi_B$$

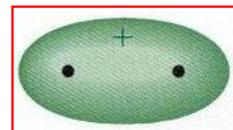


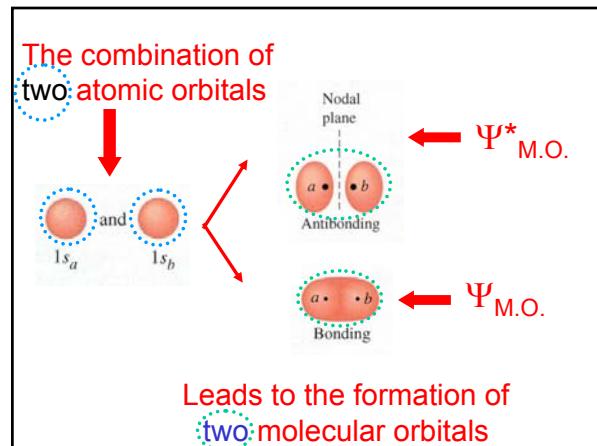
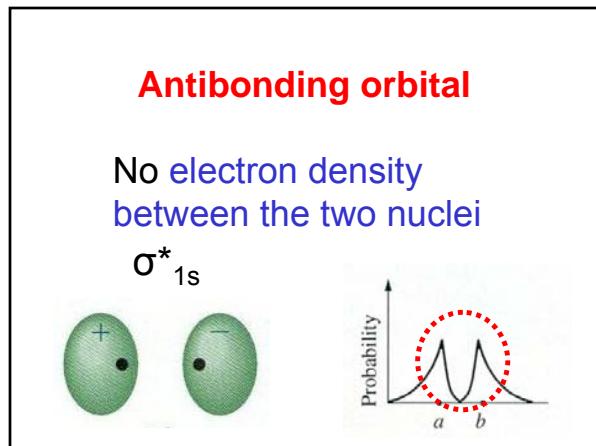
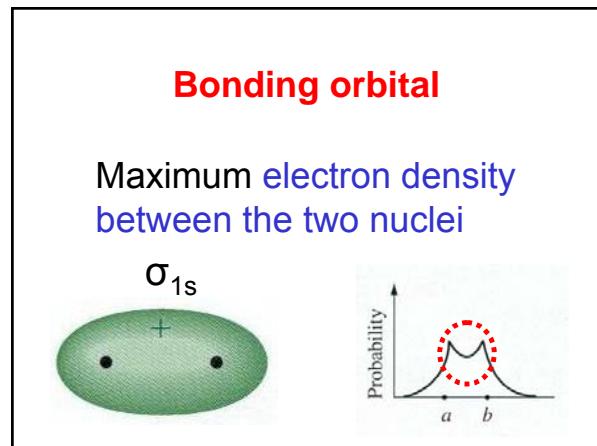
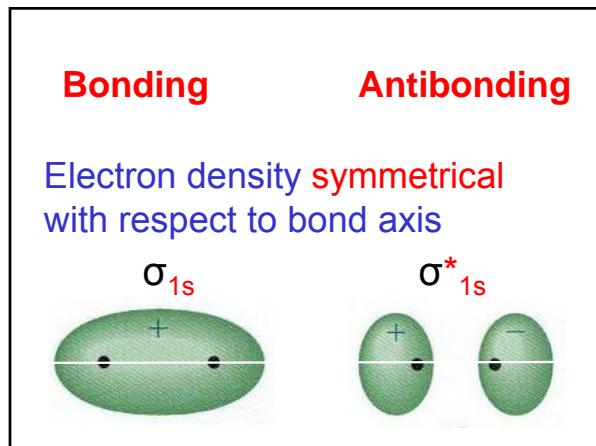
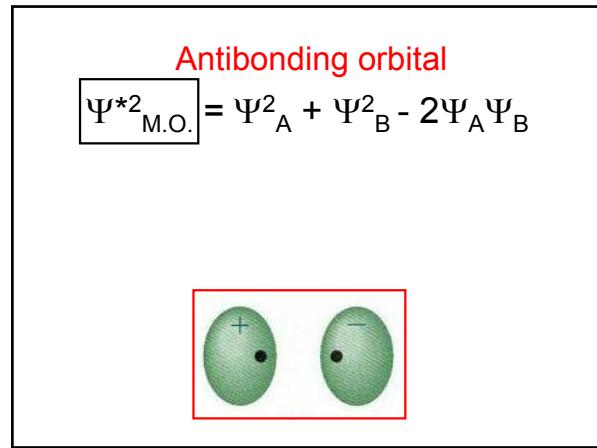
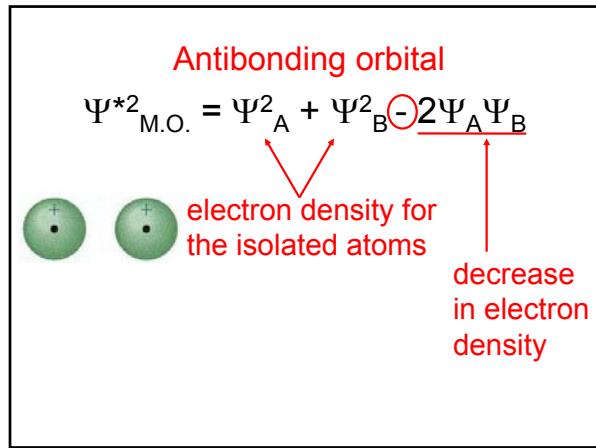
electron density for the isolated atoms

