CB VII

Molecular Orbital (MO) Theory

Ref 11: 3

Prob FUP: 11: 3, 4
E of C: 11: 32 – 37, 51

Adv Rdg 5: 1 - 5

General

further improvement on Lewis, VSEPR & VB theory;

resulting in better info on:
- bond energy
- bond order
- magnetic properties of molecules
- ……..
- ……..

Basic Principles

Wave mechanical theory
is applied to bonding in a molecule as a whole
i.e., includes interaction of **all nuclei & e⁻’s**

Schroedinger equ^n is solved for allowed wave states, or wave functions, Ψ, which, in turn, provide a description molecular orbitals (MO’s)

as a result we get a set of discrete MO’s describing energy & “location” of e^-’s

important to realize that MO’s cover the molecule as a whole (e^-’s are “delocalized”), rather than being strictly located on or between individual atoms

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Basic Ideas

- problem very complex
- no exact solutions exist
- various approximations are applied, esp. LCAO method (“linear combination of atomic orbitals”)
- start off w/ AO’s of bound atoms
- generally, combine AO’s that are close in:
  - proximity,
  - orientation,
  - energy

  to form MO’s

basic ideas ...

- use wavemechanical concepts, esp. aspects of wave interference (constructive and destructive) to construct MO's

- generally,
  # of MO's = # of "originating" AO's

  half of MO's are lower in energy than the originating AO's = **bonding MO's**

  half of MO's are higher in energy ...
  = **antibonding MO's**

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basic ideas ...

- apply principles you know from AO Theory to fill a set MO's w/ e^-'s as follows:

  "Aufbau"
  in ground state lowest energy MO's are occupied

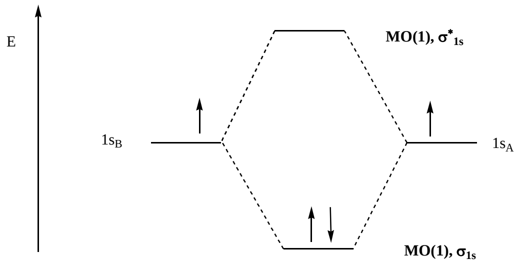
  "Pauli"
  max. of 2 e^-'s per MO;
  if 2 are present , they have opposite spins

  "Hund"
  if MO's are degenerate,
  fill MO's singly first (w/ same spin)
  before doubling up

Application to H_2 Molecule

$_{A}H - H_{B}$

Energy Diagram



MO(1) = 1 s_A + 1 s_B
MO(2) = 1 s_A – 1 s_B

2 e^-'s available,
only the bonding MO, σ_{1s}, will be filled,

∴ H_2 stable !!

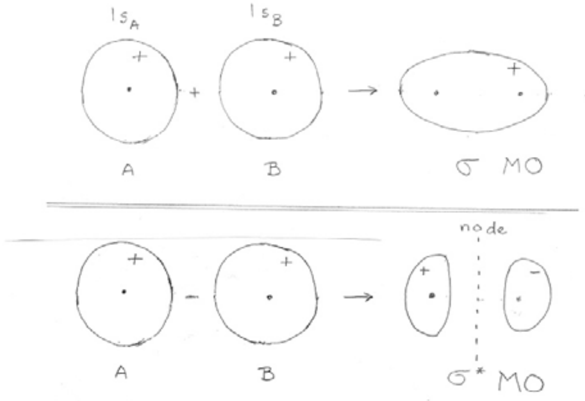
H_2 molecule ...

equivalent expression :

