CHEM F111 : General Chemistry
Semester I: AY 2017-18

Lecture-06, 19-01-2018

Notice: Quiz-01

Schedule: During 23-01-2018 to 29-01-2018 in the Tutorial Class

Syllabus: L-01 to L-06

Summary: Lecture - 05

- Particle on a ring.
- Angular momentum operator:
- Schröndinger Equation for particle on a ring:

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi} = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$$

$$-\frac{\hbar^2}{2I}\frac{d^2}{d\varphi^2}\Phi(\varphi) = E\Phi(\varphi)$$

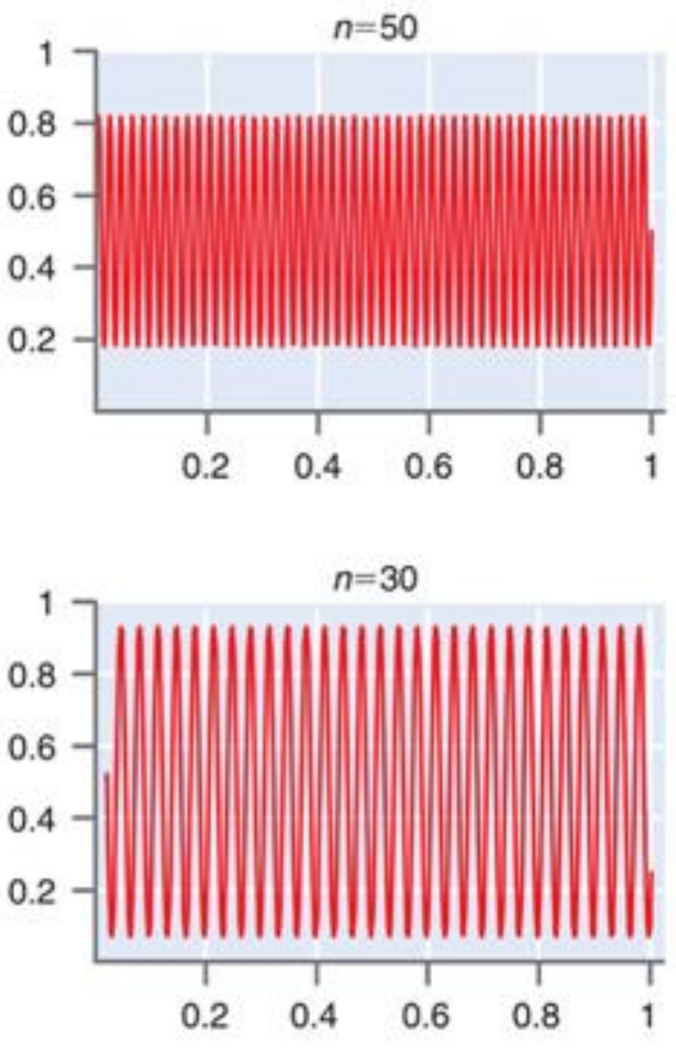
$$\Rightarrow \frac{d^2}{d\varphi^2}\Phi(\varphi) = -\frac{2I}{\hbar^2}E\Phi(\varphi)$$

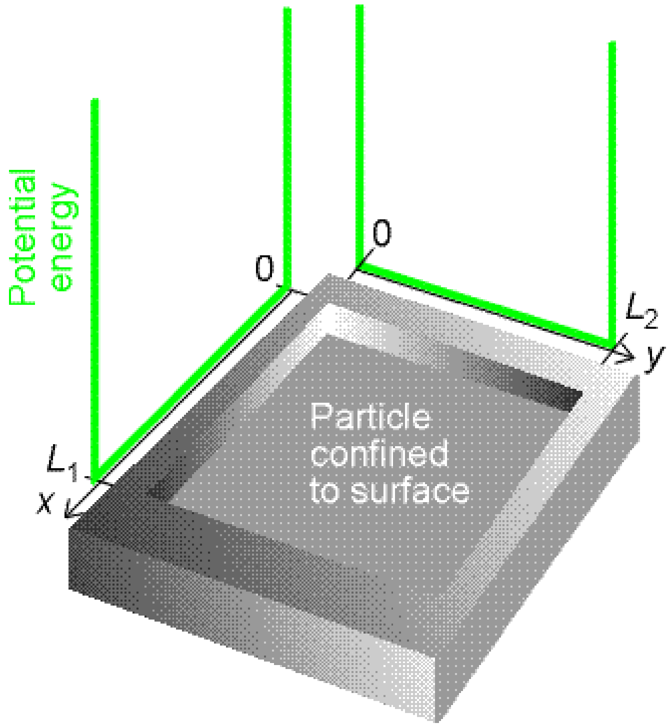
$$\boxed{\psi_m(\phi) = \frac{e^{im\phi}}{(2\pi)^{1/2}}}$$

$$\boxed{E = \frac{m^2\hbar^2}{2I}}$$

$$\boxed{L_Z = \pm m\hbar}$$

Summary: Lecture - 05





$$E = \frac{n_x^{\,2} h^2}{8mL_1^{\,2}} + \frac{n_y^{\,2} h^2}{8mL_2^{\,2}}$$

Where n_x= 1, 2, 3….

