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Department of Chemistry

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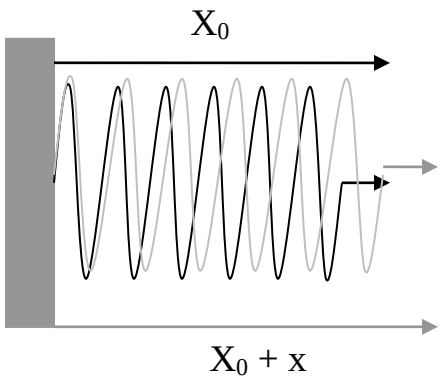
CH101

Class 7-8; Physical Chemistry

Vibrational Motion:

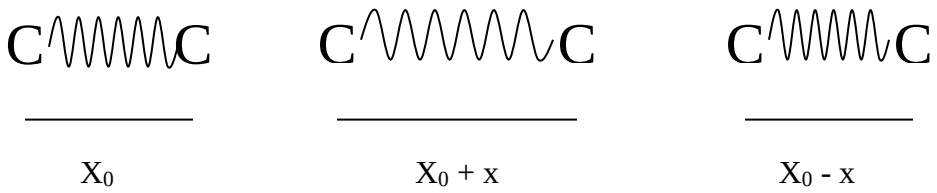
Consider the following restoring force that acts on a stretched spring (Hook's Law) $F = -k(X_0 - x)$; where k is the force constant and x is the displacement of the spring from the equilibrium position.



The potential energy is, $V = \frac{1}{2}k(X_0 - x)^2$. This is the potential energy associated with a harmonic oscillator.

X_0 is the equilibrium position of the spring.

Now, consider molecules where real chemical bonds exist. For simplicity and convenience one can assume that the vibrational motion of the chemical bonds to be harmonic and thus want to find the energy associated with the vibrational motion of the molecular bonds. Consider, for example, a carbon-carbon bond. The bond stretched and compressed between an equilibrium distance of R_0 to $R_0 \pm r$, where r is the extent of stretching (compression).



X_0 $X_0 + x$ $X_0 - x$

One can simplify the equations by setting $X_0 = 0$ (origin of coordinates).

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

One can write the Schrödinger wave equation for the system:

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

The solution of the above equation is not simple, but well known in mathematics.

The details of the solutions appear like

$$\Psi_v(x) = N_v H_v(y) e^{-\frac{y^2}{2}}\text{; where } y=\frac{x}{\alpha}\text{; and } \alpha = \{\frac{\hbar^2}{mk}\}^{\frac{1}{4}}$$

$H_v(y)$ is a Hermite polynomial. The values for different v are

$$H_0(y) = 1$$
$$H_1(y) = 2y$$
$$H_2(y) = 4y^2 - 2$$
$$H_3(y) = 8y^3 - 12y$$
$$H_4(y) = 16y^4 - 48y^2 + 12$$
$$H_5(y) = 32y^5 - 160y^3 + 120y$$
$$H_6(y) = 64y^6 - 480y^4 + 720y^2 - 120$$

Also, the Hermite polynomials are the solutions of the differential equation

$H_v'' - 2yH_v' + 2vH_v = 0$; where the primes denote differentiation.

They Hermite polynomials satisfy the following recursion relation

$$H_{v+1} - 2yH_v + 2vH_{v-1} = 0$$

An important integral related to this is

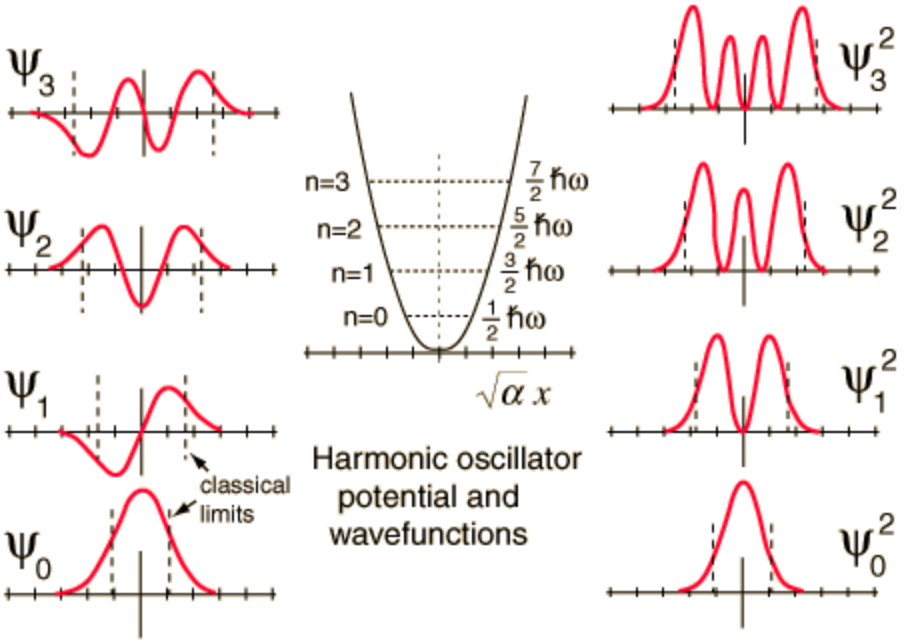
$$\int_{-\infty}^{\infty} H_{v'}H_v e^{-y^2}dy = \begin{cases} 0 & if\ ;v'\neq v \\ \sqrt{\pi}\,2^v v! & if\ ;v'=v \end{cases}$$