increase in electron density

Bonding orbital

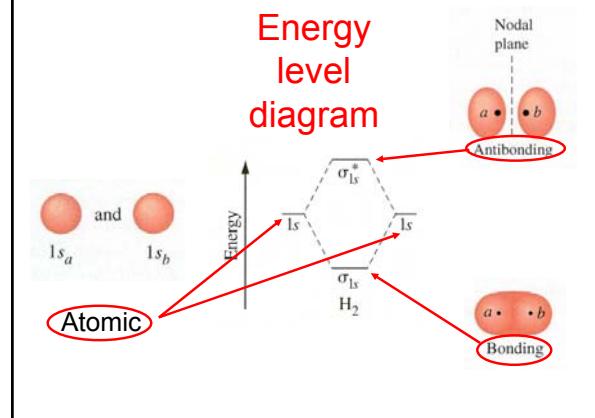
$$\Psi^2_{M.O.} = \Psi_A^2 + \Psi_B^2 + 2\Psi_A\Psi_B$$





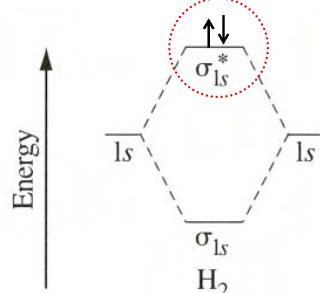
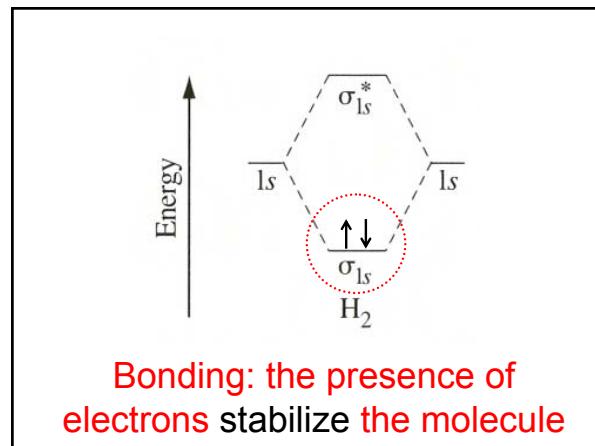
## M.O. Theory

1. Derive a set of **molecular** orbitals
2. Arrange the **molecular** orbitals in order of increasing energy

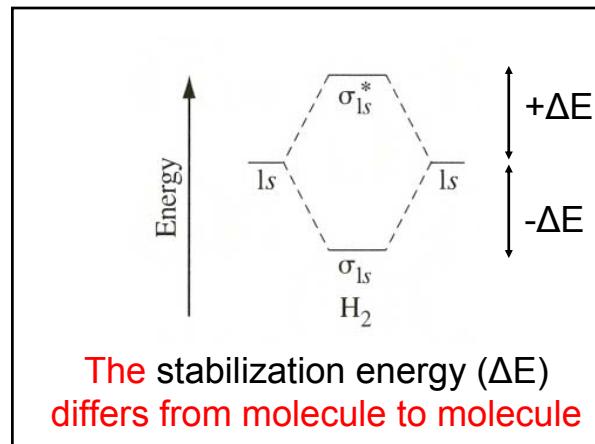


## M.O. Theory

1. Derive a set of **molecular** orbitals
2. Arrange the **molecular** orbitals in order of increasing energy
3. Distribute the electrons among the available **molecular** orbitals obeying Hund's rule and Pauli's exclusion principle



Antibonding: the presence of electrons destabilize the molecule



For bonding to occur:

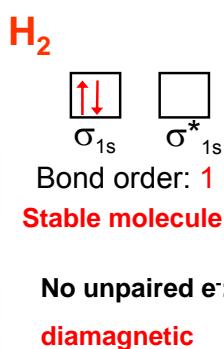
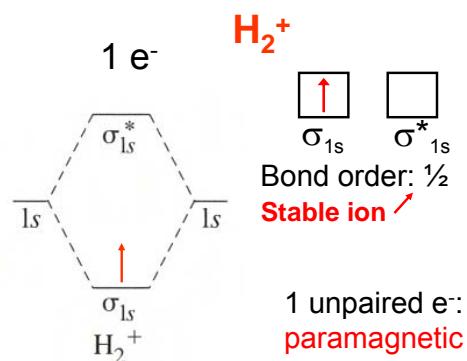
$$\frac{\# \text{ bonding e}^- - \# \text{ antibonding e}^-}{2} > 0$$

Bond Order > 0

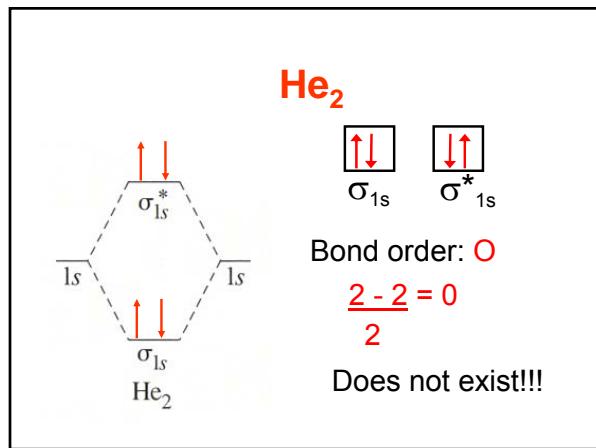
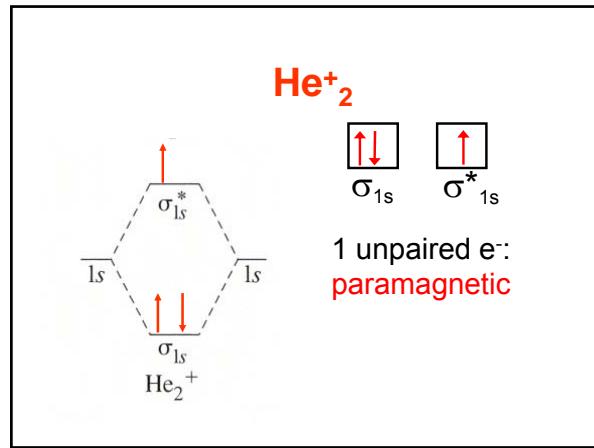
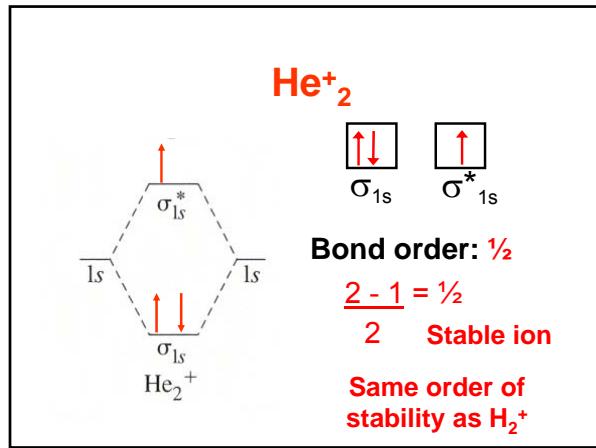
Predicting stability and magnetic properties



