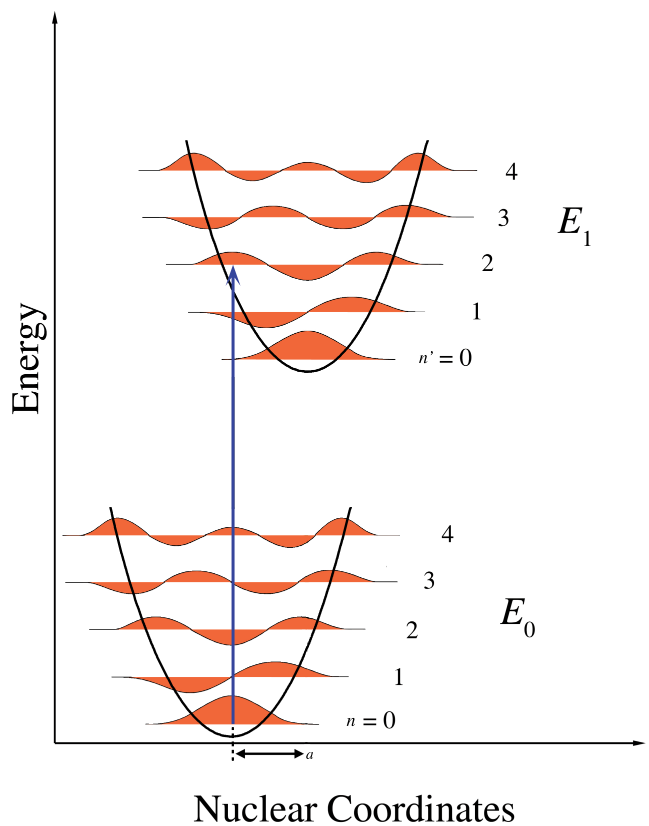
Chemistry 30321 | Fall 2012
Professor J. Daniel Gezelter | Due Fri. 11/30/2012

Problem Set 10 (Last One!)
Tunneling and Electronic Spectroscopy

1. Do problem 4-36 in McQuarrie and Simon
2. Do problem 4-37 in McQuarrie and Simon
3. Franck-Condon factors

   In vibronic spectroscopy, light excites a molecule that is on a ground electronic state (E_0) and in a ground-state vibrational level ($n = 0$) to a higher vibrational level (n') on an excited electronic state (E_1). Most excited states have equilibrium geometries that are shifted away from the equilibrium geometry of the ground state. In this figure, the excited state surface is displaced by a distance a from the ground state geometry.



The intensity of a vertical vibronic transition is governed by the "Franck-Condon overlap", $|S_{n,n'}|^2$ between two states, where

$$S_{n,n'} = \langle n|n'\rangle.$$

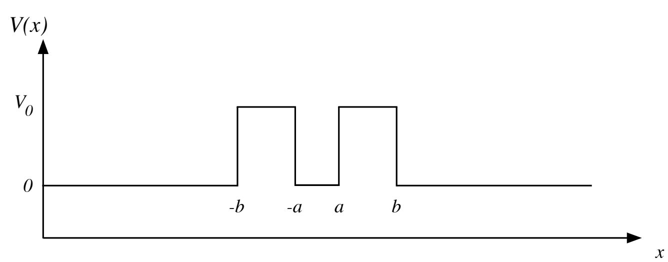
Here, $|n\rangle$ is the vibrational wavefunction of state n on the ground state, and $|n'\rangle$ is the vibrational wavefunction of state n' on the excited state. In the figure, the $(n = 0) \rightarrow (n' = 2)$ transition would be more intense than the $(n = 0) \rightarrow (n' = 0)$ transition because the overlap between the wavefunctions is larger.

Use the following wavefunctions to compute the vibronic intensities for transitions from the ground state to the first three vibrational states on the *shifted* excited state surface.

Ground State Wavefunction: $\|n\rangle$	**Excited State Wavefunctions:** $\|n'\rangle$
$\|0\rangle = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$	$\|0\rangle = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha(x-a)^2/2}$ $\|1\rangle = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} (x-a)e^{-\alpha(x-a)^2/2}$ $\|2\rangle = \left(\frac{\alpha}{4\pi}\right)^{1/4} (2\alpha(x-a)^2-1)e^{-\alpha(x-a)^2/2}$

4. Extra Credit!

Plot the transmission probability as a function of energy for the piecewise-flat M-shaped barrier shown in the picture below. You only need to do the range between 0 and V_0 (although going higher is also interesting). Specifically, consider the case where $V_0 = \frac{5h^2}{2ma^2}$ and where $b = 2a$



How do the energies of the tunnelling resonances relate to the energies of a particle in a box with infinite walls at $-a$ and a? (Hint: Construct the boundary matching equations as a matrix problem

$$\mathsf{A} \cdot \mathsf{x} = \mathsf{b}$$

where x is a vector of the amplitudes of the parts of the wavefunction, b is a vector containing only unit incoming flux (i.e. the coefficient of the incoming wave on the left side is initially 1, and the coefficient of all other parts of the wave function are initially 0), and the matrix A maps the coefficients in one region to the adjacent regions. Invert this equation (using Mathematica) to obtain the outgoing flux (i.e. the coefficient of the outgoing wave on the right side of the barriers). Since you have the incoming flux and the outgoing flux, the transmission probability is the square of outgoing flux over incoming flux...)

Interpret your results!