Lecture 18

Molecular Orbital Theory (8.12)

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Lecture 18, Knowledge and Skills

- Form molecular orbitals from atomic orbitals
  - bonding and nonbonding molecular orbitals
  - σ and π molecular orbitals
- Molecular orbital energy diagram
- Molecular electron configuration
- Predict physical properties of diatomic molecules
  - bond order; magnetism; relative bond lengths

I need to take Midterm II on Oct. 30 (Monday)

(a) Yes; (b) No

Atomic Orbitals

Atomic orbitals

- Location and energy of electron within atoms.

Atomic orbitals can be calculated by means of quantum mechanics.

You are familiar with the results of these calculations: s, p, d, f … orbitals.

Molecular Orbitals

Molecular orbitals

- can be obtained in a similar fashion by calculating the wavefunctions of electrons moving in the field of two or more nuclei.

Many similarities with atomic orbitals: the lowest orbital would have no node, the next orbital would have one node. Higher orbitals would have more nodes.

Molecular orbitals can be constructed by combining known atomic orbitals. This procedure is justified since in molecules most of the electrons are found near the nuclei of the atoms. This procedure is called "linear combination of atomic orbitals" (LCAO).

Molecular Orbitals, Basic Aspects

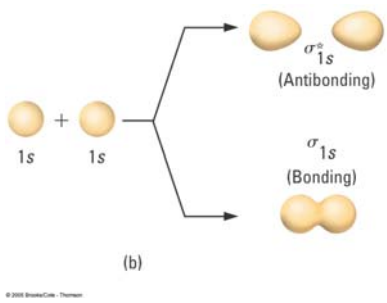
One of the basic rules for LCAO is that the number of molecular orbitals produced by combining atomic orbitals is exactly the same as the number of atomic orbitals used.

Simplest case: Dihydrogen, H_2

The combination of the 1s orbitals from the two hydrogen atoms gives exactly two molecular orbitals. One of these has no node, the other one node.

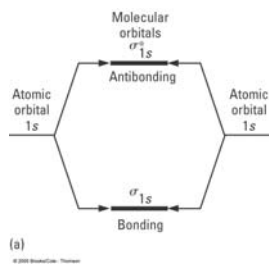
For the elements of the second period, we will also seek combinations of atomic p orbitals.

Molecular Orbitals of Dihydrogen



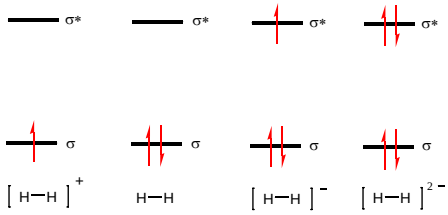
Molecular Orbital Energy Diagram

One molecular orbital is at lower energy than the orbitals of the free atoms, one is at higher energy.



Molecular Electron Configurations

The molecular electron configuration is obtained by placing the available electrons into these orbitals. Two electrons per orbital, starting with the lowest energy orbital.



Bond Order	1/2	1	1/2	0
Magnetism	param.	diam.	param.	--

Bond order: [(# of el. in bonding orb.)-(# of el. in antibond. orb.)]/2

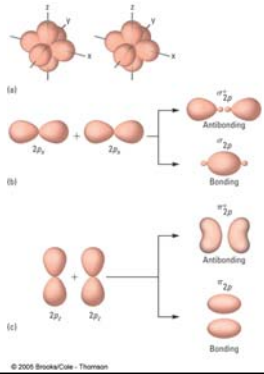
Homonuclear diatomic molecules of the second period elements

Overlap of 2s orbitals gives σ_{2s} and σ^*_{2s} orbitals.

Homonuclear diatomic molecules of the second period elements

Overlap of 2p orbitals can occur in two ways:

head-on and sideways, giving rise to two types of molecular orbitals, labeled σ and π, respectively.

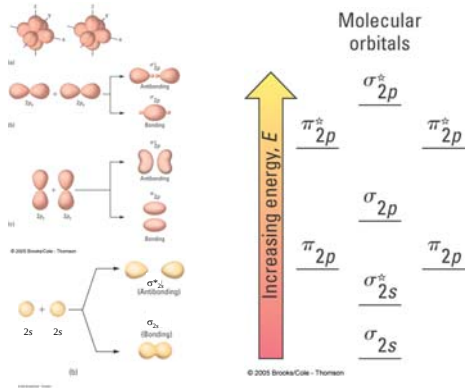


Homonuclear diatomic molecules of the second period elements

Each pair of interacting orbitals gives rise to corresponding bonding and antibonding orbitals.

The relative ordering of these orbitals is the result of subtle interactions between the electrons in these orbitals and is not the same for all diatomics under consideration. So we use a suitable generic orbital energy level diagram.

