MULTIPLE BONDS Handout - Page 1
ETHENE (ethylene):

Recall - From VB model (Fig. 14.10 text):

- Un-hybridized p AO in sp$^2$ hybridization is \( \perp \) to PLANE of 3 x sp$^2$ HAO's.

Energy Level Scheme - sp$^2$ hybridization of \( C_a \) & \( C_b \):

- \( \text{C atom} "a" \): \( sp_a^2 \), \( sp_a^2 \), \( 2p_{a} \)
- \( \text{C atom} "b" \): \( sp_b^2 \), \( sp_b^2 \), \( sp_b^2 \), \( 2p_{b} \)

\( \sigma \) bonding framework of \( C_2H_4 \):

- Each of 4 C-H \( \sigma \) bonds = sp$^2_C + 1s_H$ and
- C-C "1st" bond = \( \sigma_{CC} = sp^2_a + sp^2_b \) ("Hot Dog")
The “2nd” C-C bond in C_2H_4:
(Page 3 - Multiple Bond Handout)

• σ bonds are depicted as “sticks”.
A NEW TYPE of BOND (Localized MO) forms:
• “2nd” C-C bond = π C-C = 2p_⊥a + 2p_⊥b (z-axis) - “BUN”.

MULTIPLE BONDS Handout - Page 3
ETHYNE (acetylene):

• EACH C atom sp hybridized
• The s & p_y AO’s hybridize (Why p_y AO ?).

Energy Level Scheme - sp hybridization of C_a & C_b :
(Page 3 - Multiple Bond Handout)

• p_x & p_z AO’s ⊥ to “line” of H-C-C-H atoms.

σ bonding framework of C_2H_2 :
(Page 4 - Multiple Bond Handout)

• Each of 2 C-H σ bonds = sp_C + 1s_H and
• C-C “1st” bond = σ_C-C = sp_a + sp_b (“Hot Dog”)
The “2nd” & “3rd” C-C bonds in C_2H_2:
(Page 5 - Multiple Bond Handout)

- σ bonds are depicted as "sticks".
- TWO (2) π BONDS (Localized MO’s) form:
  - "2nd" C-C bond = π_{C-C} = 2p_{za} + 2p_{zb} (z-axis) - "1 BUN".
  - "3rd" C-C bond = π_{C-C} = 2p_{xa} + 2p_{xb} (x-axis) - "2 BUNS".

Resonance … VB Model is NOT enough…
“Delocalized” MO theory to the “rescue”:
(Pages 5 & 6 - Multiple Bond Handout)

- EXAMPLE - CARBONATE ANION - CO_3^{2-} (continued)
  3 equivalent resonance structures … 3 equivalent C-O bonds.

Summary of Bonds - VB Model:
(Page 5 - Multiple Bond Handout)

- Single Bond = σ MO or σ BOND.
- Double Bond = σ MO or σ BOND ("Hot Dog") + π MO or π BOND. ("Bun").
- Triple Bond = σ MO or σ BOND ("Hot Dog") + π MO or π BOND. (Another "Bun").

EXAMPLE - CARBONATE ANION - CO_3^{2-} (continued)
SINGLE structure "explaining" 1 1/3 B.O.:
(Page 6 - Multiple Bond Handout)

- ALL ATOMS - C & O are sp^2 hybridized - all PLANAR.
- EACH C atom has a 2p_z AO ⊥ to PLANE (4 total).
- 2 e’s in 2nd bond are DELOCALIZED over all 3 sites.
EXAMPLE - CARBONATE ANION - $\text{CO}_3^{2-}$ (continued)
(Page 6 - Multiple Bond Handout)

• A single $\pi$-type MO with electron density DELOCALIZED over ALL 3 bond sites …

ANOTHER EXAMPLE - BENZENE - $\text{C}_6\text{H}_6$:
(Figure 14.48 - text)
Equivalent "Best" structures "signal" for DELOCALIZATION … NOT the CAUSE!!

ANOTHER EXAMPLE - BENZENE - $\text{C}_6\text{H}_6$:
(Figure 14.49 - text)
6 UN-INTERUPTED sp² C atoms in a "ring":

ANOTHER EXAMPLE - BENZENE - $\text{C}_6\text{H}_6$:
(Figure 14.50 (a) & (b) - text)
"Parallel" "Picket" fence of parallel p AO’s.

DELOCALIZED $\pi$ MO … “BAGEL” ?!?!
ANOTHER EXAMPLE - NITRATE ANION - NO₃⁻:

(FIGURE 14.51 (a) - text)

"Parallel" "Picket" fence of parallel p AO's.