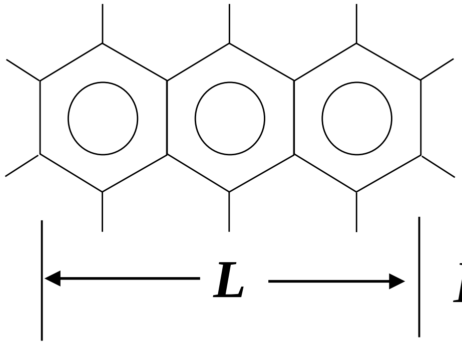
n_y= 1, 2, 3…

$$\psi(x,y) = \sqrt{\frac{2}{L_1}}\sqrt{\frac{2}{L_2}}\sin\left(\frac{n_x \pi x}{L_1}\right)\sin\left(\frac{n_y \pi y}{L_2}\right)$$

Bohr correspondence principle

Summary: Lecture - 05

PIB: Simple model of molecular energy levels



$L \approx 6\ \text{Å}$

Anthracene

π electrons – consider "free" in box of length L.

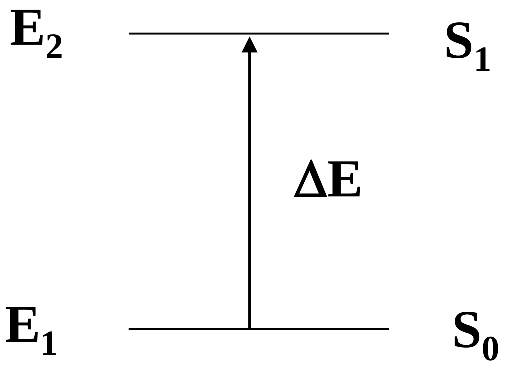
Ignore all coulomb interactions.

$$m = m_e = 9\times10^{-31}\ \text{kg}$$

$$L = 6\ \text{Å} = 6\times10^{-10}\ \text{m}$$

$$h = 6.6\times10^{-34}\ \text{Js}$$

$$\Delta E = 5.04\times10^{-19}\ \text{J}$$



Calculate wavelength of absorption of light.

Form particle in box energy level formula

$$\Delta E = E_2 - E_1 = \frac{3h^2}{8mL^2}$$

$$\Delta E = h\nu$$

$$\nu = \Delta E / h = 7.64\times10^{14}\ \text{Hz}$$

$$\lambda = c/\nu = 393\ \text{nm}$$ blue-violet

Experiment $\Rightarrow$ 400 nm

Big molecules $\longrightarrow$ absorb in red.

Small molecules $\longrightarrow$ absorb in UV.

Operators, eigen values, and observables

Postulate 2: To every observable in classical mechanics there corresponds an operator in quantum mechanics.

Postulate 3: Quantum Mechanical operators are special in nature. In any measurement of the observable associated with the operator $\hat{A}$, the only values that will be ever observed are the eigenvalues a, which satisfy the eigen value equation:

$$\hat{A}\,\psi = a\,\psi$$

Perform the following operations:

$$i)\ \hat{A}(2x), where\ \hat{A} = \frac{d^2}{dx^2}\ ;\ ii)\ \hat{A}\left(x^2\right), where\ \hat{A} = \frac{d^2}{dx^2} + 2\frac{d}{dx} + 3$$

Operators, eigen values, and observables

Time independent Schröndinger Equation (ODE)

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + u(x)\,\psi\,(x) = E\,\psi\,(x)$$

We can rewrite as,

$$\left\{-\frac{\hbar^2}{2m}\,\frac{d^2}{dx^2} + u\,(x)\right\} = \hat{H};$$

Operation: $\frac{d^2}{dx^2}$

Then multiply by $-\frac{\hbar^2}{2m}$

Then add u(x) ψ (x)

