<center>Physical Chemistry</center>

<center>Quantum harmonic and anharmonic oscillator</center>

The idea of harmonic oscillation is not a purely quantum experiment. It is well known that all classical particles expierence some form of harmonic motion. Which needs to be described and understood first before quantum harmonic oscillation can be understood. The main use of quantum harmonic oscillation is to describe and explain why spectroscopic methods produce reasonably discreet peaks rather than a large Gaussian shift.

Classical treatment of a vibrating molecule

When a molecule undergoes simple harmonic motion the force needed to separate the molecule is negatively proportional to the force that is pulling it back in. The force is dependant on a constant of the bond that is k and x is the extension.

$$F = -kx$$

It is also known that the potential energy is represented by the equation:

$$V = \frac{1}{2}kx^2$$

The potential energy is 0 when the displacement is 0 meaning that the kinetic energy and therefore the speed is at a maximum at this point.

When a molecule is vibrating its mass is centred on a fixed point this gives it an adjusted mass of μ.

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

When this is applied to Newton's second law of motion the vibration leads to the equation of:

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

This means that the force is dependant on the displacement over time. Which can be mapped by a graph with the equation:

$$x = A \sin\left[\left(\frac{k}{\mu}\right)^{\frac{1}{2}} t\right]$$

The fundamental frequency of the vibration can be given as one over the period or represented as:

$$\omega_0 = \frac{1}{\tau} = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{\frac{1}{2}}$$

It is also noted that the change in energy of a particle undergoing simple harmonix ossilation can be given as:

$$E = h\omega_0 = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}}$$

Quantum mechanical treatment of a vibrating diatomic molecule

Now we can apply some of these principles to the quantum mehcnical principles shown below. The following equation relates the eigenvalue for energy and the observable for energy being the total energy minus the potential energy.

$$-\frac{\hbar^2}{2\mu}\frac{d^2\Psi}{dx^2} = \left(E - \frac{1}{2}kx^2\right)\Psi$$

This means that the shcrodinger equation can be represented as:

$$-\frac{\hbar^2}{2\mu}\frac{d^2\Psi}{dx^2}\Psi + \frac{1}{2}kx^2\Psi = E\Psi$$

This can be converted (using calculus) to:

$$\Psi = N_v H_v\left(\frac{x}{\alpha}\right)e^{-\frac{\left(\frac{x}{\alpha}\right)^2}{2}} \qquad \alpha = \frac{\hbar^2}{mk} \qquad y = \frac{x}{\alpha}$$

This seems very complicated and it is, Here H_v represents a number of different polynomials. The first three are worth remembering:

$$v = 0 \quad H_1 = 1$$
$$v = 1 \quad H_2 = 2y$$
$$v = 2 \quad H_3 = 4y^2 - 2$$

To normalise the wavefunction is harder in these cases as the constant depends on the energy level that the molecule is at. This means that the normalisation constant can only be given as:

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

The frequency of the oscillator can be given as the zero point energy of the oscillator in the following equation

$$E_0 = \frac{1}{2}\hbar\omega_0$$

Obviously this doesn't explain the oscillation at different energies which can be explained by the following equations:

$$E_v = \left(v + \frac{1}{2}\right)\hbar\omega_0$$

This means that the energy of the simple harmonic osciallator is always separated by the same energy gap. Which is $\hbar\omega_0$.

Tunnelling in quantum harmonic motion

As the energy levels for the quantum harmonic oscillator are sloped and are not at an infinite potential it is possible for the molecule to tunnel outside of the oscillator. This means that it is possible for the particle to have a negative kinetic energy.