University of Babylon
College of Sciences
Department of Chemistry
Course No. Chsc 424

Lectures of

Quantum mechanics of Chemistry

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Lecture No. 8 ((System of Harmonic oscillator))

1-Introduction:

The harmonic oscillator system is a model for a physical system whose natural motion is described by the Schrödinger equation, such as the vibrational motion of molecules, lattice vibrations of crystals. Quantization of vibrational energies and their levels will be evolve also, a vibration quantum number is realized mathmetically to control energy level value.

Q/Give general idea about the solution of Schrödinger equation for Harmonic oscillator system.

The solution of Harmonic oscillator system give us :

1. New energetic motion term is introduced in the total energy summation(vibration motion).
2. Quantization of vibration motion at different levels to the oscillated chemical bond accourding to the vibration quantum nuber.
3. Potential energy term is important factor into total energy.
4. Fundamental principles of infrared spectroscopy that's dependeng on egin value of energy that associated to the wave function of this system.

2- **Formalism of Hamltonion Operator:**

Chemical bond is consider as the case of a point mass, m, attached to the end of a linear spring with a spring constant **k** as shown in Figure 1. The classical equation of motion is:- $F = -Kx$ ------1

Since F, K, and x are the restoring force, the force constant, and the displacement respectively. When the mass is moving away from the equilibrium position by an external effect. If the system is conserving energy, the mass is restoring to the original position.

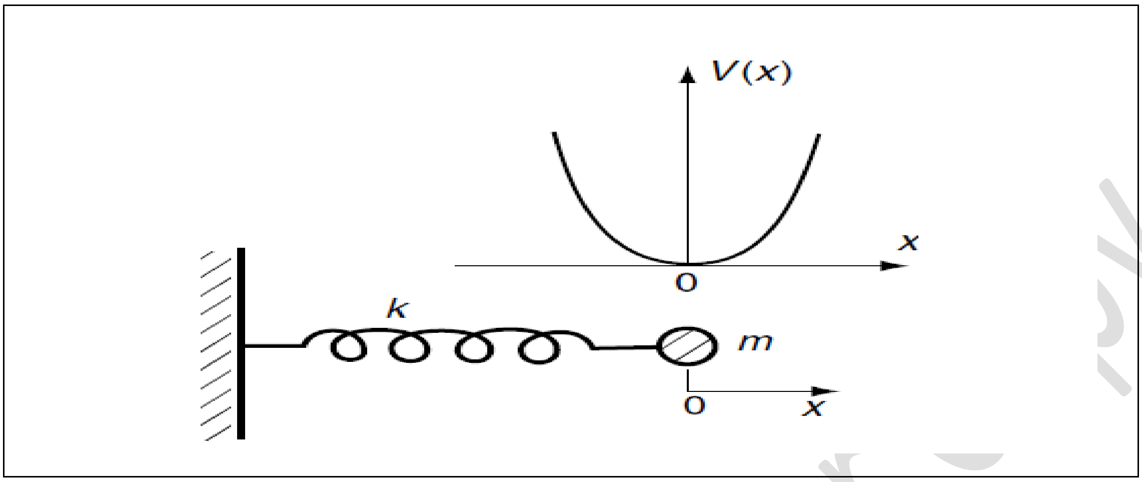

Figure 1. Schematic diagram of a harmonic oscillator.

The potential energy of the particle varies with the deviation from its equilibrium position (x=0). So that according to quantum mechanics :

$$F = \frac{-\partial V_x}{\partial x} \text{ ------2} \qquad \text{Since } V_x \text{ is potential energy}$$

According to Newton's law $F = m.\left(\frac{dx}{dt}\right)^2$ ----3

For the same true system must be eq.2 = eq. 3

$$\frac{-\partial Vx}{\partial x} = m.\left(\frac{dx}{dt}\right)^2 \text{ ------4}$$

by taking the integral and rearrangement

$$\frac{1}{2}.m.\left(\frac{dx}{dt}\right)^2 + Vx = C \text{ ---------5}$$

Eq. 5 is agreement with the conservation energy system due to the summation of kinetic energy and potential energy is constant and this phenomenon didn't depend on the time, therefore the eq. 2 is true and therefore eq.1=eq.2

$$-K.x = \frac{-\partial V_x}{\partial x} \qquad \text{by rearrangement}$$

$$K.x\, \partial x = \partial V_x \text{ -----6} \qquad \text{By integral}$$

$V_x = \frac{1}{2} k.x^2$-------7   The potential energy of harmonic oscillator.

The kinetic energy of the system is equal to ($E = \frac{P^2}{2m}$)in the form of linear momentum.

The Hamiltonian operator is $\hat{H}$= T+V= $-\frac{h^2}{8\pi^2 m}.\frac{\partial^2}{\partial x^2} + \frac{1}{2}K.x^2$

3-Harmonic oscillator system in one dimension:

$\hat{H}\Psi = E\Psi$ the Schrödinger equation of Harmonic oscillator is

$$[\left(-\frac{h^2}{8\pi^2 m}.\frac{\partial^2}{\partial x^2} + \frac{1}{2}K.x^2\right)\varphi_x = E\varphi_x)] \quad \text{or}$$

$$[\left(-\frac{h^2}{8\pi^2 m}.\frac{\partial^2 \varphi_x}{\partial x^2} + \frac{1}{2}\varphi_x K.x^2\right) = E\varphi_x)]$$

$$[\left(-\frac{h^2}{8\pi^2 m}.\frac{\partial^2 \varphi_x}{\partial x^2}\right) = E\varphi_x - \frac{1}{2}\varphi_x K.x^2)]$$

this equation is multiple by ($-\frac{8\pi^2 m}{h^2}$) and rearrangement to became as follow:

$$\left(\frac{\partial^2 \varphi_x}{\partial x^2}\right) = -\frac{8\pi^2 m}{h^2}E\varphi_x + \frac{1}{2}\frac{8\pi^2 m}{h^2}\varphi_x K.x^2)]$$

$$\left(\frac{\partial^2 \varphi_x}{\partial x^2}\right) = -\frac{8\pi^2 m}{h^2}(E\varphi_x - \frac{1}{2}\varphi_x K.x^2)]$$

$$\frac{\partial^2 \varphi}{\partial x^2} + \left(\frac{8\pi^2 m}{h^2}(E_x - \frac{k.x^2}{2})\right)\varphi_x = 0$$

Or

$$\frac{\partial^2 \varphi}{\partial x^2} + \left(\frac{8\pi^2 m E_x}{h^2} - \frac{4\pi^2 m k}{h^2}.x^2\right)\varphi_x = 0 \text{ -----9}$$

To solve the eq. 9 must be supposed the following: $\beta^2 = \frac{4\pi^2 mk}{h^2}$, $\alpha = \frac{8\pi^2 m E_x}{h^2}$
And subsitued this terms in eq.9 .

Equation of one-dimensional Harmonic oscillator system is

$$\frac{\partial^2\varphi}{\partial x^2} + (\propto -\beta^2 . x^2).\Psi_x = 0 \text{ -----10}$$

And If supposed that $y^2 = \beta^2 . x^2$, since $\frac{\partial y}{\partial x} = \sqrt{\beta}$ and the $\frac{\partial^2 y}{\partial x^2} = 0$

According to this hypothesis; $\frac{\partial^2\varphi}{\partial x^2} = \frac{\partial}{\partial x} . \left(\frac{\partial\varphi}{\partial x}\right) = \frac{\partial}{\partial x}(\frac{\partial y}{\partial x} . \frac{\partial\varphi}{\partial y})$

$$= \frac{\partial^2 y}{\partial x^2} . \frac{\partial\varphi}{\partial y} + \frac{\partial y}{\partial x} . \frac{\partial}{\partial x} . \frac{\partial\varphi}{\partial y}$$

$$= \frac{\partial^2 y}{\partial x^2} . \frac{\partial\varphi}{\partial y} + \frac{\partial y}{\partial x} . (\frac{\partial y}{\partial x} . \frac{\partial\varphi}{\partial y}) . \frac{\partial}{\partial y} by$$

substituted our hypothesis

$$= 0 + \sqrt{\beta} \ .(\sqrt{\beta} \ . \frac{\partial^2\varphi}{\partial y^2})$$

So that

$\frac{\partial^2\varphi}{\partial x^2} = \beta . \frac{\partial^2\varphi}{\partial y^2}$ ------------11 because the $\frac{\partial^2 y}{\partial x^2} = 0$

By introducing eq.10 into eq.11 to get on

$$\beta . \frac{\partial^2\varphi}{\partial y^2} + (\propto -\beta^2 . y^2).\Psi = 0 \text{ -----12}$$

by divided into β

$$\frac{\partial^2\varphi}{\partial y^2} + (\frac{\propto}{\beta} - \beta . y^2).\Psi = 0 \text{ -----13}$$

The mathematic solution of this equation is

$$\Psi = e^{\pm\frac{y^2}{2}} \text{ -----14}$$

In eq. 14 the value of y is very important because when the value is very large the term is becoming nil value approximately so that the eq. 14 can be solved by using a function that has the following foundation:-

$\Psi = U(Y) . e^{-\frac{y^2}{2}}$ -----15 the function $e^{-\frac{y^2}{2}}$ becomes to infinity

When y=∞ that’s mean the displacement (x) becomes infinity toward the position of equilibrium. Must be using standard formalism to find the solutions (Hermit equation) the final solution is Hermit polynomial.

