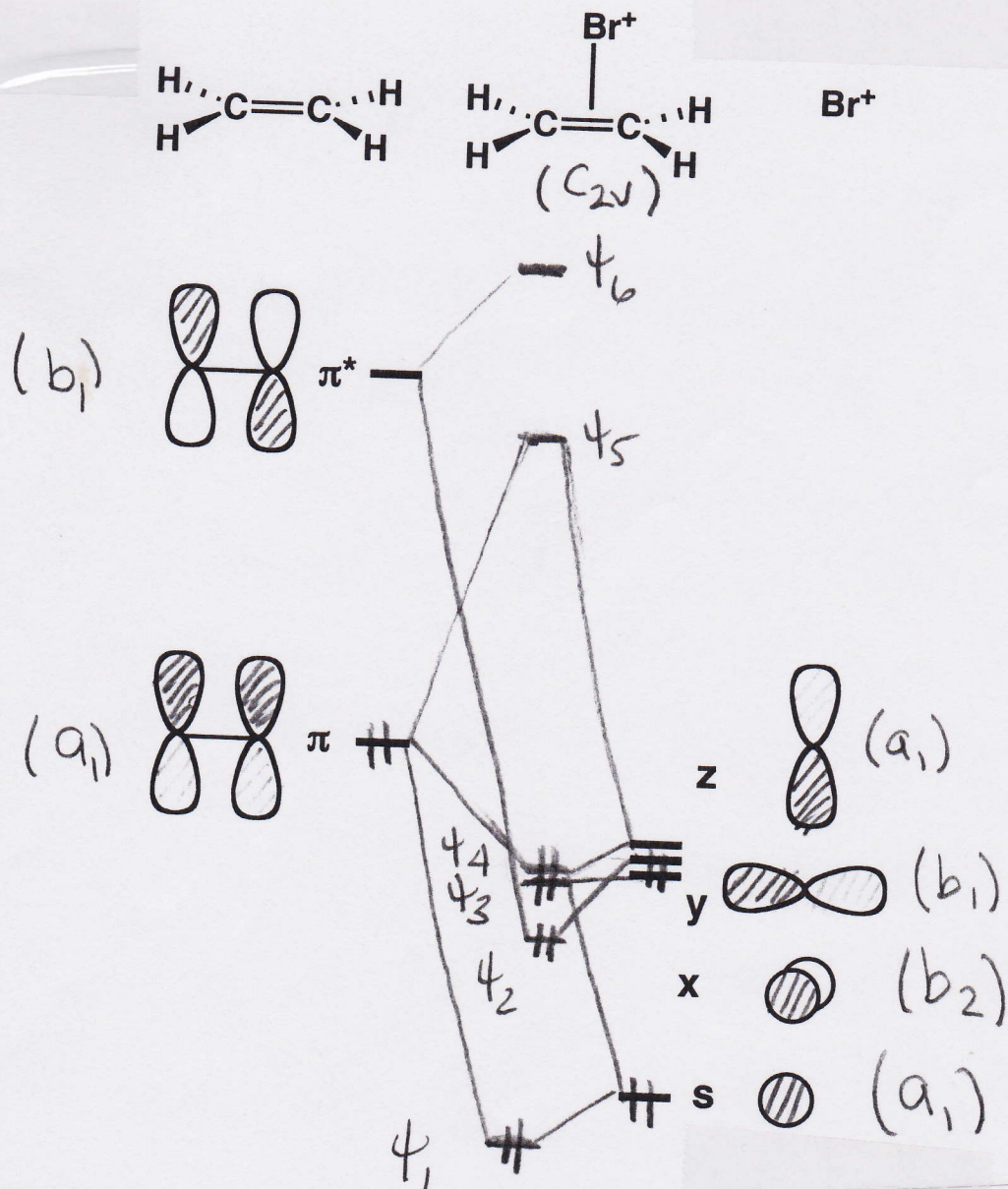


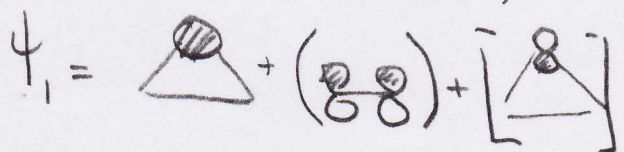
Answers - Chapter 11

1.



$$\psi_1 \approx \psi_s^0 + t_{\pi,s}^{(1)} \psi_\pi^0 + t_{z,s}^{(2)} \psi_s^0$$

$$t_{\pi,s}^{(1)} \propto \frac{-\tilde{S}_{s,\pi}}{e_s^0 - e_\pi^0} = \frac{(-)(+)}{(-)} = (+)$$

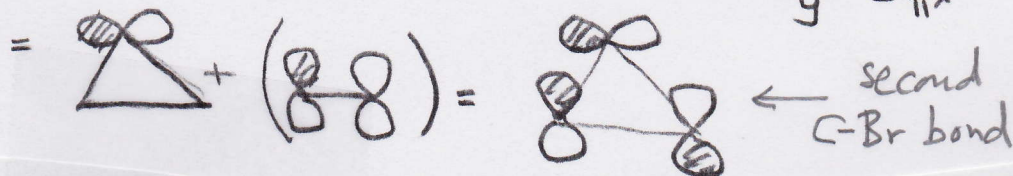


$$t_{z,s}^{(2)} \propto \frac{\tilde{S}_{s,\pi} \tilde{S}_{z,\pi}}{(e_s^0 - e_z^0)(e_s^0 - e_\pi^0)} = \frac{(+)(+)}{(-)(-)} = (+)$$



$$t_2 \approx \psi_y^0 + t_{\pi^*,y}^{(1)} \psi_{\pi^*}^0$$

$$t_{\pi^*,y}^{(1)} \propto \frac{-\tilde{S}_{\pi^*,y}}{e_y^0 - e_{\pi^*}^0} = \frac{(-)(+)}{(-)} = (+)$$



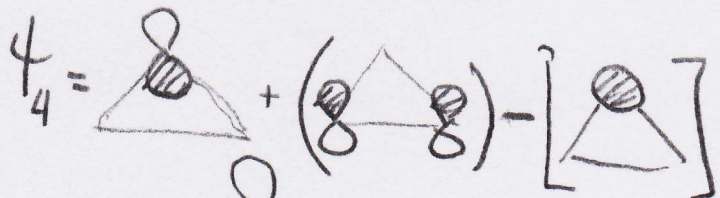
$$\psi_3 = \psi_x^0 \text{ (unperturbed)}$$



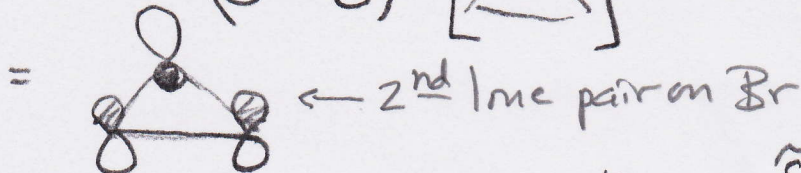
← lone pair on Br

$$\psi_4 \approx \psi_z^0 + t_{\pi,z}^{(1)} \psi_{\pi}^0 + t_{s,z}^{(2)} \psi_s^0$$

$$t_{\pi,z}^{(1)} \propto \frac{-\tilde{S}_{\pi,z}}{e_z^0 - e_{\pi}^0} = \frac{(-)(+)}{(-)} = (+)$$