Energy Operator or Hamiltonian

Operators, eigen values, and observables

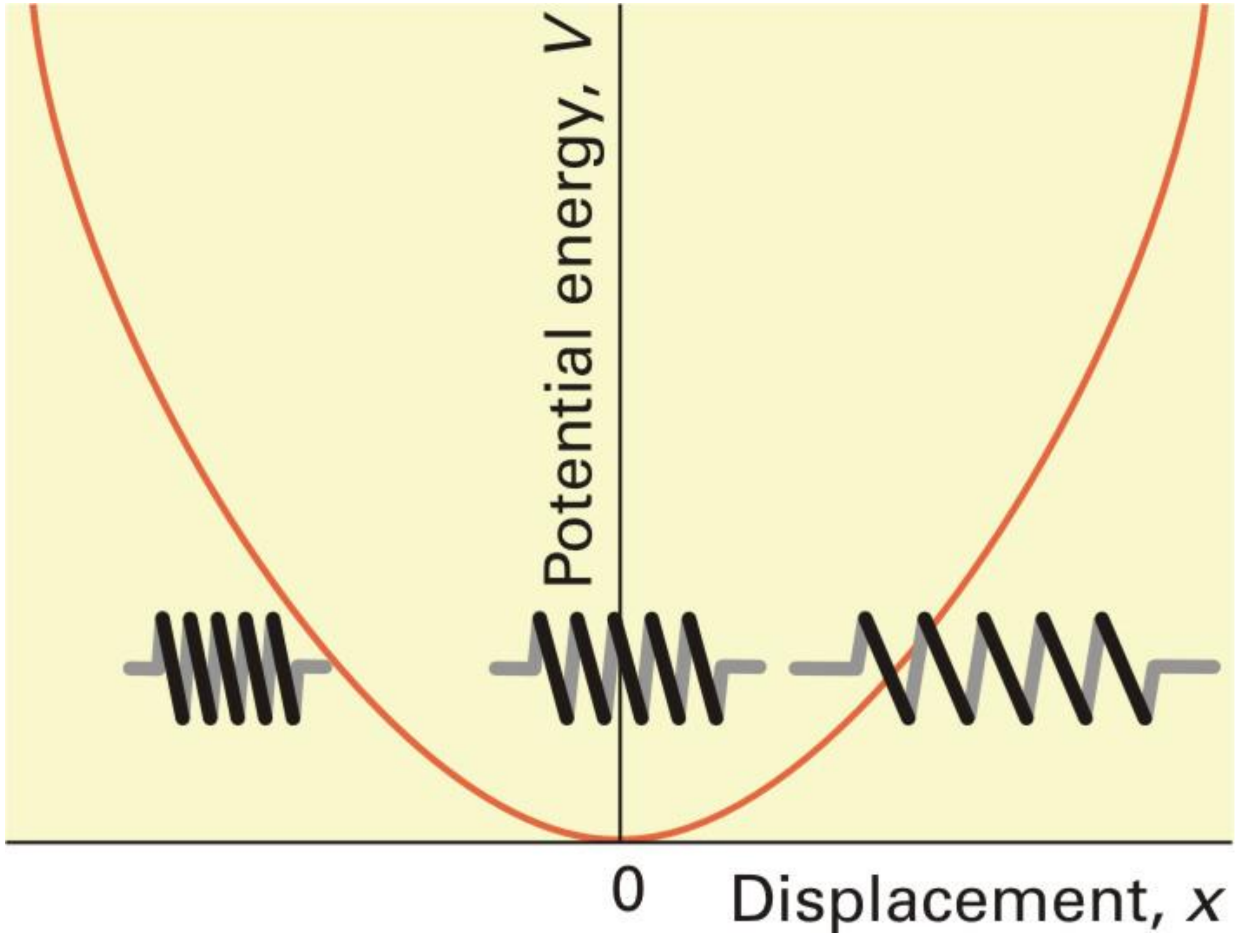
i) Show that e^{ikx} is an eigen function of the momentum operator. What is the eigen value?

ii) Is e^{ikx} is an eigen function of the energy operator for a free particle? What is the eigen value?

iii) Consider PIB problem. Is $\psi_n(x)$ is an eigen function of the energy operator? What is the energy eigen value? Is $\psi_n(x)$ is an eigen function of the momentum operator?

iv) Write down the form of Hamiltonian operator for a free particle and a particle constrained to move in a one-dimensional box. Is there any difference between the Hamiltonian of these two systems?

Vibrations: Harmonic Oscillator



Hooke's law:

Restoring force = – kx

(k – force constant,

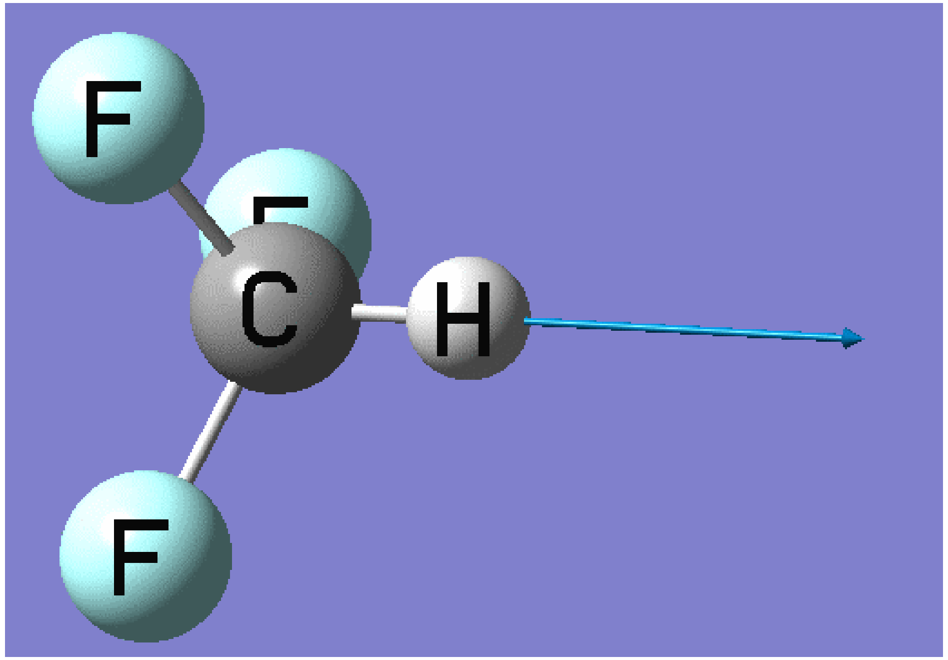
x – displacement from equilibrium)

