CHEM110 – Chapter 5
Chemical Bonding and Molecular Structure

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5.7 Molecular Orbital Theory : Diatomic Molecules

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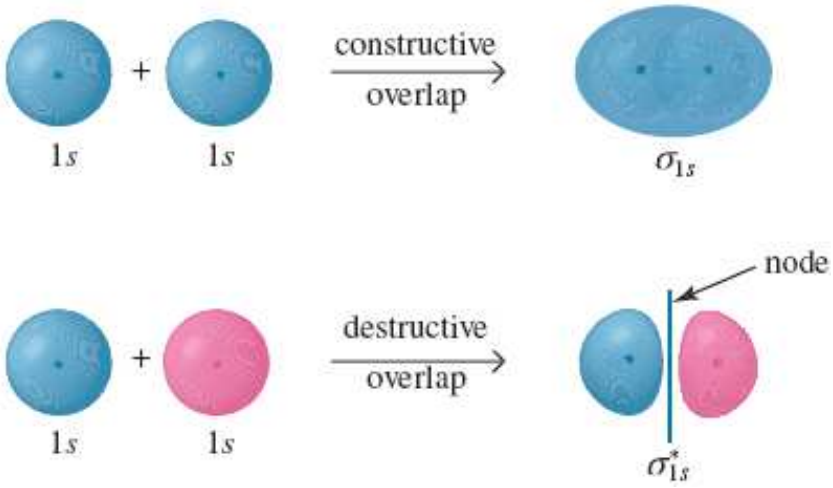
- Molecular orbital theory can predict and explain molecular properties
- Differs fundamentally from valence bond theory (it is more complex)
- Electrons within a molecule are not localised, instead they occupy molecular orbitals (MOs)
- *N* atomic orbitals will generate *N* molecular orbitals (i.e. combination 2 atomic orbitals gives 2 molecular orbitals)

5.7 Molecular Orbital Theory : Diatomic Molecules

Molecular orbitals of H_2

- When two hydrogen 1s atomic orbital interact, they generate two molecular orbitals :

  one **bonding** σ one **anti bonding** σ*



- The region of zero amplitude is called a node

5.7 Molecular Orbital Theory : Diatomic Molecules

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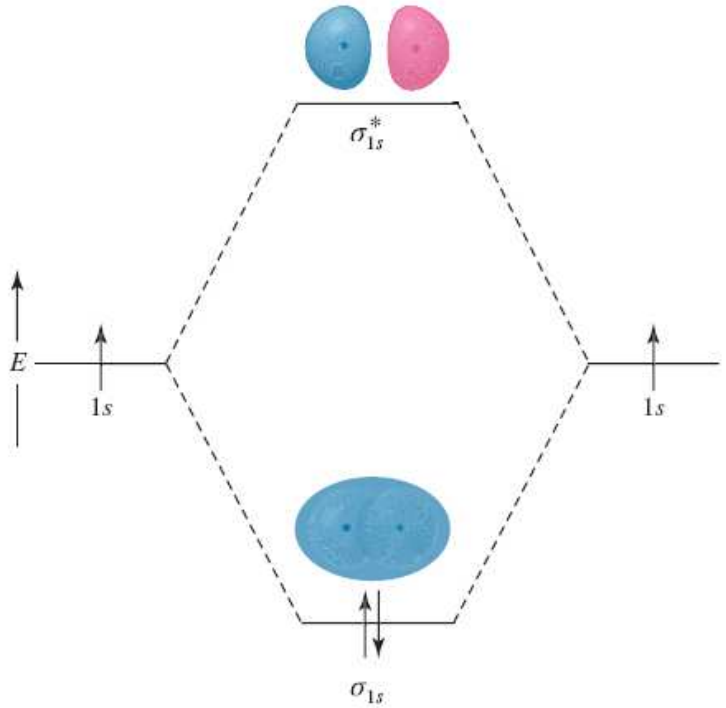
Molecular orbitals of H_2

- Molecular orbital diagrams show the relative energies of atomic and molecular orbitals