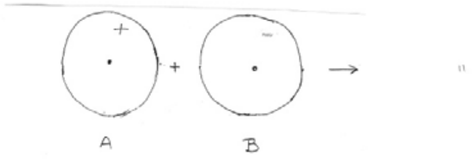
$1s_A$ & $1s_B$ AO's combine

in - phase to form bonding MO's
&
out - of - phase to form antibonding MO's

Orbital Diagrams for H_2

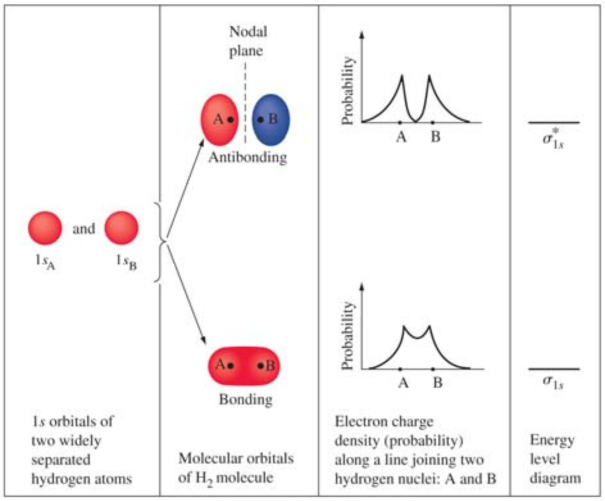


or equivalent



same as $a - (+b) = a + (-b)$

Pet. Fig.11.20 MO Theory for H_2



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Bond Order by MO Theory

General:

$$\text{B.O.} = \frac{\text{bonding } e^{-}\text{'s} - \text{antibonding } e^{-}\text{'s}}{2}$$

for H_2:

$$\text{B.O.} = \frac{2 - 0}{2} = 1 \quad (\textit{single bond})$$

in this case, agrees w/ Lewis theory

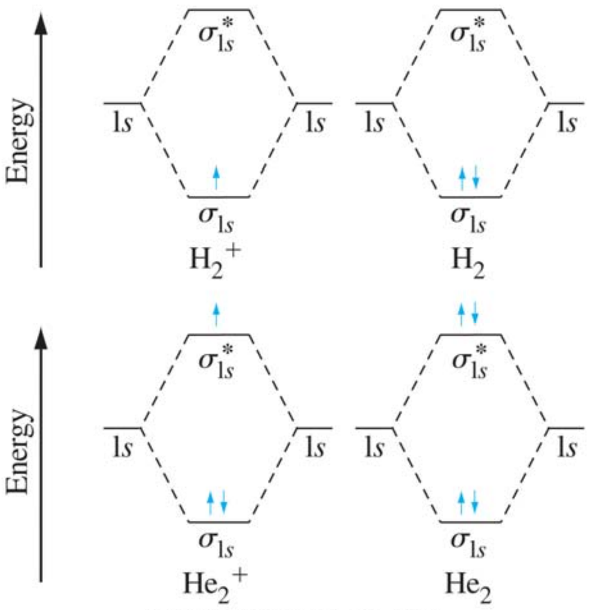
Other Row 1 Species

see Pet. Fig. 11.21

evaluate for B.O. and stability:

species	B.O.	Existence
H_2^+	0.5	known
He_2^+	0.5	“expected
He_2	0	unknown, not expected

Pet. Fig. 11.21 MO diagrams for diatomic row 1 species



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MO Theory for Row 2 Molecules (diatomic, homonuclear)

Generally,

can ignore core AO's (i.e., 1s AO's)

(because weak interaction;
also, bonding & antibonding MO's cancel)

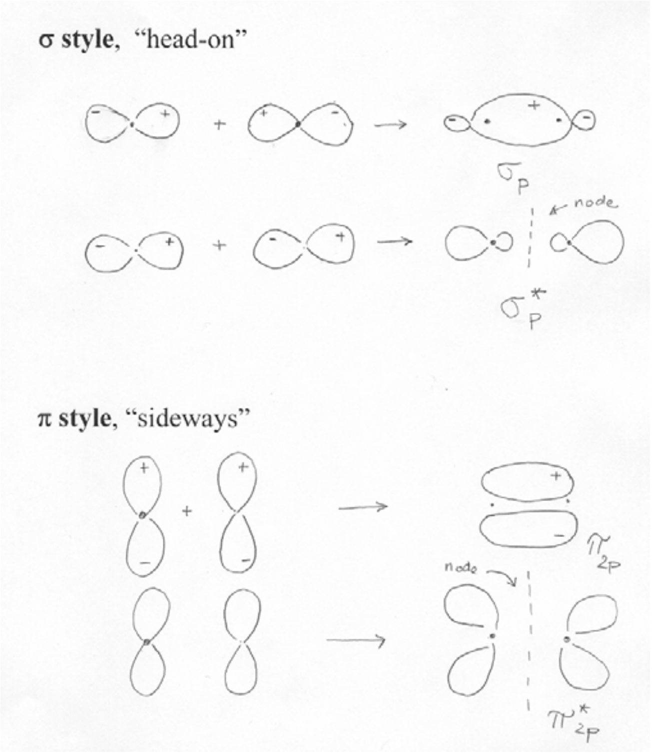
i.e., work w/ valence e^-'s

significant combinations in row 2 orbitals:

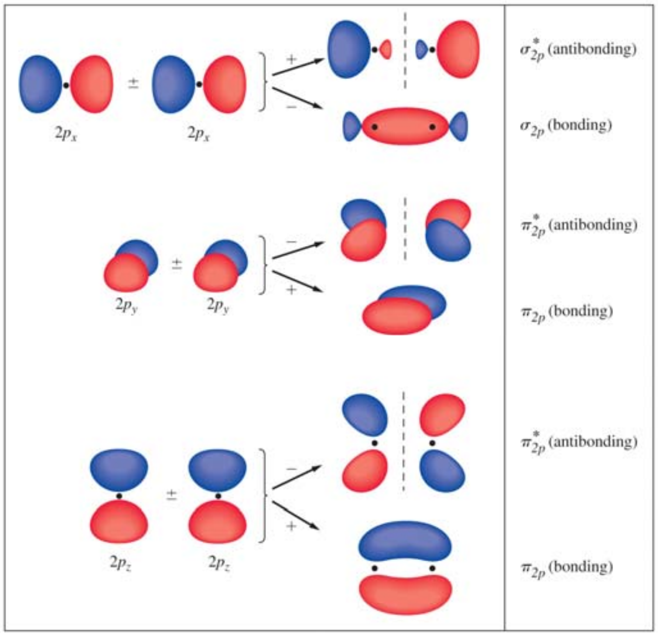
2s AO's ⟶ σ_{2s} MO

2p AO's ⟶ $\begin{cases} \sigma_{2p} \text{ MO} \\ \pi_{2p} \text{ MO} \end{cases}$

Combination of p AO's



Pet. Fig. 11.23 MO's from 2p AO's



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MO Energy Diagrams

σ_{2s} lower than σ_{2p}, π_{2p}

(b/c originating 2s AO's are lower than 2p AO)

expect that σ_{2p} is lower than π_{2p}
(σ_{2p} has more overlap than π_{2p})

"expected" MO diagram
(HT Fig. 14.1)

but exceptions are common

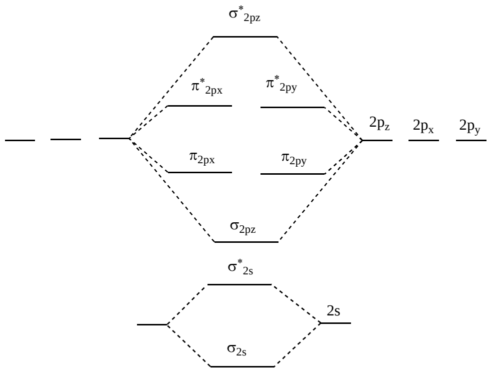
"modified" MO diagram
(HT Fig. 14.2)

General MO Energy Diagram

Expected

valid for O_2, F_2, (Ne_2)