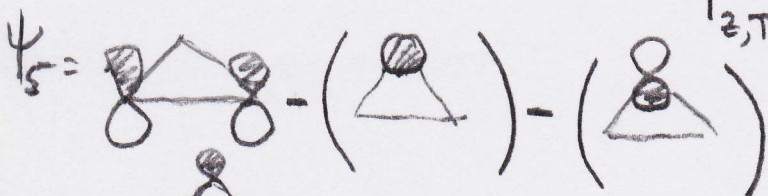
$$t_{s,z}^{(2)} \propto \frac{\tilde{S}_{\pi,z} \tilde{S}_{\pi,s}}{(e_z^0 - e_s^0)(e_z^0 - e_{\pi}^0)} = \frac{(+)(+)}{(+)(-)} = (-)$$



$$\psi_5 \approx \psi_{\pi}^0 + t_{s,\pi}^{(1)} \psi_s^0 + t_{z,\pi}^{(1)} \psi_z^0$$

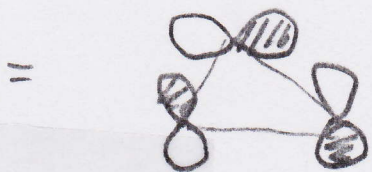
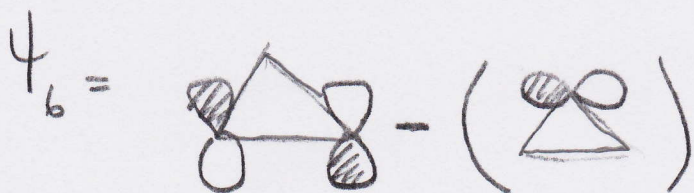
$$\psi_{s,\pi}^{(1)} = \frac{-\tilde{S}_{\pi,s}}{e_{\pi}^0 - e_s^0} = \frac{(-)(+)}{(+)} = (-)$$

$$\psi_{z,\pi}^{(1)} = \frac{-\tilde{S}_{\pi,z}}{e_{\pi}^0 - e_z^0} = \frac{(-)(+)}{(+)} = (-)$$

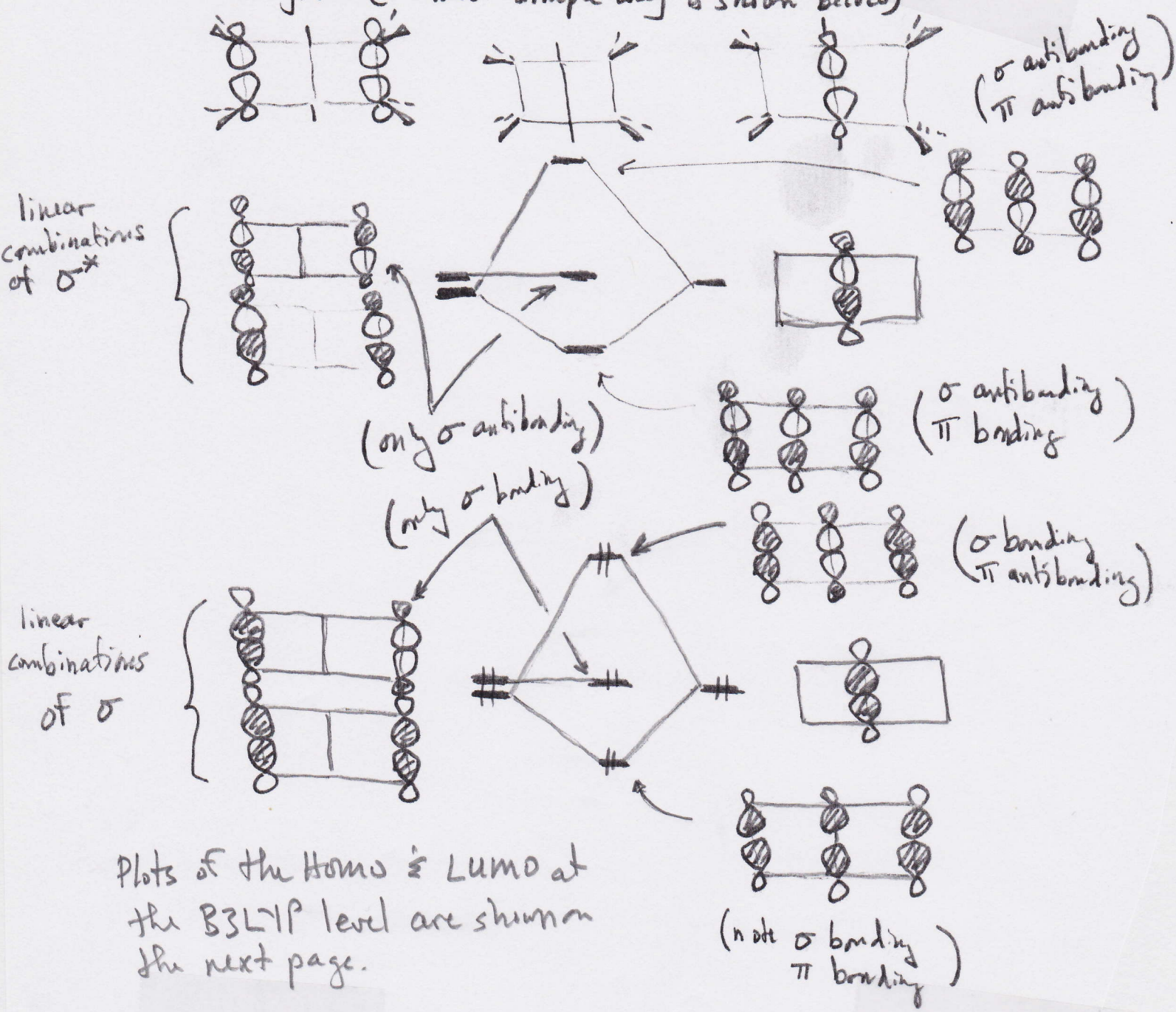


$$\psi_6 \approx \psi_{\pi^*}^0 + t_{y,\pi^*}^{(1)} \psi_y^0$$

$$t_{y,\pi^*}^{(1)} \propto \frac{-\tilde{S}_{\pi^*,y}}{e_{\pi^*}^0 - e_y^0} = \frac{(-)(+)}{(+)} = (-)$$

