CHEM 550
Homework 9. Due Fri. Dec. 9 at 5pm in Prof. Ginger's mailbox.   Page ½
Another soft one to let you rest up for the final. If you want to save yourself time on the
final I recommend making sure you have complete solutions to the Maple exercises
presented throughout the term.

CIRCLE YOUR ANSWERS AND KEY INTERMEDIATE RESULTS
STAPLE YOUR PAPERS TOGETHER
INCLUDE ALL COMPUTER PRINTOUTS

1) Use Hückel MO theory to estimate if the linear state (H-H-H+) or triangular state

(each H bonded to two others in a triangle) of H_3^+ is more stable. Repeat for neutral H_3

and for H_3^-

2) Verify the equivalence of secular determinants and the geometric 'Frost Circle'

method (which is a geometric realization of the general form of the 'circulant' type

secular determinants that result). *Explicitly* calculate the MO Energy levels (and draw the

labeled MO energy levels) for the cyclopentadienyl radical ($C_5H_5^{\cdot}$), and benzene BOTH

by writing down and solving their secular determinants in the Hückel approximation, and

by using the 'Frost Circle' method.

2) Draw MO diagrams, fill with e- according to Hund's rule, and deduce which of the

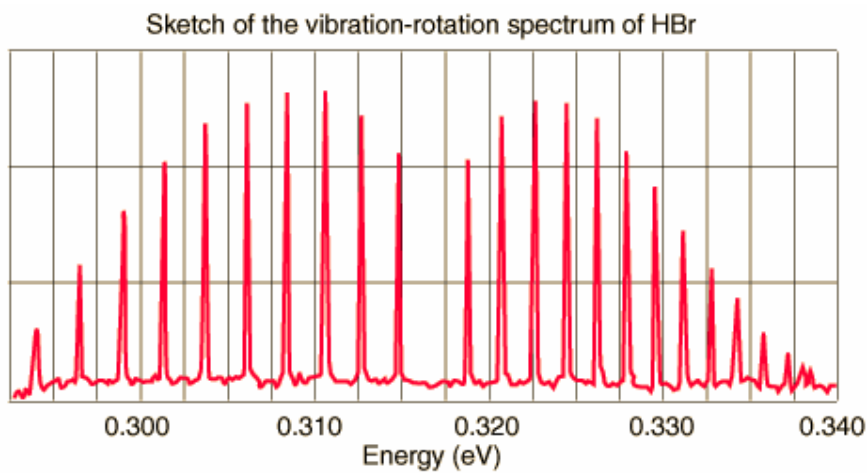following molecules are aromatic, radicals, or diradicals (use Hückel's 4n+2 rule):
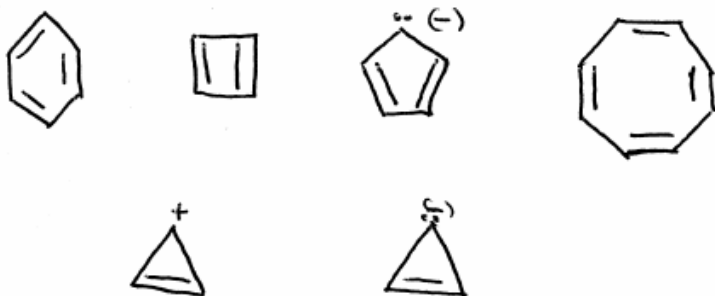
3) In our derivation of Bloch's Theorem we defined the 'displacement' operator by

Df(x)=f(x+a) associated with a potential of the form *V(x)=V(x+a)*. Prove that [D,H]=0,

and thus that simultaneous eigenfunctions exist for *D* and *H*.

4) a) Explain in relation to the Einstein emission and absorption coefficients, why a laser requires a population inversion to sustain laser action.

b) Explain why it is very difficult to make a conventional two-state laser for short wavelength light. Calculate the ratio of the Einstein coefficients for stimulated emission and absorption for 70.8 pm x-rays, and 500 nm visible light.

5) Explain the general shapes of the following spectra, and label the peaks in each transition with the initial and final rotational/vibrational/electronic quantum #'s as appropriate.

a) infrared:

Sketch of the vibration-rotation spectrum of HBr

b) visible: