1) Use the Equivalent Bond Orbital method to derive expressions for the individual hybrid orbitals for a molecule with a) a trigonal planar geometry (sp^2 bonding) and b) a square planar geometry (dsp^2 bonding).

2.) a) Show using projection operators that the LCAO molecular orbitals which form bases for the irreducible representations of benzene (in addition to a_{2u} derived in class) are:

$$\Psi(B_{2g}) = \frac{1}{\sqrt{6}}(\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6)$$

$$\Psi_1(E_{1g}) = \frac{1}{\sqrt{12}}(2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6)$$

$$\Psi_2(E_{1g}) = \frac{1}{\sqrt{12}}(\phi_1 + 2\phi_2 + \phi_3 - \phi_4 - 2\phi_5 - \phi_6)$$

$$\Psi_1(E_{2u}) = \frac{1}{\sqrt{12}}(2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 - \phi_6)$$

$$\Psi_2(E_{2u}) = \frac{1}{\sqrt{12}}(\phi_1 - 2\phi_2 + \phi_3 + \phi_4 - 2\phi_5 + \phi_6)$$

Use the ZOA approximation to determine normalization factors and check wave functions for orthogonality. Make use of the numbering system for the carbon atoms used in class, which is reproduced at the end of the problem.
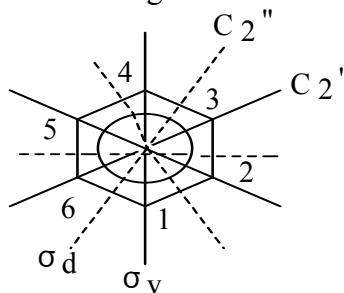
b) Show that the molecular orbitals

$$e_{1g}(1) = \frac{1}{\sqrt{3}}(\Psi_1(E_{1g}) + \Psi_2(E_{1g}))$$

$$e_{1g}(2) = (\Psi_1(E_{1g}) - \Psi_2(E_{1g}))$$

are normalized and orthogonal. Find similarly the pair of orthonormal MOs for the E_{2u} representation.

c) Use your results to confirm how the signs of the MOs vary around the ring the nodal planes.

Benzene molecule, carbon numbering, and some of the symmetry elements

3.) Like benzene, the D_{2h} cyclobutadiene dianion, $C_4H_4^{2-}$, has 6 electrons in a delocalized π-system.
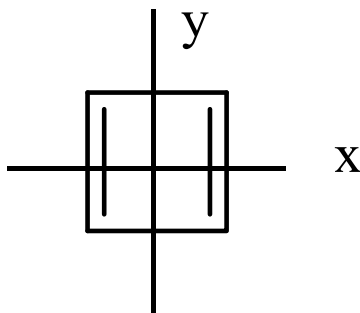
a) Use group theory and projection operators to develop a qualitative π-MO scheme for this species. Draw the MOs and label them by their irreducible representations. Indicate the nodal planes if present.

b) Derive the Hückel energies and explain why $C_4H_4^{2-}$ is less stable than benzene even though both species have six π-electrons.

4.) Consider the *trans*-butadiene molecule.
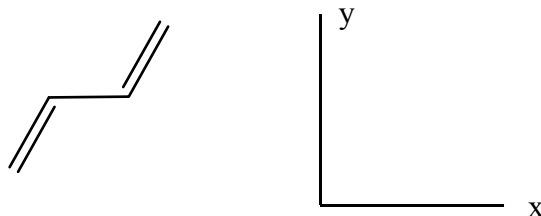
a) As drawn what is its point group?
b) Derive the irreducible representation for the molecular orbitals (MOs) using the set of 4 p_z orbitals on the labelled carbons.
c) **Without** using projection operators, make pictorial representations of these MOs. Make an energy level diagram based on the nodal structure of the MOs.
d) What is the ground electronic configuration of π-system? What is the irreducible representation of the resultant ground state? What is the electronic configuration of the first excited state obtained by promoting one electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO)? What is the irreducible representation of the resultant state?
e) Is the HOMO → LUMO transition electric dipole allowed? Recall a transition is allowed here if $\Gamma(LUMO)\otimes\Gamma(HOMO)\subset\Gamma_{(x,y,z)}$ or if $\Gamma(LUMO)\otimes\Gamma_{(x,y,z)}\otimes\Gamma(HOMO)\subset\Gamma_1$. Γ_1 is the totally symmetric representation.

5.) Borane, BH_3 is an unstable compound whose geometry is probably trigonal planar. Develop a general MO scheme for BH_3 and display this in a standard MO diagram. Assume that only the boron 2s and 2p orbitals interact with the hydrogen 1s orbitals; that is, the boron 1s orbital is non-bonding.

6.) Although BH_3 is unstable, the BX_3 trihalides (X = F, Cl, Br) are stable but reactive. BF_3 in particular has strong pπ-bonding between the $2p_z$ orbital of boron and the three $2p_z$ of the Fs.
a) Develop a general MO scheme for the pπ-MOs of BF_3.
b) Although the 2s orbitals on fluorine may be assumed to nonbonding, projection operators can still be used to form the symmetry adapted linear combinations of atomic orbitals among them. Do so, and label each combination by their irreducible representation.
c) Assume that each of the F atoms uses a 2p orbital directed towards the B atom to form σ-interactions. What are the symmetries of the three MOs that can be formed from the three σ-symmetry 2p orbitals on the F atoms?
d) In addition to the F 2p orbitals engaged in σ- and π-bonding, there are 3 2p orbitals lying in the plane of the molecule that may be assumed to be non-bonding. What are the symmetries of the three symmetry adapted MOs that can be formed from these 2p orbitals?
e) Use the results in a) through d) to develop a complete MO scheme for BF_3 and display this in a standard MO diagram.
f) In part d) it was assumed that the F 2p-orbitals not involved in σ-bonding were non-bonding. On the basis of symmetry, are antibonding and bonding interactions with B precluded for these orbitals? If bonding is possible, how might that qualitatively affect the MO scheme developed in e)?