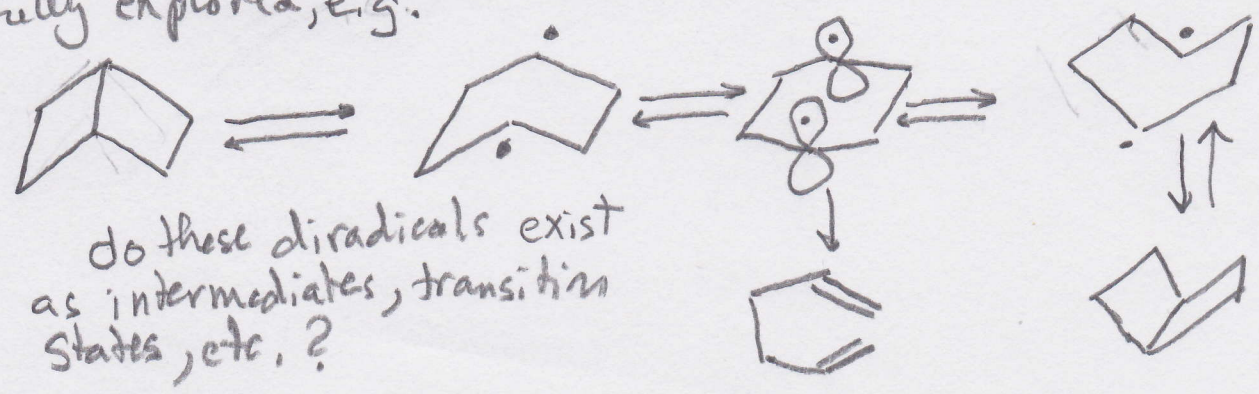


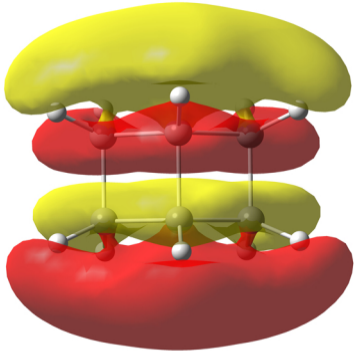
2. Use σ & σ^* as the 1st step; then do an interaction diagram (the most simple way is shown below)



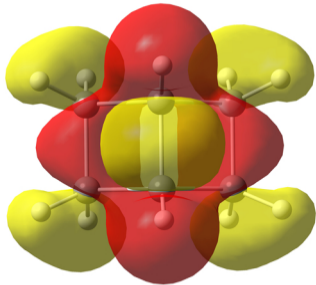
Plots of the HOMO & LUMO at the B3LYP level are shown on the next page.

There is interesting dynamical issues that have not been fully explored, e.g.



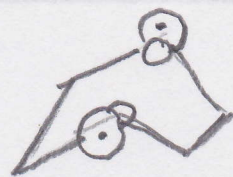


LUMO



HOMO

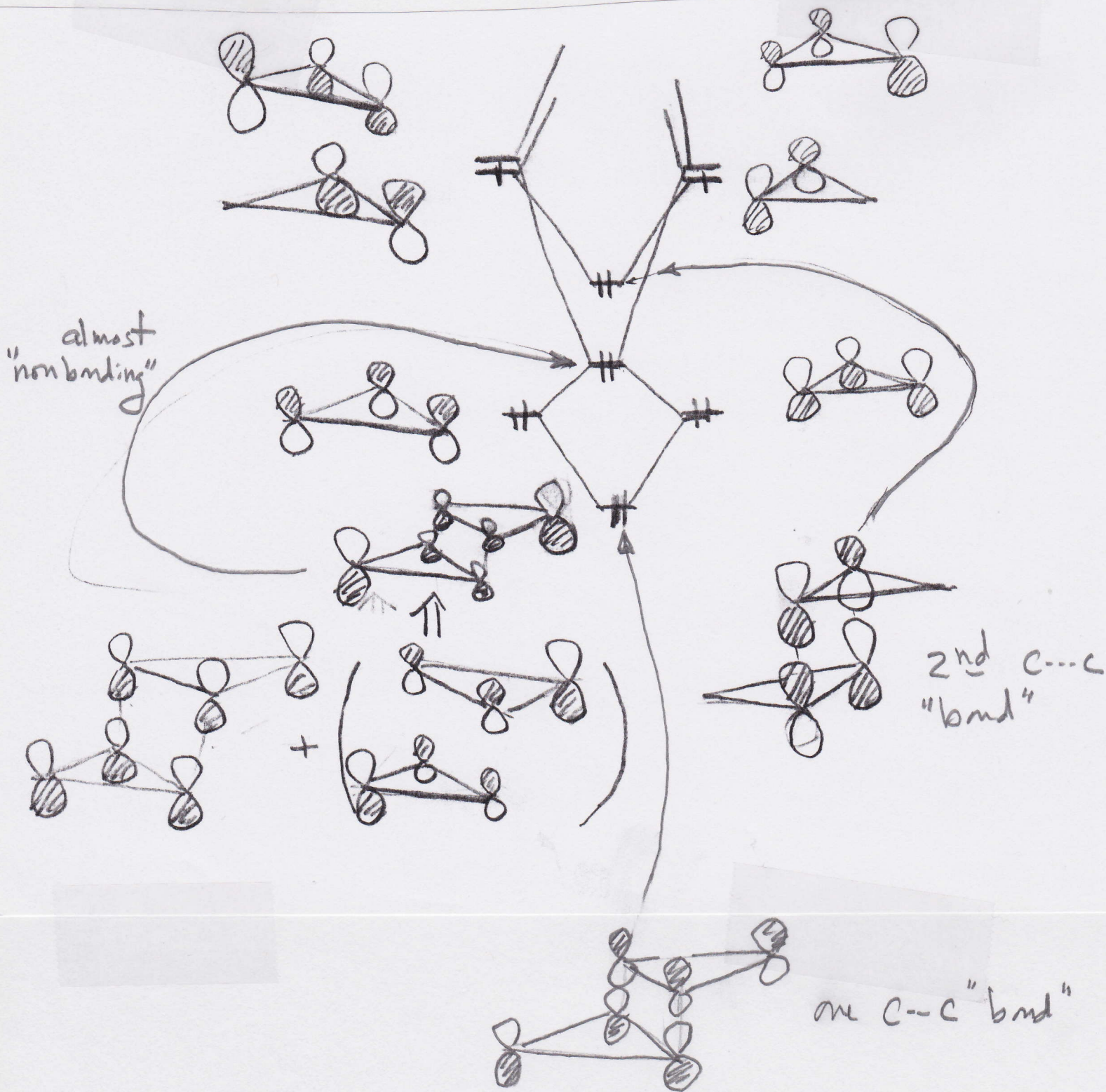
If



diradical exists - through bond conjugation

should put the S combination empty and above the A combination.

3.



4. The net results are as follows:

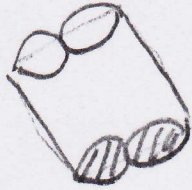
For $\alpha_1 - \alpha_4$:

$\psi_{a_{1g}}$

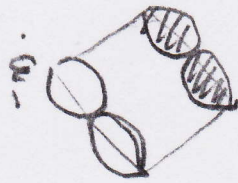


$$\alpha_1 + \alpha_2 + \alpha_3 + \alpha_4$$

ψ_{e_u}

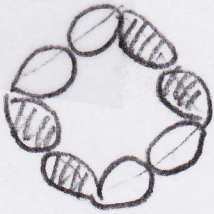


$$\alpha_2 - \alpha_4$$



$$\alpha_1 - \alpha_3$$

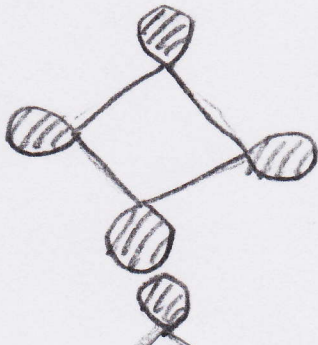
$\psi_{b_{2g}}$



$$\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4$$

For $\alpha_5 - \alpha_8$:

$\psi_{a_{1g}}$

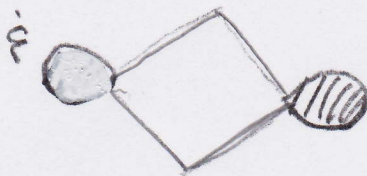


$$\alpha_5 + \alpha_6 + \alpha_7 + \alpha_8$$

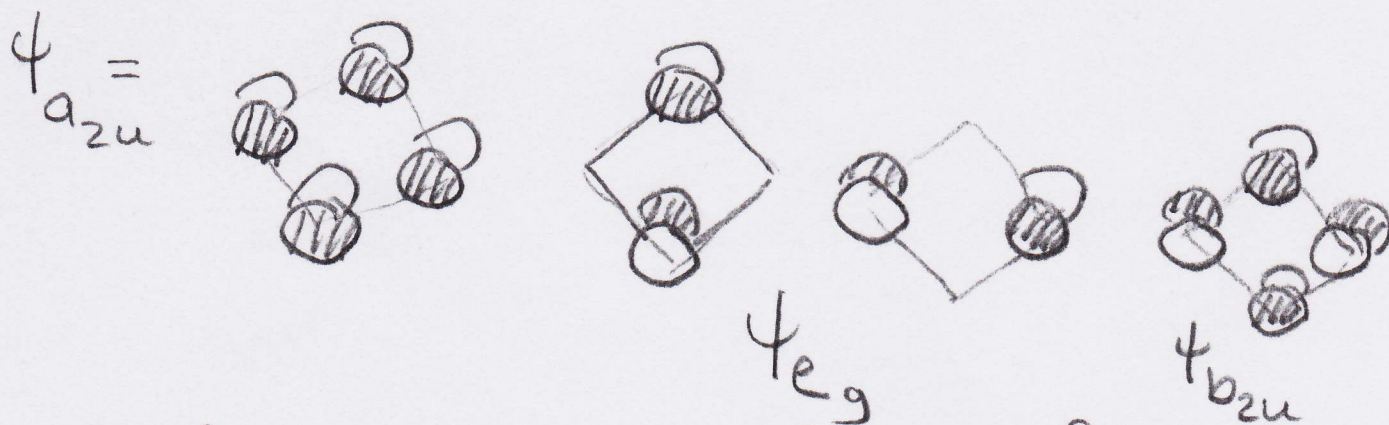
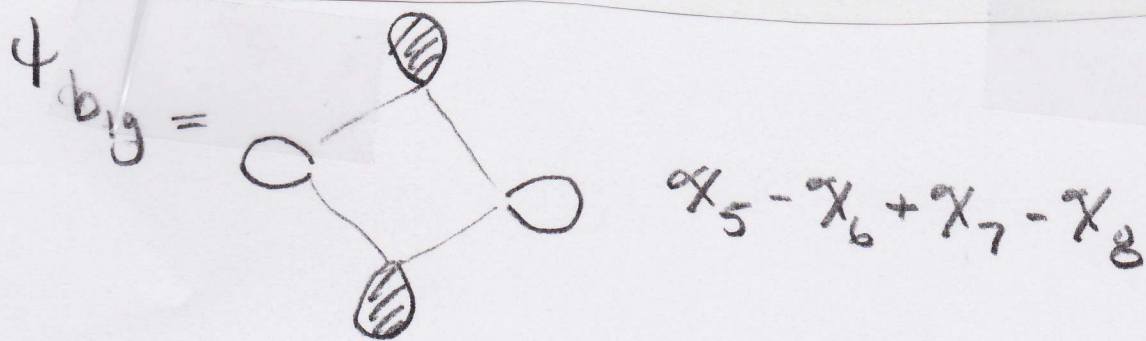
ψ_{e_u}



$$\alpha_5 - \alpha_7$$

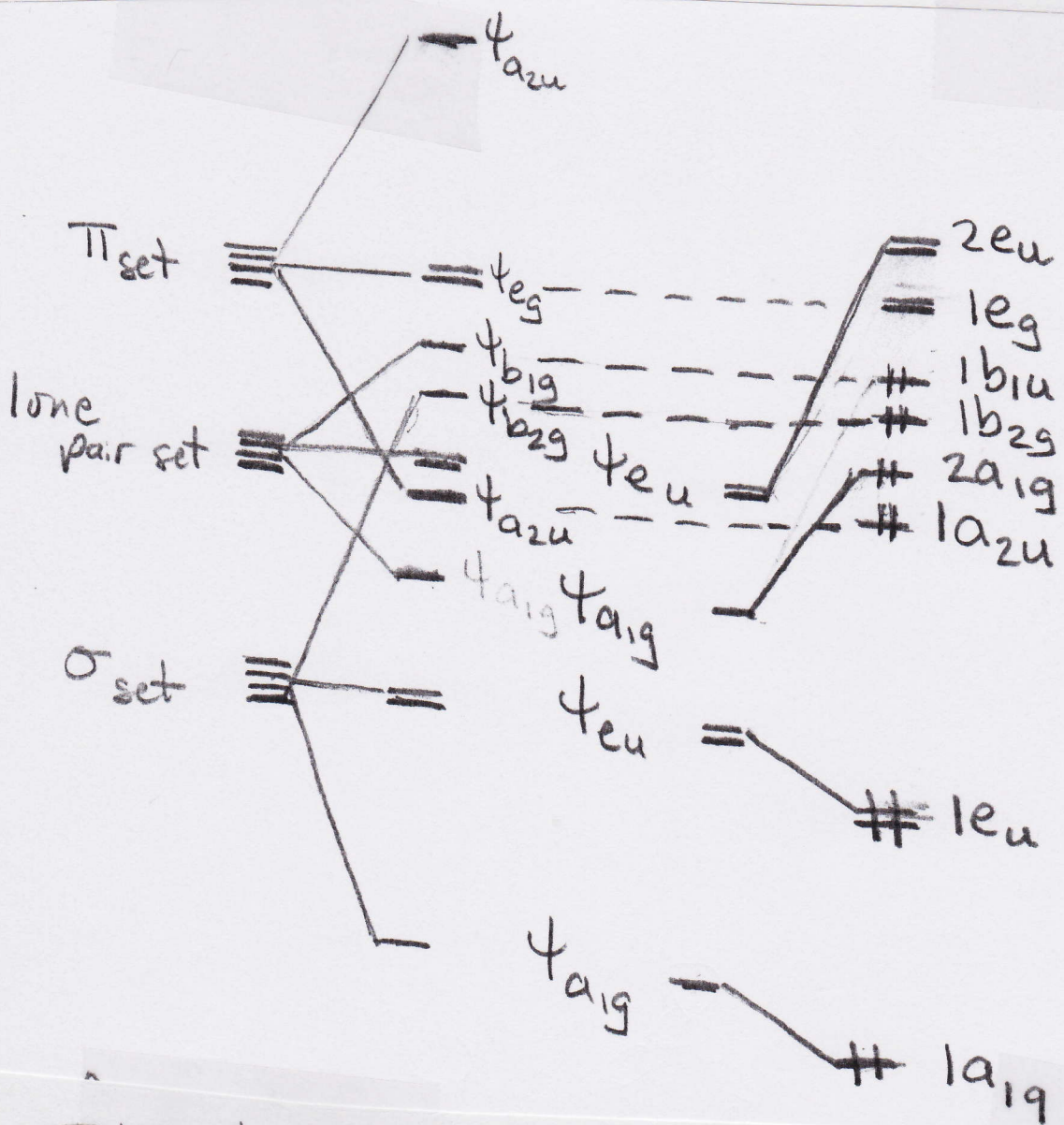


$$\alpha_6 - \alpha_8$$

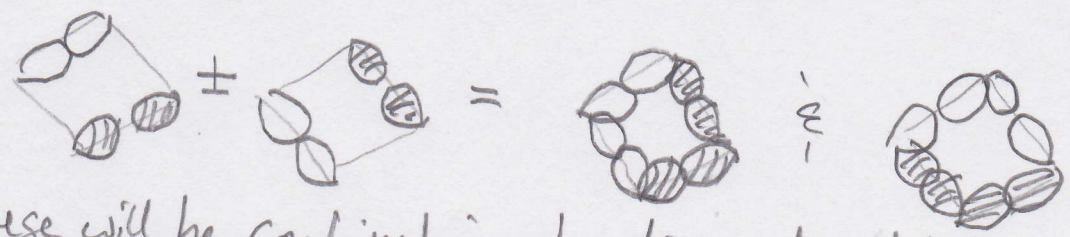


note that all have the same functional form.

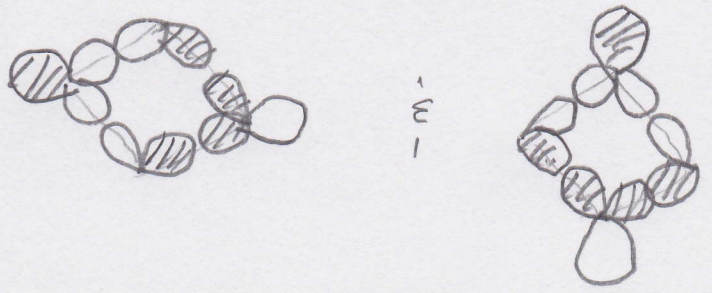
One might expect that the σ bonds will lie before combining them below the lone pair and the π MO's before perhaps at the same or higher energy than the lone pairs (we are starting the π MO's from just p AOs on the Al atoms). So the splitting that one would expect from constructing the SALCs is shown on the left side on the next page. HOWEVER, this is not what the MO's from the extended Hückel calculation yield. The e_u and a_{1g} sets of lone pair combinations are pushed up to higher energies, as shown on the right side. They have mixed with the σ sets of the same symmetry.



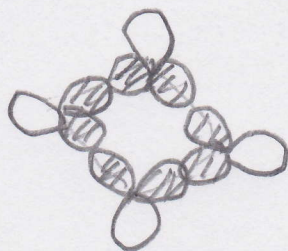
Taking linear combinations of the e_u set of σ orbitals gives



These will be combined in a bonding and antibonding way with the e_u lone pair set, e.g., the antibonding combination looks like

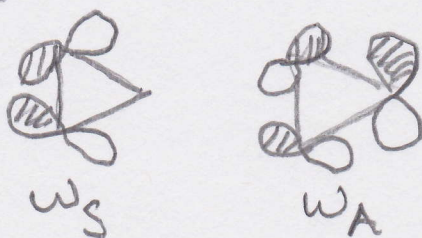


The same occurs with the a_{1g} set so the antibonding combination is



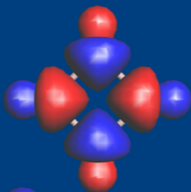
Extended Hückel plots of these MO's are shown on the next page.

5. Let $w_S \hat{=} w_A$ stand for the two Walsh orbitals in cyclopropane:

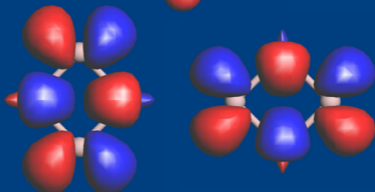


For the cyclopropane PE spectrum these MO's correspond to peak ①. They have e' symmetry in D_{3h} so $C_3H_6^+$ is Jahn-Teller unstable and there are two peaks, each with considerable vibrational progressions. For methylene cyclopropane peak ① clearly is the π orbital. It's IP of 9.6 eV is very close to that in $\begin{matrix} \text{CH}_3 \\ \diagdown \\ \text{C} \\ \diagup \\ \text{CH}_3 \end{matrix}$ (9.5). The Walsh set is split in energy w_A goes up in energy by ~ 0.5 eV and w_S is lowered by about the same amount. In the former the in-plane π_{CH_2} orbital mixes into and destabilizes w_A . For the latter w_S and the exocyclic C-C σ bond mix together so w_S is stabilized. Both MO's from a B3LYP calculation are shown on the next page.

