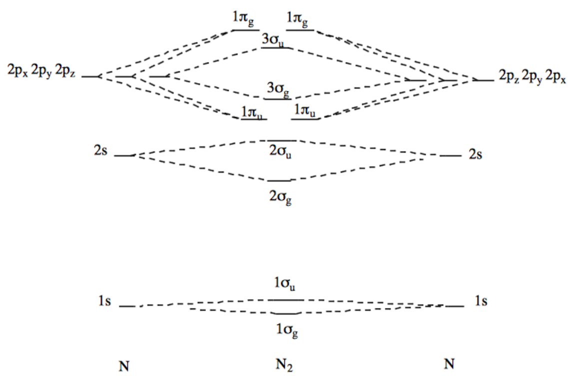
22.2.6: vi. Problem Solutions

1.

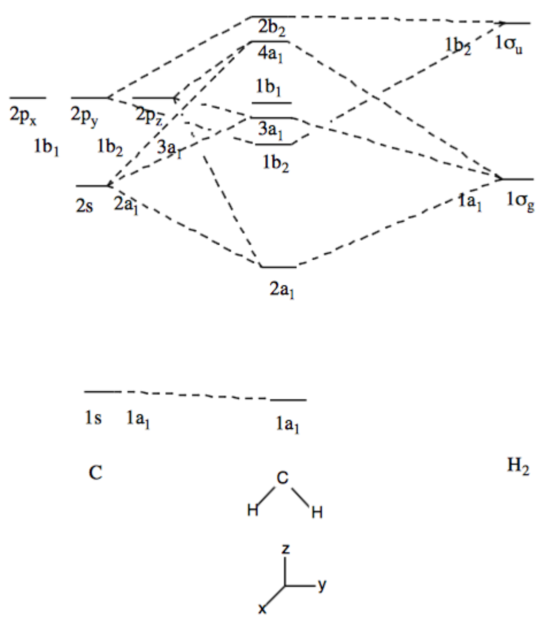


The above diagram indicates how the SALC-AOs are formed from the 1s, 2s, and 2p N atomic orbitals. It can be seen that there are $3\sigma_g$, $3\sigma_u$, $1\pi_{ux}$, $1\pi_{uy}$, $1\pi_{gx}$, and $1\pi_{gy}$ SALC - AOs. The Hamiltonian matrices (Fock matrices) are given. Each of these can be diagonalized to give the following MO energies:

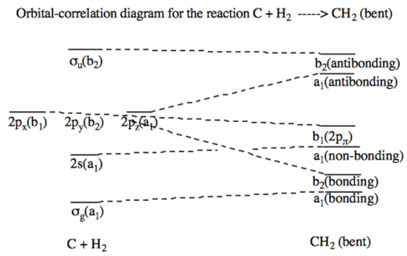
$3\sigma_g$; -15.52, -1.45, and -0.54 (hartrees)
$3\sigma_u$; -15.52, -0.72, and 1.13
$1\pi_{ux}$; -0.58
$1\pi_{uy}$; -0.58
$1\pi_{gx}$; 0.28
$1\pi_{gy}$; 0.28

It can be seen that the $3\sigma_g$ orbitals are bonding, the $3\sigma_u$ orbitals are antibonding, the $1\pi_{ux}$ and $1\pi_{uy}$ orbitals are bonding, and the $1\pi_{gx}$ and $1\pi_{gy}$ orbitals are antibonding. The eigenvectors one obtains are in the orthogonal basis and therefore pretty meaningless. Back transformation into the original basis will generate the expected results for the 1e$^-$ MOs (expected combinations of SALC-AOs).

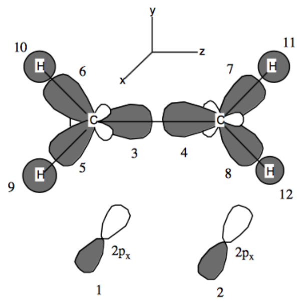
2. Using these approximate energies we can draw the following MO diagram:



This MO diagram is **not** an orbital correlation diagram but can be used to help generate one. The energy levels on each side (C and H_2) can be "superimposed" to generate the left side of the orbital correlation diagram and the center CH_2 levels can be used to form the right side. Ignoring the core levels this generates the following orbital correlation diagram.



3.



Using D_{2h} symmetry and labeling the orbitals $(f_1 - f_{12})$ as shown above proceed by using the orbitals to define a reducible representation which may be subsequently reduced to its irreducible components. Use projectors to find the SALC-AOs for these irreps.