Overlapping orbitals and energy level diagram



Homonuclear diatomic molecules of the second period elements

One of the most remarkable facts is that even the simplest level of molecular orbital theory correctly predicts the paramagnetism of the dioxygen molecule.

Bond order: [(# of el. in bonding orb.)-(# of el. in antibond. orb.)]/2

Magnetism: molecules (atoms) with unpaired electrons are paramagnetic, those with only paired electrons are diamagnetic

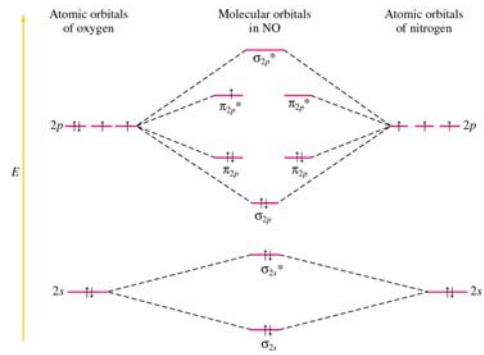
Bond length: expected to correlate with bond order

TABLE 8.4 Predicted and Observed Properties of Diatomic Molecules of Second-Period Elements

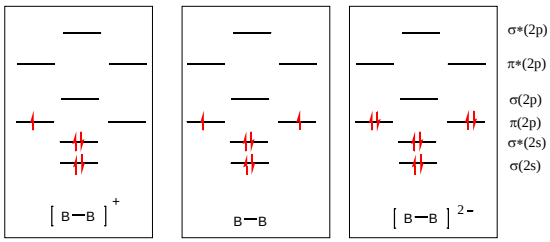
	Occupancy of Orbitals							
	σ_{2s}	σ^*_{2s}	π_{2p}	π_{2p}	σ_{2p}	π^*_{2p}	π^*_{2p}	σ^*_{2s}
Li_2	(↑↓)	( )	( )	( )	( )	( )	( )	( )
Be_2	(↑↓)	(↑↓)	( )	( )	( )	( )	( )	( )
B_2	(↑↓)	(↑↓)	(↑)	(↑)	( )	( )	( )	( )
C_2	(↑↓)	(↑↓)	(↑↓)	(↑↓)	( )	( )	( )	( )
N_2	(↑↓)	(↑↓)	(↑↓)	(↑↓)	(↑↓)	( )	( )	( )
O_2	(↑↓)	(↑↓)	(↑↓)	(↑↓)	(↑↓)	(↑)	(↑)	( )
F_2	(↑↓)	(↑↓)	(↑↓)	(↑↓)	(↑↓)	(↑↓)	(↑↓)	( )
Ne_2	(↑↓)	(↑↓)	(↑↓)	(↑↓)	(↑↓)	(↑↓)	(↑↓)	(↑↓)

	Predicted Properties		Observed Properties	
	Number of unpaired e^-	Bond Order	Number of Unpaired e^-	Bond Energy (kJ/mol)
Li_2	0	1	0	105
Be_2	0	0	0	Unstable
B_2	2	1	2	289
C_2	0	2	0	598
N_2	0	3	0	946
O_2	2	2	2	498
F_2	0	1	0	158
Ne_2	0	0	0	Nonexistent

Nitric oxide (NO) diagram



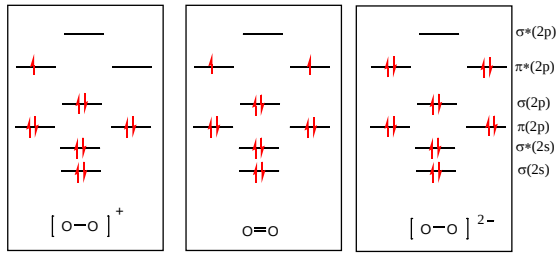
Diboron



	[B—B] +	B—B	[B—B] 2-
B. O.	1/2	1	2
Magn.	param.	param.	diam.
B. L.	longer than in BB		shorter

Complete same analysis for: [B—B] -

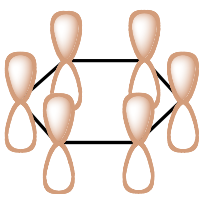
Dioxygen



	[O—O] +	O=O	[O—O] 2-
Bond O.	2.5	2	1
Magn.	param.	param.	diam.
Bond L.	shorter than in O=O		longer than in O=O

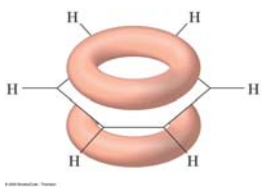
Complete same analysis for: [O—O] 2+ and [O—O] -

π Electron System of Benzene



6 atomic p orbitals

their combination gives 6 molecular π orbitals



This is the π orbital with no node (lowest energy). This picture may also be used to represent the entire π electron system.