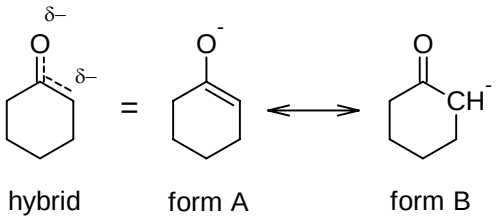
Problem Set 3
Due Fri, Sept 15

Background: Chapters 2 & 3
Problems: P2.21, P2.23, P2.24ab, P2.25ab, P2.27 (*Mathematica* problem – see below), P2.29, P2.30

Extra: It is often desirable to express a wave function as a linear combination of two more convenient wave functions. The mathematical version of resonance theory does exactly this. An organic chemist draws:



to say that the enolate (resonance hybrid) somehow combines the properties of the two resonance forms. A quantum chemist expresses this same situation in mathematical terms:

$$\psi_{hybrid} = N\,(c_A\,\psi_A + c_B\,\psi_B)$$

where each ψ represents a wave function that depends simultaneously on the (x, y, z) coordinates of every electron in these molecules: (I won't explain how ψ_A and ψ_B must differ mathematically in order to produce different bonding patterns, but it is possible.[1])

Assume the following relationships hold (integrals are taken over all possible values of all electron coordinates, $d\tau$):

$1 = \int \psi_A^*\,\psi_A\,d\tau = \int \psi_B^*\,\psi_B\,d\tau$	$S = \int \psi_A^*\,\psi_B\,d\tau = \int \psi_B^*\,\psi_A\,d\tau$
$E_A = \int \psi_A^*\,\hat{H}\,\psi_A\,d\tau$	$E_B = \int \psi_B^*\,\hat{H}\,\psi_B\,d\tau$
$E_{AB} = \int \psi_A^*\,\hat{H}\,\psi_B\,d\tau = \int \psi_B^*\,\hat{H}\,\psi_A\,d\tau$	

a. What must N be in order to normalize ψ_{hybrid}?
b. Let $\psi_{hybrid2} = N_2\,(c_B\,\psi_A - c_A\,\psi_B)$. Show that $\psi_{hybrid2}$ is orthogonal to ψ_{hybrid} and determine N_2.

[1] You might imagine that each wave function combines a set of bond orbitals. In this case, the different bond patterns would lead to different combinations of bond orbitals.

c. Suppose ψ_{hybrid} and $\psi_{hybrid2}$ are good estimates of the eigenfunctions of this molecule. Suppose also that $c_A > c_B$ and $E_A < E_B$, what is the energy of a molecule in the state represented by ψ_{hybrid}? What is the energy of a molecule in the state represented by $\psi_{hybrid2}$? Which state is lower in energy? (Hint: see postulates 3 & 4 in Chapter 3 for guidance on how to set up the energy calculations.)

Mathematica Problem

P2.27 – You don't have to solve the problem using *Mathematica*, but I at least want to see a *Mathematica* notebook containing a graph of your Fourier series expansion.

Examples of plots, both single and double, can be found in this notebook:
http://academic.reed.edu/chemistry/alan/333/Lecture/3_090106.nb

(If you are using the PCs in the Chemistry computer lab, go to
http://academic.reed.edu/chemistry/alan/333/lecture_schedule.html
right-click, and select **Save Link As …**, to save the notebook to your computer)