PROBLEM SET 3, BCMB/CHEM 8190

1) An adenine in a bulge of a poly A – poly U nucleic acid helix is said to be flipped out in solution instead of being stacked between adenine rings of adjacent base pairs. Assume the six membered rings of adenine act like benzene rings and the H2 proton of the adenine in question is above and below the center of rings before and after the central adenine by 3 Å. In the flipped out position assume the distance to the center of the other adenine rings is large. Using the remote group model for benzene to approximate the effect of the adenine rings, what would you expect for the chemical shift of the H2 proton of the flipped out adenine compared to other adenine H2s?

2) What would you expect for the alpha carbon chemical shift of an alanine when it was in an alpha helix of a protein as compared to a beta sheet?

3) See how many of the multiplets you can assign in the spectrum below using your knowledge of multiplet structure from three bond H-H couplings and general chemical shift trends.
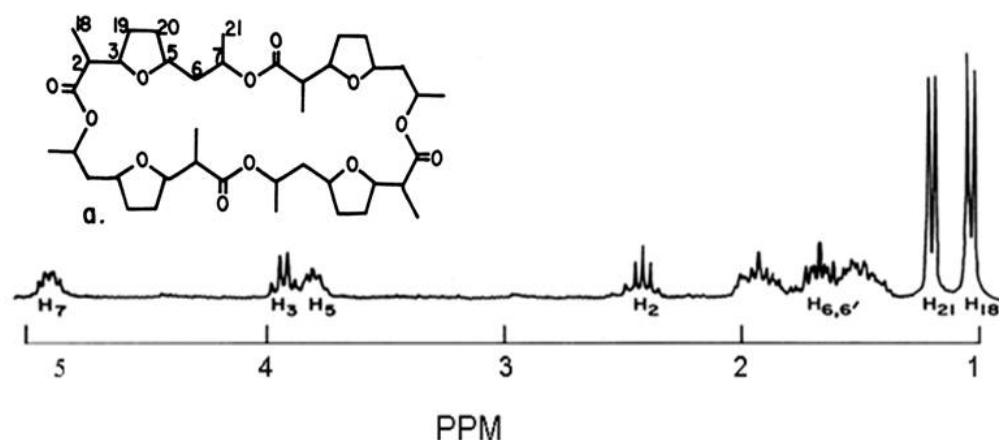
4) Write down a Hamiltonian for a pair of spin 1/2 spins in a static B_0 field using the z-component spin operators I_{z1}, I_{z2}, their coupling constant $J_{1,2}$, and their offsets due to chemical shieldings, ν_1 and ν_2. Assume $J_{1,2}$ is positive and $\nu_1 \ll \nu_2$. Make an energy level diagram showing the positions of levels for the four simple product spin functions. Show the allowed one-quantum transitions and calculate the energy differences associated with them. Sketch and label the corresponding lines in a frequency resolved spectrum.