5.7 Molecular Orbital Theory : Bond Order

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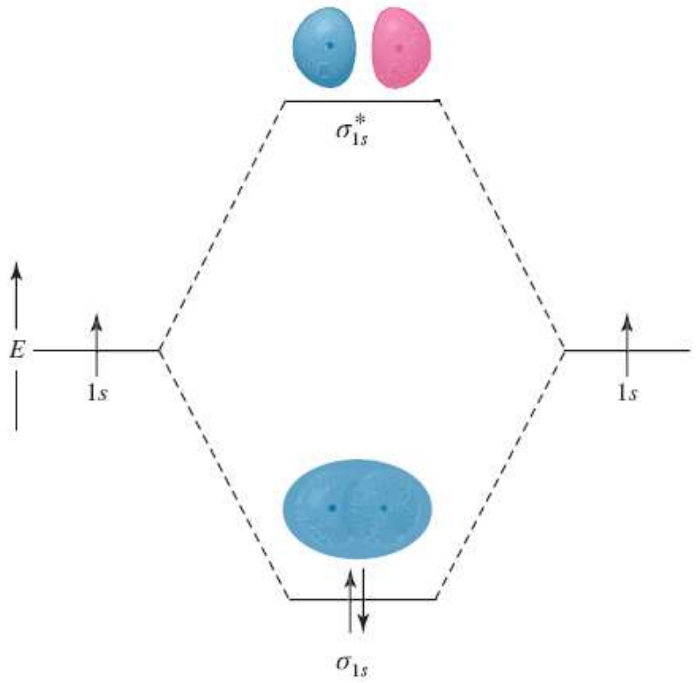
- Bond order (BO) can be calculated and used to establish whether a molecule will form (or not)
- Bonds will not form if there is no energy advantage (i.e. bond order = 0)
- Molecules with BO > 0 can exist (i.e. there is an energetic advantage)
- Note than BO can be non integer e.g. $\frac{1}{2}$, $1\frac{1}{2}$ etc.

5.7 Molecular Orbital Theory : Bond Order

- Bond order (BO) = ½ (number of e^- in bonding MO) – (number of e^- in antibonding MO)



Example H_2:

BO= ½ x (2-0) = 1

i.e. H_2 has 1 single bond

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Worked Example 5.9 (page 200):

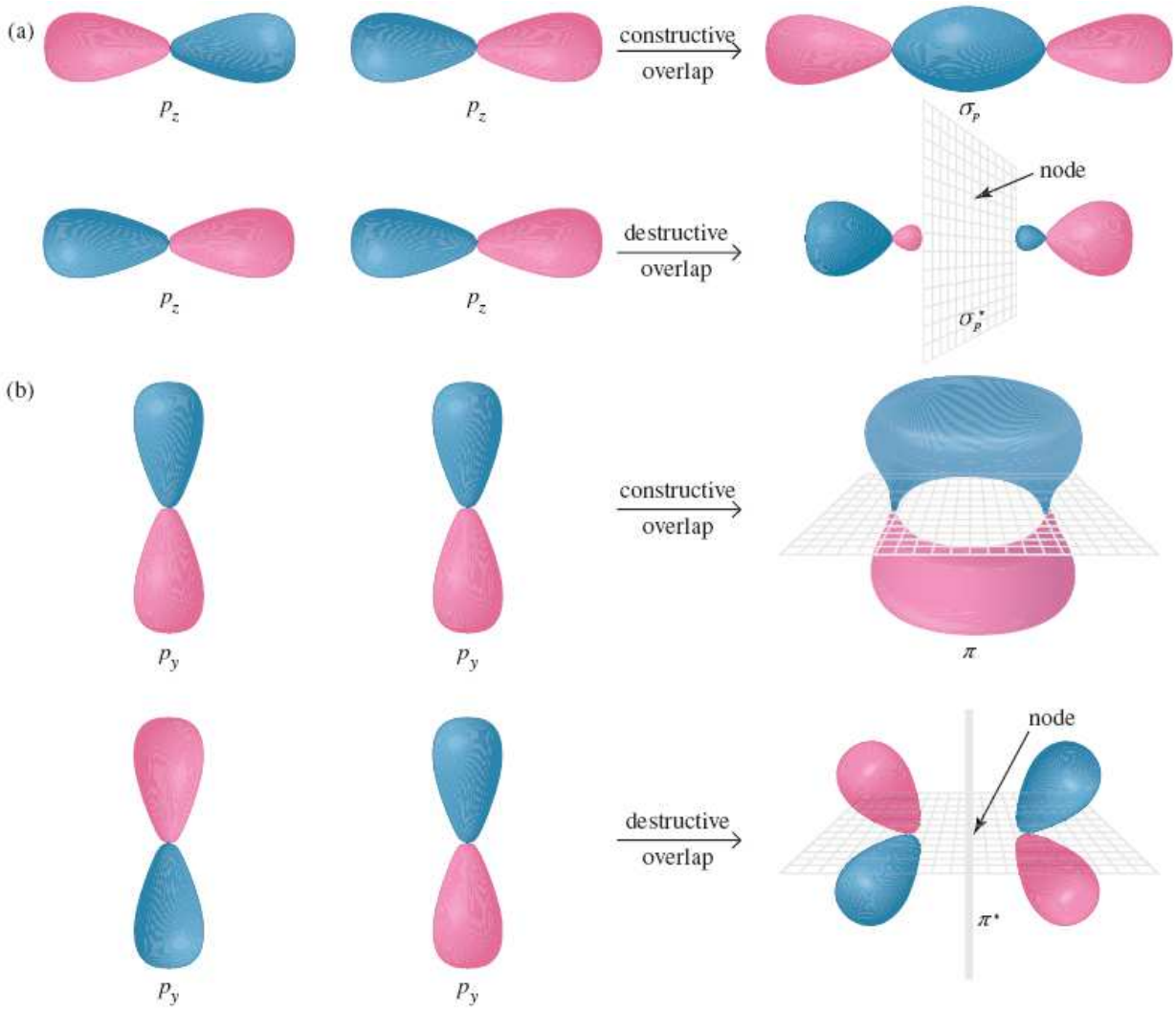
Use a molecular orbital diagram to predict if it is possible to form the He_2^+ cation.

