Quiz 6
CHEM 325
Spring 2009

Name: ____

1a. (6 Points) The simple harmonic oscillator wavefunctions have the un-normalized form $\psi_v = H_v(y)e^{-y^2/2}$, where v is the vibrational quantum number, $H_v(y)$ is one of the real Hermite polynomials and y is a unitless parameter involving the spring constant for the oscillator, the displacement from its equilibrium position, the oscillator's reduced mass and Planck's constant. Normalize ψ_v.

A potentially useful relationship is $\int_{-\infty}^{+\infty} H_{v'}(y)H_v(y)e^{-y^2}dy = \begin{cases} 0 \text{ if } v' \neq v \\ \pi^{1/2}2^v v! \text{ if } v' = v \end{cases}$.

To normalize a function we need to solve the following integral for N: $N^2\int_{-\infty}^{+\infty}\psi^*\psi d\tau = 1$.

Since the Hermite polynomials are real, and therefore equal to their complex conjugates, the expression that we need is $N^2\int_{-\infty}^{+\infty}\left(H_v(y)e^{-y^2/2}\right)\left(H_v(y)e^{-y^2/2}\right)dy = 1$**, which may be simplified to** $N^2\int_{-\infty}^{+\infty}H_v(y)H_v(y)e^{-y^2}dy = 1$**.**

Since the v's are the same, the integral may be evaluated from the given information.

$$N^2\left(\pi^{1/2}2^v v!\right) = 1$$

$$N = \left(\frac{1}{\pi^{1/2}2^v v!}\right)^{1/2}$$

So, the normalization constant for the Hermite polynomials is $\left(\frac{1}{\pi^{1/2}2^v v!}\right)^{1/2}$**, although its exact value will vary because v will be different for each Hermite polynomial.**

b. (3 Points) What does it mean for the Hermite polynomials when the potentially useful integral in part *a* equals 0 when $v' \neq v$?

When $v' \neq v$, the integral is zero, which means that the Hermite polynomials are orthogonal to each other when the vibrational quantum numbers don't match.

2. (10 Points) The wavenumber of the fundamental vibrational transition of $^{35}Cl_2$ is 564.9 cm^{-1}. Calculate the force constant of the bond assuming that the molecule is a simple harmonic oscillator and given that the isotopic mass of ^{35}Cl is 34.9688 amu.

Start with $G(v)=\left(v+\frac{1}{2}\right)\tilde{\nu}-\left(v+\frac{1}{2}\right)^2 x_e\tilde{\nu}$ **, with the second term equal to 0 (no anharmonicity). The wavenumber of a vibrational transition is thus**

$$G(v+1)-G(v)=\left(v+\frac{3}{2}\right)\tilde{\nu}-\left(v+\frac{1}{2}\right)\tilde{\nu}=\left(v+\frac{3}{2}-v-\frac{1}{2}\right)\tilde{\nu}=\tilde{\nu}$$

The vibrational frequency of a quantum mechanical simple harmonic oscillator, $\tilde{\nu}$ **, is related to the force constant by the expression** $\tilde{\nu}=\frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2}$ **. Rearranging and solving for *k* gives** $k=(2\pi c\tilde{\nu})^2\mu$**.**

First determine the reduced mass, and then substitute into this expression to find *k*.

$$\mu=\frac{m_1m_2}{m_1+m_2}=\frac{(34.9688)^2\text{ amu}}{2(34.9688)}=17.4844\text{ amu}\left(\frac{1.66054x10^{-27}\text{ kg}}{1\text{ amu}}\right)$$

$$\mu=2.90335_5x10^{-26}\text{ kg}$$

$$k=(2\pi c\tilde{\nu})^2\mu=\left(2\pi\left(2.99792458x10^{10}\text{ cm}\cdot\text{s}^{-1}\right)\left(564.9\text{ cm}^{-1}\right)\right)^2\left(2.90335_5x10^{-26}\text{ kg}\right)$$

$$k=328.7\text{ s}^{-2}\cdot\text{kg}\left(\frac{1\text{ N}}{1\text{ kg}\cdot\text{m}\cdot\text{s}^{-2}}\right)=328.7\text{ N}\cdot\text{m}^{-1}$$

The force constant for $^{35}Cl_2$ is 328.7 N·m^{-1}.