CHE-372 Gustavus Adolphus College

Assignment #3

Recommended Problems (not to be handed in)
All of these problems are from McQuarrie & Simon.
D-4, D-6, D-8; 5-37, 5-28; 13-20, I-3, I-13

Required Problems (**Due March 16 at 3 pm**)
You will want/need to use Excel or other plotting program for some of these problems.
1. McQuarrie & Simon: D-2, D-7, D-12; 5-33, 5-35; 13-16, 13-33, 13-34, 13-35, 13-36

2. a) Show that $\sigma_x = \langle x^2 \rangle^{1/2}$ for the harmonic oscillator. When this relationship is true, the standard deviation is often called the root-mean-square-displacement.
   b) Find the expressions of $<\psi_v|x^2|\psi_v>$ for the first two states of the harmonic oscillator. (Note the use of Dirac notation.) See Problem 5-20 if you get stuck.
   c) Using the fundamental vibrational frequencies given in Table 1, calculate the root-mean-square-displacement for each molecule in the v=0 state and compare the magnitude of the root-mean-square-displacement to the equilibrium bond lengths, R_e.

Table 1: Info for Problem #2

Molecule	$\tilde{\nu}$ / cm^{-1}	R_e / pm
H_2	4401	74.1
$^{35}Cl^{35}Cl$	554	198.8
$^{14}N^{14}N$	2330	109.4

3. The Morse potential is an analytical expression which more accurately models the internuclear potential than the harmonic oscillator model. (See Example 5-2 for more on the Morse potential.) A Maclaurin expansion of the Morse potential yields:

$$V(x) = D\beta^2 x^2 + ...$$

Given that $D = 8.19 \times 10^{-19}$ J/molecule, $\tilde{\nu}_o$=1580.0 cm^{-1}, and R_e = 121 pm for $^{16}O_2$, calculate the force constant of $^{16}O_2$. Plot the More potential for $^{16}O_2$ and the corresponding harmonic oscillator potential on the same graph. (It should look like Figure 5.5).

4. Given the following parameters for $^{12}C^{16}O$: $\tilde{T}_e = 6.508043 \times 10^4$ cm^{-1}, $\tilde{\nu}_e' = 1514.10$ cm^{-1}, $\tilde{x}_e'\tilde{\nu}_e' = 17.40$ cm^{-1}, $\tilde{\nu}_e'' = 2169.81$ cm^{-1}, and $\tilde{x}_e''\tilde{\nu}_e'' = 13.29$ cm^{-1}, make a table of the first four vibrational states in the first two electronic states. In addition, determine the allowed transitions from v" = 0 (put these values in a second table).

5. Calculate the moment of inertia and rotational constant, B, of H_2O around its twofold axis of symmetry (the bisector of the HOH angle). The bond angle is 104.5° and each bond length is 95.7 pm. Recall $I = \Sigma m_i r_i$ where m_i is the mass of each atom and r_i is the perpendicular distance from the axis of rotation.