Potential energy $V(x) = ½ kx^2$

Classical Oscillator

- Spring is stretched and released. At the point of release total energy is PE
- The mass accelerates as it moves back toward the center of the parabolic potential.
- At the center, total energy is KE – mass continues to move – spring gets compressed – reaches a point with total PE.
- Classical turning points: Mass stops as the total energy is PE.
- A classical harmonic oscillator can have any energy – energy value is continuous.
- Energy is determined by how much the spring is stretched – value of PE at the turning points.
- Motion of the mass is oscillatory.
- Position varies simultaneously with time.
- Oscillator is moving faster at the center – spends least time near the center.
- Oscillators may have zero energy – not moving.

Quantum oscillator



uncertainty principle????

A quantum oscillator is supposed to behave very differently:

Lowest energy state of a quantum oscillator can not be zero

x is well defined; p_X is also well defined = 0

Vibration in diatomic molecules

- We can use the concept of quantum mechanical oscillator.
- Need to solve Schröndinger Equation – simple system could be 1D.
- Hamiltonian for 1D harmonic oscillator:

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

Energy eigen value equation:

$$\hat{H}\psi = \mathrm{E}\,\psi \Rightarrow (\hat{H} - E)\psi = 0$$

Quantum Harmonic Oscillator

Aim:

1. Energy eigen value of quantum harmonic oscillator.

Solution of this differential equation is not so easy – need to adopt polynomial method.

Solution of the differential equation can be represented in terms of Hermite Polynomials:

$$\psi_v(x) = N_v \, H_V \, (y) \, e^{-y^2/2}$$

Normalization constant (N_v)

Hermite Polynomials (H_V)

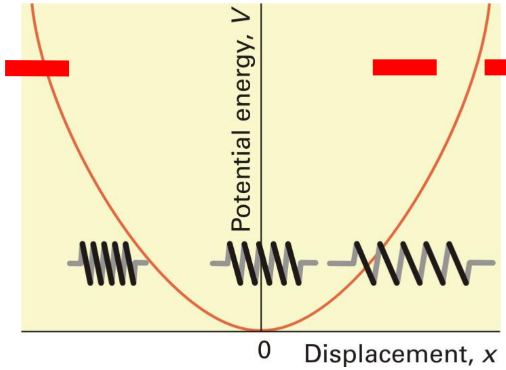
Gaussian Function ($e^{-y^2/2}$)

$$y = \frac{x}{\alpha}$$

$$\alpha = \left(\frac{\hbar^2}{mk_f}\right)^{1/4}$$

Energy states of Quantum Oscillator

-∞ ← — — — — — — → +∞



Solve the Schrodinger equation and apply the boundary conditions ($\psi \to 0$ as $x \to \pm\infty$) to get:

$$E_v = \left(v + \frac{1}{2}\right) h\nu, v = 0, 1, 2, \ldots \, (\textit{vibrational quantum number})$$

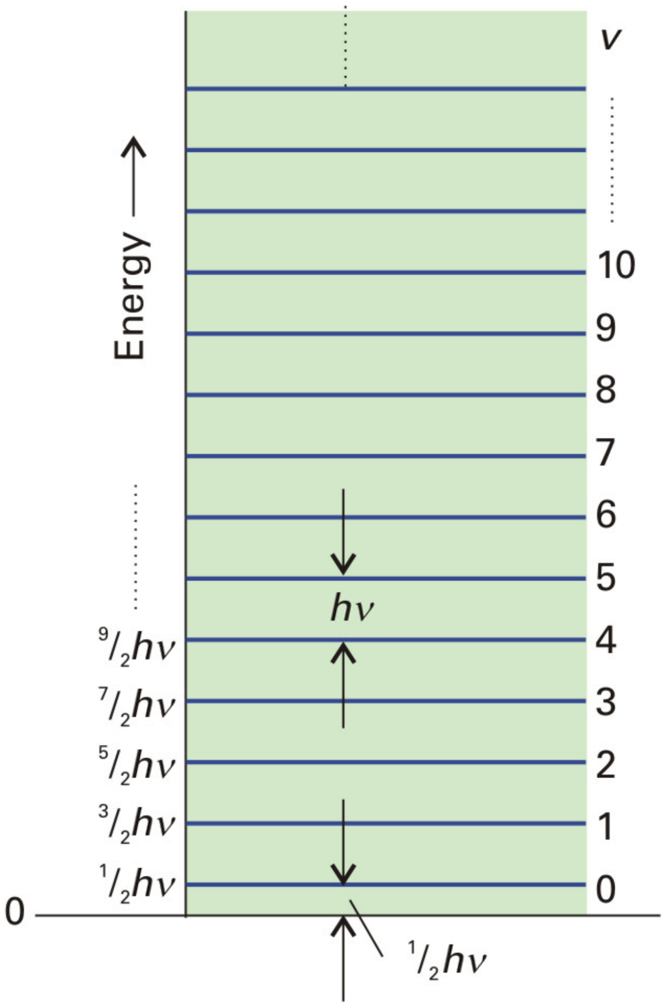
Ground state: v = 0, $E_0 = \frac{1}{2} h\nu = \frac{1}{2} \hbar\omega$

