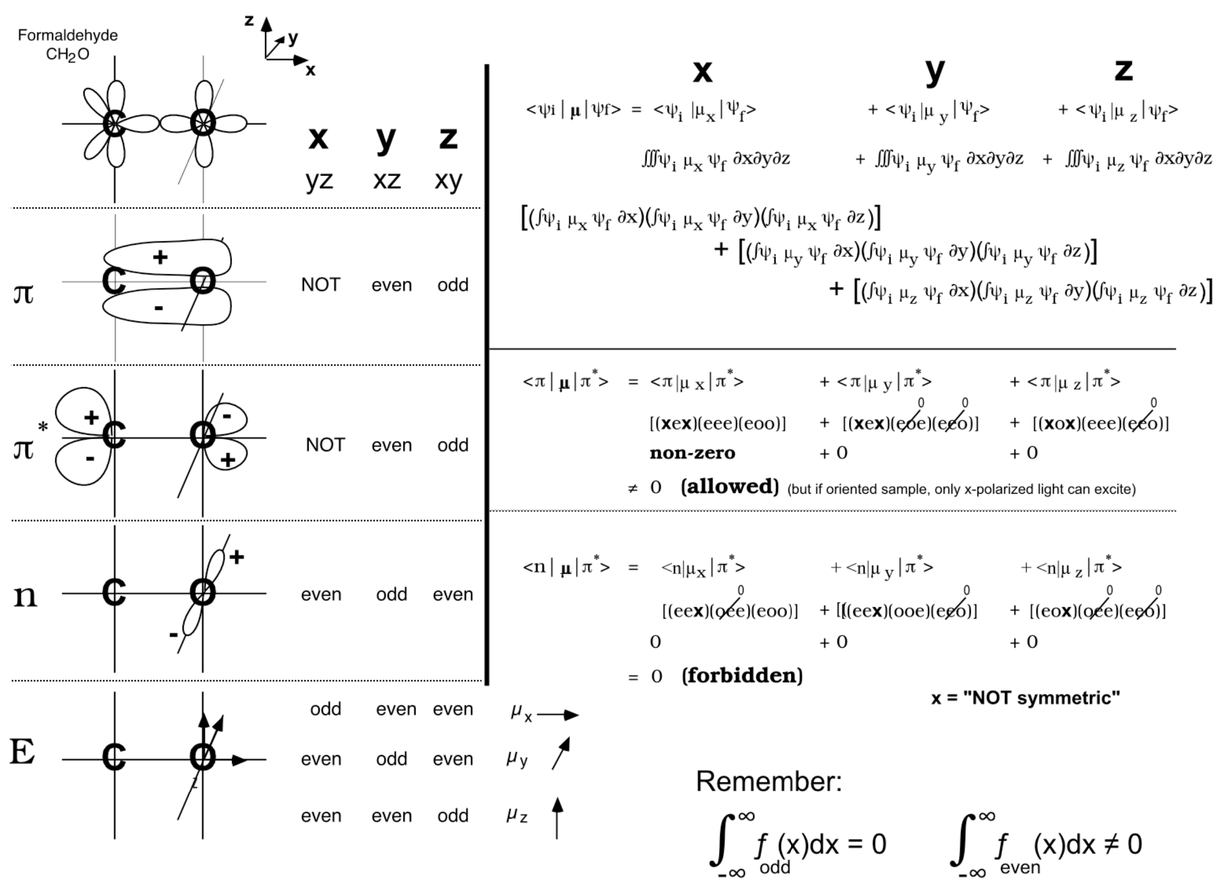
Core Course 2002
Homework Part II, Problem Set 2

1. a) In the example of formaldehyde discussed in class, we concluded that the n->π* transition was strictly forbidden. For formaldehyde, you can make a very simple argument that in fact, this is not strictly true. Symmetry dictates that the transition will not be completely forbidden. **Explain** (bring some of what you learned from the first half of the course; the conclusion *would* be true for ethylene).

   Since the electronegativities of C and O are different, the π and π* orbitals will be distorted (the π orbital electron density towards O).
   WHOOPS! My error. As detailed below, the transitions are still as before

   b) Reevaluate the integrals as we did in class, but now using your new understanding of formaldehyde. For single crystals of formaldehyde, predict whether light polarized along x, y, and z will induce each transition.

   The π and π* orbitals will now no longer have odd symmetry with respect to the x–axis (but symmetry with respect to y or z will remain unchanged). The symmetries won't be even either, so the effect is that the integrals containing transitions to or from these orbitals can no longer go completely to zero when the light inducing the transition is polarized along the x axis.