HT Fig. 14.1

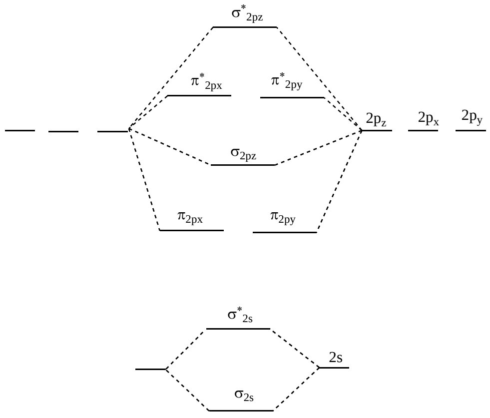


General MO Energy Diagram

Modified

valid for Li_2 .... N_2

HT Fig.14.2



Practice

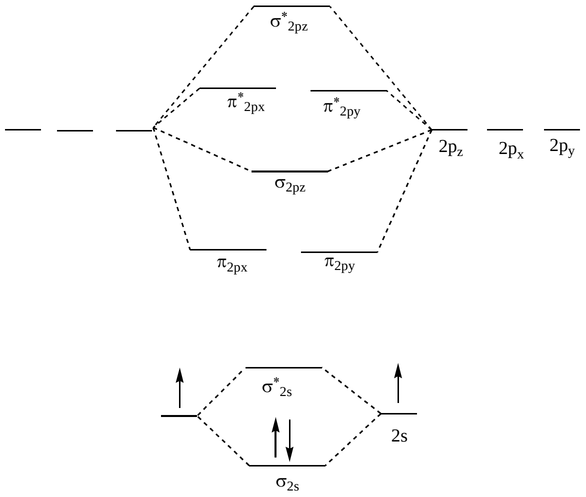
Complete MO Energy Diagrams for

Li_2, B_2, N_2, O_2

- fill MO diagrams w/ e^-'s
- determine B.O.
- assess magnetism

For completeness sake, you may want to do Be_2, C_2, F_2, Ne_2 also

MO Energy Diagram for **Li_2**

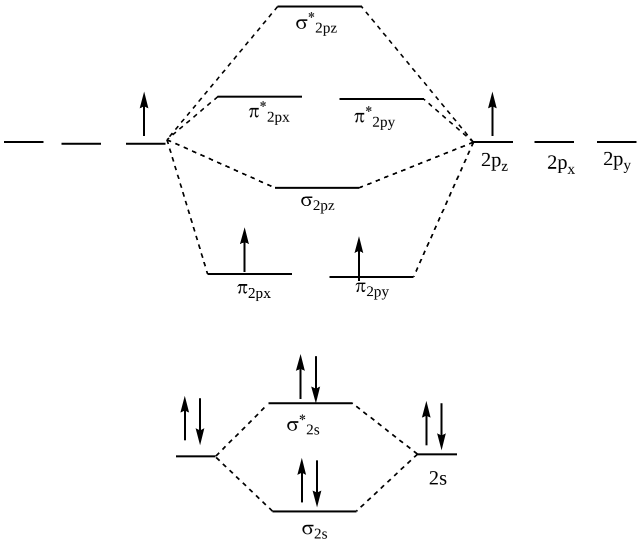


$$\text{B.O.} = \frac{2-0}{2} = 1$$

all e^-'s paired

∴ diamagnetic

MO Energy Diagram for **B_2**

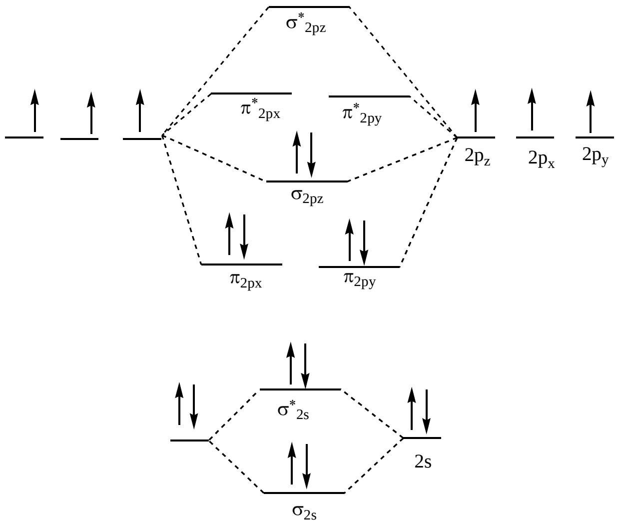


$$\text{B.O.} = \frac{4-2}{2} = 1$$

2 e^-'s unpaired

∴ paramagnetic

MO Energy Diagram for **N_2**

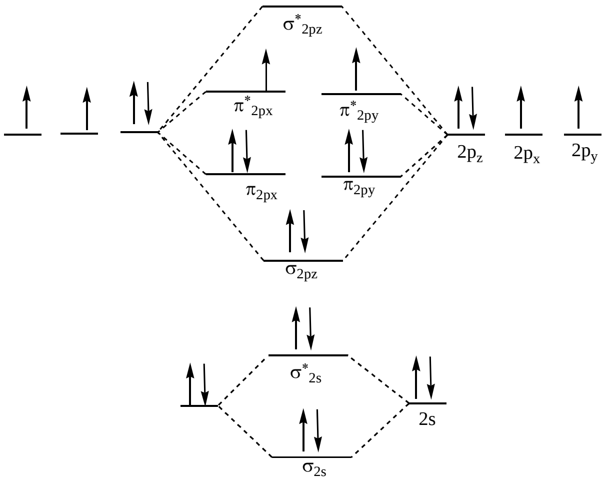


$$\text{B.O.} = \frac{8-2}{2} = 3$$

all e^-'s paired

∴ diamagnetic

MO Energy Diagram for **O_2**



$$\text{B.O.} = \frac{8-4}{2} = 2$$

2 e^-'s unpaired

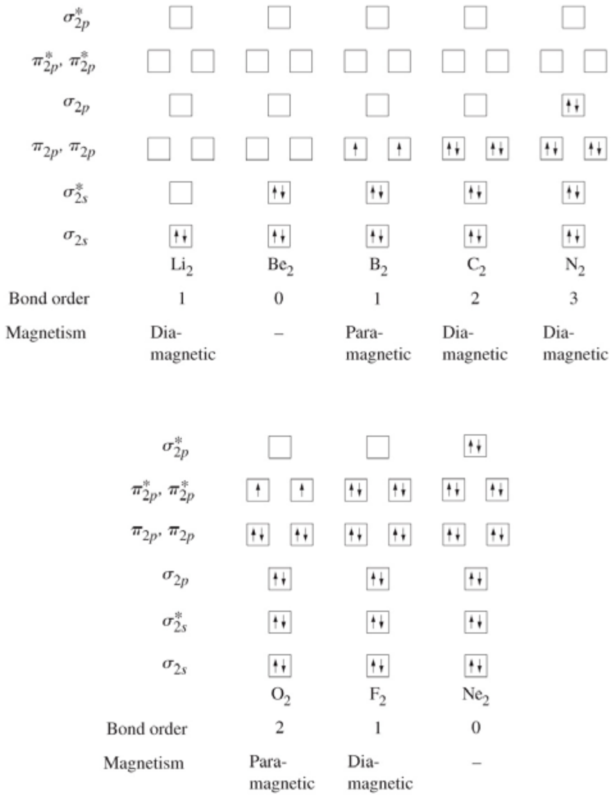
∴ paramagnetic

Summary

Pet. Fig. 11.25 provides a summary of MO’s for all row 2 diatomic homonuclear molecules.

Derive, don’t memorize

Pet.Fig. 11.23 Summary of MO theory for row 2 diatomics