## Hydrogen

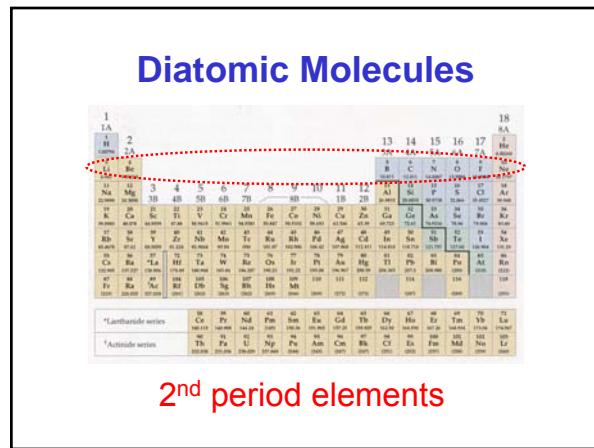


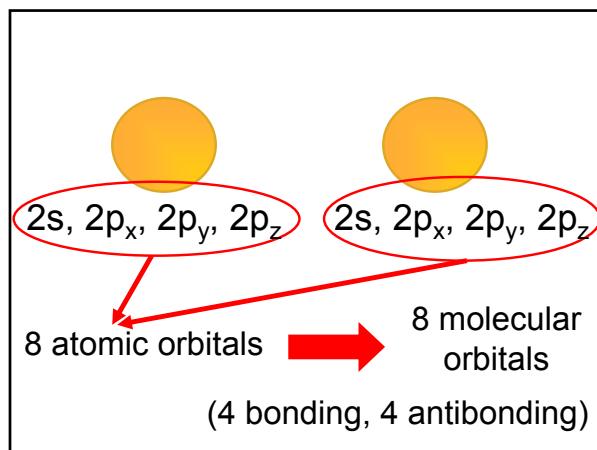
## Helium



Compare predictions with experimentally determined values

Molecule	Bond order	Unpaired electrons	ΔHf kcal/mol	Magnetism
H <sub>2</sub> <sup>+</sup>	1/2	1	-61	Paramagnetic
H <sub>2</sub>	1	0	-103	Diamagnetic
He <sub>2</sub> <sup>+</sup>	1/2	1	-60	Paramagnetic
He <sub>2</sub>	0	0		Non-existent