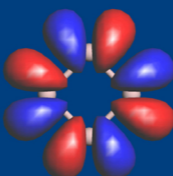
$2b_{1g}$



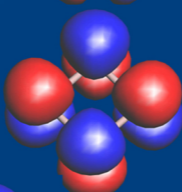
$3e_u$



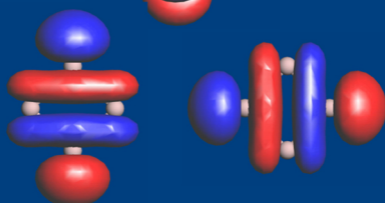
$1a_{2g}$



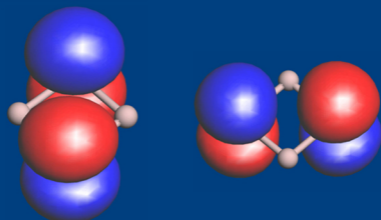
$1b_{2u}$



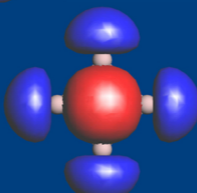
$2e_u$



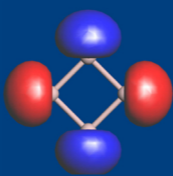
$1e_g$



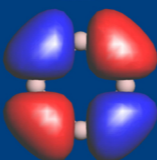
$2a_{1g}$



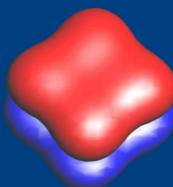
$1b_{1g}$



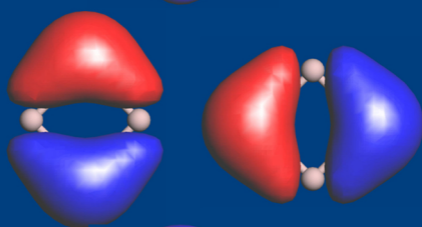
$1b_{2g}$



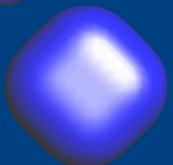
$1a_2''$

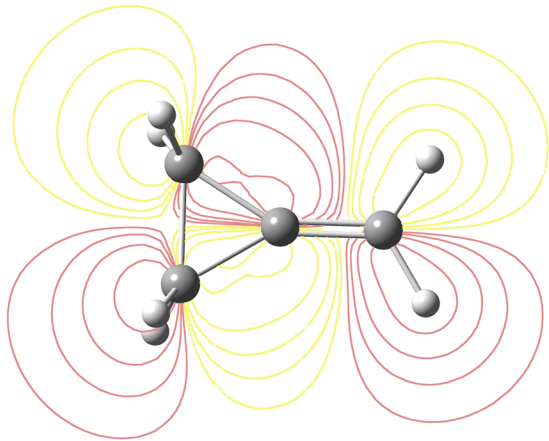


$1e_u$

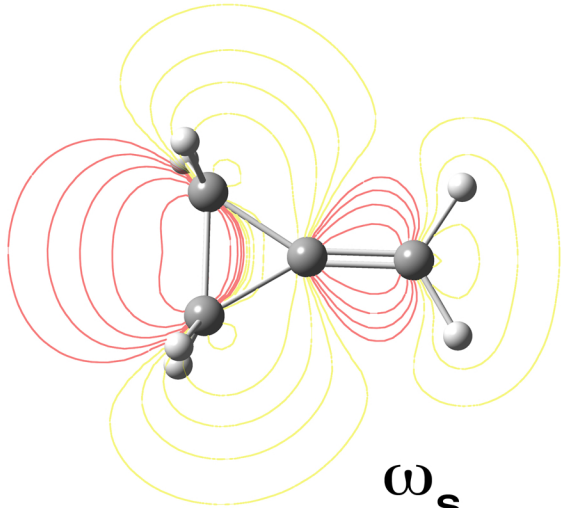


$1a_{1g}$





ω_A

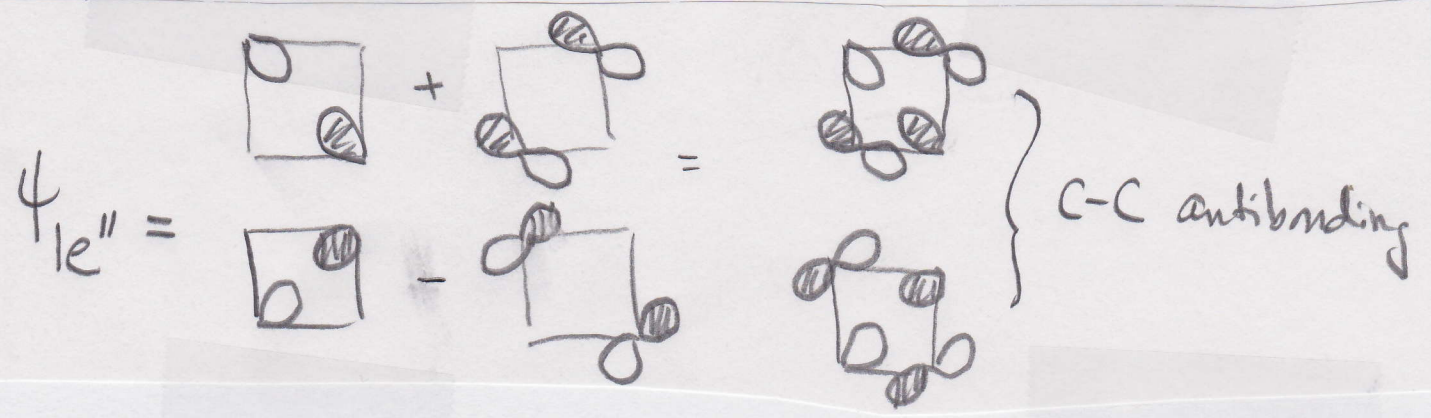


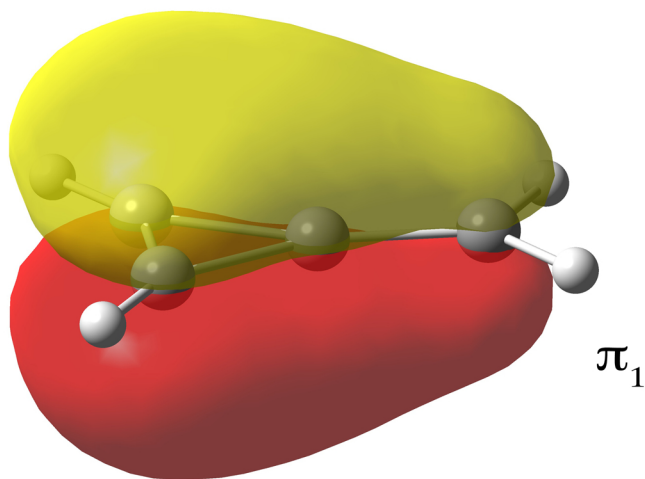
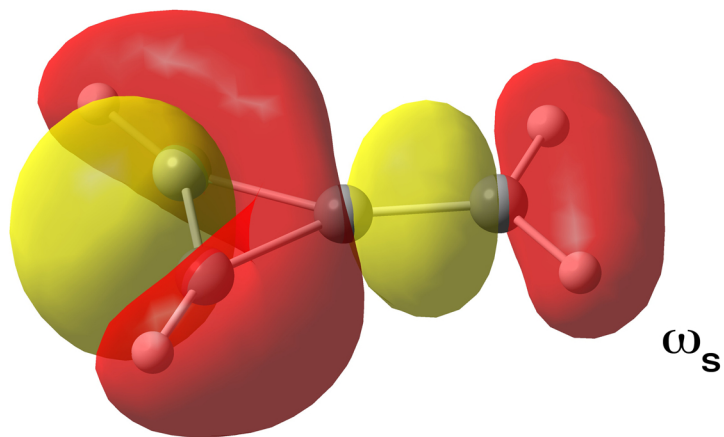
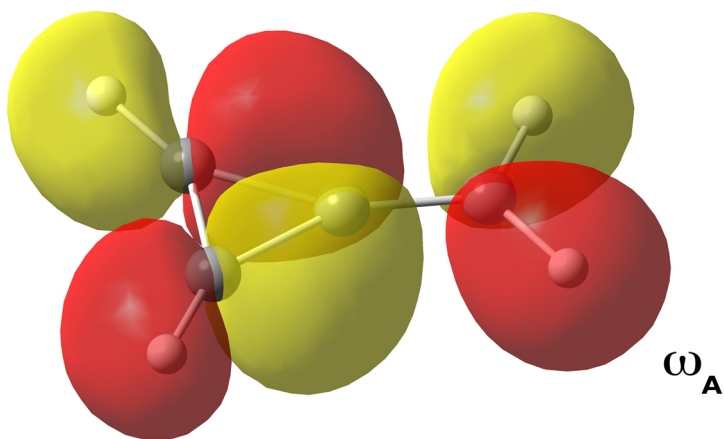
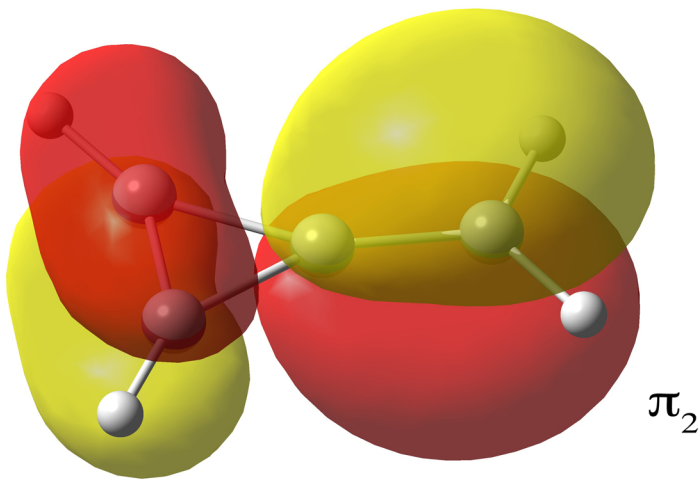
ω_S