3. a. The $2P_x$ orbitals on each carbon form the following reducible representation:

$$\begin{array}{lccccccc} D_{2h} & E & C_2(z) & C_2(y) & C_2(x) & i\ \sigma(xy) & \sigma(xz) & \sigma(yz) \\ \Gamma_{2p_x} & 2 & -2 & 0 & 0 & 0\ 0 & 2 & -2 \end{array} \tag{22.2.6.1, 22.2.6.2}$$

The number of irreducible representations may be found by using the following formula:

$$n_{irrep} = \frac{1}{g}\sum_R \chi_{red}(R)\chi_{irrep}(R),$$

where g = the order of the point group (8 for D_{2h}).

$$n_{A_g} = \frac{1}{8}\sum_R \Gamma_{2p_x}(R)A_g(R) \tag{22.2.6.3}$$

$$= \frac{1}{8}[(2)(1)+(-2)(1)+(0)(1)+(0)(1)+(0)(1)+(0)(1)+(2)(1)+(-2)(1)] = 0 \tag{22.2.6.4}$$

Similarly,

$$n_{B_{1g}} = 0 \tag{22.2.6.5}$$

$$n_{B_{2g}} = 1 \tag{22.2.6.6}$$

$$n_{B_{3g}} = 0 \tag{22.2.6.7}$$

$$n_{A_u} = 0 \tag{22.2.6.8}$$

$$n_{B_{1u}} = 0 \tag{22.2.6.9}$$

$$n_{B_{2u}} = 0 \tag{22.2.6.10}$$

$$n_{B_{3u}} = 1 \tag{22.2.6.11}$$

Projectors using the formula:

$$P_{irrep} = \sum_R \chi_{irrep}(R)R,$$

may be used to find the SALC-AOs for these irreducible representations.

$$P_{B_{2g}} = \sum_R \chi_{B_{2g}}(R)R,$$

$$P_{B_{2g}} = (1)Ef_1 + (-1)C_2(z)f_1 + (1)C_2(y)f_1 + (-1)C_2(x)f_1 + (1)if_1 + (-1)\sigma(xy)f_1 + (1)\sigma(xz)f_1 + (-1)\sigma(yz)f_1 \tag{22.2.6.12}$$

$$= (1)f_1 + (-1) - f_1 + (1) - f_2 + (-1)f_2 + (1) - f_2 + (-1)f_2 + (1)f_1 + (-1) - f_1 \tag{22.2.6.13}$$

$$= f_1 + f_1 - f_2 - f_2 - f_2 - f_2 + f_1 + f_1 \tag{22.2.6.14}$$

$$= 4f_1 - 4f_2 \tag{22.2.6.15}$$

Normalization of this SALC-AO (and representing the SALC-AOs with ϕ) yields:

$$\int N(f_1 - f_2)N(f_1 - f_2)d\tau = 1$$

$$N^2\left(\int f_1 f_1 d\tau - \int f_1 f_2 d\tau - \int f_2 f_1 d\tau + \int f_2 f_2 d\tau\right) = 1$$

$$N^2(1+1) = 1$$

$$2N^2 = 1$$

$$N = \frac{1}{\sqrt{2}}$$

$$\phi_{1b_{2g}} = \frac{1}{\sqrt{2}}(f_1 - f_2).$$

The B_{3u} SALC-AO may be found in a similar fashion:

$$\begin{aligned} P_{B_{3u}} f_1 = & (1)f_1 + (-1) - f_1 + (-1) - f_2 + (1)f_2 + (-1) - f_2 + (1)f_2 + (1)f_1 + (-1) - f_1 && (22.2.6.16) \\ = & f_1 + f_1 + f_2 + f_2 + f_2 + f_2 + f_1 + f_1 && (22.2.6.17) \\ = & 4f_1 + 4f_2 && (22.2.6.18) \end{aligned}$$

Normalization of this SALC-AO yields:

$$\phi_{1b_{3u}} = \frac{1}{\sqrt{2}}(f_1 + f_2).$$

Since there are only two SALC-AOs and both are of different symmetry types these SALC-AOs are MOs and the 2x2 Hamiltonian matrix reduces to 2 1x1 matricies.

$$\begin{aligned} H_{1b_{2g},1b_{2g}} = & \int \frac{1}{\sqrt{2}}(f_1 - f_2) H \frac{1}{\sqrt{2}}(f_1 - f_2) d\tau && (22.2.6.19) \\ = & \frac{1}{2}\left(\int f_1 H f_1 d\tau - 2\int f_1 H f_2 d\tau + \int f_2 H f_2 d\tau\right) && (22.2.6.20) \\ = & \frac{1}{2}(\alpha_{2p\pi} - 2\beta_{2p\pi-2p\pi} + \alpha_{2p\pi}) && (22.2.6.21) \\ = & \alpha_{2p\pi} - \beta_{2p\pi-2p\pi} && (22.2.6.22) \\ = & -11.4 - (-1.2) = -10.2 && (22.2.6.23) \\ H_{1b_{3u},1b_{3u}} = & \int \frac{1}{\sqrt{2}}(f_1 + f_2) H \frac{1}{\sqrt{2}}(f_1 + f_2) d\tau && (22.2.6.24) \\ = & \frac{1}{2}\left(\int f_1 H f_1 d\tau + 2\int f_1 H f_2 d\tau + \int f_2 H f_2 d\tau\right) && (22.2.6.25) \\ = & \frac{1}{2}(\alpha_{2p\pi} + 2\beta_{2p\pi-2p\pi} + \alpha_{2p\pi}) && (22.2.6.26) \\ = & \alpha_{2p\pi} + \beta_{2p\pi-2p\pi} && (22.2.6.27) \\ = & -11.4 + (-1.2) = -12.6 && (22.2.6.28) \end{aligned}$$