$$\boxed{\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}}$$

Zero point energy

Energy states of Quantum Oscillator

innovate achieve lead



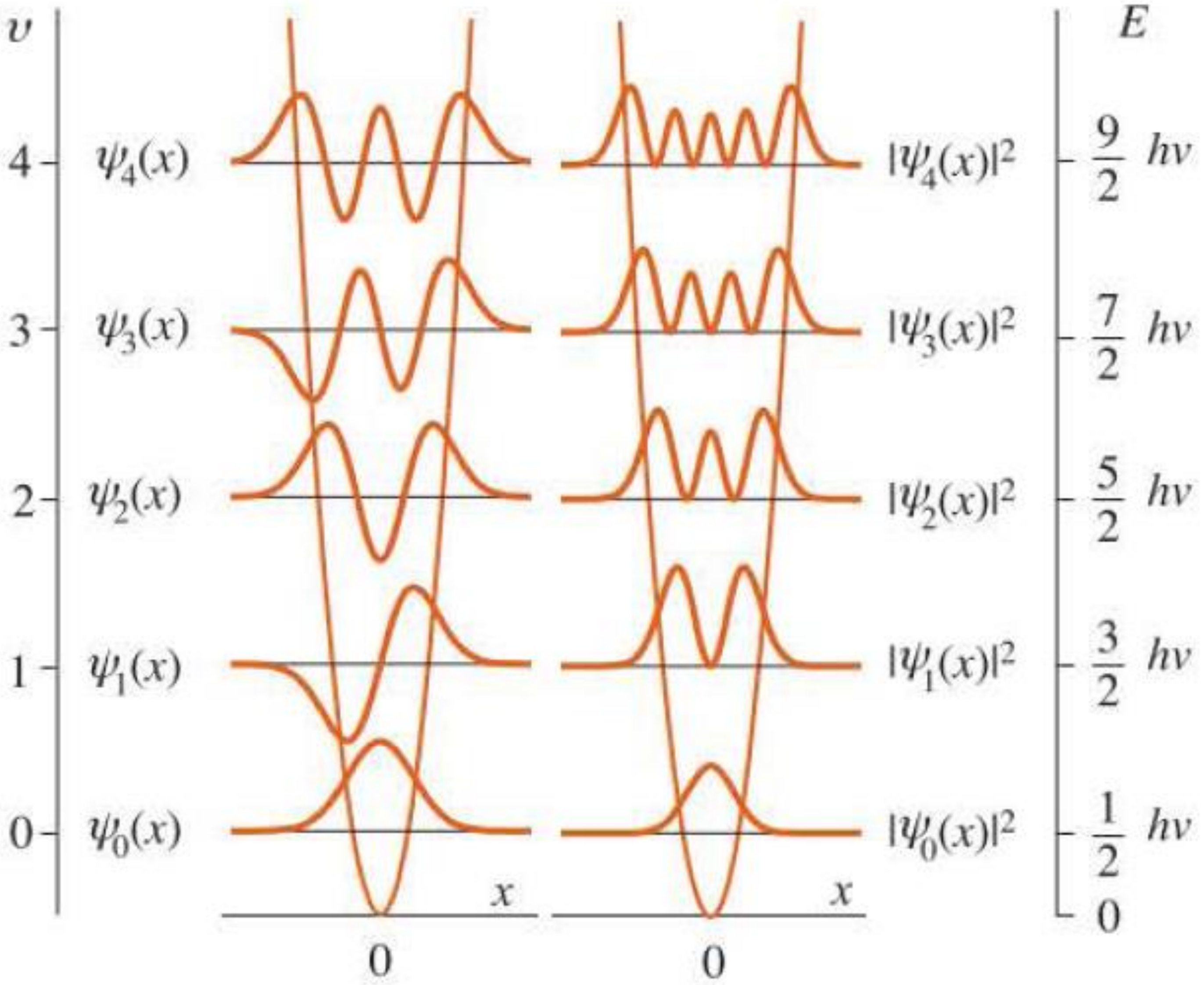
Vibrational spectroscopy

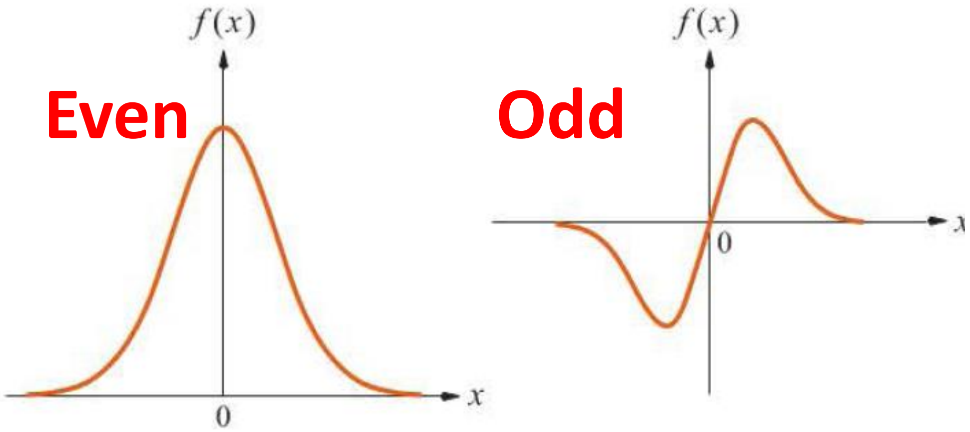
- Evenly spaced energy levels.
- Spacing = hν
- Ground state energy = ½ hν