$$H_v(y) = (-1)\, v .\, e^{y^2} . \frac{d^v}{\partial y^v} .\; e^{-y^2} \quad \text{---------16}$$

V is the vibrational quantum number, so the formula of the final solution for the Schrödinger equation is:-

$$\Psi_v(y) = N_v .\, H_v .\, e^{-y^2/2} \quad \text{---------17}$$

The normalization constant of function can be calculated as follows:-

$$N_v = \int_{-\infty}^{+\infty} [H\text{v}(y)]^2 . e^{-y^2} . \partial y = 1 \quad \text{-------------18}$$

$$N_v = \left(\frac{1}{\pi}\right)^{\frac{1}{4}} . (2^v . v!)^{-\frac{1}{2}} = \{\{ \sqrt[4]{\frac{1}{\pi}} . \frac{1}{\sqrt{(2^v . v!)}} \}\} \quad \text{---------------19}$$

Therefore the equation of harmonic Oscillator is

$$\Psi_v(y) = \left(\frac{1}{\pi}\right)^{\frac{1}{4}} . (2^v . v!)^{-\frac{1}{2}} . H_v(y) .\, e^{-y^2} \quad \text{---------20}$$

To calculate the Eigenvalue (**E_v**) that's associated with equation 20

Must remember the approximation of:

$\alpha = \frac{8\pi^2 m E_x}{h^2}$ and $\beta = \frac{2\pi}{h} . (k/m)^{1/2}$ due that $\frac{\propto}{\beta} - 1 = 2v$

Therefore

$$\frac{\frac{8\pi^2 m Ex}{h^2}}{\frac{2\pi}{h} . (k/m)^{1/2}} - 1 = 2v \quad \text{---------21}$$

By rearrangement:

$$E_v = \left(v + \frac{1}{2}\right) . \frac{h}{2\pi} . (k/m)^{0.5} \quad \text{----------------22}$$

By substituting the value of vibration frequency (v) from the equation of angular frequency for the oscillator (w) into equation 21.

$w = 2\boldsymbol{\pi\nu} = (k/m)^{0.5}$ So that $E_v = \left(v + \frac{1}{2}\right) . \frac{h}{2\pi} . 2\pi\boldsymbol{\nu}$ $E_v = \left(\mathrm{v} + \frac{1}{2}\right) hv$ --23

Eigenvalue of the system

Q// Several notes that's can released from this equation, what are this?

Answer:

1-The vibrational energy value is proportional directly with vibration quantum number (v). Force constant of bond(k) therefor at high values of vibration quantum number the vibrational energy value will be very large and the harmonic oscillator body will be a longer vibrated motion. At the sam time high value of k will needed high value of vibrational energy. The vibrational energy value is inversely proportional with suquar root of the reduced mass of bonded atoms.

2- The increasing vibrational energy value, will increase the elongation of the chemical bond and tend to be broken(lost harmonicity).

3- The lowest value of vibrational quantum numbers(v), is zero; therefore, the zero-point energy value of the harmonic oscillator system is equal to $E_0 = (\frac{1}{2}\ h\boldsymbol{\nu})$.

Equation 23 is the basis of infrared spectroscopy, is the zero-point energy.

Figure 2. It represents the little part of the energy level of vibration energy for the harmonic oscillator system.

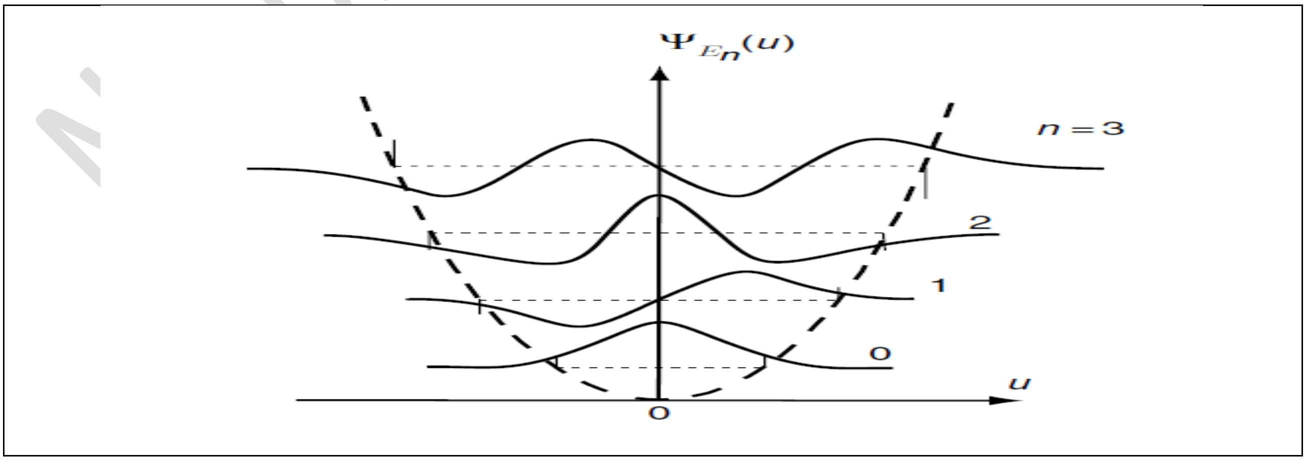

Figure 2. Eigenfunction of some vibration levels energies for the harmonic oscillator.