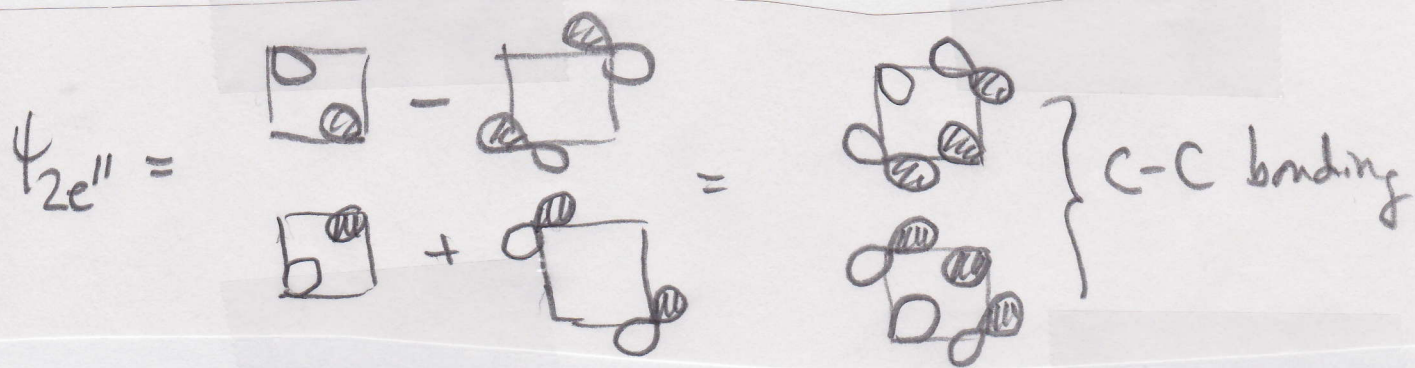
In cyclopropene the formation of a $C=C$ bond shortens the $C-C$ bond length from 1.51 \AA in cyclopropane to 1.30 \AA . Thus w_s is stabilized by (it is bonding between these two carbons) and w_A is destabilized slightly (it is antibonding between these two carbons). In methylenecyclopropene one has the same factors as in the previous two compounds for the Walsh set. Furthermore, the two π orbitals mix to form a bonding and antibonding combination (with a larger and smaller IP, respectively, than in methylenecyclopropane and cyclopropene). B3LYP plots of these four MOs are illustrated on the next page.

b. Combining the e'' sets

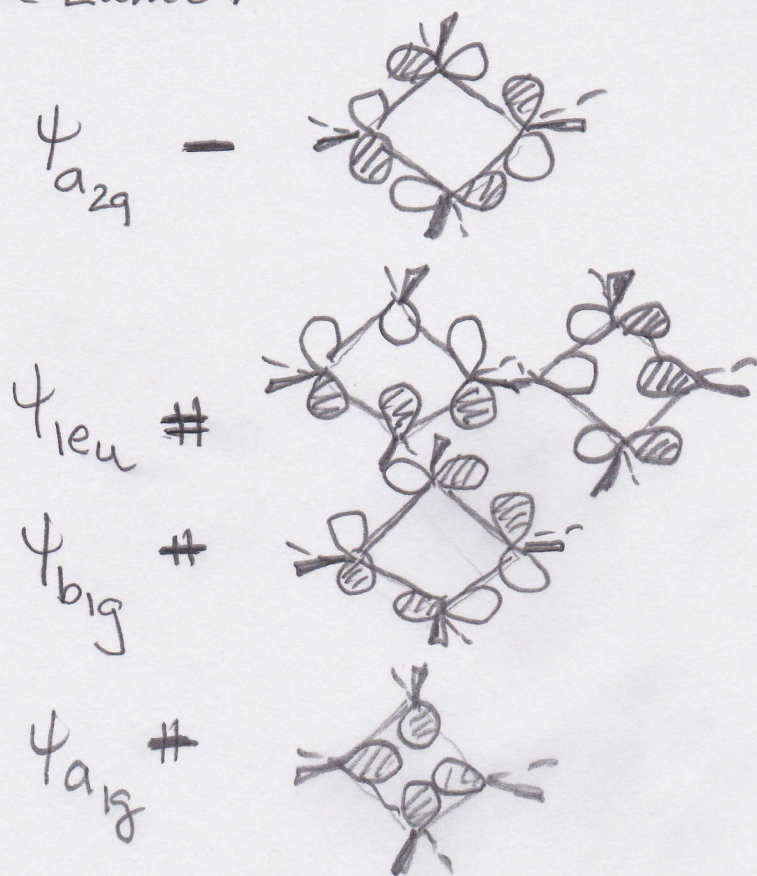
a)