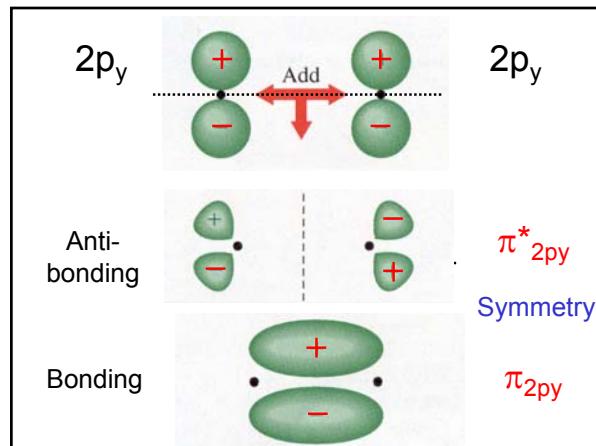
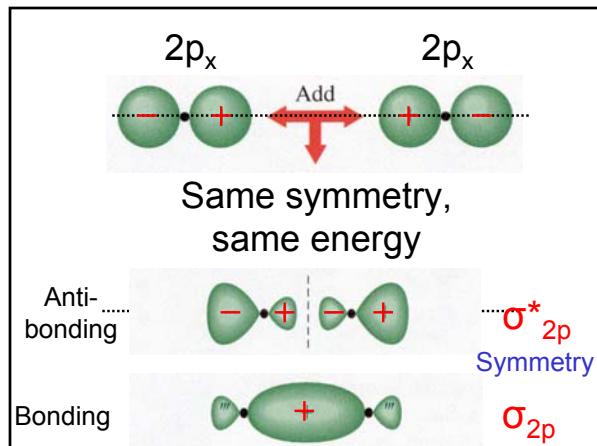
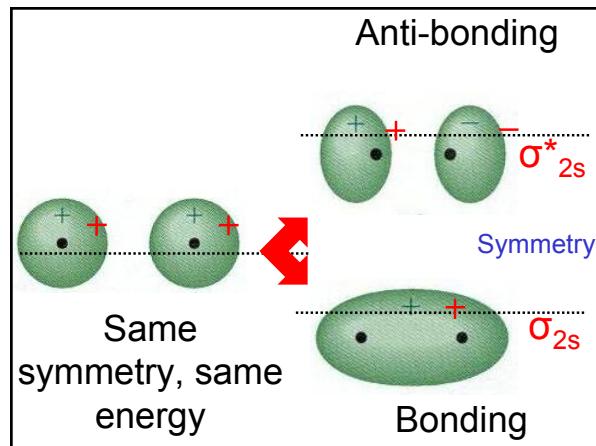
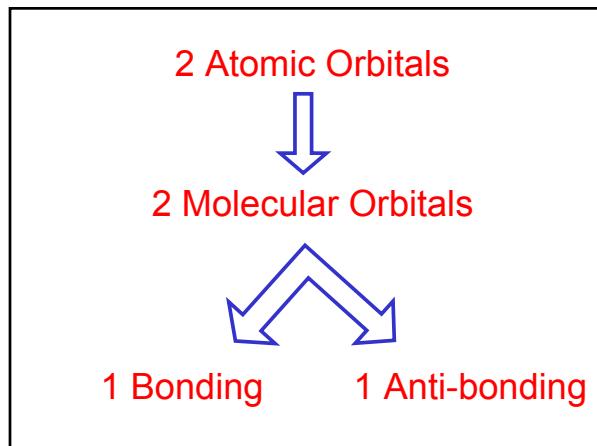