This results in a $\pi \rightarrow \pi^*$ splitting of 2.4 eV.

3. b. The sp^2 orbitals forming the C-C bond generate the following reducible representation:

$$\begin{array}{lllllllll} D_{2h} & E & C_2(z) & C_2(y) & C_2(x) & i & \sigma(xy) & \sigma(xz) & \sigma(yz) \\ \Gamma^2_{C_{sp}} & 2 & 2 & 0 & 0 & 0 & 0 & 2 & 2 \end{array} \qquad (22.2.6.29),\ (22.2.6.30)$$

This reducible representation reduces to $1A_g$ and $1B_{1u}$ irreducible representations.

Projectors are used to find the SALC-AOs for these irreducible representations.

$$\begin{aligned} P_{A_g} f_3 = & (1)Ef_3 + (1)C_2(z)f_3 + (1)C_2(y)f_3 + (1)C_2(x)f_3 + (1)if_3 + (1)\sigma(xy)f_3 + (1)\sigma(xz)f_3 + (1)\sigma(yz)f_3 && (2 \\ (1)f_3 + (1)f_3 + (1)f_4 + (1)f_4 + (1)f_4 + (1)f_4 + (1)f_3 + (1)f_3 & && (2 \\ = & 4f_3 + 4f_4 && (2 \end{aligned}$$

Normalization of this SALC-AO yields:

$$\phi_{1a_g} = \frac{1}{\sqrt{2}}(f_3 + f_4).$$

The B_{1u} SALC-AO may be found in a similar fashion:

$$\begin{aligned} P_{B_{1u}} f_3 = & (1)f_3 + (1)f_3 + (-1)f_4 + (-1)f_4 + (-1)f_4 + (-1)f_4 + (1)f_3 + (1)f_3 && (22.2.6.34) \\ = & 4f_3 - 4f_4 && (22.2.6.35) \end{aligned}$$

Normalization of this SALC-AOs yields:

$$\phi_{1b_{3u}} = \frac{1}{\sqrt{2}}(f_3 - f_4).$$

Again sine there are only two SALC-AOs and both are of different symmetry types these SALC-AOs are MOs and the 2x2 Hamiltonian matrix reduces to 2 1x1 matrices.

$$\begin{aligned} H_{1a_g,1a_g} = & \int \frac{1}{\sqrt{2}}(f_3 + f_4) H \frac{1}{\sqrt{2}}(f_3 + f_4) d\tau && (22.2.6.36) \\ = & \frac{1}{2}\left(\int f_3 H f_3 d\tau + 2\int f_3 H f_4 d\tau + \int f_4 H f_4 d\tau\right) && (22.2.6.37) \\ = & \frac{1}{2}(\alpha_{sp^2} + 2\beta_{sp^2-sp^2} + \alpha_{sp^2}) && (22.2.6.38) \\ = & \alpha_{sp^2} + \beta_{sp^2-sp^2} && (22.2.6.39) \\ = & -14.7 + (-5.0) = -19.7 && (22.2.6.40) \\ H_{1b_{1u},1b_{1u}} = & \int \frac{1}{\sqrt{2}}(f_3 - f_4) H \frac{1}{\sqrt{2}}(f_3 - f_4) d\tau && (22.2.6.41) \\ = & \frac{1}{2}\left(\int f_3 H f_3 d\tau - 2\int f_3 H f_4 d\tau + \int f_4 H f_4 d\tau\right) && (22.2.6.42) \\ = & \frac{1}{2}(\alpha_{sp^2} - 2\beta_{2p^2-2p^2} + \alpha_{sp^2}) && (22.2.6.43) \\ = & \alpha_{sp^2} - \beta_{sp^2-sp^2} && (22.2.6.44) \\ = & -14.7 - (-5.0) = -9.7 && (22.2.6.45) \end{aligned}$$

3. c. The C sp^2 orbitals and the H s orbitals forming the C-H bonds generate the following reducible representation:

$$\begin{array}{lllllllll} D_{2h} & E & C_2(z) & C_2(y) & C_2(x) & i & \sigma(xy) & \sigma(xz) & \sigma(yz) \\ \Gamma_{sp^2-s} & 8 & 0 & 0 & 0 & 0 & 0 & 0 & 8 \end{array} \qquad (22.2.6.46),\ (22.2.6.47)$$

This reducible representation reduces to $2A_g, 2B_{3g}, 2B_{1u},$ and $2B_{2u}$ irreducible representation.

