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Exact Solution

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Wave equation for a Harmonic oscillator:

For a diatomic molecule, there is only one vibration mode, so there will be only a single set of vibrational wave functions with associated energies for this system. For polyatomic molecules, there will be a set of wavefunctions with associated energy with each vibrational mode.

For the free particle and the particle in a box, the potential energy term used in the Hamiltonian was zero.

(a) Potential energy (V) of a simple harmonic oscillator. The work done in stretching the bond increases the potential energy of the system. If the potential energy for the equilibrium length of the bond is zero and that for the length 'x' is given by

$$V = \int_0^x (-F)\,dx$$

But $F = -Kx$

Thus $V = \int_0^x Kx\,dx$ or $V = \frac{1}{2}Kx^2$ — (1)

(b) Wave equation for a simple harmonic oscillator

The Schrodinger's equation along x axis is given by

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m[E-V]\psi}{h^2} = 0 \quad (2)$$

The potential energy along x axis is

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

Substituting the value of V in equation (2) we get

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h}\left(E - \frac{1}{2}Kx^2\right)\psi = 0$$

— (3)

If we change over to two new independent dimensionless variables ξ and α which are defined as

$$\xi = \left(\frac{2\pi}{h}\sqrt{Km}\right)^{1/2} x \quad \text{— (4)}$$

$$K = 4\pi^2 m\nu^2$$

Substituting the value of K in equation (4) we have

$$\xi = \left[\frac{2\pi}{h}\sqrt{4\pi^2 m\nu^2 \cdot m}\right]^{1/2} x \quad \text{— (5)}$$

$$\xi = \left(\frac{4\pi^2 m\nu}{h}\right) x$$

$$\alpha = \frac{4E\pi}{h}\sqrt{m/K}$$

Substituting $K = 4\pi^2 m\nu^2$ we have

$$\alpha = \frac{4\pi E}{h}\sqrt{\frac{m}{4\pi^2 m\nu^2}}$$

or $\alpha = \frac{4\pi E}{h} \cdot \frac{1}{2\pi\nu}$ or $\alpha = \frac{2E}{h\nu}$ — (6)

from equation (5) we get

$$\xi^2 = \frac{4\pi^2 m\nu}{h} x^2$$

$$x^2 = \frac{\xi^2 h}{4\pi^2 m\nu} \quad \text{— (7)}$$

from equation (6) we have

$$E = \frac{h\nu\alpha}{2} \quad \text{— (8)}$$

NO $\frac{d^2\psi}{dx^2} = \frac{d}{dx}\left(\frac{d\psi}{dx}\right)$

$$= \frac{d}{dx} \cdot \frac{d\psi}{d\xi} \cdot \frac{d\xi}{dx} = \frac{d}{d\xi} \cdot \frac{d\psi}{dx} \cdot \frac{d\xi}{dx}$$

$$= \frac{d}{d\xi}\left(\frac{d\psi}{d\xi} \cdot \frac{d\xi}{dx}\right)\frac{d\xi}{dx} =$$

$$= \frac{d^2\psi}{dx^2} = \frac{d^2\psi}{d\xi^2}\left(\frac{d\xi}{dx}\right)^2 \quad \text{— (9)}$$

Now from eqn (5)

$$y = \left(\frac{4\pi^2 m\nu}{h}\right)^{\frac{1}{2}} x$$

$$\therefore \frac{dy}{dx} = \left(\frac{4\pi^2 m\nu}{h}\right)^{\frac{1}{2}}$$

On squaring both sides we have

$$\left(\frac{dy}{dx}\right)^2 = \frac{4\pi^2 m\nu}{h} \quad -(10)$$

Substituting this value in equation (9) we we have,

$$\frac{d^2\psi}{dx^2} = \frac{d^2\psi}{dy^2}\left(\frac{4\pi^2 m\nu}{h}\right) \quad -(11)$$

