Biophysics 206: Problem Set 1, Quantum Mechanics

You are welcome to work together on this problem set, and ask me or the TAs questions about it. You will be graded on making a reasonable effort. We will go over the solutions in class.

1) The Morse oscillator potential can be written as

$$U(x) = D\left[1 - e^{-\beta x}\right]^2$$

Expand U(x) in a Taylor series around x=0 and show that the first term is quadratic in x (i.e., "harmonic").

2) Apply first-order perturbation theory to the ground vibrational state of HCl. The potential energy curve can be approximated as a Morse oscillator with D = 7.31 x 10^{-19} J and β = 1.82 x 10^{10} m^{-1}. Here's how to approach this:

a) The overall Hamiltonian can be written as $-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + U(x)$, where μ is the reduced mass of the H and Cl nuclei. Using your results from (1), write the Hamiltonian as a sum of a zero-order part, which you choose to be a harmonic oscillator Hamiltonian, and a perturbation, which is the rest of the potential (i.e., H.O. potential – M.O. potential).

b) The ground state of the harmonic oscillator Hamiltonian $-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$ is $\psi_0(x) = \sqrt[4]{\frac{\alpha}{\pi}}e^{-\alpha x^2/2}$, where $\alpha = \sqrt{\frac{k\mu}{\hbar^2}}$, with energy $E_0 = \frac{\hbar}{2}\sqrt{\frac{k}{\mu}}$. Using this result, what is the "zero-order" (harmonic) eigenenergy and eigenfunction for HCl?

c) Now calculate the first-order perturbation theory correction to the energy. I would not recommend trying to calculate the integral analytically! But it's pretty easy to do it numerically using Excel. Just calculate the integrand at, perhaps, 100 discrete points and add it up.

3) Apply the variational method to find the ground vibrational state of HCl, using as a basis set the ground state and first excited state of the harmonic oscillator, as in (2b). The first excited state of the HO is $\psi_1(x) = \sqrt[4]{\frac{\alpha}{4\pi}}\left(2\sqrt{\alpha}x\right)e^{-\alpha x^2/2}$, with energy $E_1 = \frac{3\hbar}{2}\sqrt{\frac{k}{\mu}}$. This involves computing 2 more integrals relative to what you already did in (2c) (actually you can get away with just one more), and then evaluating the secular determinant.