Projectors are used to find the SALC-AOs for these irreducible representations.

$$\begin{aligned}
P_{A_g} f_6 = & \quad (1)Ef_6 + (1)C_2(z)f_6 + (1)C_2(y)f_6 + (1)C_2(x)f_6 + (1)if_6(1)\sigma(xy)f_6 + (1)\sigma(xz)f_6 + (1)\sigma(yz)f_6 && (22.2.6.48)\\
= & \quad (1)f_6 + (1)f_5 + (1)f_7 + (1)f_8 + (1)f_8 + (1)f_7 + (1)f_5 + (1)f_6 && (22.2.6.49)\\
= & \quad 2f_5 + 2f_6 + 2f_7 + 2f_8 && (22.2.6.50)
\end{aligned}$$

Normalization yields: $\phi 2a_g = \frac{1}{2}(f_5 + f_6 + f_7 + f_8)$.

$$\begin{aligned}
P_{A_g} f_{10} = & \quad (1)Ef_{10} + (1)C_2(z)f_{10} + (1)C_2(y)f_{10} + (1)C_2(x)f_{10} + (1)if_{10} + (1)\sigma(xy)f_{10} + (1)\sigma(xz)f_{10} + (1)\sigma(yz)f_{10} && (22.2.6.51)\\
= & \quad (1)f_{10} + (1)f_9 + (1)f_{11} + (1)f_{12} + (1)f_{12} + (1)f_{11} + (1)f_9 + (1)f_{10} && (22.2.6.52)\\
= & \quad 2f_9 + 2f_{10} + 2f_{11} + 2f_{12} && (22.2.6.53)
\end{aligned}$$

Normalization yields: $\phi_{3a_g} = \frac{1}{2}(f_9 + f_{10} + f_{11} + f_{12})$.

$$\begin{aligned}
P_{B_{3g}} f_6 = & \quad (1)f_6 + (-1)f_5 + (-1)f_7 + (1)f_8 + (1)f_8 + (-1)f_7 + (-1)f_5 + (1)f_6 && (22.2.6.54)\\
= & \quad -2f_5 + 2f_6 - 2f_7 + 2f_8 && (22.2.6.55)
\end{aligned}$$

Normalization yields: $\phi_{1b_{3g}} = \frac{1}{2}(-f_5 + f_6 - f_7 + f_8)$.

$$\begin{aligned}
P_{B_{3g}} f_{10} = & \quad (1)f_{10} + (-1)f_9 + (-1)f_{11} + (1)f_{12} + (1)f_{12} + (-1)f_{11} + (-1)f_9 + (1)f_{10} && (22.2.6.56)\\
= & \quad -2f_9 + 2f_{10} - 2f_{11} + 2f_{12} && (22.2.6.57)
\end{aligned}$$

Normalization yields: $\phi_{2b_{3g}} = \frac{1}{2}(-f_9 + f_{10} - f_{11} + f_{12})$.

$$\begin{aligned}
P_{B_{1u}} f_6 = & \quad (1)f_6 + (1)f_5 + (-1)f_7 + (-1)f_8 + (-1)f_8 + (-1)f_7 + (1)f_5 + (1)f_6 && (22.2.6.58)\\
= & \quad 2f_5 + 2f_6 - 2f_7 - 2f_8 && (22.2.6.59)
\end{aligned}$$

Normalization yields: $\phi_{2b_{1u}} = \frac{1}{2}(f_5 + f_6 - f_7 - f_8)$.

$$\begin{aligned}
P_{B_{1u}} f_1 0 = & \quad (1)f_{10} + (1)f_9 + (-1)f_{11} + (-1)f_{12} + (-1)f_{12} + (-1)f_{11} + (1)f_9 + (1)f_{10} && (22.2.6.60)\\
= & \quad 2f_9 + 2f_{10} - 2f_{11} - 2f_{12} && (22.2.6.61)
\end{aligned}$$

Normalization yields: $\phi_{3b_{1u}} = \frac{1}{2}(f_9 + f_{10} - f_{11} - f_{12})$.

$$P_{B_{2u}} f_6 = (1)f_6 + (-1)f_5 + (1)f_7 + (-1)f_8 + (-1)f_8 + (1)f_7 + (-1)f_5 + (1)f_6 \quad = \quad -2f_5 + 2f_6 + 2f_7 - 2f_8 \tag{22.2.6.62}$$

Normalization yields: $\phi_{1b_{2u}} = \frac{1}{2}(-f_5 + f_6 - f_7 - f_8)$.

$$P_{B_{2u}} f_{10} = (1)f_{10} + (-1)f_9 + (1)f_{11} + (-1)f_{12} + (-1)f_{12} + (1)f_{11} + (-1)f_9 + (1)f_{10} \quad = \quad -2f_9 + 2f_{10} + 2f_{11} - 2f_{12} \tag{22.2.6.63}$$

Normalization yields: $\phi_{2b_{2u}} = \frac{1}{2}(-f_9 + f_{10} + f_{11} - f_{12})$.