Combining equation 3, 7, 8 and (11) we get-

$$\left(\frac{4\pi^2 m\nu}{h}\right)\frac{d^2\psi}{dy^2} + \frac{8\pi^2 m}{h^2}\left[\frac{h\nu\alpha}{2} - \left(\frac{1}{2}4\pi^2 m\nu^2\right)\left(\frac{y^2 h}{\pi\pi^2 m\nu}\right)\right]\psi = 0$$

dividing both side by $\frac{4\pi^2 m\nu}{h}$ we get,

$$\frac{d^2\psi}{dy^2} + \frac{2}{h\nu}\left[\frac{h\nu\alpha}{2} - \frac{1}{2}\nu h y^2\right]\psi = 0$$

$$\frac{d^2\psi}{dy^2} + (\alpha - y^2)\psi = 0 \quad -(12)$$

$$\frac{d^2\psi}{dy^2} = (y^2 - \alpha)\psi \quad - \quad (13)$$

$$\left(\frac{d^2\psi}{dy^2} / y^2 - \alpha\right)\psi = 1 \quad -(14)$$

Equation (12), (13) and (14) are different form of the wave equation for the simple harmonic oscillator.

(c) Asymptotic solution of the wave equation of simple harmonic oscillator is-

$$\frac{d^2\psi}{dy^2} / (y^2 - \alpha)\psi = 1 \quad -(15)$$

As $\xi \to \pm\alpha$, $\xi^2 >>> \alpha$ thus the equation (15) may be written as

$$\lim_{\xi \to \alpha} \left[\frac{d^2\psi}{d\xi^2} / \xi^2 \psi \right] = 1 \quad -(16)$$

The equation (16) has the solution of the form

$$\psi_\alpha = e^{\pm\frac{1}{2}\xi^2}$$
$$= \exp(\pm\tfrac{1}{2}\xi^2) \quad -(17)$$

Now as $\xi \to \pm\alpha$, $\xi^2 \to +\alpha = (+\frac{1}{2}\xi^2)$ becomes larg. Therefore, boundary conditions allow us only to retain negative sign in equ (17). Hence the equation

$$\psi_\alpha = \exp(-\tfrac{1}{2}\xi)^2 \quad — (18)$$

(d) Energy levels — If we consider a Solution of the type

$$\psi = y e^{-\frac{1}{2}\xi^2} \quad —(19)$$

Then equation (12) becomes

$$\frac{d^2y}{d\xi^2} - 2\xi \frac{dy}{d\xi} + (\alpha - 1) y = 0 \quad - (20)$$

The equation (20) resembles Hermite's equation which is differential equation of type

$$\frac{d^2y}{dx^2} - 2x \cdot \frac{dy}{dx} + 2ny = \quad (21)$$

Thus, the solution (12) is any solution $H(\xi)$ of Hermite equation multiplied by $\exp(-\frac{1}{2}\xi^2)$ i.e

$$\psi = H(\xi) \cdot \exp(\tfrac{1}{2}\xi^2) \quad -(22)$$

Hermite differential equation is defined as - for is a non negative integer i.e the solution of Hermite's aquation are often referred to as Hermite Polynomials.

The recursion formula becomes

$$\frac{A_{n+2}}{n} = \frac{2n+1-\alpha}{(n+1)(n+2} \quad -(23)$$

As $n \to \alpha$

$$\lim_{n\to\alpha}\left(\frac{A_{n+2}}{A_n}\right) = \frac{2n}{n^2} = \frac{2}{n} \quad - 24$$

Consider the series

$$e^{n^2} = 1 + \xi^2 + \frac{\xi^4}{\lfloor 2} + \cdots \frac{\xi^n}{\lfloor(\frac{1}{2}\xi)}$$

with the recursion expression

$$\frac{\beta_{n+2}}{\beta_n} = \frac{(\lfloor\frac{1}{2}n)}{(\lfloor\frac{1}{2}n+1)} = \frac{1}{\frac{n}{2}+1}$$

$$\lim_{n\to\alpha}\left(\frac{\beta_{n+2}}{\beta_n}\right) = \frac{1}{n/2} = \frac{2}{n}$$

Thus, for a large n, The $H(\xi)$ series behaves like the exponential series $\exp(\xi^2)$. This mean.

$$\underset{\xi \to \text{Large}}{\psi(\xi)} = H(\xi)\, e^{-\frac{1}{2}\xi^2} = e^{\frac{1}{2}\xi^2},$$

It $E_0 = \frac{1}{2}h\nu$ is know as zero Poin energy