4-Harmonic oscillator system at three dimensions:

All components of Schrödinger formalism are treatment in three dimensions.

T = $\frac{(xP^2.yP^2.zP^2)}{2m}$, $V = \frac{1}{2}$k(x^2+y^2+z^2), therefore H = $\frac{(xP^2.yP^2.zP^2)}{2m}$ + $\frac{1}{2}k$.(x^2+y^2+z^2)

The represented equation is

$$\left[\!\left[-\frac{h^2}{8\pi^2 m}.\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)-\frac{1}{2}.k(x^2+y^2+z^2)\right]\!\right]\Psi_{x,\,y,\,z}=E\Psi_{x,\,y,\,z}$$

Or

$$\left[\!\left[\left(\frac{\partial^2\varphi}{\partial x^2}+\frac{\partial^2\varphi}{\partial y^2}+\frac{\partial^2\varphi}{\partial z^2}+\frac{8\pi^2 m}{h^2}\right)E-\frac{1}{2}.k(x^2+y^2+z^2)\right]\!\right]\Psi_{x,\,y,\,z}=0 \text{ ----25}$$

By some approximations $\left(\frac{8\pi^2 m}{h^2}\right)E=\lambda$, $\frac{4\pi^2 mk}{h^2}=\alpha^2$ the equation becomes

$$\left[\!\left[.\left(\frac{\partial^2\varphi}{\partial x^2}+\frac{\partial^2\varphi}{\partial y^2}+\frac{\partial^2\varphi}{\partial z^2}+\frac{8\pi^2 m}{h^2}\right)+\lambda-\propto^2 x^2+\propto^2 y^2+\propto^2 z^2)\right]\!\right]\Psi_{x,\,y,\,z}=0 \text{ ----26}$$

The solutions of this equation is come by separation of the mathematical terms using single wave functions depending on single variables for each of them.

Since:

$$\Psi_{x,y,z}= Xx . Yy. Zz \text{ ----------------------27}$$

By taking the differential of the wave function of eq. 27 for two times into each sub-function with constant the other two sub-function and repeating the process for all. The result substituted in equation 26 and divided the resultant equation on **X.Y.Z** and rearrangement the final equation:

$$\left(\left(\frac{1}{X}.\frac{\partial^2 X}{\partial x^2}-\propto^2 x^2\right)+\left(\frac{1}{Y}.\frac{\partial^2 Y}{\partial y^2}-\propto^2 y^2\right)+\left(\frac{1}{Z}.\frac{\partial^2 Z}{\partial z^2}-\propto^2 z^2\right)\right)+\lambda=0 \text{ -------28}$$

Equation 28 is symmetrical (equatorial terms), because of the real symmetry, can be separated into three sub equation all of them equal to zero.

$$\frac{\partial^2 X}{\partial x^2} + (\lambda x - \propto^2 x^2)X = 0; \quad \frac{\partial^2 Y}{\partial y^2} + (\lambda y - \propto^2 y^2)Y = 0 \text{ ----------29}$$

$$\frac{\partial^2 Z}{\partial z^2} + (\lambda z - \propto^2 z^2)Z = 0$$

The total energy of the system is λ=(λ_x+ λ_y+ λ_z), it's the Eigenvalue of the Eigen wave function ($\Psi_{x, y, z}$). Every equation of 29 is like equation 10(harmonic oscillator for one dimension. The solution of equation 29 is done in the same way as equation 10 and the final solution has come from the multiple products of equation 29. The Eigenvalue (energy value of system) is equal to:

$$E = h\left[\left(V_x + \frac{1}{2}\right).V_x + \left(V_y + \frac{1}{2}\right).V_y + \left(V_z + \frac{1}{2}\right).V_z\right] \text{----30}$$

5- Applications:

Calculate the required energy by (h**ν**) units for transitions between vibrational levels at v=3 and v=4.

Solve:- By using the Eigen value equation

E_v= (v+1/2)h**ν** E_3=(3+1/2) h**ν** = 7/2 h**ν** E_4= 9/2 h**ν**

Required energy for transition E_4-E_3=(9/2-7/2) h**ν**=2/2 h**ν**=1 h**ν**
