Chemistry 30321 Fall 2012
Professor J. Daniel Gezelter Due Mon. 10/8/2012

Problem Set 5
(Mostly harmonic oscillator)

1. Do problem 5-7 in McQuarrie and Simon.

2. Do problem 5-8 in McQuarrie and Simon.

3. Do problem 5-14 in McQuarrie and Simon.

4. A simple potential function which models many of the properties of diatomic molecules is the *Morse potential*,
$$V(x) = D_e \left(1 - e^{-\beta x}\right)^2 \tag{1}$$
where x is the displacement of the bond from its equilibrium position and D_e is the value of $V(x)$ at large separations. Expand $V(x)$ in a Taylor series about $x = 0$ to obtain
$$V(x) = D_e \beta^2 x^2 - D_e \beta^3 x^3 + \cdots \tag{2}$$
Given that $D_e = 7.31 \times 10^{-19}$ J $\cdot$ molecule^{-1} and $\beta = 1.82 \times 10^{10}$ m^{-1} for HCl, calculate the force constant of HCl. Plot the Morse potential for HCl and plot the corresponding harmonic oscillator potential on the same graph. A computer will be helpful in making this graph.

   Hint: See Example 5-2 in McQuarrie and Simon to get you started.

5. Do problem D-7 in McQuarrie and Simon.

6. Do problem D-9 in McQuarrie and Simon.

7. Extra Credit

   Consider a harmonic oscillator that is operating under *classical mechanics*. The probability ($P(x)dx$) of being found between x and $x + dx$ is proportional to $1/v(x)$ where $v(x)$ is the velocity at point x. Suppose our classical harmonic oscillator is given the same total energy as the ground state of the quantum harmonic oscillator, $E = \hbar\omega/2$.

   a) Where are the classical turning points at this energy?
   b) Use the fact that the kinetic energy is $E - V(x)$ to derive an expression for the velocity as a function of position ($v(x)$) that will work if we are between the classical turning points.
   c) Use your expression for $v(x)$ to normalize the classical probability distribution $P(x)$ between the classical turning points.

d) Plot on the same graph, the potential energy, the classical probability distribution, and the quantum probability distribution, $|\psi_0(x)|^2$ for the harmonic oscillator. A computer will be helpful in making this graph.