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Comments

- Use the same diagrams to analyze
  (stability, B.O., magnetism …)
  charged homonuclear species,
  such as N_2^+, O_2^- , etc.

- similar analysis applies
  to **row 3** diatomic molecules
  Na_2 ……. Ar_2
  Combine 3s and 3p AO’s to get
  σ_{3s}, σ_{3p}, π_{3p} MO’s
  (again bonding & antibonding etc.)

Heteronuclear Diatomics

(e.g., CO, NO)

when molecule contains O

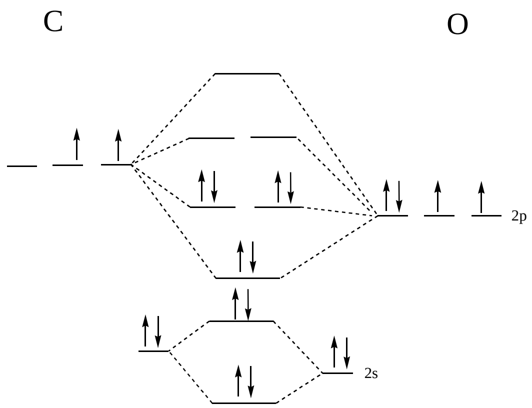
apply “**expected**” MO energy diagram,

but in a “distorted” form

(originating AO’s of more e/n atom are lower in energy, causing this distortion)

see CO as an example, HT Fig.14.3

HT Fig. 14.3 MO Energy Diagram for CO



$$\text{B.O.} = \frac{6-0}{2} = 3$$

all e^-'s paired

∴ diamagnetic

Overall Comment on Bonding

- MO theory generally gives best results,
  but often very complicated

- in many cases, simpler theories are satisfactory

- "practicing chemists" use a mixture of all theories,
  "whatever works best"

- e.g., in organic chem.:

  for σ bonds: use VB theory, including hybridization of AO's

  for π bonds: use MO theory, including resonance ideas from Lewis theory