5.7 Molecular Orbital Theory : Diatomic Molecules

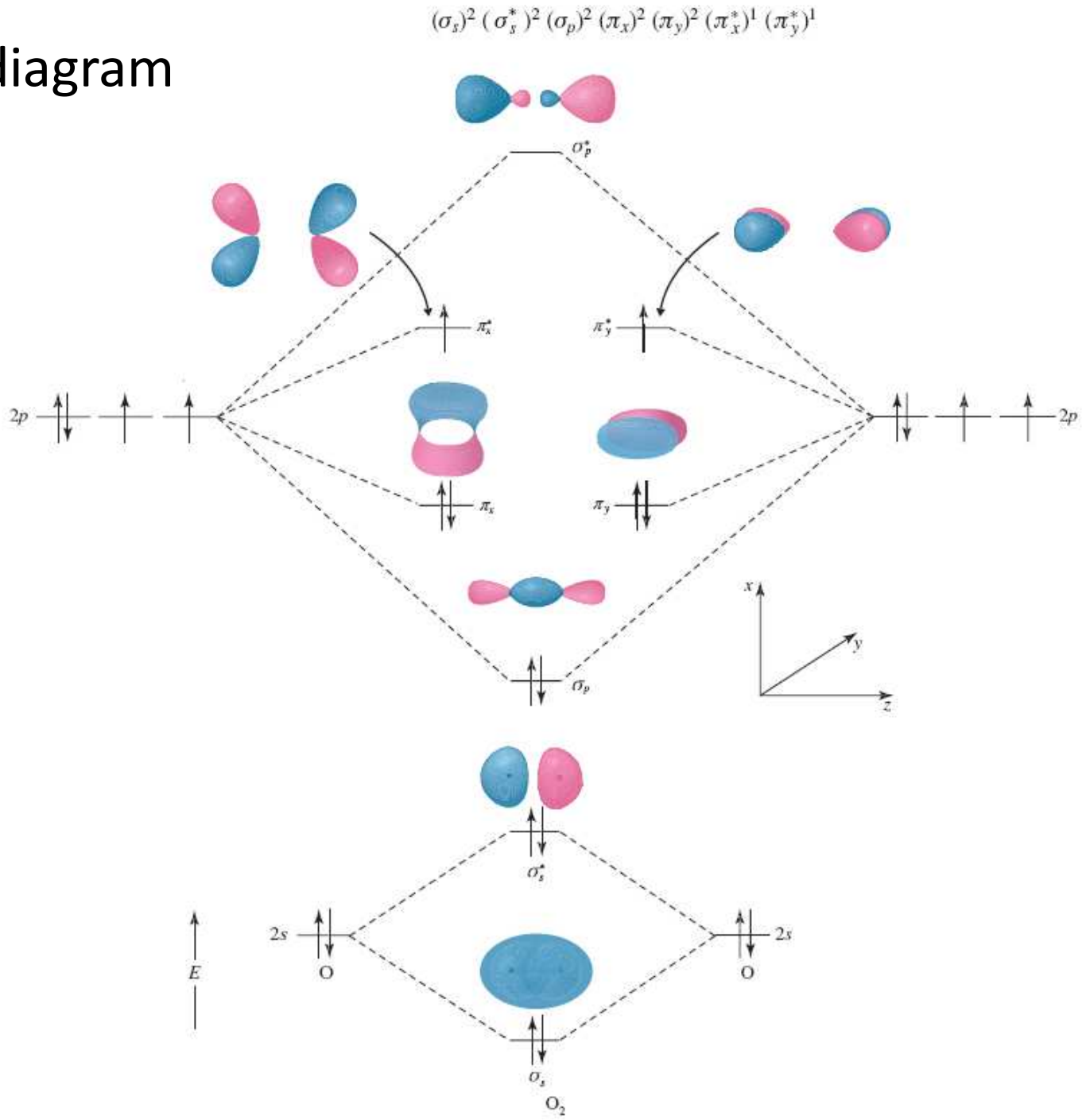
Example: Molecular orbitals of O_2

- Core MOs (σ_s and σ^*_s) contribute little to bonding
- The bonding and antibonding σ_s orbitals have the lowest energy
- The two π bonding orbitals are degenerate (equivalent)
- The antibonding orbitals formed from the atomic 2p orbitals are highest in energy, with the σ^*_p orbital higher than the π^*

5.7 Molecular Orbital Theory : Diatomic Molecules



O_2 MO diagram