MO Theory Handout - Page 1

Homonuclear Diatomic Molecule (X₂):

• MUST SOLVE SCHRODINGER WAVE EQUATION (SWE)...
• IF USE AO's to construct MO's ... MUST TAKE ALL POSSIBLE Linear Combinations of Atomic Orbitals to construct Molecular Orbitals ... LCAO-MO.
• CONSTRUCTIVE (BONDS) &
• DESTRUCTIVE (???) ... "Worse than bonds" ... HOMONUCLEAR DIATOMIC MOLECULES (X₂):
• "Like" AO's IDENTICAL on EACH atom (in energy & form):
  1sₐ = 1sₐ ; 2sₐ = 2sₐ ; 2pₓA = 2pₓB ; 2pᵧA = 2pᵧB ;
  2p₂A = 2p₂B.

• ALL POSSIBLE EQUAL COMBO's of IDENTICAL AO's ...

NITRATE ANION - NO₃⁻ (continued):

(FIGURE 14.51 (b) - text)

DELOCALIZED π MO ...
MO Theory Handout (X₂) (continued):

• Only $\Psi^2$ is the important quantity - Probability Density.

THUS:

• $(MO_{IV})^2 = (-1s_A - 1s_B)^2 = (-1)^2(1s_A + 1s_B)^2 = (MO)^2$

• $(MO_{II})^2 = (-1s_A + 1s_B)^2 = (-1)^2(1s_A - 1s_B)^2 = (MO^*)^2$

Thus - only 2 unique combos:

• CONSTRUCTIVE = $AO_A + AO_B = BONDING MO$.
• DESTRUCTIVE = $AO_A - AO_B = ANTIBONDING MO = (MO)^*$.

What do they look like?
• How do they stack ENERGETICALLY? …
  • Do they INTERLEAVE?…

MO Theory Handout (X₂) (continued)
(PAGE 3 of MO Handout):

2s BONDING MO & 2s ANTIBONDING MO:

MO Theory Handout (X₂) (continued)
(PAGE 4 of MO Handout):

2p BONDING MO (ALONG bond axis):

MO Theory Handout (X₂) (continued)
(PAGE 4 of MO Handout):

2p ANTIBONDING MO (ALONG bond axis):
MO Theory Handout (X₂) (continued)  
(PAGE 5 of MO Handout):  
2p BONDING MO’s (⊥ to bond axis):  

2p_yA + 2p_yB  

Bonding Combo  

& another set along x-axis.  

π_{2p}  

MO Theory Handout (X₂) (continued)  
(PAGE 5 of MO Handout):  
2p ANTI-BONDING MO’s (⊥ to bond axis):  

2p_yA - 2p_yB  

Antibonding Combo  

& another set along x-axis.  

π^*_{2p}  

MO Theory Handout (X₂) (continued)  
(PAGE 2 of MO Handout):  

- STACK the COMBO’s … Notice that they INTERLEAVE …  
  Li through N:  

MO Theory Handout (X₂) (continued)  
(PAGE 2 of MO Handout):  

- ANOTHER SCHEME: O, F, & Ne:  

\[ 2p_{y,A}, 2p_{z,A}, 2p_{x,A}, 2p_{y,B}, 2p_{z,B}, 2p_{x,B}, 2s_A, 1s_A, 2s_B, 1s_B \]
MO Theory Handout (X2) (continued)

Where are the bonds?
(PAGE 6 of MO Handout)

• Bond Order (B.O.) =

\[(1/2) \cdot [\text{Tot. \# of Bonding } e^-\text{s} - \text{Tot. \# of Antibonding } e^-\text{s}]\]

• If B.O. = 0; molecule predicted to NOT form.
  He₂, Be₂ & Ne₂.

• ALSO - MAGNETIC PROPERTIES … similar to atoms
  • PARAMAGNETIC (any unpaired e'-'s) &
  • DIAMAGNETIC (NO unpaired e'-'s)

MO Theory Handout (X2) - Page 1 (continued):

HOMONUCLEAR X₂ (atoms “A” & “B”):
• “List of AO’s for 2nd ROW Molecules:
  \(1sₐ = 1sₐ ; 2sₐ = 2sₐ ; 2pₓₐ = 2pₓₐ ; 2pᵧₐ = 2pᵧₐ ; 2p₂ₐ = 2p₂ₐ\).

• ALL POSSIBLE EQUAL COMBO’s of IDENTICAL AO’s …
EXAMPLE with \(1sₐ & 1sₐ\):
• \(MO_I = + 1sₐ + 1sₐ\)
• \(MO_{II} = + 1sₐ - 1sₐ\)
• \(MO_{III} = - 1sₐ + 1sₐ = - MO_{II}\)
• \(MO_{IV} = - 1sₐ - 1sₐ = - MO_{I}\)

• Only \(\Psi²\) is the important quantity - Probability Density..

