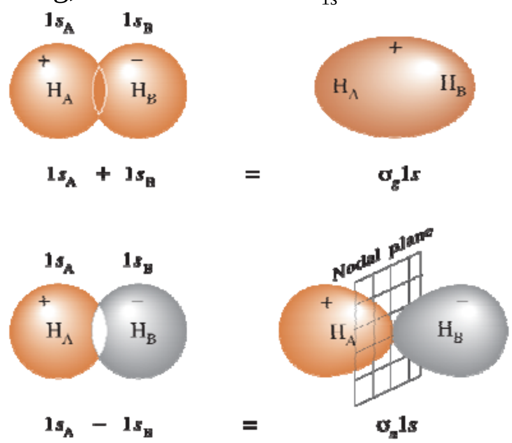
Chapter 11 – Qualitative Theory of Chemical Bonding

Background: We have briefly mentioned bonding but it now time to talk about it for real. In this chapter we will delocalized orbitals and introduce Hückel MOT.

* More MO Theory – time to talk formally about σ and π
  - The σ MO
    -- is completely symmetric about internuclear axis
    -- there are two possible combos:
      --- bonding, σ: $1s_A + 1s_B \rightarrow \sigma_{1s}$
      --- antibonding, σ^*: $1s_A + 1s_B \rightarrow \sigma_{1s}^*$



    -- symmetry argument:
      --- when the sign of the MO does not change with respect to its center of inversion it is even and we would call it gerade (German word for even) or σ_g

$$\sigma_{1s} = \frac{1}{\sqrt{2(1+S)}}(1s_A + 1s_B) = \sigma_g 1s$$

      --- if the sign does change it is called ungerade or σ_u

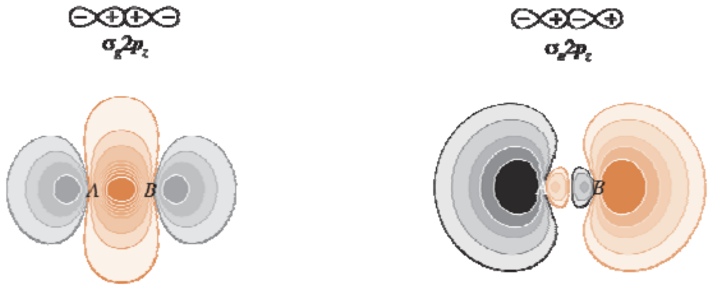
$$\sigma_{1s} = \frac{1}{\sqrt{2(1+S)}}(1s_A - 1s_B) = \sigma_u 1s$$

    -- only AOs with similar energies are combined in this way otherwise there will be very little overlap btwn them
      --- the combs btwn 2s orbitals are very similar to 1s:

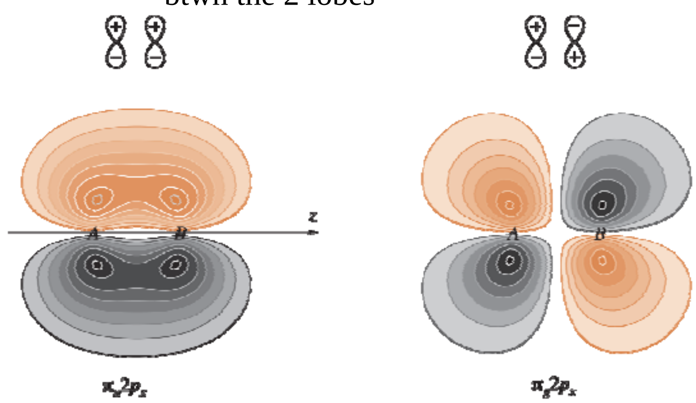
$$2s_A + 2s_B \rightarrow \sigma_g 2s \quad 2s_A - 2s_B \rightarrow \sigma_u 2s$$