Each of these four 2x2 symmetry blocks generate identical Hamitonian matrices. This will bve demonstrated for the B_{3g} symmetry, the others proceed analogously:

$$\begin{aligned}
H_{1b_{3g},1b_{3g}} = & \quad \int \frac{1}{2}(-f_5 + f_6 - f_7 + f_8) H \frac{1}{2}(-f_5 + f_6 - f_7 + f_8) d\tau && (22.2.6.64)\\
= & \quad \frac{1}{4}\Big[\int f_5 H f_5 d\tau - \int f_5 H f_6 d\tau + \int f_5 H f_7 d\tau - \int f_5 H f_8 d\tau && (22.2.6.65)\\
& - \int f_6 H f_5 d\tau + \int f_6 H f_6 d\tau - \int f_6 H f_7 d\tau + \int f_5 H f_8 d\tau && (22.2.6.66)\\
& + \int f_7 H f_9 d\tau - \int f_7 H f_{10} d\tau + \int f_7 H f_{11} d\tau - \int f_7 H f_{12} d\tau && (22.2.6.67)\\
& - \int f_8 H f_9 d\tau + \int f_8 H f_{10} d\tau - \int f_8 H f_{11} d\tau + \int f_8 H f_{12} d\tau\Big] && (22.2.6.68)\\
= & \quad \frac{1}{4}[\beta_{sp^2-s} - 0 + 0 - 0 - 0 + \beta_{sp^2-s} - 0 + 0 + 0 - 0 + \beta_{sp^2-s} - 0 - 0 + 0 - 0 + \beta_{sp^2-s}] = \beta_{sp^2-s} && (22.2.6.69)\\
H_{1b_{3g},2b_{3g}} = & \quad \int \frac{1}{2}(-f_5 + f_6 - f_7 + f_8) H \frac{1}{2}(-f_9 + f_{10} - f_{11} + f_{12}) d\tau && (22.2.6.70)\\
= & \quad \frac{1}{4}\Big[\int f_5 H f_9 d\tau - \int f_5 H f_{10} d\tau + \int f_5 H f_{11} d\tau - \int f_5 H f_{12} d\tau && (22.2.6.71)\\
& - \int f_6 H f_9 d\tau + \int f_6 H f_{10} d\tau - \int f_6 H f_{11} d\tau + \int f_5 H f_{12} d\tau && (22.2.6.72)\\
& + \int f_7 H f_9 d\tau - \int f_7 H f_{10} d\tau + \int f_7 H f_{11} d\tau - \int f_7 H f_{12} d\tau && (22.2.6.73)\\
& - \int f_8 H f_9 d\tau + \int f_8 H f_{10} d\tau - \int f_8 H f_{11} d\tau + \int f_8 H f_{12} d\tau\Big] && (22.2.6.74)\\
= & \quad \frac{1}{4}[\beta_{sp^2-s} - 0 + 0 - 0 - 0 + \beta_{sp^2-s} - 0 + 0 + 0 - 0 + \beta_{sp^2-s} - 0 - 0 + 0 - 0 + \beta_{sp^2-s}] = \beta_{sp^2-s} && (22.2.6.75)\\
H_{2b_{3g},2b_{3g}} = & \quad \int \frac{1}{2}(-f_9 + f_{10} - f_{11} + f_{12}) H \frac{1}{2}(-f_9 + f_{10} - f_{11} + f_{12}) d\tau && (22.2.6.76)\\
= & \quad \frac{1}{4}\Big[\int f_9 H f_9 d\tau - \int f_9 H f_{10} d\tau + \int f_9 H f_{11} d\tau - \int f_9 H f_{12} d\tau && (22.2.6.77)\\
& - \int f_{10} H f_9 d\tau + \int f_{10} H f_{10} d\tau - \int f_{10} H f_{11} d\tau + \int f_{10} H f_{12} d\tau && (22.2.6.78)\\
& + \int f_{11} H f_9 d\tau - \int f_{11} H f_{10} d\tau + \int f_{11} H f_{11} d\tau - \int f_{11} H f_{12} d\tau && (22.2.6.79)\\
& - \int f_{12} H f_9 d\tau + \int f_{12} H f_{10} d\tau - \int f_{12} H f_{11} d\tau + \int f_{12} H f_{12} d\tau\Big] && (22.2.6.80)\\
= & \quad \frac{1}{4}[\alpha_s - 0 + 0 - 0 - 0 + \alpha_s - 0 + 0 + 0 - 0 + \alpha_s - 0 - 0 + 0 - 0 + \alpha_s] = \alpha_s && (22.2.6.81)
\end{aligned}$$

