(1) Perform Hückel calculations on the 4 hydrocarbons below. A web-based calculator can be found at http://www.chem.ucalgary.ca/SHMO/ — this will do the computational work if you input the graph of the molecule correctly. The SHMO calculator makes the usual Hückel assumption that all C-C bonds are equal in length (and therefore only one $\beta$ is necessary). Note: Think about D before beginning work on it. Consider only $\pi$-$\pi$ overlaps — if you are careful with it, you can do this problem with a standard Hückel MO computer program.

In all cases, construct appropriate SALCs and set up the secular determinant as if you were going to do the calculation by hand. In all cases, draw a complete $\pi$ MO diagram, including orbital irreducible representation labels. Draw figures showing the form of each $\pi$ orbital. One or more of these molecules does not have a “closed shell” configuration – calculate the unpaired spin density expected for each atom (as discussed for the naphthalene radical anion in class). Compute $\pi$ bond orders in the manner described in the text for naphthalene.

(2) Read the Perturbation Theory and Subgroups handout before attempting this problem. Do the group-subgroup orbital correlations in part (a) before applying perturbation theory in part (b) – it saves a lot of time in calculation too!

Despite Hückel’s $(4n + 2)\pi$-electron rule, [10]annulene molecule is not possess ‘aromatic stability’ like benzene. Large angle strain in the all-cis $D_{10h}$ conformation (E, next page) precludes the geometry most conducive to aromatic stabilization. Nevertheless, let’s see how we can relate the $\pi$ orbitals of [10]annulene to those of naphthalene (F) if we realize that if we make the assumption that [10]annulene could adopt the structure $E'$ (also otherwise unrealistic due to H…H crowding) – which wouldn’t alter the energies or atomic orbital coefficients of the $\pi$ orbitals. All we need to account for is the perturbation introduced by adding a bond between the C₁ and C₆ atoms as indicated by the dashed lines (and, of course, removing the hydrogen atoms).

(a) Draw a correlation diagram relating the $\pi$ orbitals of all-cis $D_{10h}$ [10]annulene (E) to those of the (unperturbed) $\pi$ orbitals of the $D_{2h}$ [10]annulene (E') and then further to the $\pi$ orbitals of the $D_{2h}$ naphthalene (F).

(b) Using [10]annulene as your zeroth-order system, use perturbation theory to calculate the $\pi$ energies and molecular orbitals of naphthalene. Employ the same parameters and
approach taken in the handout (as in the handout, assume the value of $\beta$ is the same for all bonds). Make a table of the naphthalene $\pi$ orbital energies obtained from perturbation theory and those obtained by doing the Hückel calculation. Taking the total energy as just the sum of the orbital energies ($\times 2$ – to account for two electrons in each orbital), which has the more stable $\pi$ system?

![Diagram of naphthalene molecules]

(3) Before attempting this problem, read the “translation groups” handouts.

Let’s consider the subject of single-walled carbon nanotubes. Such nanotubes can be constructed (on paper) by taking a slice from a graphite layer and “rolling it up”. A nanotube so constructed propagates in a direction that is normal to the so-called “rolling vector”. The rolling vector is expressed in terms of multiples of the unit cell vectors. On the attached sheets, two rolling vectors, (11,2) and (11,4), are illustrated along with the slices of the graphite sheet that are used to “roll-up” two distinct carbon nanotubes. ((11,2) and (11,4) respectively correspond to $11a + 2b$ and $11a + 4b$.)

Nanotubes with certain rolling vectors are electrically conducting (metallic), while others are semiconducting. The electronic structures of all the nanotubes are closely related to graphite; but only certain rolling vectors will give nanotubes that have, like graphite, no band gap. Which of the two illustrated rolling vectors, (11,2) and (11,4), will yield a metallic nanotube and which will give a semiconducting nanotube? Explain, and give a formula that will enable one to generally predict the answer for all rolling vectors. (Hint: For a metallic nanotube, the form of the orbitals where the lower and upper graphite $\pi$-bands meet must “carry over” to the nanotube, or the nanotube will have a $\pi$-band gap.)

![Explanation of Figures]

Explanation of Figures: Both the attached figures show how rolling vectors are defined as the vector sum of the $a$ and $b$ components that make them up. To put together a nanotube, shaded slices are ‘cut out’ and rolled up so that opposite edges meet with the two ends of the rolling vector joined together to make a circular ring around the nanotube; the cut C–C bonds are stitched back together!