(Zero point energy)

Work out: Calculate zero point energy of a harmonic oscillator consisting of a particle of mass 2.33×10^{-26} kg and force constant 155 N m^{-1}.

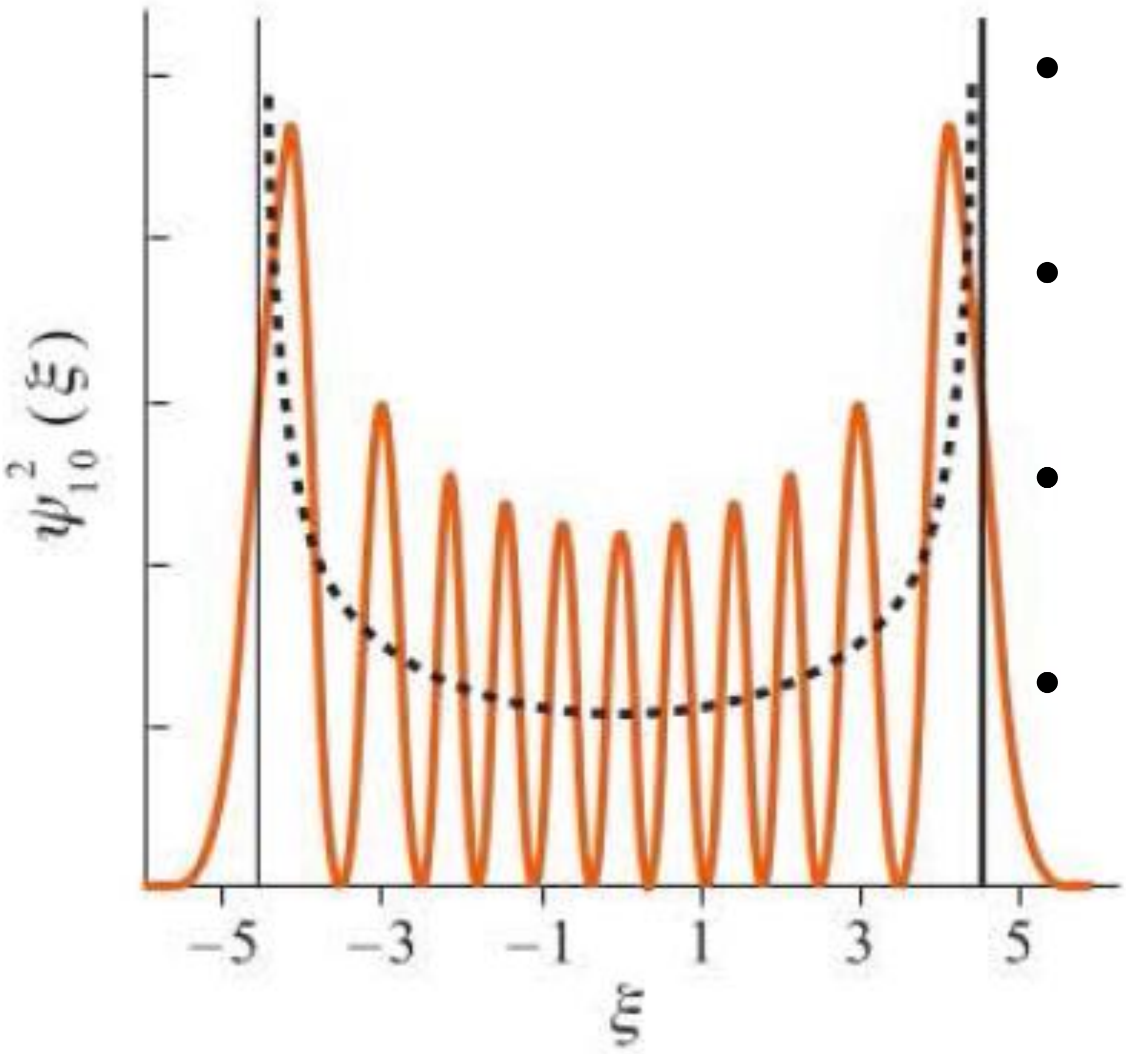
Quantum Harmonic Oscillator





- Number of nodes is v
- Wavefunctions are alternately symmetric or antisymmetric about x = 0.

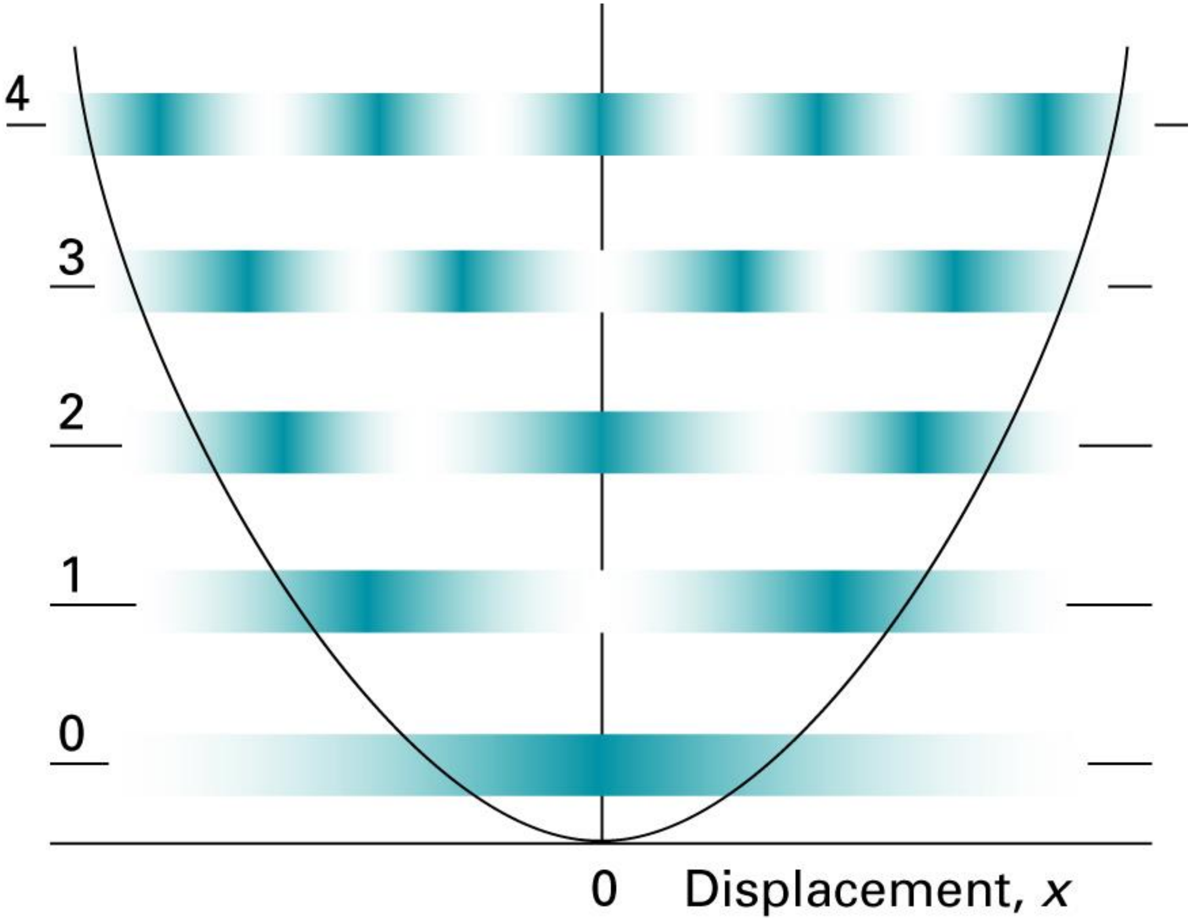
Classical limit



- Probability distribution associated with ψ_{10} (x) to the classical distribution.
- Probability of finding the particle at the center of the potential well is less.
- Probability of finding the particle near the turning points increases.
- Probability distribution moves towards the classical limit.

Characteristics

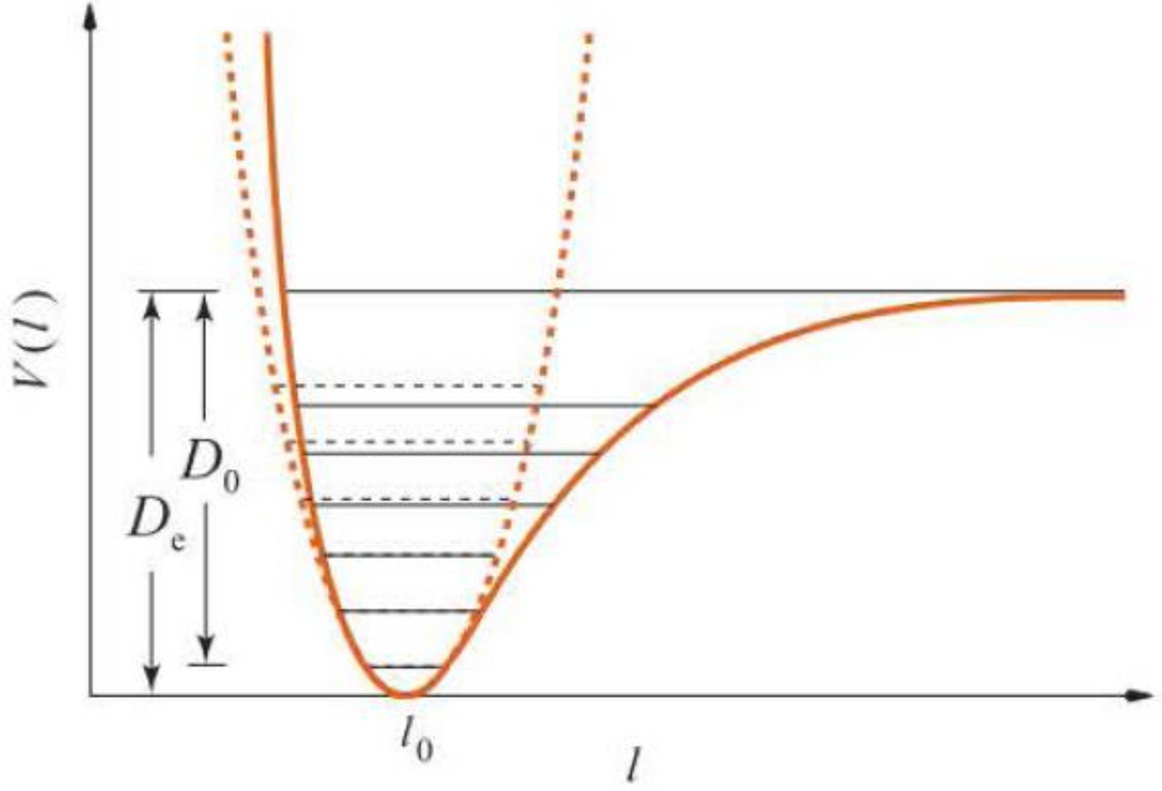
The wavefunction leaks into the classically forbidden region – TUNNELING.

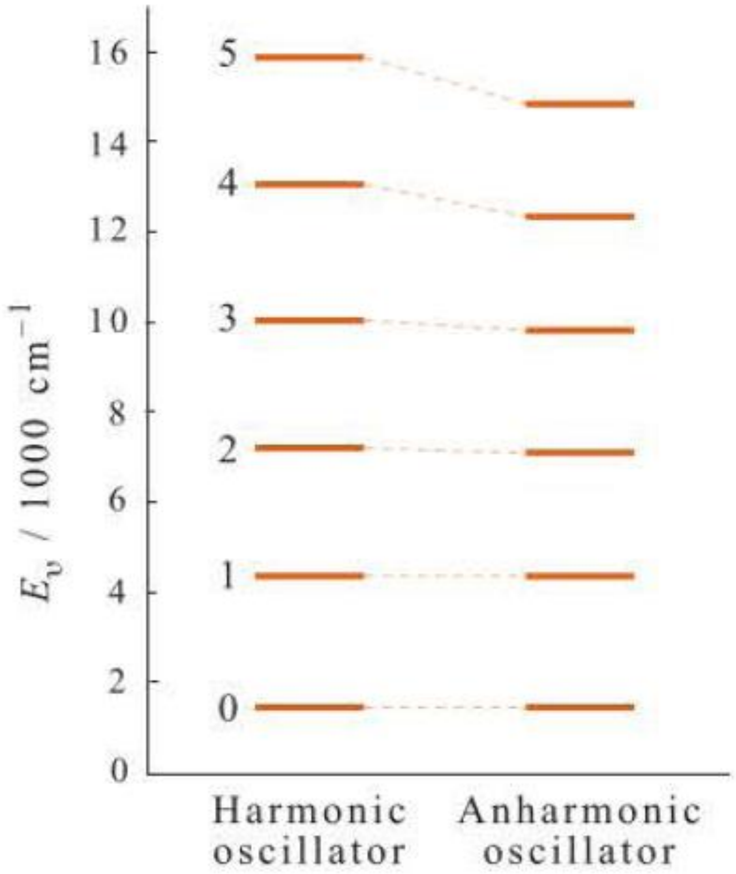


Anharmonicity

Molecular vibrations are really harmonic?

Chemical reactions??





Interested in equilibrium geometry

We have discussed..........

- Schröndinger Equation
- Free particle in one dimension
- Particle in one dimensional box
- Particle in two dimensional box
- Particle on a ring
- Quantum mechanical oscillator

World is not about one dimension

Three dimensional problem

Hamiltonian in 3-D

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(x, y, z)$$

$$= -\frac{\hbar^2}{2m}\nabla^2 + V(x, y, z)$$

∇^2 is known as Laplacian operator

Aim:

- Rotation in three dimension – very close to H-atom problem.
- Simple system would be a rigid rotor

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2$$

Read: *The separation of variable procedure {Further information 12.1 of Text Book};