5.7 Molecular Orbital Theory : Diatomic Molecules

Homonuclear diatomic molecules

- Until now we have assumed that 2s and 2p atomic orbitals act independently

- A more refined treatment of MO theory considers interactions between the 2s and 2p orbitals

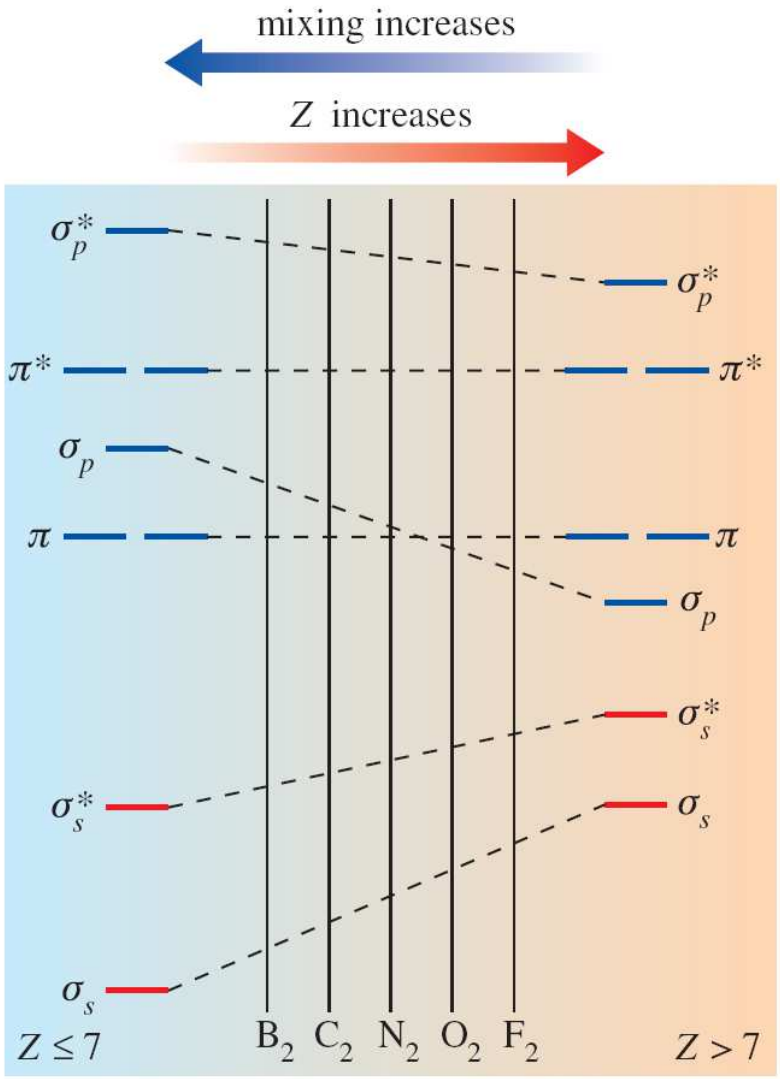
- Orbital mixing causes the σ_s and σ_p molecular orbitals to move further apart in energy

- The amount of mixing depends on the difference in energy between 2s and 2p atomic orbitals

(Mixing is largest when orbital energies are nearly the same)

5.7 Molecular Orbital Theory : Diatomic Molecules

Homonuclear



5.7 Molecular Orbital Theory : Diatomic Molecules

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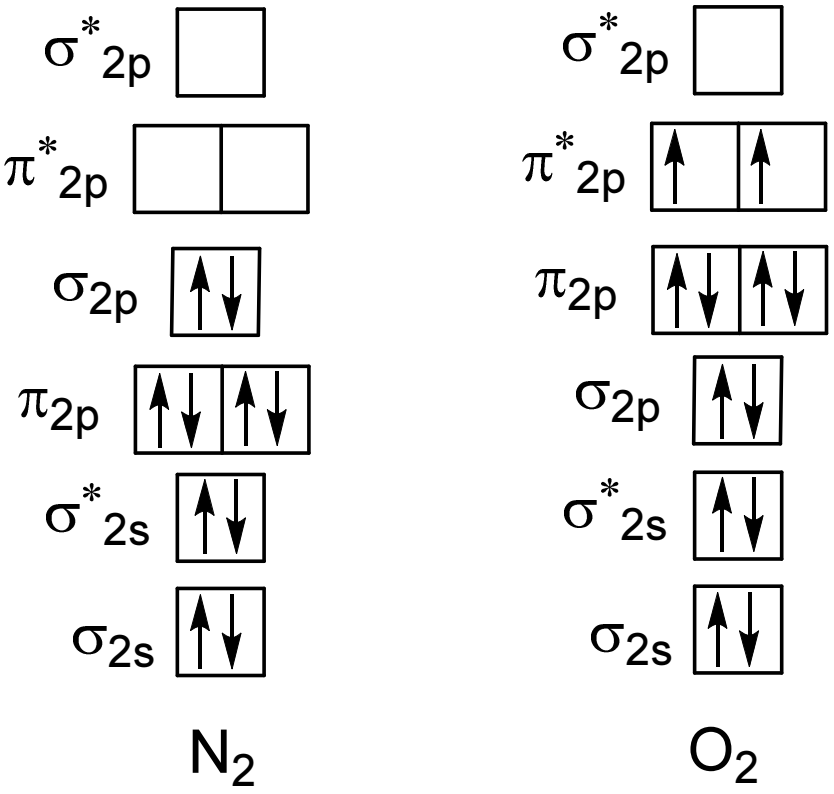
[Liquid Nitrogen vs Liquid Oxygen Video]



Also see Figure 5.50 in textbook

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Worked Example 5.10 (page 204):

Use molecular orbital diagrams to explain the trend in the following bond energies: B_2 = 290 kJ mol^{-1}; C_2 = 600 kJ mol^{-1}; N_2 = 942 kJ mol^{-1}

5.7 Molecular Orbital Theory : Diatomic Molecules

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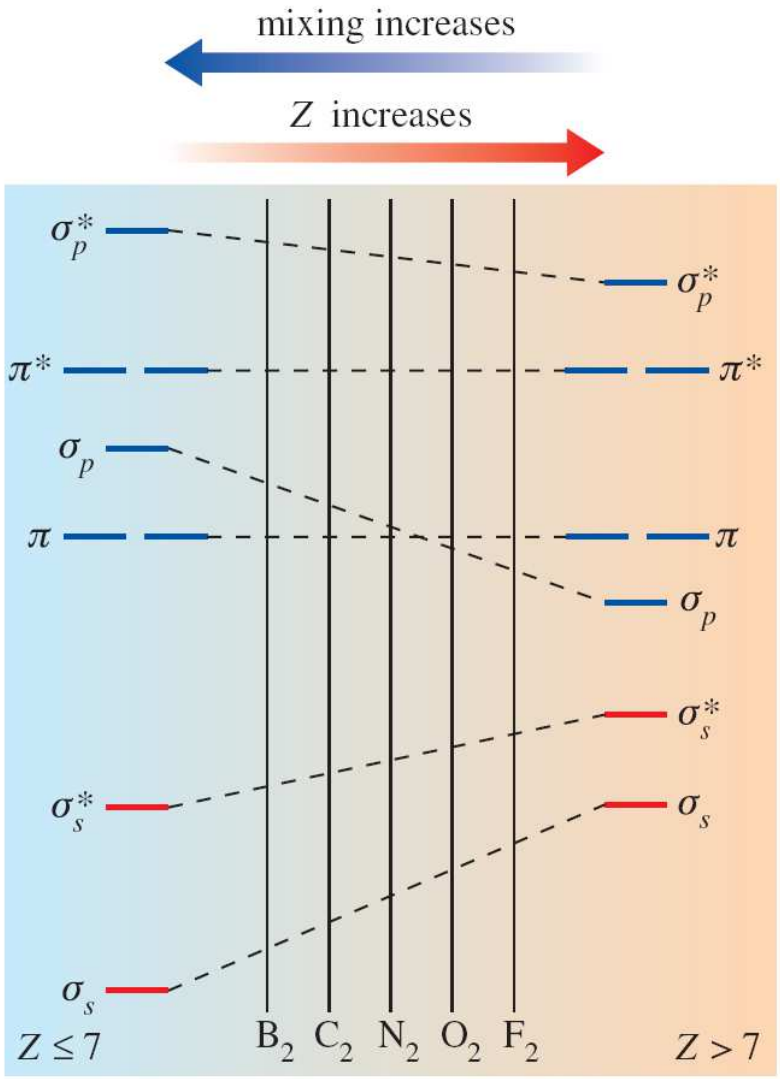
Homonuclear



5.7 Molecular Orbital Theory : Diatomic Molecules

Heteronuclear diatomic molecules

Qualitative features of orbital overlap do not depend on the identity of atoms

The same sets of orbitals that describe homonuclear diatomic molecules can be used

But which ones?

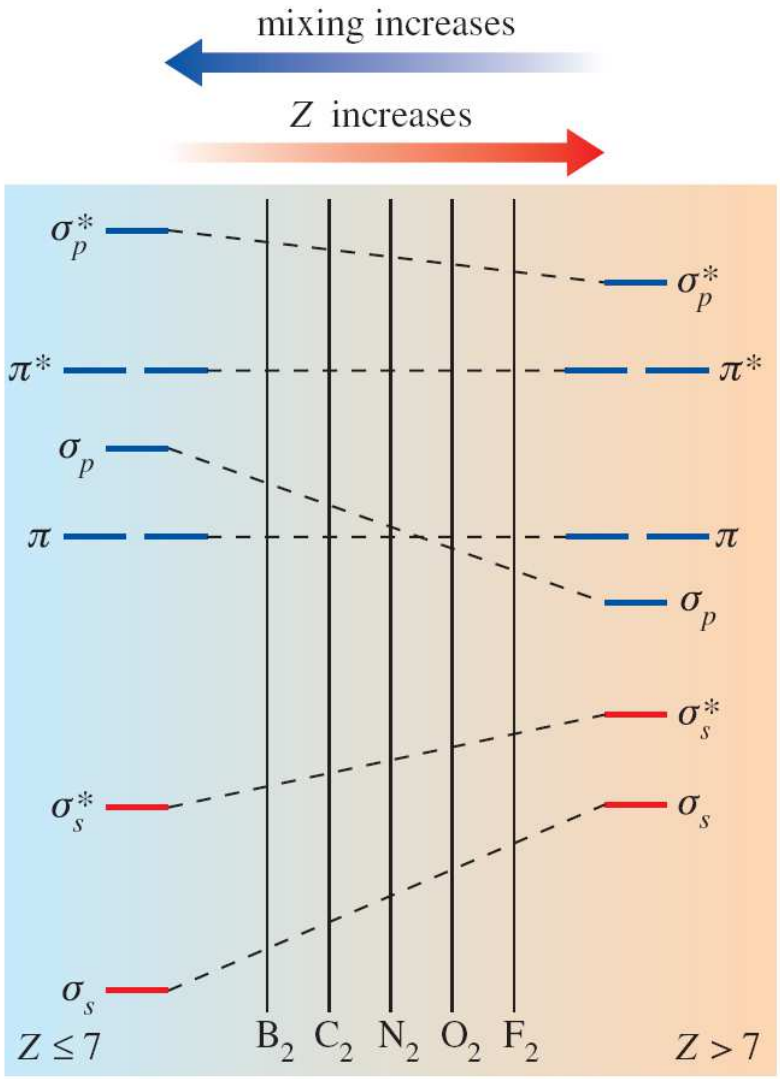
5.7 Molecular Orbital Theory : Diatomic Molecules