      --- the primary bonding axis is the z-axis which is where the σ_{2p} bonds

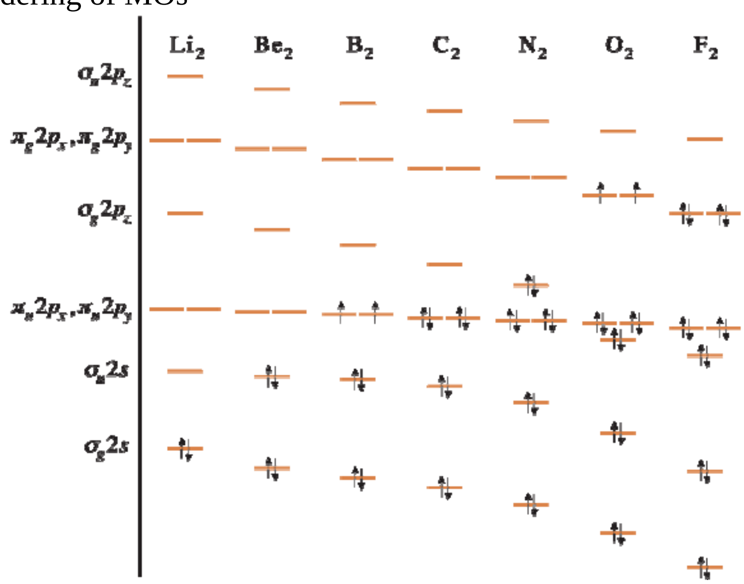
$$2p_{zA} + 2p_{zB} \rightarrow \sigma_g 2p_z \quad 2p_{zA} - 2p_{zB} \rightarrow \sigma_u 2p_z$$



- The π MO
  - -- for $2p_x$ and $2p_y$ they are perpendicular to each other and $2p_z$ so there is no net overlap between them
    - --- they only have overlap with each other
    - --- $2p_{xA} + 2p_{xB} \rightarrow \pi_u 2p_x \quad 2p_{xA} - 2p_{xB} \rightarrow \pi_g 2p_x$
      - ---- this delineation is based on a center of inversion argument
      - ---- when we invert across the center for π_u we have a sign change btwn the 2 lobes



    - --- we get the same result for $2p_y$ combos
- Energy Ordering of MOs



* Bond Order and molecular electronic configurations

- $Bond\ Order = \frac{1}{2}\left[no.of\ \ bonding\ e^{-}'s - no.of\ \ antibonding\ e^{-}'s\right]$

Species	No. of e^-s	Ground State Electron Config	Bond Order	Bond Length (pm)	Binding E (kJ/mol)
H_2^+	1	$(\sigma_g 1s)^1$	$\frac{1}{2}$	106	268
H_2	2	$(\sigma_g 1s)^2$	1	74	457
He_2^+	3	$(\sigma_g 1s)^2(\sigma_u 1s)^1$	$\frac{1}{2}$	108	241
He_2	4	$(\sigma_g 1s)^2(\sigma_u 1s)^2$	0	≈6000	<<1

- Pauli Exclusion Principle
  - -- placement of e-'s in MOs follows the PEP and the ordering follows Hund's rules
  - -- e.g. O_2

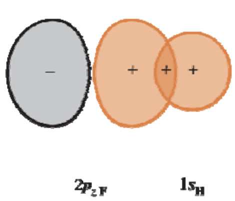
$$(\sigma_g 1s)^2(\sigma_u 1s)^2(\sigma_g 2s)^2(\sigma_u 2s)^2(\sigma_g 2p_z)^2(\pi_u 2p_x)^2(\pi_u 2p_y)^2(\pi_g 2p_x)^1(\pi_g 2p_y)^1$$

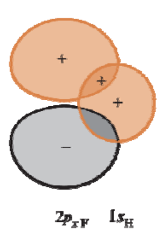
or $KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\sigma_g 2p_z)^2(\pi_u 2p_x)^2(\pi_u 2p_y)^2(\pi_g 2p_x)^1(\pi_g 2p_y)^1$

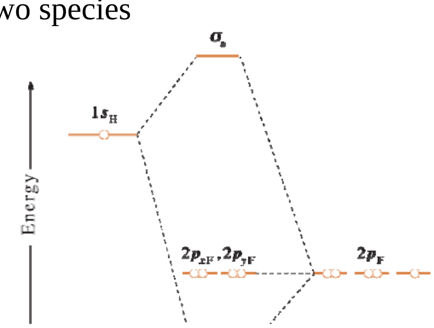
where KK is the filled n = 1 shell

B.O. = 2 so oxygen is predicted to have a double bond

* Heteronuclear Diatomics and Molecular Orbital Theory
- we can extend MOT to heteronuclear diatomic molecules
- the difference is that the J, S, and K integrals are dependent on how close in energy the atomic orbitals on adjacent atoms are
- the more EN an atom is the lower the AOs
  - -- e.g. CO is close enough so that the orbital overlaps occur btwn the same AOs on each atom
  - -- e.g. for HF the 1s AO on hydrogen overlaps with the $2p_z$ orbital on F to give rise to the single bond btwn the two species







* Molecular Term Symbols for Linear Molecules
- we start by evaluating the total angular momentum of e-'s in the MOs:
  e.g. $m_l = 0$ for σ and $m_l = \pm 1$ for π
- we use capitalized Greek symbols to specify term symbols for our linear molecules

$\lvert M_L \rvert$	Symbol
0	Σ
1	Π
2	Δ
3	Φ

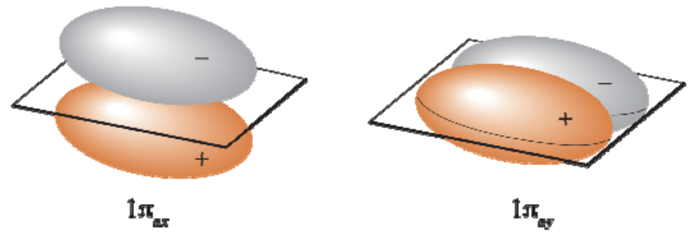
- the term symbol is represented by: ${}^{2S+1}\lvert M_L \rvert$
  - -- where M_S is again the sum of spin and S is the total spin
- Examples:
  - -- H_2 ground state: $\left(1\sigma_g\right)^2$
    - --- our only M_L is 0 so Σ is our symbol
    - --- in the ground state our e-'s are paired so $M_s = \frac{1}{2} - \frac{1}{2} = 0 \quad 2S + 1 = 1$
    - --- so our ground state is a singlet sigma: ${}^1\Sigma$
  - -- B_2 ground state: $\left(1\sigma_g\right)^2 \left(1\sigma_u\right)^2 \left(2\sigma_g\right)^2 \left(2\sigma_u\right)^2 \left(2\pi_u\right)^1 \left(2\pi_u\right)^1$
    - --- everything is paired up until we get to the π orbitals so these are the only e-s we need to consider
    - --- $m_l = \pm 1 \rightarrow M_L$ = -1 + -1 = -2, 0, or +1 for π
    - --- $m_s = \pm ½ \rightarrow M_L$ = +1, 0, or -1

-1	$+1$				-1	$+1$			
$\uparrow$	$\uparrow$	$\left(-1^+, +1^+\right)$	$L = 0$	$S = 1$	$\downarrow$	$\downarrow$	$\left(-1^-, +1^-\right)$	$L = 0$	$S = -1$
$\uparrow\downarrow$		$\left(-1^+, -1^-\right)$	$L = -2$	$S = 0$		$\uparrow\downarrow$	$\left(+1^-, +1^-\right)$	$L = +2$	$S = 0$
$\uparrow$	$\downarrow$	$\left(-1^+, +1^-\right)$	$L = 0$	$S = 0$	$\downarrow$	$\uparrow$	$\left(-1^-, +1^+\right)$	$L = 0$	$S = 0$

    - --- we follow the same rules we used to determine the atomic term symbols
      - ---- the largest L = 2 so Δ and 2S + 1 = 2S(0) + 1 = 1 $\rightarrow {}^1\Delta$
      - ---- next L = 0 with 2S + 1 = 3 $\rightarrow {}^3\Sigma$
      - ---- lastly, L = 0 with 2S + 1 = 1 $\rightarrow {}^1\Sigma$
    - --- the largest spin state is the ground state or ${}^3\Sigma$

* Symmetry and term symbols

- when both MOs are gerade then $g \bullet g = g$ for the overall symmetry
- when both MOs are ungerade then $u \bullet u = g$ for the overall symmetry
- when the MOs are opposite symmetry then $u \bullet g = u$ for the overall symmetry
- e.g. the term symbol for B_2 is then ${}^3\Sigma_g$
- Plane of Inversion and term symbols
  - -- for σ obitals the reflection thru a plane is always +
  - -- with π orbitals the reflection thru a plane will be either + or – depending upon the plane we use to define our system



-- for our π_x the sign will be – and for π_y the sign will be +

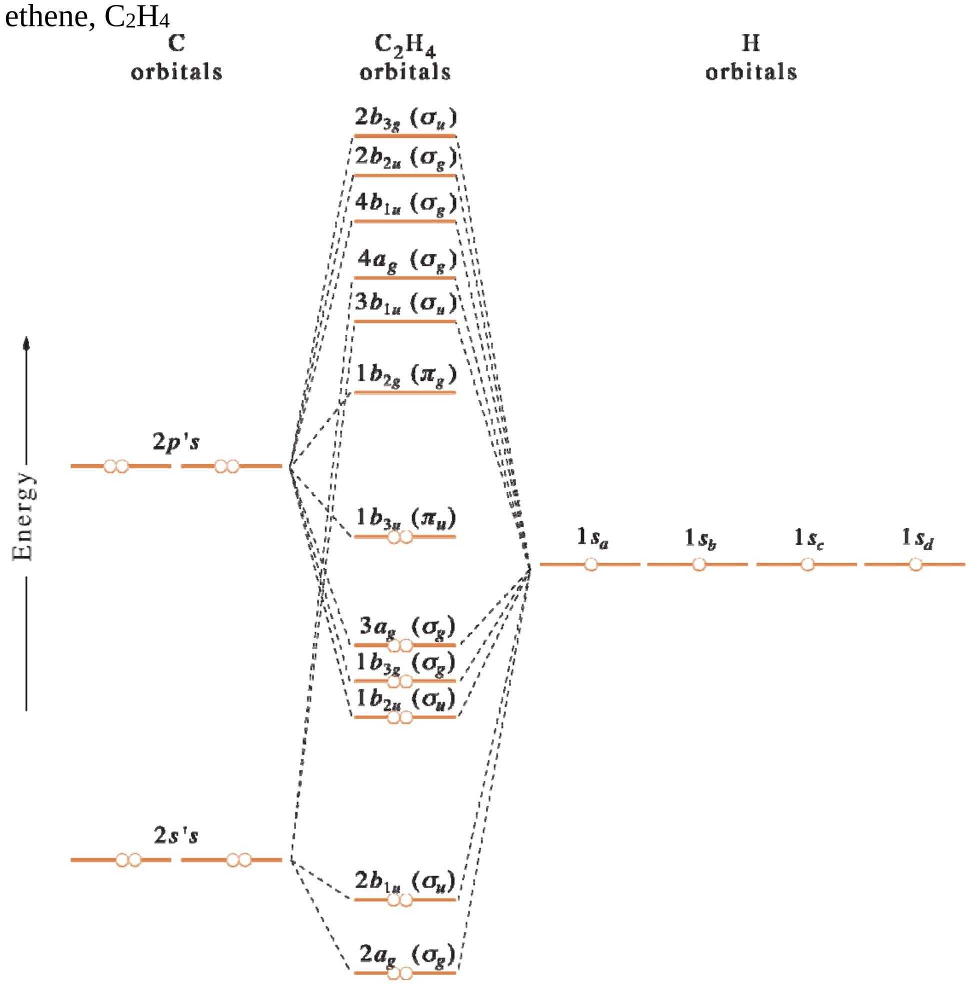
-- e.g. the complete term symbol for B_2 is then ${}^3\Sigma_g^-$ since we have an e- in each of these MOs

