**NORTH CAROLINA STATE UNIVERSITY**

Department of Chemistry Name________________________________

Physical Chemistry CH437 Problem Set #2

Due Date: September 4, 2015

1. Using formulae for the associated LeGendre polynomial determine the rotational transition moment for the transition from $\ell$ = 1 to $\ell$ = 2. This derives from the general selection rule $\Delta\ell$ = 1 or -1 and $\Delta$m = 0.

$$(1-x^2)\frac{\partial^2 P(x)}{\partial x^2} - 2x\frac{\partial P(x)}{\partial x} + \left(\ell(\ell+1) - \frac{m^2}{1-x^2}\right)P(x) = 0$$

You may assume the case of m = 0. For this case the Legendre polynomials are:

$P_0(x)=1$ $P_2(x)=1/2\ (3x^2 - 1)$

$P_1(x)=x$ $P_3(x)=1/2\ (5x^3 - 3x)$

2. Consider two masses $m_1$ and $m_2$ in one dimension, interacting through a potential that depends only upon their relative separation ($x_1 - x_2$), so that $V(x_1,x_2) = V(x_1 - x_2)$. Given that the force acting upon the jth particle is $f_j = -(\partial V/\partial x_j)$, show that f1 = -f2. Show your work throughout this problem.

A. What physical law is this?

Newton's equations for $m_1$ and $m_2$ are:

$$m_1 \frac{d^2x_1}{dt^2} = -\frac{\partial V}{\partial x_1} \quad and \quad m_2 \frac{d^2x_2}{dt^2} = -\frac{\partial V}{\partial x_2}$$

Now introduce center-of-mass and relative coordinates by:

$$X = \frac{m_1x_1 + m_2x_2}{M} \quad , \qquad x = x_1 - x_2$$

where $M = m_1 + m_2$, and solve for $x_1$ and $x_2$ to obtain:

$$x_1 = X + \frac{m_2}{M}x \quad , x_2 = X + \frac{m_1}{M}x$$

Show that Newton's equations in these coordinates are:

$$m_1 \frac{d^2X}{dt^2} + \frac{m_1m_2}{M}\frac{d^2x}{dt^2} = -\frac{\partial V}{\partial x}$$

and

$$m_2 \frac{d^2X}{dt^2} - \frac{m_1m_2}{M}\frac{d^2x}{dt^2} = +\frac{\partial V}{\partial x}$$

Now add these equations to find

$$M\frac{d^2X}{dt^2} = 0$$

B. Interpret this result.

Now divide the first equation by $m_1$ and the second by $m_2$ and subtract to obtain:

$$\frac{d^2x}{dt^2} = -\left(\frac{1}{m_1} + \frac{1}{m_2}\right)\frac{\partial V}{\partial x}$$

Or

$$\mu\frac{d^2x}{dt^2} = -\frac{\partial V}{\partial x}$$

Give the definition of $\mu$.

C. Interpret this result and discuss how the original two-body problem has been reduced to two one-body problems.

3. Calculate the expectation value (average value of <r> (i.e. the mean radius) for the normalized 2s and 2p wavefunctions. You will need the following integral.

$$\int_0^\infty r^n e^{-ar} dr = \frac{n!}{a^{n+1}}$$

4. The root-mean-square motion of a harmonic oscillator is given by:

$$\sqrt{< Q^2 >_0} = \sqrt{\int_{-\infty}^{\infty} \chi_0 \, Q^2 \chi_0 dQ}$$

Using a general formula for the r.m.s. motion of a harmonic oscillator in quantum level v, determine the change in amplitude of motion of the diatomic CO for the transition from v = 0 to v = 1. Assume that the vibrational frequency of is 2143 $cm^{-1}$.