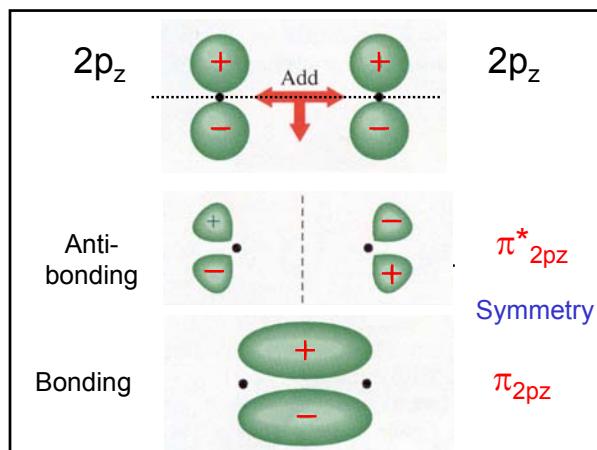


Atomic orbitals with **compatible** symmetry and energy

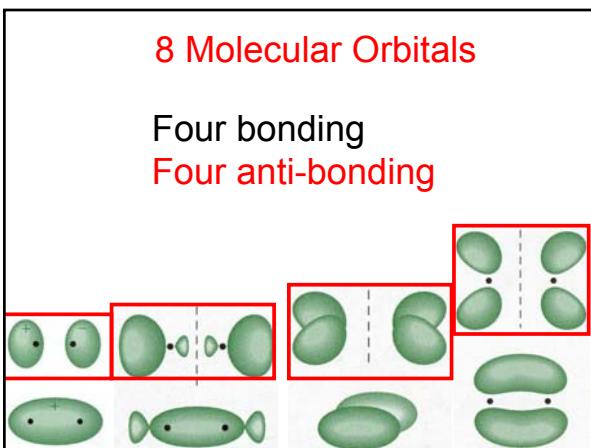
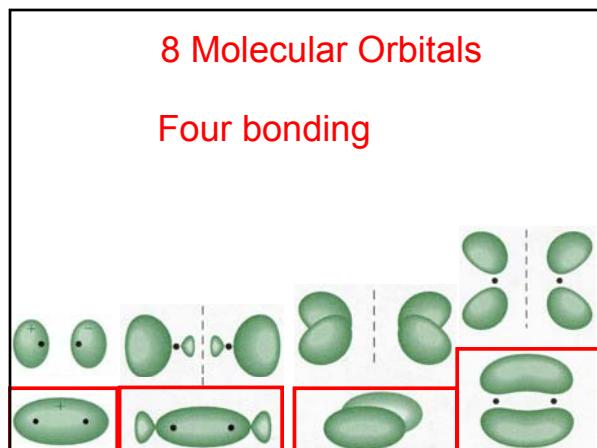
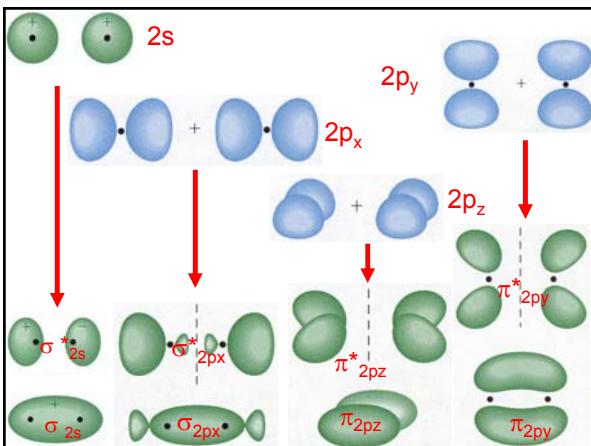
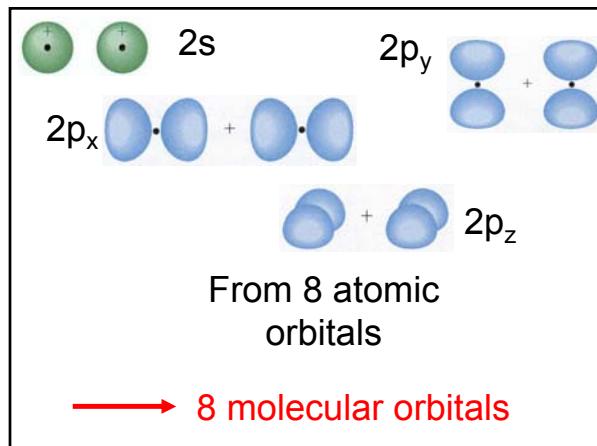
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Molecular orbitals

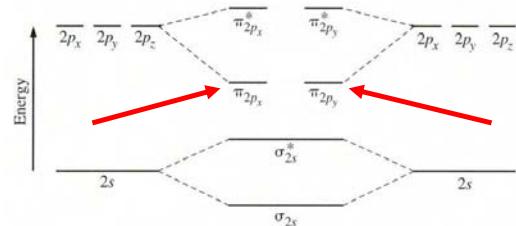




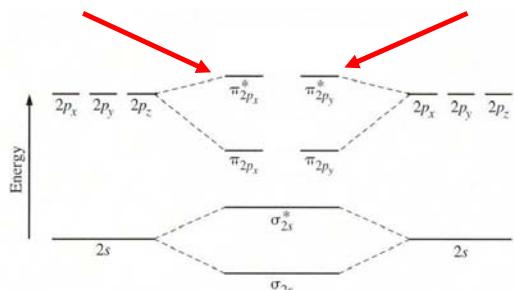
Overview:



## Molecular Orbital Energy Diagram

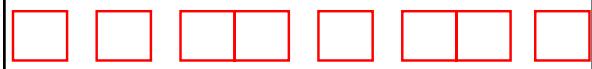


The two  $\pi$  bonding orbitals are of the same energy (degenerate)



The two  $\pi$  antibonding orbitals are of the same energy (degenerate)

## Relative order of energy



$$\sigma_{2s} < \sigma_{2s}^* < \pi_{2p} < \sigma_{2p} < \pi_{2p}^* < \sigma_{2p}^*$$

## Relative order of energy



$$\sigma_{2s} < \sigma_{2s}^* < \sigma_{2p} < \pi_{2p} < \pi_{2p}^* < \sigma_{2p}^*$$

For  $O_2$  and  $F_2$ , the order is inverted!

## Predicting stability and magnetic properties

### Examples

2<sup>nd</sup> period elements

Li Be B C N O F

**Li<sub>2</sub>**

2 valence electrons



$$\sigma_{2s} < \sigma^*_{2s} < \pi_{2p} < \sigma_{2p} < \pi^*_{2p} < \sigma^*_{2p}$$

Bond order:  $\frac{2}{2} = 1$       Stable  
(in gas phase)

**Li<sub>2</sub>**

2 valence electrons



$$\sigma_{2s} < \sigma^*_{2s} < \pi_{2p} < \sigma_{2p} < \pi^*_{2p} < \sigma^*_{2p}$$

Unpaired electrons = 0

Diamagnetic

2<sup>nd</sup> period elements

Li Be B C N O F

**Be<sub>2</sub>**

4 valence electrons



$$\sigma_{2s} < \sigma^*_{2s} < \pi_{2p} < \sigma_{2p} < \pi^*_{2p} < \sigma^*_{2p}$$

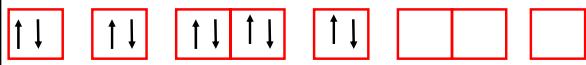
Bond order:  $\frac{2-2}{2} = 0$       Unstable

2<sup>nd</sup> period elements

Li Be B C N O F

## N<sub>2</sub>

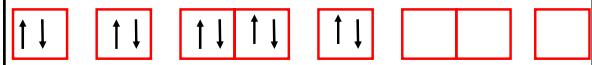
10 valence electrons



Bond order:  $\frac{8 - 2}{2} = 3$       Stable

## N<sub>2</sub>

10 valence electrons

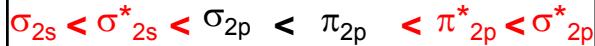
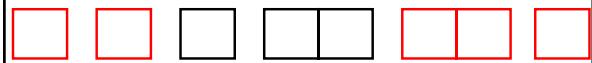

$$\sigma_{2s} < \sigma^*_{2s} < \pi_{2p} < \sigma_{2p} < \pi^*_{2p} < \sigma^*_{2p}$$

Unpaired electrons = 0      { VB Theory :N≡N: }  
Diamagnetic

## 2<sup>nd</sup> period elements

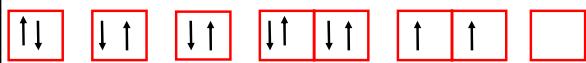
Li    Be    B    C    N    O    F

## Recall for O<sub>2</sub>



## O<sub>2</sub>

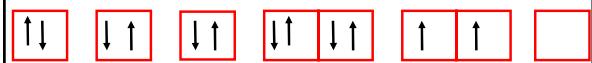
12 valence electrons



Bond order:  $\frac{8 - 4}{2} = 2$       { VB Theory : $\ddot{\text{O}}=\ddot{\text{O}}$ : }

## Recall for O<sub>2</sub>

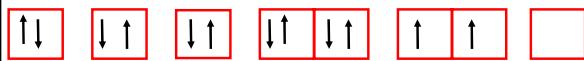
12 valence electrons



Unpaired electrons : 2      { VB Theory : $\ddot{\text{O}}=\ddot{\text{O}}$ : }  
Paramagnetic