This matrix eigenvalue problem then becomes:

$$\begin{vmatrix} \alpha_{sp^2}-\epsilon & \beta_{sp^2-s} \\ \beta_{sp^2-s} & \alpha_s-\epsilon \end{vmatrix} = 0$$

$$\begin{vmatrix} -14.7-\epsilon & -4.0 \\ -4.0 & -13.6 \end{vmatrix} = 0$$

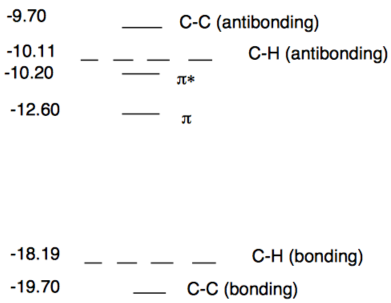
Solving this yields eigenvalues of:

$$\begin{vmatrix} -18.19 & -10.11 \end{vmatrix} \tag{22.2.6.82}$$

and corresponding eigenvectors:

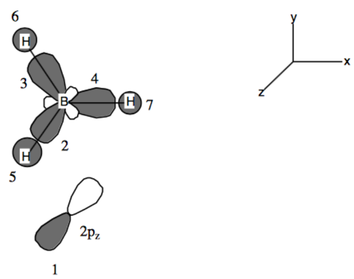
$$\begin{vmatrix} -0.7537 & -0.6572 \\ -0.6572 & 0.7537 \end{vmatrix} \tag{22.2.6.83}$$

This results in an orbital energy diagram:



For the ground state of ethylene you would fill the bottom 3 levels (the C-C, C-H, and π bonding orbitals), with 12 electrons.

4.



Using the hybrid atomic orbitals as labeled above (functions $f_1 - f_7$) and the D_{3h} point group symmetry it is easiest to construct three sets of reducible representations:

i. the B $2p_z$ orbital (labeled function 1)
ii. the 3 B sp^2 hybrids (labeled functions 2 - 4)
iii. the 3 H 1s orbitals (labeled functions 5 - 7).

i. The B $2p_z$ orbital generates the following irreducible representation:

$$\begin{array}{cccccc} D_{3h} & E & 2C_3 & 3C_2 & \sigma_h & 2S_3\,3\sigma_v \end{array} \tag{22.2.6.84}$$

$$\begin{array}{cccccc} \Gamma_{2p_z} & 1 & 1 & -1 & -1 & -11 \end{array} \tag{22.2.6.85}$$

This irreducible representation is A_2'' and is its own SALC-AO.

ii. The B sp^2 orbitals generate the following reducible representation:

$$\begin{vmatrix} D_{3h} & E & 2C_3 & 3C_2 & \sigma_h & 2S_3 & 3\sigma_v \\ \Gamma_{2p} & 3 & 0 & 1 & 3 & 0 & 1 \end{vmatrix}$$

This reducible representation reduces to $1A_1'$ and 1E'
irreducible representations.
Projectors are used to find the SALC-AOs for these irreducible representations.
Define: C_3 = 120 degree rotations, $C_3' = 240$ degree rotation,
C_2 = rotation around f_4, C_2' = rotation around f_2, and
C_2 = rotation adound f_3. S_3 and S_3' are defined analogous
to C_3 and C_3' with accompanying horizontal reflection.
σ_v = a reflection plane through f_4, σ_v' = a reflection plane
through f_2, and σ_v'' = a reflection plan through f_3

$$P_{A_1'} f_2 = (1)Ef_2 + (1)C_3 f_2 + (1)C_3' f_2 + (1)C_2 f_2 + (1)C_2' f_2 + (1)C_2'' f_2 + (1)\sigma_h f_2 + (1)S_3 f_2 + (1)S_3' f_2 + (1)\sigma_v f_2$$
$$+ (1)\sigma_v' f_2 + (1)\sigma_v'' f_2$$
$$= (1)f_2 + (1)f_3 + (1)f_4 + (1)f_3 + (1)f_2 + (1)f_4 + (1)f_2 + (1)f_3 + (1)f_4 + (1)f_3 + (1)f_2 + (1)\sigma f_4$$
$$= 4f_2 + 4f_3 + 4f_4$$

Normalization yields: $\phi_{1e'} = \frac{1}{\sqrt{6}}(2f_2 - f_3 - f_4)$.

To find the second e' (orthogonal to the first), projection of f_3 yields $(2f_3 - f_2 - f_4)$ and projection on f_4 yields $(2f_4 - f_2 - f_3)$. Neither of these functions are orthogonal to the first, but a combination of the two $(2f_4 - f_2 - f_4) - (2f_4 - f_2 - f_3)$ yields a function which is orthogonal to the first.

Normalization yields: $\phi_{2e'} = \frac{1}{\sqrt{2}}(f_3 - f_4)$. \

iii. The H 1s orbitals generate the following reducible representation:

$$\begin{array}{cccccc} D_{3h} & E & 2C_3 & 3C_2 & \sigma_h & 2S_3 3\sigma_v \\ \Gamma_{sp^2} & 3 & 0 & 1 & 3 & 0 \quad 1 \end{array} \tag{22.2.6.86, 22.2.6.87}$$

This reducible representation reduces to $1A_1'$ and 1E' irreducible representations exactly like part ii. and in addition the projectors used to find the SALC-AOs for these irreducible representations is exactly analogous to part ii.

$$\phi_{2a_1'} = \frac{1}{\sqrt{3}}(f_5 + f_6 + f_7)$$

$$\phi_{3e'} = \frac{1}{\sqrt{6}}(2f_5 - f_6 - f_7).$$

$$\phi_{4e'} = \frac{1}{\sqrt{2}}(f_6 - f_7).$$

So, there are $1A_2''$, $2A_1'$ and 2E' orbitals. Solving the Hamiltonian matrix for each symmetry block yields:

A_2'' Block:

$$H_{1a_{2''},1a_{2''}} = \int f_1 H f_1 d\tau \tag{22.2.6.88}$$

$$= \alpha_{2p\pi} \tag{22.2.6.89}$$

$$= -8.5 \tag{22.2.6.90}$$

A_1' Block:

$$H_{1_{a1'},1_{a2'}} = \int \frac{1}{\sqrt{3}}(f_2+f_3+f_4)H\frac{1}{\sqrt{3}}(f_2+f_3+f_4)d\tau = \frac{1}{3}[\int f_2Hf_2d\tau + \int f_2Hf_3d\tau + \int f_2Hf_4d\tau + \tag{22.2.6.91}$$

$$+ \int f_3Hf_2d\tau + \int f_3Hf_3d\tau + \int f_3Hf_4d\tau + \tag{22.2.6.92}$$

$$+ \int f_4Hf_2d\tau + \int f_4Hf_3d\tau + \int f_4Hf_4d\tau] \tag{22.2.6.93}$$

$$= \frac{1}{3}[\alpha_{sp^2} + 0 + 0 + 0 + \alpha_{sp^2} + 0 + 0 + 0 + \alpha_{sp^2}] = \alpha_{sp^2} \tag{22.2.6.94}$$

$$H_{1_{a1'},2_{a1'}} = \int \frac{1}{\sqrt{3}}(f_2+f_3+f_4)H\frac{1}{\sqrt{3}}(f_5+f_6+f_7)d\tau = \frac{1}{3}[\int f_2Hf_5d\tau + \int f_2Hf_6d\tau + \int f_2Hf_7d\tau + \tag{22.2.6.95}$$

$$+ \int f_3Hf_5d\tau + \int f_3Hf_6d\tau + \int f_3Hf_7d\tau + \tag{22.2.6.96}$$

$$+ \int f_4Hf_5d\tau + \int f_4Hf_6d\tau + \int f_4Hf_7d\tau] \tag{22.2.6.97}$$

$$= \frac{1}{3}[\beta_{sp^2-s} + 0 + 0 + 0 + \beta_{sp^2-s} + 0 + 0 + 0 + \beta_{sp^2-s}] = \beta_{sp^2-s} \tag{22.2.6.98}$$

$$H_{2_{a1'},2_{a1'}} = \int \frac{1}{\sqrt{3}}(f_5+f_6+f_7)H\frac{1}{\sqrt{3}}(f_5+f_6+f_7)d\tau = \frac{1}{3}[\int f_5Hf_5d\tau + \int f_5Hf_6d\tau + \int f_5Hf_7d\tau + \tag{22.2.6.99}$$

$$+ \int f_6Hf_5d\tau + \int f_6Hf_6d\tau + \int f_6Hf_7d\tau + \tag{22.2.6.100}$$

$$+ \int f_7Hf_5d\tau + \int f_7Hf_6d\tau + \int f_7Hf_7d\tau] \tag{22.2.6.101}$$

$$= \frac{1}{3}[\alpha_s + 0 + 0 + 0 + \alpha_s + 0 + 0 + 0 + \alpha_s] = \alpha_s \tag{22.2.6.102}$$

This matrix eigenvalue problem then becomes:

\befin{align}

$$\begin{vmatrix} \alpha_{sp^2-\epsilon} & \beta_{sp^2-s} \\ \beta_{sp^2-s} & \alpha_s - \epsilon \end{vmatrix} \tag{22.2.6.103}$$

& = & 0 \\

$$\begin{vmatrix} -10.7-\epsilon & -3.5 \\ -3.5 & -13.6-\epsilon \end{vmatrix} \tag{22.2.6.104}$$

& = & 0 \end{align}

Solving this yields eigenvalues of:

$$\begin{vmatrix} -15.94 & -8.36 \end{vmatrix} \tag{22.2.6.105}$$

and corresponding eigenvectors:

$$\begin{vmatrix} -0.5555 & -0.8315 \\ -0.8315 & 0.5555 \end{vmatrix} \tag{22.2.6.106}$$

E' Block:

This 4x4 symmetry block factors to two 2x2 blocks: where one 2x2 block includes the SALC-AOs

$$\phi_{e'} = \frac{1}{\sqrt{6}}(2f_2 - f_3 - f_4) \tag{22.2.6.107}$$

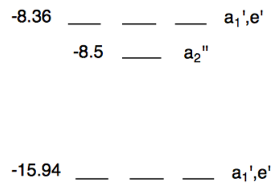
$$\phi_{e'} = \frac{1}{\sqrt{6}}(2f_5 - f_6 - f_7), \tag{22.2.6.108}$$

and the other includes the SALC-AOs

$$\phi_{e'} = \frac{1}{\sqrt{2}}(f_3 - f_4) \quad (22.2.6.109)$$

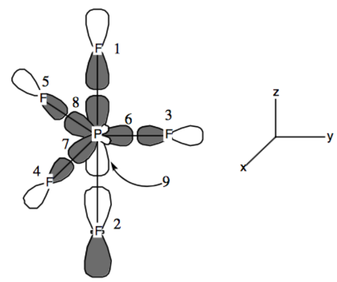
$$\phi_{e'} = \frac{1}{\sqrt{2}}(f_6 - f_7). \quad (22.2.6.110)$$

Both of these 2x2 matrices are identical to the A_1' 2x2 array and therefore yield identical energies and MO coefficients.
This results in an orbital energy diagram:



For the ground state of BH_3 you would fill the bottom level (B-H bonding), a_1' and e' orbitals, with 6 electrons.

5.



5. a. The two F p orbitals (top and bottom) generate the following reducible representation:

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3 3\sigma_v$	
Γ_p	2	2	0	0	0 2	(22.2.6.111) (22.2.6.112)

This reducible representation reduces to $1A_1'$ and $1A_2''$ irreducible representations.
Projectors may be used to find the SALC-AOsfor these irreducible representations.

$$\phi_{a_1'} = \frac{1}{\sqrt{2}}(f_1 - f_2) \quad (22.2.6.113)$$

$$\phi_{a_2}'' = \frac{1}{\sqrt{2}}(f_1 + f_2) \quad (22.2.6.114)$$

5. b. The three trigonal F p orbitals generate the following reducible representation:

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3 3\sigma_v$	
Γ_p	3	0	1	3	0 1	(22.2.6.115) (22.2.6.116)

This reducible representation reduces to $1A_1'$ and 1E' irreducible representations.
Projectors may be used to find the SALC-AOs for these irreducible representations (but they are exactly analogous to the previous few problems):

$$\phi_{a_1'} = \frac{1}{\sqrt{3}}(f_3 + f_4 + f_5) \quad (22.2.6.117)$$

$$\phi_{e'} = \frac{1}{\sqrt{6}}(2f_3 - f_4 - f_5) \quad (22.2.6.118)$$

$$\phi_{e'} = \frac{1}{\sqrt{2}}(f_4 - f_5). \quad (22.2.6.119)$$

5. c. The 3 P sp^2 orbitals generate the following reducible representation:

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3 3\sigma_v$	
Γ_p	3	0	1	3	0 1	(22.2.6.120) (22.2.6.121)

This reducible representation reduces to $1A_1'$ and 1E' irreducible representations. Again, projectors may be used to find the SALC-AOs for these irreducible representations.(but again they are exactly analogous to the previous few problems):

$$\phi_{a_1'} = \frac{1}{\sqrt{3}}(f_6 + f_7 + f_8) \quad (22.2.6.122)$$

$$\phi_{e'} = \frac{1}{\sqrt{6}}(2f_6 - f_7 - f_8) \quad (22.2.6.123)$$

$$\phi_{e'} = \frac{1}{\sqrt{2}}(f_7 - f_8). \quad (22.2.6.124)$$

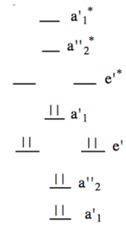
The leftover P p_z orbital generate the following irreducible representation:

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3\ 3\sigma_v$	
Γ_p	1	1	−1	−1	−11	(22.2.6.125) (22.2.6.126)

This irreducible representation is an A_2''

$$\phi_{a_2''} = f_9.$$

Drawing an energy level diagram using these SALC-AOs would result in the following:


a'1*
a''2*
e'*
a'1
e'
a''2
a'1