-- Table 11.13 summarizes the complete term symbols for all the possible diatomics up to F_2

-- We can also apply these same steps to determine excited states for our diatomics

* Pi Bonding

- ethene, C_2H_4



-- let’s say the $2p_z$ orbitals are responsible for the pi MOs is formed

$$\psi_\pi = c_1\psi_{2p_zA} + c_2\psi_{2p_zB}$$

-- we can solve this system using variational methods

$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} \\ H_{21}-ES_{21} & H_{22}-ES_{22} \end{vmatrix} = 0 \quad \begin{matrix} H_{ij} = \int \psi_{2p_zi} \hat{H} \psi_{2p_zj} d\tau \\ S_{ij} = \int \psi_{2p_zi} \psi_{2p_zj} d\tau \end{matrix}$$

where $H_{11} = H_{22}$ since the C-atoms on ethene are equivalent

--- the diagonal elements of the Hamiltonian operator are the Coulomb integrals

--- the off-diagonal ones are the Exchange integrals/resonance integrals

- Hückel Molecular Orbital Theory
  - -- this is an approximation method that simplifies the secular determinant for pi systems
  - -- the method:

--- the overlap integrals, S_{ij}, are set to the Kroenecker delta:

$$S_{ij} = \begin{cases} \delta_{ij} = 0 & i \neq j \\ \delta_{ij} = 1 & i = j \end{cases}$$

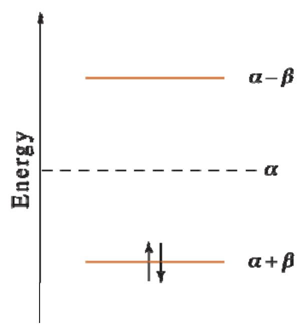
--- the Coulomb integrals are the same for all C-atoms and are denoted by α

--- the resonance/exchange integrals represent nearest neighbor interactions and are assumed to be the same and are denoted by β

--- all remaining resonance integrals are set to zero

-- applied to ethene our secular determinant becomes:

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0 \quad (\alpha - E)^2 - \beta^2 = 0 \rightarrow \alpha - E = \pm\beta \rightarrow E = \alpha \pm \beta$$



--- where $E = \alpha + \beta$ and $E = \alpha - \beta$ are the bonding and antibonding MOs, respectively

--- the experimental value of β is -75 kJ/mol

--- now we can use HMOT to obtain our wavefunctions

---- we start by rewritting the secular determinant as two equations with the two unknown coefficients

$$c_1(\alpha - E) + c_2\beta = 0 \quad c_1\beta + c_2(\alpha - E) = 0$$

---- next we plug in our energy, $E = \alpha + \beta$

$$c_1(\alpha - \alpha - \beta) + c_2\beta = 0 \rightarrow -c_1\beta + c_2\beta = 0 \rightarrow \beta(c_2 - c_1) = 0 \rightarrow c_1 = c_2$$

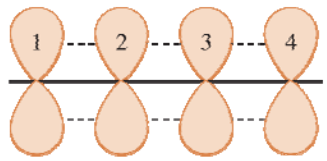
$$\psi_{nb} = c\left(\psi_{2p_{zA}} + \psi_{2p_{zB}}\right) = \frac{1}{\sqrt{2}}\left(\psi_{2p_{zA}} + \psi_{2p_{zB}}\right)$$

---- for $E = \alpha - \beta$

$$c_1(\alpha - \alpha + \beta) + c_2\beta = 0 \rightarrow c_1\beta + c_2\beta = 0 \rightarrow c_1 = -c_2$$

$$\psi_{nb} = c\left(\psi_{2p_{zA}} - \psi_{2p_{zB}}\right) = \frac{1}{\sqrt{2}}\left(\psi_{2p_{zA}} - \psi_{2p_{zB}}\right)$$

-- butadiene – time for a delocalized pi-system, $\psi_i = \sum_{j=1}^{4} c_{ij}\psi_{2p_{zi}}$



--- our secular determinant

$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} & H_{14}-ES_{14} \\ H_{21}-ES_{21} & H_{22}-ES_{22} & H_{23}-ES_{23} & H_{24}-ES_{24} \\ H_{31}-ES_{31} & H_{32}-ES_{32} & H_{33}-ES_{33} & H_{34}-ES_{34} \\ H_{41}-ES_{41} & H_{42}-ES_{42} & H_{43}-ES_{43} & H_{44}-ES_{44} \end{vmatrix} = 0$$

--- applying our HMOT approximation our determinant becomes:

$$\begin{vmatrix} \alpha-E & \beta & 0 & 0 \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ 0 & 0 & \beta & \alpha-E \end{vmatrix} = 0 \quad \text{if we let } x = \frac{\alpha-E}{\beta} \text{ then } \beta^4 \begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0$$

this leads to a secular equation of: $x^4 - 3x^2 + 1 = 0 \rightarrow x^2 = \frac{3 \pm \sqrt{5}}{2}$ therefore,

$x = \pm 1.618, \pm 0.618$

--- the total pi-electronic energy is: $E_\pi = 2(\alpha - 1.618\beta) + 2(\alpha + 0.618\beta) = 4\alpha + 4.472\beta$

--- now, if we compare this energy to double the energy we obtained for ethene we will see there is a stabilization energy which results from our delocalization

$$E_{deloc} = E_{\pi\_but} - 2E_{\pi\_eth} = 0.472\beta < 0 \rightarrow E_{deloc} = 0.472\left(-75\, {}^{kJ}\!/_{mol}\right) = -35\, {}^{kJ}\!/_{mol}$$

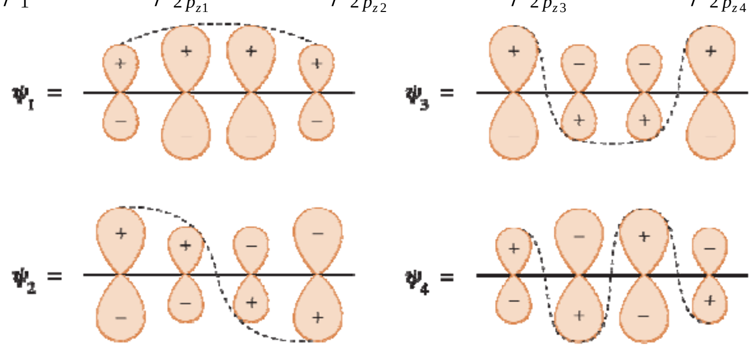
-- we can solve for our coefficients and derive wavefunctions for our MOs:

$$\psi_1 = 0.3717\psi_{2p_{z1}} + 0.6015\psi_{2p_{z2}} + 0.6015\psi_{2p_{z3}} + 0.3717\psi_{2p_{z4}} \qquad E_1 = \alpha + 1.618\beta$$

$$\psi_2 = 0.6015\psi_{2p_{z1}} + 0.3717\psi_{2p_{z2}} - 0.3717\psi_{2p_{z3}} - 0.6015\psi_{2p_{z4}} \qquad E_1 = \alpha + 0.618\beta$$

$$\psi_1 = 0.6015\psi_{2p_{z1}} - 0.3717\psi_{2p_{z2}} - 0.3717\psi_{2p_{z3}} + 0.6015\psi_{2p_{z4}} \qquad E_1 = \alpha - 0.618\beta$$

$$\psi_1 = 0.3717\psi_{2p_{z1}} - 0.6015\psi_{2p_{z2}} + 0.6015\psi_{2p_{z3}} - 0.3717\psi_{2p_{z4}} \qquad E_1 = \alpha - 1.618\beta$$



* Sections 11.7-11.8 – Skip!