Thus the wavefunction for the ground state is: $\Psi_0(x) = N_0 e^{-\frac{y^2}{2}} = N_0 e^{-\frac{x^2}{2\alpha^2}}$

The wavefunction for the first excited state is

$$\Psi_1(x) = N_1 2y e^{-\frac{y^2}{2}} = N_1 2(\frac{x}{\alpha}) e^{-\frac{x^2}{2\alpha^2}}$$

In the figures below assume n = v



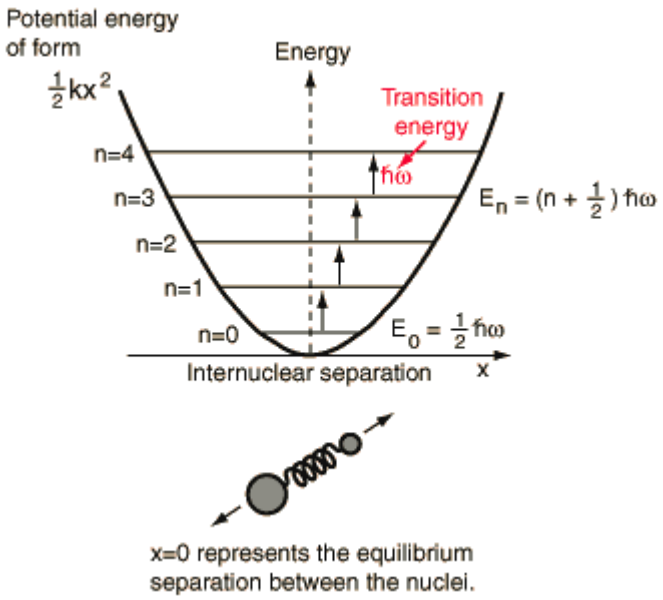
The energy expression for the harmonic oscillator is

$$E_V = (v + \frac{1}{2})\hbar\omega$$

v is the quantum number and takes the values of v = 0, 1, 2, 3,……

$$\omega = \sqrt{\frac{k}{m}}$$

When v = 0, the minimum energy is $\frac{1}{2}\hbar\omega$.



This is called zero point energy

Explanation for zero point energy. Just like the particle in a box, the oscillator here is confined in a potential well. Hence its position is not completely uncertain (that is its position uncertainty is not infinity). Hence its momentum is not zero. Thus its kinetic energy is not zero. Hence the zero point energy.

Normalization of the wavefunction $\Psi_v(x) = N_v H_v(y) e^{-\frac{y^2}{2}}$

N_v is not known. The function needs to be normalized.

$$1 = \int_{-\infty}^{\infty} \Psi_v^* \Psi_v dx = \alpha \int_{-\infty}^{\infty} \Psi_v^* \Psi_v dy = \alpha \int_{-\infty}^{\infty} N_v^2 H_v^2(y) e^{-y^2} dy = \alpha N_v^2 \pi^{\frac{1}{2}} 2^v v!$$

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

One can show that for a harmonic oscillator

$$\langle x \rangle = 0$$

$$\langle x^2 \rangle = \left(v + \frac{1}{2} \right) \frac{\hbar}{\sqrt{(mk)}}$$

Thus
$$\langle V \rangle = \left\langle \frac{1}{2} k x^2 \right\rangle = \frac{1}{2} k \left(v + \frac{1}{2} \right) \frac{\hbar}{\sqrt{(mk)}} = \frac{1}{2} \left(v + \frac{1}{2} \right) \hbar \omega$$

Since the total energy is E= T + V

$$\langle V \rangle = \frac{1}{2} \langle E_v \rangle$$

and

$$\langle T \rangle = \frac{1}{2} \langle E_v \rangle$$

$$\langle x \rangle = \int_{-\infty}^{\infty} \Psi_v^* x \Psi_v dx = N_v^2 \int_{-\infty}^{\infty} \left(H_v e^{-y^2/2} \right) x \left(H_v e^{-y^2/2} \right) dx$$

$$= N_v^2 \alpha^2 \int_{-\infty}^{\infty} \left(H_v e^{-y^2/2} \right) y \left(H_v e^{-y^2/2} \right) dy$$

$$= N_v^2 \alpha^2 \int_{-\infty}^{\infty} (H_v) y (H_v) e^{-y^2} dy$$

$u \sin g, recursion - relation$

$$y H_v = v H_{v-1} + \frac{1}{2} H_{v+1}$$

get

$$\int_{-\infty}^{\infty} (H_v) y (H_v) e^{-y^2} dy$$

$$= v \int_{-\infty}^{\infty} (H_{v-1})(H_v) e^{-y^2} dy + \frac{1}{2} \int_{-\infty}^{\infty} (H_{v+1})(H_v) e^{-y^2} dy = 0 + 0$$

$$\therefore \langle x \rangle = 0$$