Thus

Transition	light polarized along	Transition is	(Transition was)
π -> π*	x	Allowed	Allowed
	y	Forbidden	Forbidden
	z	Forbidden	Forbidden
n -> π*	x	Forbidden	Forbidden
	y	Forbidden	Forbidden
	z	Forbidden	Forbidden

2. We have seen that quenching of fluorescence can depend on the concentration of the quenching agent. Assuming that quenching is first order with respect to the quencher Q (with a first order rate constant of k_q), derive an expression for the ratio of the fluorescence in the absence of quencher to that in the presence of quencher, F_o/F_Q, as a function of [Q], k_q, and τ_o (the lifetime of the excited state in the absence of quencher).

$$\phi_o = \frac{k_f}{k_f + k_{ic} + k_{is}} \qquad \phi_Q = \frac{k_f}{k_f + k_{ic} + k_{is} + k_Q Q}$$

$$\frac{F_o}{F_Q} = \frac{\phi_o}{\phi_Q} = \frac{k_f}{k_f + k_{ic} + k_{is}} \; \frac{k_f + k_{ic} + k_{is} + k_Q Q}{k_f}$$

$$\frac{F_o}{F_Q} = \frac{k_f + k_{ic} + k_{is} + k_Q Q}{k_f + k_{ic} + k_{is}} = \frac{k_f + k_{ic} + k_{is}}{k_f + k_{ic} + k_{is}} + \frac{k_Q Q}{k_f + k_{ic} + k_{is}}$$

$$\frac{F_o}{F_Q} = 1 + \frac{k_Q Q}{k_f + k_{ic} + k_{is}} \qquad but \qquad \tau_o = \frac{1}{k_f + k_{ic} + k_{is}}$$

therefore

$$\frac{F_o}{F_Q} = 1 + k_Q \tau_o Q$$

3. For the particle in a box problem,
   a) show that the following is an eigenfunction of H.

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$$

Potentially useful equations:

$$\int \cos(ax)dx = \frac{\sin(ax)}{a}$$

$$\int x\cos(ax)dx = \frac{\cos(ax)}{a^2} + \frac{x\sin(ax)}{a}$$

$$\int x^2\cos(ax)dx = \frac{2x}{a^2}\cos(ax) + \left(\frac{x^2}{a} - \frac{2}{a^3}\right)\sin(ax)$$

$$\int \cos^2(ax)dx = \frac{x}{2} + \frac{\sin(2ax)}{4a}$$

$$\int \sin^2(ax)dx = \frac{x}{2} - \frac{\sin(2ax)}{4a}$$

$$\int x\cos^2(ax)dx = \frac{x^2}{4} + \frac{x\sin(2ax)}{4a} + \frac{\cos(2ax)}{8a^2}$$

$$\int x\sin^2(ax)dx = \frac{x^2}{4} - \frac{x\sin(2ax)}{4a} - \frac{\cos(2ax)}{8a^2}$$

$$\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\psi_n(x) = \sqrt{\frac{2}{L}}\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\sin\left(\frac{n\pi x}{L}\right)$$

$$= \sqrt{\frac{2}{L}}\frac{-\hbar^2}{2m}\frac{n\pi}{L}\frac{d}{dx}\cos\left(\frac{n\pi x}{L}\right) = -\sqrt{\frac{2}{L}}\frac{-\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2\sin$$

$$= \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right) = \frac{1}{2m}\left(\frac{n\hbar\pi}{L}\right)^2\psi_n(x)$$

   b) show that this is a normalized wavefunction

$$\int_0^L \psi_n^2(x)dx = \int_0^L \frac{2}{L}\sin^2\left(\frac{n\pi x}{L}\right)dx$$

$$= \frac{2}{L}\int_0^L \sin^2\left(\frac{n\pi x}{L}\right)dx = \frac{2}{L}\left[\frac{x}{2} - \frac{\sin\left(\frac{2n\pi x}{L}\right)}{\frac{4n\pi}{L}}\right]_0^L$$

$$= \frac{2}{L}\left\{\left[\frac{L}{2} - \frac{\sin\left(\frac{2n\pi L}{L}\right)}{\frac{4n\pi}{L}}\right] - \left[\frac{0}{2} - \frac{\sin\left(\frac{2n\pi 0}{L}\right)}{\frac{4n\pi}{L}}\right]\right\} = \frac{2}{L}\left\{\left[\frac{L}{2} - 0\right] - \left[\frac{0}{2} - 0\right]\right\} = 1$$