### Recall for O<sub>2</sub>

12 valence electrons



Unpaired electrons : 2       $\left\{ \begin{array}{c} \text{VB Theory} \\ \cancel{\ddot{\text{O}}=\ddot{\text{O}}} \end{array} \right\}$   
Paramagnetic

### Paramagnetism of Oxygen:



A triumph of the M.O. theory

$\sigma_{2p}^*$	□	□	□	□	□
$\pi_{2p}^*, \pi_{2p}^*$	□	□	□	□	□
$\sigma_{2p}$	□	□	□	□	↑
$\pi_{2p}, \pi_{2p}$	□	□	□	↑	↑
$\sigma_{2s}^*$	□	↑	↑	↑	↑
$\sigma_{2s}$	↑	↑	↑	↑	↑
Bond order	1	0	1	2	3
Magnetism	Di-magnetic	-	Para-magnetic	Di-magnetic	Di-magnetic

$\sigma_{2p}^*$	□	□	↑
$\pi_{2p}^*, \pi_{2p}^*$	↑	↑	↑
$\pi_{2p}, \pi_{2p}$	↑	↑	↑
$\sigma_{2p}$	↑	↑	↑
$\sigma_{2s}^*$	↑	↑	↑
$\sigma_{2s}$	↑	↑	↑
Bond order	2	1	0
Magnetism	Para-magnetic	Di-magnetic	-

Molecule	Bond order	# unpaired e <sup>-</sup>	Bond length (Å)	$\Delta H_f$ kcal/mol	Magnetism
Li <sub>2</sub>	1	0	1	-26.3	Di-magnetic
Be <sub>2</sub>	0	0		Unknown	
B <sub>2</sub>	1	2	1.59	-69	Para-magnetic
C <sub>2</sub>	2	0	1.24	-150	Di-magnetic

Molecule	Bond order	Unpaired electrons	Bond length (Å)	$\Delta H_f$ kcal/mol	Magnetism
N <sub>2</sub>	3	0	1.10	-225	Di-magnetic
O <sub>2</sub>	2	2	1.21	-118	Para-magnetic
F <sub>2</sub>	1	0	1.4	-37	Di-magnetic

### M.O. theory shortcomings

M.O. theory does not always predict most stable state.

### LITHIUM

Most stable state under standard conditions is in metallic crystals.

However,  $\text{Li}_2$  has been observed in the vapor phase at high temperatures

### CARBON

Most stable state under standard conditions is in molecular networks (graphite, diamond)

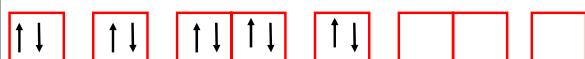
However  $\text{C}_2$  has been observed in the vapor phase at high temperatures.

Extend M.O. theory to molecular ions

Predict the relative stability and magnetic properties of  $\text{N}_2^+$  and  $\text{N}_2^{2+}$

### $\text{N}_2$

10 valence electrons



Bond order: 3

No unpaired electrons: diamagnetic

### $\text{N}_2^+$

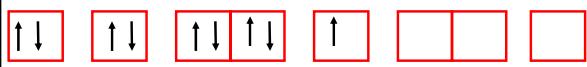
9 valence electrons



Bond order:  $\frac{7-2}{2} = 2.5$  Stable but less than  $\text{N}_2$

$\text{N}_2^+$

9 valence electrons



Unpaired electrons = 1

Paramagnetic

In agreement with experimental data

	ΔH <sub>f</sub> kcal/mol	Magnetism
N <sub>2</sub>	-225	Diamagnetic
N <sub>2</sub> <sup>+</sup>	-201	Paramagnetic

## MO THEORY

### PRACTICE

Review: Ch. 11.5-11.5

Practice Examples: 11.5 -11.7(A & B)

Exercises: 25-36

Quizzes: Petrucci website