MO Theory Handout (X2) (continued):

• Only \(\Psi²\) is the important quantity - Probability Density..

THUS:
• \((MO_I)² = (-1)²(1sₐ + 1sₐ)^² = (MO)²\)
• \((MO_{II})² = (-1)²(1sₐ - 1sₐ)^² = (MO)²\)

• Thus - only 2 unique combos:
  • CONSTRUCTIVE = \(AO_A + AO_B = BONDING\ MO\).
  • DESTRUCTIVE = \(AO_A - AO_B = ANTI\ BONDING\ MO = (MO)*\).

What do they look like?
• How do they stack ENERGETICALLY? …
  • Do they INTERLEAVE?…

MO Theory Handout (X2) (continued)

(PAGE 3 of MO Handout):

2s BONDING MO & 2s ANTIBONDING MO:

![Bonding Combo](image1)

\[2s_A + 2s_B \rightarrow \sigma_{2s}^+\]

![Antibonding Combo](image2)

\[2s_A - 2s_B \rightarrow \sigma_{2s}^-\]
MO Theory Handout (X₂) (continued)
(PAGE 4 of MO Handout):
2p BONDING MO (ALONG bond axis):

\[ 2p_z^A + 2p_z^B \rightarrow \sigma_{2p} \]

MO Theory Handout (X₂) (continued)
(PAGE 4 of MO Handout):
2p ANTIBONDING MO (ALONG bond axis):

\[ 2p_z^A - 2p_z^B \rightarrow \sigma^{*}_{2p} \]

MO Theory Handout (X₂) (continued)
(PAGE 5 of MO Handout):
2p BONDING MO's (L to bond axis):

\[ 2p_y^A + 2p_y^B \rightarrow \pi_{2p} \& \text{another set along x-axis.} \]

MO Theory Handout (X₂) (continued)
(PAGE 5 of MO Handout):
2p ANTIBONDING MO's (L to bond axis):

\[ 2p_y^A - 2p_y^B \rightarrow \pi^{*}_{2p} \& \text{another set along x-axis.} \]
MO Theory Handout (X2) (continued)
(PAGE 2 of MO Handout):
• STACK the COMBO’s … Notice that they INTERLEAVE …
  Li through N:

MO Theory Handout (X2) (continued)
(PAGE 2 of MO Handout):
• ANOTHER SCHEME: O, F, & Ne:

MO Theory Handout (X2) - Ground State Config’s
Fill them in … follow Pauli & Hund …

MO Theory Handout (X2) - Ground State Config’s
Fill them in … follow Pauli & Hund …
Heteronuclear Diatomic Molecules … Page 7 of MO Handout - CO Example (valence shell):

MO Theory Handout (X2) - Ground State Config’s
Fill them in … follow Pauli & Hund …

\[
\begin{align*}
\text{MO Theory Handout (X2) - Ground State Config's} & \quad O_2, F_2, & \text{Ne}_2 \quad \sigma_{2p} & \text{& } \pi_{2p} \text{ MO's “switch”} \\
\end{align*}
\]

Heteronuclear Diatomic Molecules … Page 8 of MO Handout - HF Example (valence shell):

\[
\begin{align*}
\text{MO Theory Handout (X2) - Ground State Config's} & \quad O_2, F_2, & \text{Ne}_2 \quad \sigma_{2p} & \text{& } \pi_{2p} \text{ MO’s “switch”} \\
\end{align*}
\]
Heteronuclear Diatomic Molecules …

Page 9 of MO Handout - HF MO's:

\[
\begin{align*}
1s_H & \rightarrow \sigma = 1s_H + 2p_zF \text{ Bonds} \\
-2p_{zF} & \Rightarrow \sigma^* = 1s_H - 2p_zF \text{ Antibonds} \\
+2p_{zF} & \Rightarrow \pi = 1s_H + 2p_{zF} \text{ Bonds}
\end{align*}
\]

Multiple Bonds Handout … PAGE 8

Conjugated Polyenes - 1,3-Butadiene - \( \pi \) MO scheme:
( | are nodal planes \( \perp \) to bond axis)

\[
\begin{align*}
\pi_4 & \leftrightarrow \pi_4^* \\
\pi_3 & \leftrightarrow \pi_3^* \text{ - LUMO Lowest Unoccupied MO} \\
\pi_2 & \leftrightarrow \pi_2 \text{ - HOMO Highest Occupied MO} \\
\pi_1 & 
\end{align*}
\]

Another Example … Conjugated Polyenes

1,3,5-Hexatriene - \( \pi \) MO scheme: