NORTH CAROLINA STATE UNIVERSITY

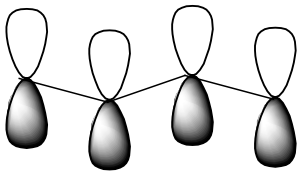
Department of Chemistry Name_____

Physical Chemistry CH437 Problem Set #6

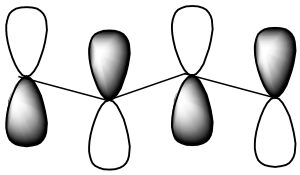
Due Date: October 13, 2015

1. The molecular orbitals for the p-system of butadiene are given below.

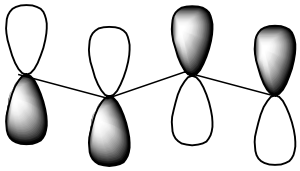
A



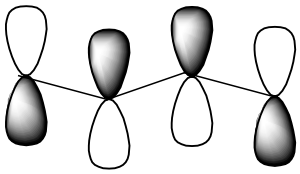
B



C



D



ϕ_1 ϕ_2 ϕ_3 ϕ_4

A. What is the point group of trans-butadiene?

Point group is _____.

B. Identify the molecular orbitals below with the appropriate letter corresponding to the figure above.

$\chi_1 = \phi_1 + \phi_2 + \phi_3 + \phi_4$ corresponds to _____ and has irrep _____.

$\chi_2 = \phi_1 + \phi_2 - \phi_3 - \phi_4$ corresponds to _____ and has irrep _____.

$\chi_3 = \phi_1 - \phi_2 - \phi_3 + \phi_4$ corresponds to _____ and has irrep _____.

$\chi_4 = \phi_1 - \phi_2 + \phi_3 - \phi_4$ corresponds to _____ and has irrep _____.

B. How many nodes does each molecular orbital have in total?

Nodes in χ_1 = _____.

Nodes in χ_2 = _____.

Nodes in χ_3 = _____.

Nodes in χ_4 = _____.

C. Which orbitals are filled (occupied) and which are empty (unoccupied).

χ_1 is _____.

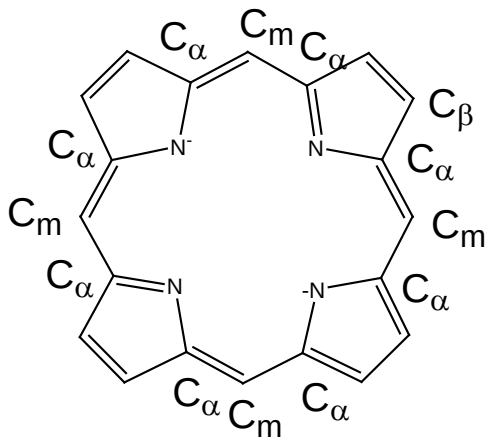
χ_2 is _____.

χ_3 is _____.

χ_4 is _____.

D. Is the HOMO → LUMO transition allowed? If so, what is it's polarization?

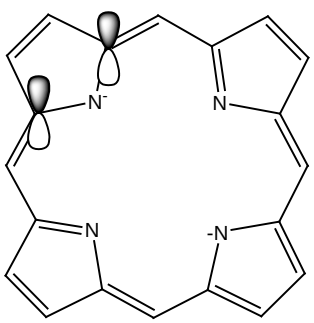
2. Metalloporphyrins are important molecules in nature. They form the basic skeleton for chlorophyll in photosynthesis and heme in heme proteins such as myoglobin, hemoglobin, peroxidase, cytochrome P450, cytochrome c oxidase, cytochrome c, etc. Let's consider two alternative models of the transitions of the metalloporphyrin π-system.
   A. The free electron model
   B. Huckel theory



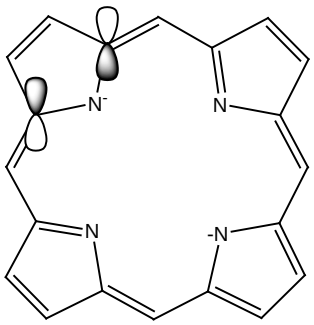
A. In the free electron model (FEM) you may use the particle-on-a-wire model for the electron. Consider that there are 18 π-electrons and fill the energy levels of the particle-on-a-wire energy levels to the highest level. Finally consider the transitions. There are two types, allowed and forbidden. Sketch the energy levels and estimate the transition energy if the radius of the wire is 3.5 A.

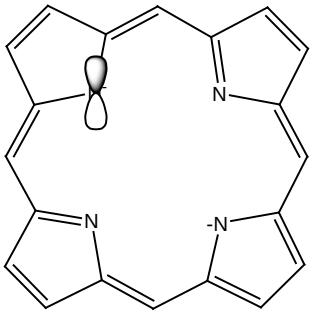
B. Using the Huckel model we find that there are three different types of p electrons, N, Cα, and Cm (m = meso). Each of these types has a reducible representation. Note that the charge on the porphyrin is 2^- so that there are 16 orbitals in this model, but 18 electrons as was the case in the FEM.

B.1. Determine the reducible representation for the basis consisting of N, Cα and Cm. Note that both Cα's transform the same way so they are interchangeable. You can use the one on the left to determine the reducible representation.

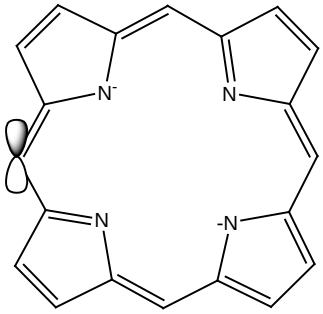


Cα





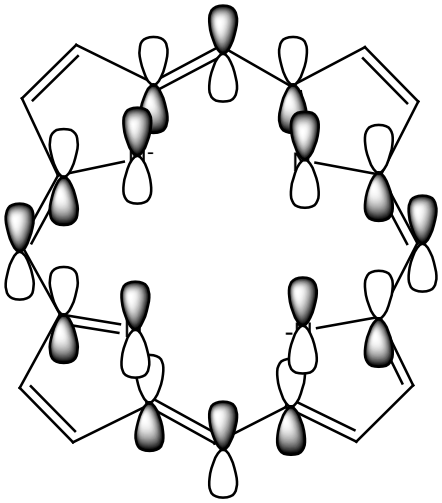
N



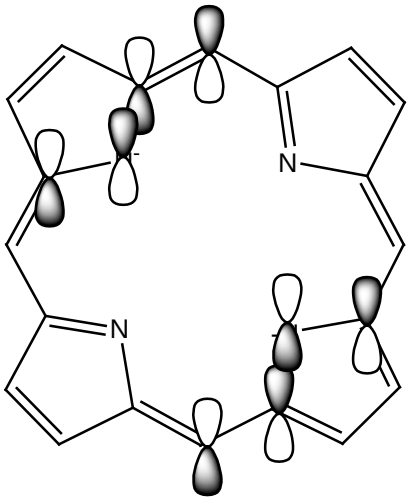
Cm

B.2 Decompose the reducible representations into irreps.

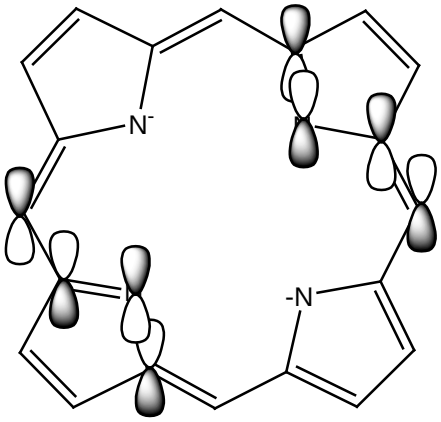
B.3 Identify the MOs obtained using the the projection operator method. How many nodes does each quantum level have, i.e. what is the value of m (number of nodes)? [You not need to include the node of the p-orbitals, but you will not be wrong if you do so consistently]



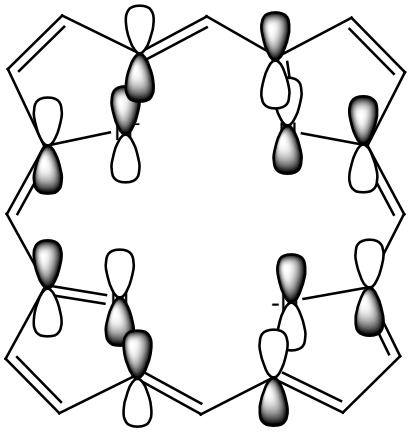
Irrep = _____. m = _____.



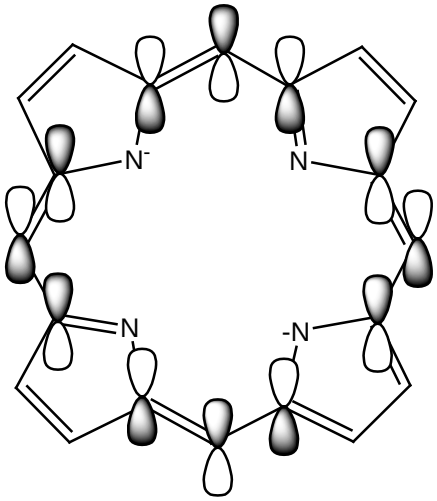
Irrep = _____. m = _____.



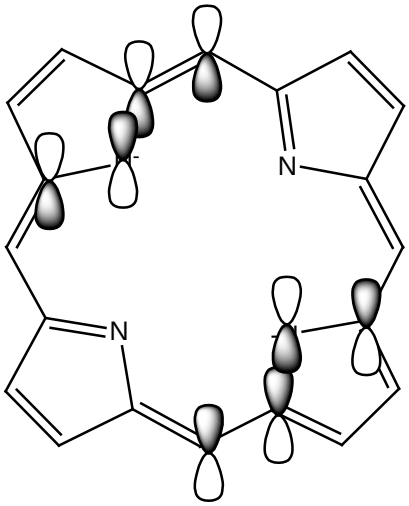
Irrep = _____. m = _____.



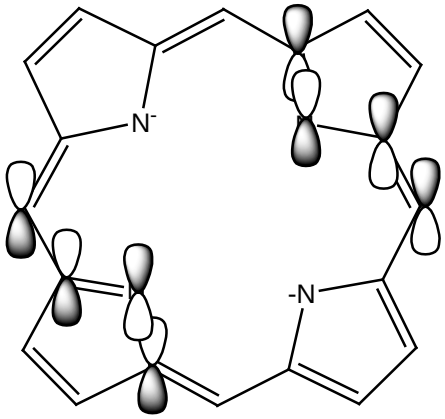
Irrep = _____. m = _____.



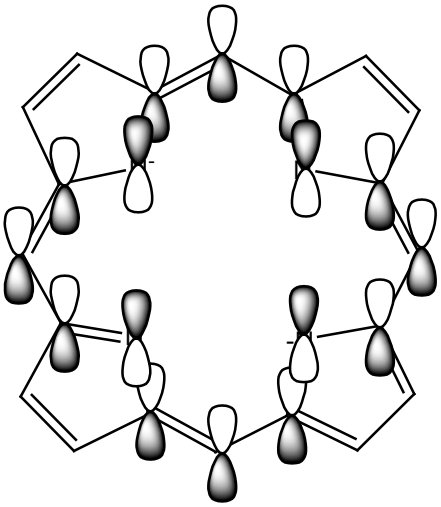
Irrep = _____. m = _____.



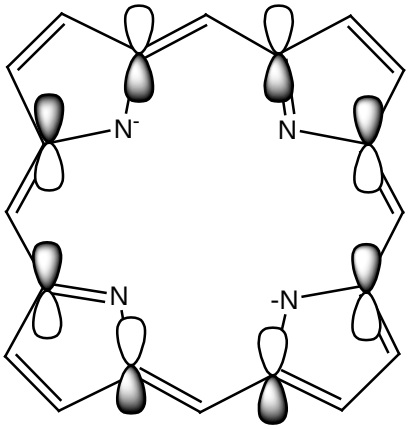
Irrep = _____. m = _____.



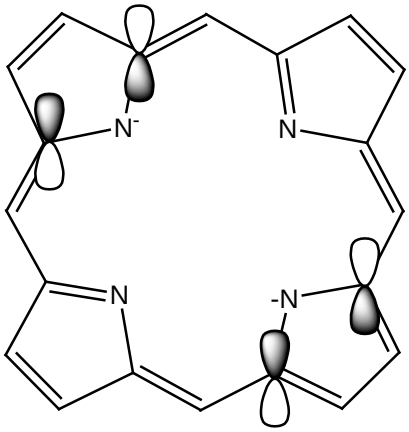
Irrep = _____. m = _____.



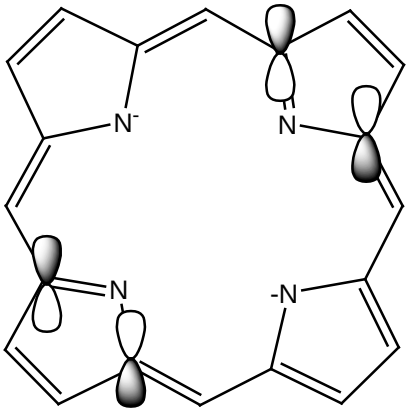
Irrep = _____. m = _____.



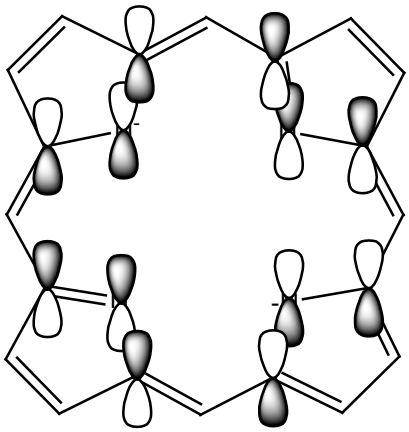
Irrep = _____. m = _____.



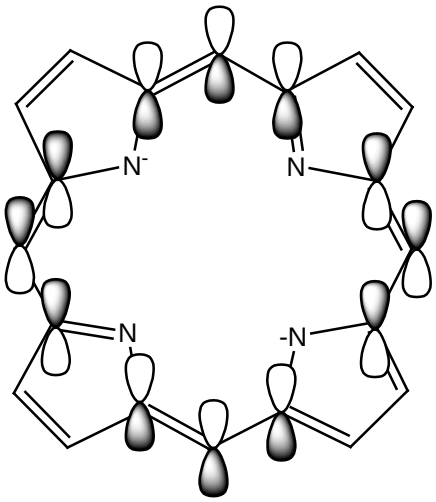
Irrep = _____. m = _____.



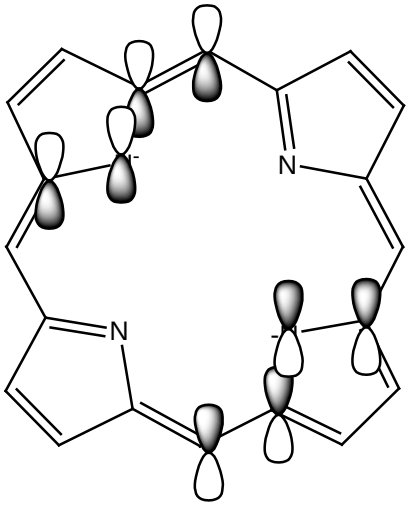
Irrep = _____. m = _____.



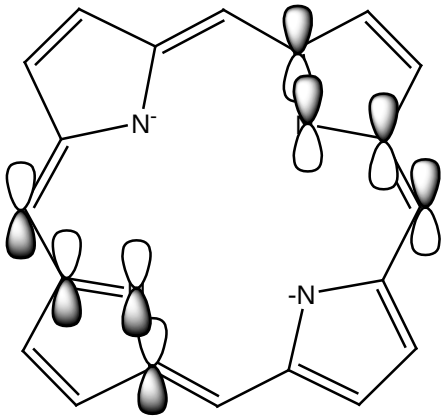
Irrep = _____. m = _____.



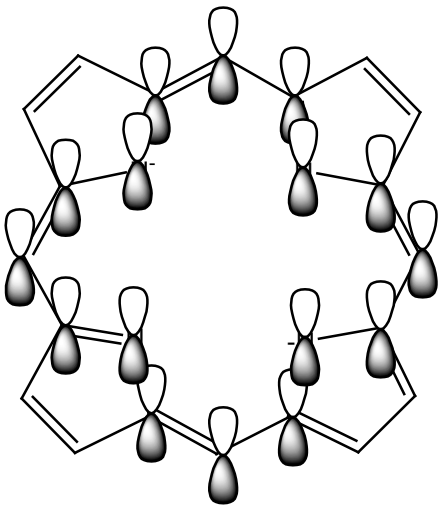
Irrep = _____. m = _____.



Irrep = _____. m = _____.



Irrep = _____. m = _____.



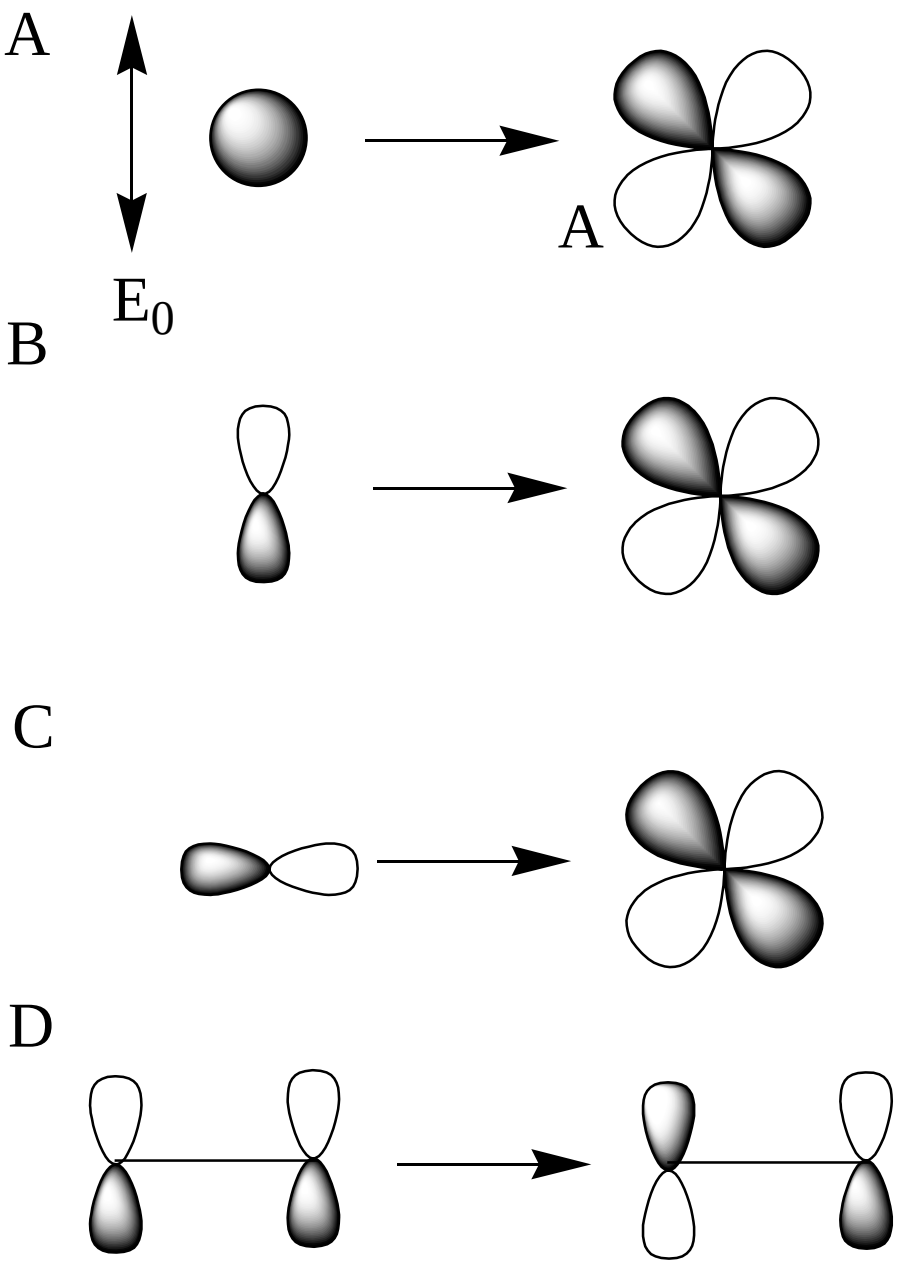
Irrep = _____. m = _____.

.

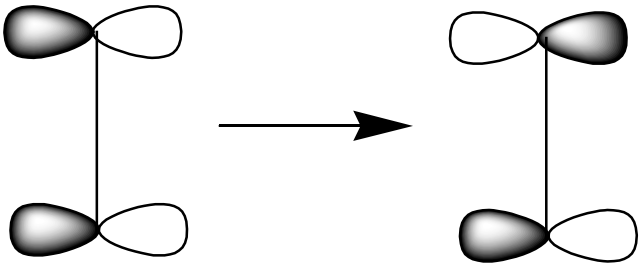
B.4 Which transitions are the π- π^* transitions of a porphyrin?

B.5 Use the direct product to determine the symmetries of vibrational modes that couple these transitions.

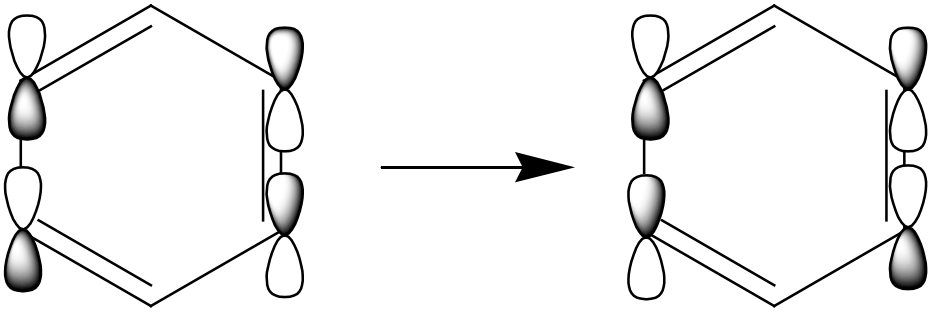
3. Use symmetry considerations or common sense to determine whether the transitions indicated are allowed or forbidden. The polarization of the electric vector for all of the configurations is perpendicular as shown in A.


A
E0
A
B
C
D

E



F



Plane of benzene ring is in the page and p-orbitals pointing perpendicular to page

4.Calculate the transition dipole moment of the hydrogen atom for the 1s → 2pz transition including both the angular and radial parts.