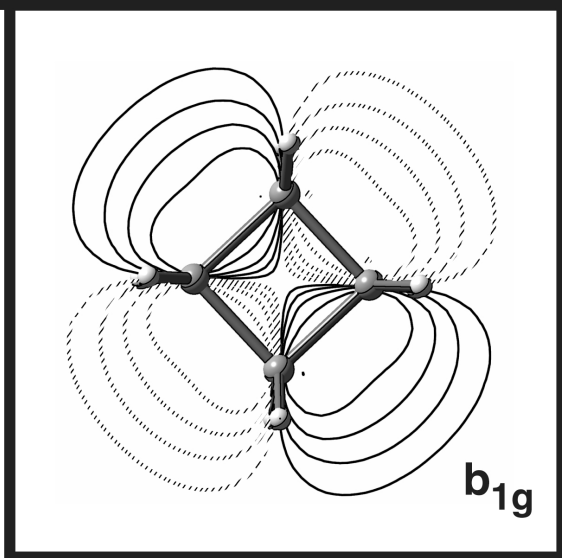
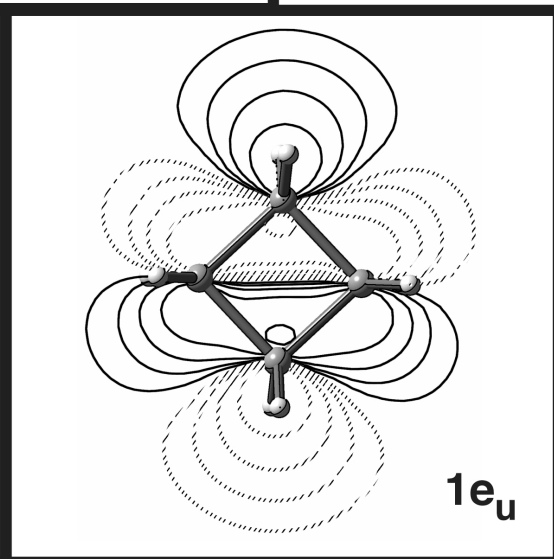
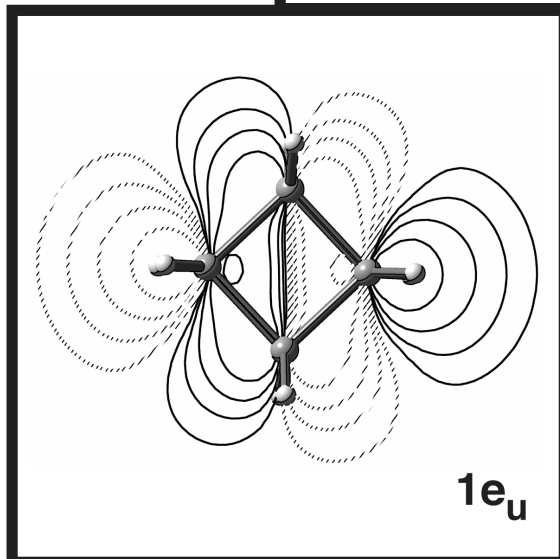
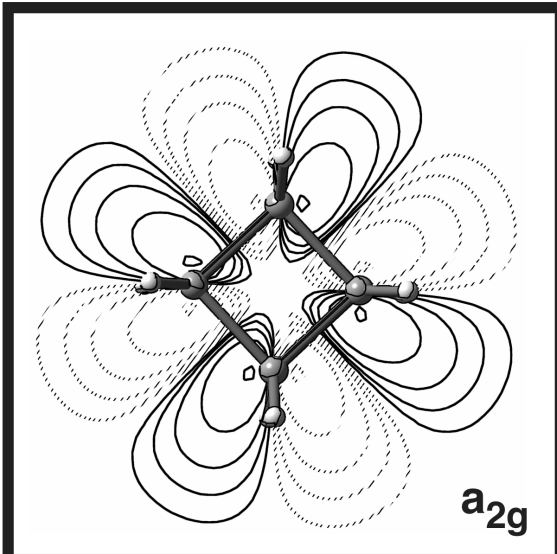


So we have filled MO's (now in D_{4h} symmetry) and the LUMO:

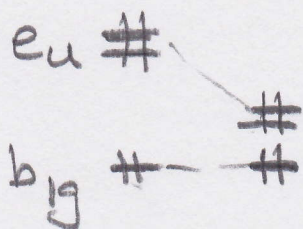
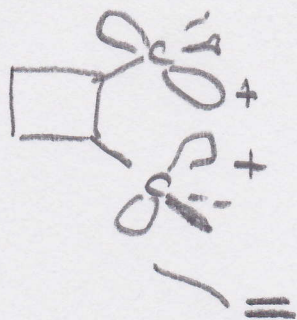


A plot of these MO's at the HF 3-21G level is shown on the next page (except for a_{1g}).

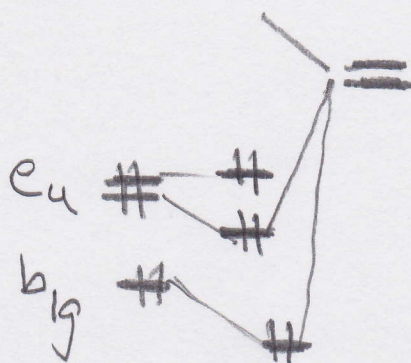
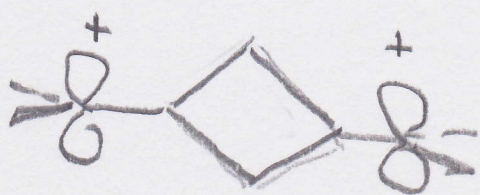
b) For the bis methylene dications, the stabilizing interactions will occur between the empty p AO's and filled orbitals on the cyclobutane fragment.



For the first structure one can use both members of e_u to interact with the p AO's, i.e.

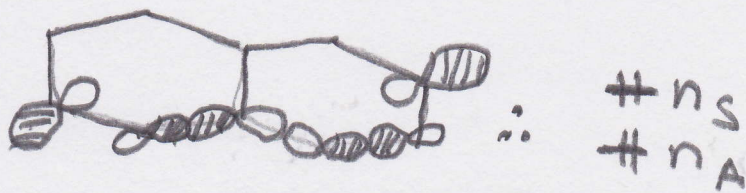
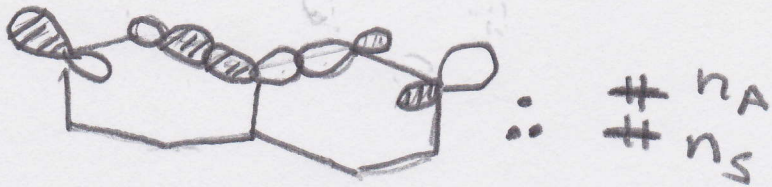
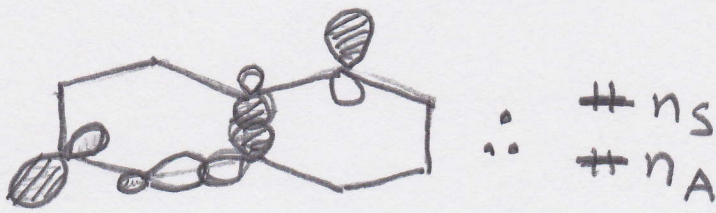
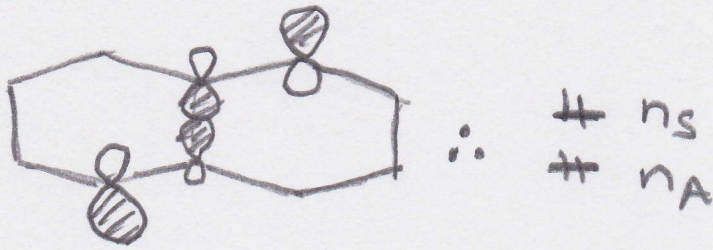
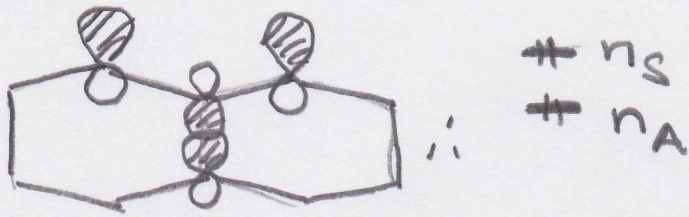


For the alternative structure, one uses one member of e_u and b_g :



So both structures are stabilized, perhaps the first a little more.
 In principle both C-C bond σ and σ^* combinations could combine with the lone pairs on nitrogen, but in practice σ^* lies very high

in energy so the mixing with σ^* is pretty small. So we will only show the highest σ combination destabilizing either n_S or n_A :



8.

