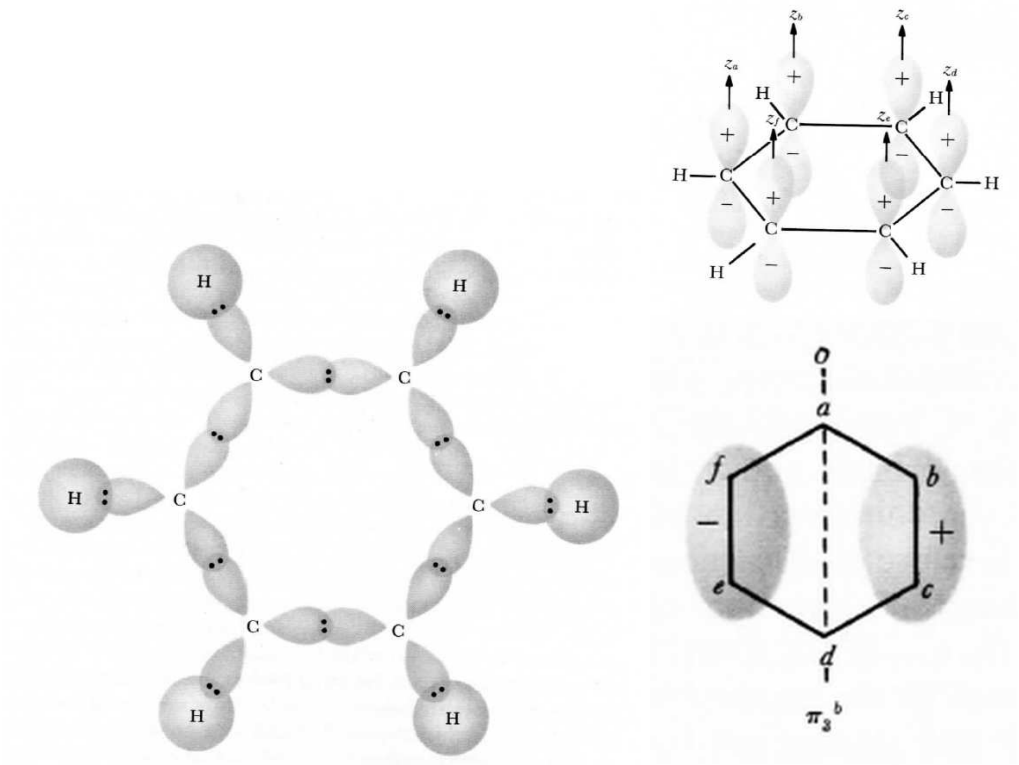
Cohesion of Benzene.

Benzene is a planar molecule consisting of a hexagonal ring of carbon atoms surrounded by hydrogen atoms bonded to the carbons. Each hydrogen atom has a single valence electron (1s) and each carbon atom has four valence electrons ($2s^2 2p^2$). Three of the carbon electrons, and the hydrogen electron, occupy sp^2 hybrid orbitals and form a σ bonded network within the plane of the molecule. A single 2p electron for each carbon atom remains, with its orbital ($2p_z$) perpendicular to the plane of the molecule. These six electrons will occupy molecular π orbitals. Figures below illustrate the Benzene structure and these two orbital types. Note: you may wish to review Cohen-Tannoudji complement G_{XI}.



(a) Use the p_z atomic orbitals as the basis for a subspace (LCAO) solution of Schrodinger's equation. Let $|i\rangle$ be the atomic $2p_z$ orbital on the i^{th} carbon atom, with $i = 0, \cdots, 5$, and identify $i = 6$ with $i = 0$. Denote the non-zero matrix elements as $\langle i|H|i\rangle \equiv Q$, $\langle i|H|i+1\rangle \equiv R < 0$, and $\langle i|i+1\rangle \equiv S$. Obtain the eigenvalues and orthonormal eigenvectors of the Hamiltonian. Draw and label an energy level diagram (note that specific values of the parameters are not important).

(b) For each energy level, consider the transformation of the eigenfunctions under rotations of the molecule by 60° about its 6-fold symmetry axis. Using your six eigenfunctions as a basis, write down the matrix representing a 60° rotation. Identify the angular momentum of each irreducible representation, as defined by its phase change under rotation.

(c) Sketch the eigenfunctions (molecular orbitals) and indicate any nodal planes. An example of one of the eigenfunctions is given on the previous page. In this particular orbital, the electron does not visit two of the carbon atoms.

(d) How do the six $2p_z$ electrons distribute themselves among the six molecular π orbitals? Describe the electronic charge density and describe how this contributes to stability of the Benzene molecule.