CEM 882 Problem Set 5 – Due Thursday, April 10 – Please email a pdf to weliky@chemistry.msu.edu

1. In this problem, the molecular orbital model will be applied to understand the $\pi^* \leftarrow \pi$ absorption of phenylalanine. The absorption will be considered in the context of the molecular orbital model of LectureNotes_8 with the lower energy state as the right-side, second-row from the bottom orbital and the higher energy state as the left-side, third-row from the bottom orbital. The atomic p_z orbitals are denoted $|p_1\rangle$, …, $|p_6\rangle$ with $|p_1\rangle$ on the C atom on the bottom of the ring and clockwise numbering of $|p_1\rangle$, …, $|p_6\rangle$. Consider $\langle p_j | p_j \rangle = 1$ and $\langle p_j | p_k \rangle = 0$ for $j \neq k$. Consider the Hamiltonian H with $\langle p_j | H | p_j \rangle = \alpha$, $\langle p_j | H | p_k \rangle = \beta$ if C_j and C_k are directly bonded, and $\langle p_j | H | p_k \rangle = 0$ if C_j and C_k are not directly bonded. The α and β each correspond to a specific energy value and both α and β are negative.

a. (20 points) Show by calculation that the molecular orbital for the initial state of the transition is normalized. Show by calculation that the molecular orbital for the final state of the transition is normalized.

b. (40 points) Evaluate the average total energy of the initial state where your answer is in terms of α and β. Evaluate the average total energy of the final state where your answer is in terms of α and β.

c. (10 points) Use the **b** result to determine the transition energy in terms of α and β.

d. (20 points) Use the spectrum on page 15 of Lectures 3 to determine the experimental $\pi^* \leftarrow \pi$ transition energy of phenylalanine to three significant figures in units of kJ/mole.

e. (10 points) Use the **c** and **d** results to determine β to three significant figures in units of kJ/mole.

f. (20 points) One way of understanding the $\pi^* \leftarrow \pi$ transition is conversion of a specific number of double C=C bonds in the aromatic ring to single C-C bonds. Use the molecular orbital diagram to determine this specific number and explain your determination.

g. (20 points) Provide the literature energy of a C=C bond to three significant figures in units of kJ/mole. Provide the literature energy of a C-C bond to three significant figures in units of kJ/mole. Provide the reference(s) for these literature values. Use these values in the **f** model to estimate the $\pi^* \leftarrow \pi$ transition energy to three significant figures in units of kJ/mole.

h. (10 points) Are the **d** and **g** values in semi-quantitative agreement or are they not in semi-quantitative agreement? Provide a reasoned explanation for your choice.