Heteronuclear diatomic molecules

Example: NO

5.7 Molecular Orbital Theory : Diatomic Molecules

Homonuclear



5.7 Molecular Orbital Theory : Diatomic Molecules

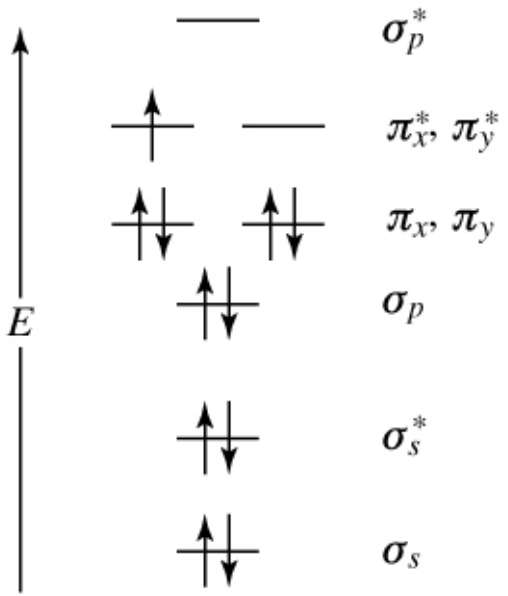
Example: NO

- Crossover point for energy rankings of the σ_p and π orbital is between N and O so we can expect energies to be about the same

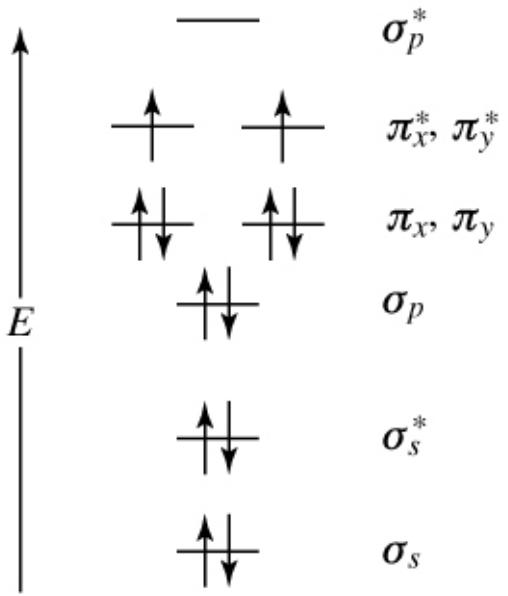
- Experiments show that that σ_p is slightly more stable than π (lower in energy)
- therefore energy levels of NO are the same order as O_2

5.7 Molecular Orbital Theory : Diatomic Molecules

Example: NO



Compare O_2

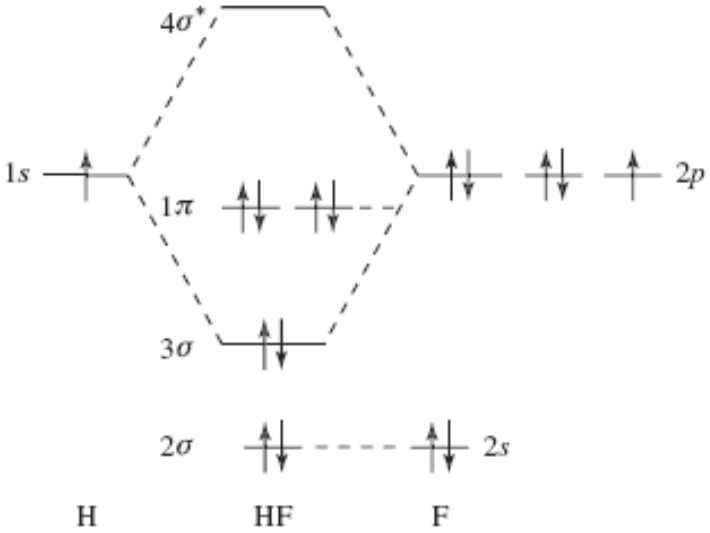


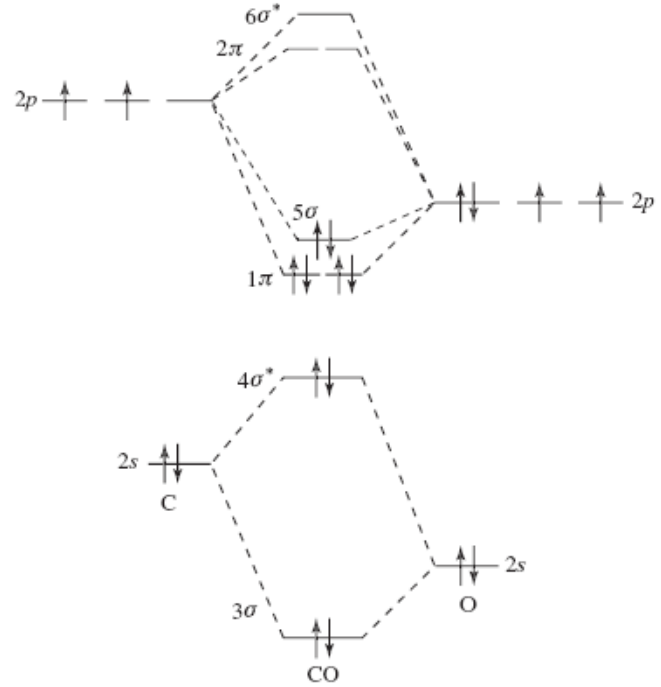
Species	Bond length	Bond energy	Configuration	Bond order
O_2	121 pm	495 kJ mol^{-1}	$\ldots (\sigma_p)^2 (\pi_x)^2 (\pi_y)^2 (\pi_x^*)^1 (\pi_y^*)^1$	2
NO	115 pm	605 kJ mol^{-1}	$\ldots (\sigma_p)^2 (\pi_x)^2 (\pi_y)^2 (\pi_{x,y}^*)^1$	2.5
N_2	110 pm	945 kJ mol^{-1}	$\ldots (\pi_x)^2 (\pi_y)^2 (\sigma_p)^2$	3

5.7 Molecular Orbital Theory : Diatomic Molecules

Heteronuclear diatomic molecules

For diatomic molecules composed of atoms with very different energies of their atomic orbitals, the MO diagram becomes more complicated





Chapter Summary

Fundamentals of bonding

- Covalent bonds are formed as a result of the sharing of electrons between nuclei
- Unequal sharing of electrons gives a polar covalent bond (electronegativity)

Ionic bonding

- Ionic compounds are formed between elements with very different electronegativities

Chapter Summary

Lewis structures

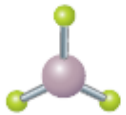
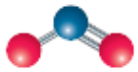
- Lewis structures show the distribution of valence electrons within a molecule and can be built following a 5 step procedure

VSEPR theory

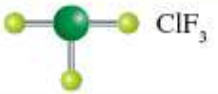
- To determine the geometry of a molecule, electron-pair repulsions are minimised by placing them as far apart as possible

Chapter Summary

TABLE 5.4 Features of molecular geometries.

Number of sets of electron pairs	Number of outer atoms	Lone pairs	Geometry of sets of electron pairs	Molecular shape	Bond angles	Dipole moment[a]	Example
2	2	0	linear	linear	180°	no	CO_2
3	3	0	trigonal planar	trigonal planar	120°	no	 BF_3
	2	1	trigonal planar	bent	<120°	yes	 NO_2^- (plus other resonance structures)
4	4	0	tetrahedral	tetrahedral	109.5°	no	CH_4
	3	1	tetrahedral	trigonal pyramidal	<109.5°	yes	NH_3
	2	2	tetrahedral	bent	<109.5°	yes	H_2O

Chapter Summary

5	5	0	trigonal bipyramidal	trigonal bipyramidal	90°, 120°	no	PCl_5
	4	1	trigonal bipyramidal	seesaw	<90°, <120°	yes	SF_4
	3	2	trigonal bipyramidal	T shaped	<90°, <120°	yes	 ClF_3
	2	3	trigonal bipyramidal	linear	180°	no	I_3^-
6	6	0	octahedral	octahedral	90°	no	SF_6
	5	1	octahedral	square pyramidal	<90°	yes	ClF_5
	4	2	octahedral	square planar	90°	no	XeF_4

(a) Applies only to molecules with identical outer atoms.

Chapter Summary

Properties of covalent bonds

- Dipole moment, bond length, bond energies

Valence bond theory

- Bonding in molecules using localised bonds formed from orbital overlap of hybrid orbitals

TABLE 5.5 A summary of valence orbital hybridisation.

Number of sets of electron pairs	Electron group geometry	Hybridisation	Number of hybrid orbitals	Number of unused *p* orbitals	Diagram[a]
2	linear	*sp*	2	2	
3	trigonal planar	sp^2	3	1	
4	tetrahedral	sp^3	4	0	

(a) Apart from one half (pink or blue) of the unhybridised p_z atomic orbital, all orbitals are of the same phase. The different colours are used for clarity only. Diminished lobes of opposite phase have also been omitted.

Chapter Summary

Molecular orbital theory : diatomic molecules

Bonding is describing in terms of delocalised bonds

The relative energies of the resulting orbitals are shown on a MO diagram and electrons are placed into this diagram

Bond order can be calculated

(we can use this to predict if molecules should exist!)