

## Chapter 4

### The Harmonic Oscillator

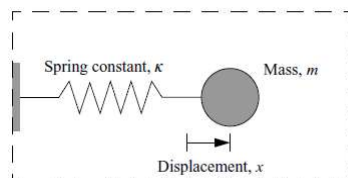


### The one-dimensional harmonic oscillator



- Classical-Mechanical Treatment
- Quantum-Mechanical Treatment

## The one-dimensional harmonic oscillator: Classical treatment



Closed system with no exchange of energy outside the system implies conservation of energy.

Illustration showing a classical particle mass  $m$  attached to a spring and constrained to move in one dimension. The displacement of the particle from its equilibrium position is  $x$ . The box drawn with a broken line indicates a closed system.

## The one-dimensional harmonic oscillator: Classical treatment



$$F = ma$$

$$F_x = -kx$$

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

$$c = (k/m)^{1/2}$$

$$x = A \sin(2\pi\nu t + b)$$

$$\nu = \frac{1}{2\pi} \left( \frac{k}{m} \right)^{1/2}$$

$$y''(x) + c^2 y(x) = 0$$

$$y = A \cos cx + B \sin cx$$

$$y = D \sin(cx + e)$$

## The one-dimensional harmonic oscillator: Classical treatment



$$F_x = -\frac{\partial V}{\partial x}, \quad F_y = -\frac{\partial V}{\partial y}, \quad F_z = -\frac{\partial V}{\partial z}$$

$$F_x = -\frac{dV}{dx} = -kx$$

$$V = \int kx dx = \frac{1}{2}kx^2 + C$$

$$V = \frac{1}{2}kx^2 \quad C = 0$$

$$V = 2\pi^2\nu^2 mx^2$$

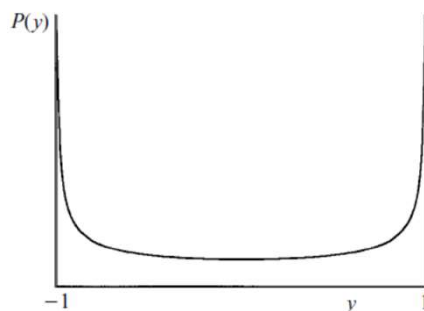
$$T = \frac{1}{2}m(dx/dt)^2$$

$$E = T + V = \frac{1}{2}kA^2 = 2\pi^2\nu^2 mA^2$$

$$x = A \sin(2\pi\nu t + b)$$

$$\frac{dx}{dt} = A \times 2\pi\nu \cos(2\pi\nu t + b)$$

## The one-dimensional harmonic oscillator: Classical treatment



Classical probability density for an oscillating particle.

## The one-dimensional harmonic oscillator: Quantum treatment



Hamiltonian function

$$H(x, p) = \frac{p^2}{2m} + V(x) = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$$

Hamiltonian operator

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + 2\pi^2\nu^2 m x^2 = -\frac{\hbar^2}{2m} \left( \frac{d^2}{dx^2} - \alpha^2 x^2 \right)$$

$$\alpha \equiv 2\pi\nu m / \hbar$$

$$\frac{d^2\psi}{dx^2} + (2mE\hbar^{-2} - \alpha^2 x^2)\psi = 0$$

There are **two procedures** available for solving this differential equation.

**1) The Frobenius or series solution method**

**2) The ladder operator procedure**

## The one-dimensional harmonic oscillator: Quantum treatment



**1) The Frobenius or series solution method**

A substitution that simplify the procedure is:

$$\psi = e^{-\alpha x^2/2} f(x)$$

$$\psi'' = e^{-\alpha x^2/2} (f'' - 2\alpha x f' - \alpha f + \alpha^2 x^2 f)$$

$$\frac{d^2\psi}{dx^2} + (2mE\hbar^{-2} - \alpha^2 x^2)\psi = 0$$



$$f''(x) - 2\alpha x f'(x) + (2mE\hbar^{-2} - \alpha)f(x) = 0$$

## The one-dimensional harmonic oscillator: Quantum treatment



$$f(x) = \sum_{n=0}^{\infty} c_n x^n$$

$$f'(x) = \sum_{n=1}^{\infty} n c_n x^{n-1} = \sum_{n=0}^{\infty} n c_n x^{n-1}$$

$$f''(x) = \sum_{n=2}^{\infty} n(n-1) c_n x^{n-2}$$

$$= \sum_{j=0}^{\infty} (j+2)(j+1) c_{j+2} x^j = \sum_{n=0}^{\infty} (n+2)(n+1) c_{n+2} x^n$$

$$f''(x) - 2\alpha x f'(x) + (2mE\hbar^{-2} - \alpha) f(x) = 0$$

## The one-dimensional harmonic oscillator: Quantum treatment



$$\sum_{n=0}^{\infty} (n+2)(n+1) c_{n+2} x^n - 2\alpha \sum_{n=0}^{\infty} n c_n x^n + (2mE\hbar^{-2} - \alpha) \sum_{n=0}^{\infty} c_n x^n = 0$$

$$\sum_{n=0}^{\infty} [(n+2)(n+1) c_{n+2} - 2\alpha n c_n + (2mE\hbar^{-2} - \alpha) c_n] x^n = 0$$

$$(n+2)(n+1) c_{n+2} - 2\alpha n c_n + (2mE\hbar^{-2} - \alpha) c_n = 0$$

$$c_{n+2} = \frac{\alpha + 2\alpha n - 2mE\hbar^{-2}}{(n+1)(n+2)} c_n$$

Two term recursion relation.  
Thus, there is two arbitrary constants:  $c_0$  and  $c_1$

## The one-dimensional harmonic oscillator: Quantum treatment



If  $c_1 = 0$

$$\psi = e^{-\alpha x^2/2} f(x) = e^{-\alpha x^2/2} \sum_{n=0,2,4,\dots}^{\infty} c_n x^n = e^{-\alpha x^2/2} \sum_{l=0}^{\infty} c_{2l} x^{2l}$$

If  $c_0 = 0$

$$\psi = e^{-\alpha x^2/2} \sum_{n=1,3,\dots}^{\infty} c_n x^n = e^{-\alpha x^2/2} \sum_{l=0}^{\infty} c_{2l+1} x^{2l+1}$$

The general solution:

$$\psi = A e^{-\alpha x^2/2} \sum_{l=0}^{\infty} c_{2l+1} x^{2l+1} + B e^{-\alpha x^2/2} \sum_{l=0}^{\infty} c_{2l} x^{2l}$$

## The one-dimensional harmonic oscillator: Quantum treatment



We now must see if the boundary conditions on the wave function lead to any restrictions on the solution.

How the two infinite series behave for large  $x$ :

$$c_{n+2} = \frac{\alpha + 2\alpha n - 2mE\hbar^{-2}}{(n+1)(n+2)} c_n$$

$$n = 2l$$

$$\frac{c_{2l+2}}{c_{2l}} = \frac{\alpha + 4\alpha l - 2mE\hbar^{-2}}{(2l+1)(2l+2)}$$

## The one-dimensional harmonic oscillator: Quantum treatment



Assuming that for large values of  $x$  the later terms are the dominant ones:

$$\frac{c_{2l+2}}{c_{2l}} \sim \frac{4\alpha l}{(2l)(2l)} = \frac{\alpha}{l}$$

For  $n = 2l + 1$

$$\frac{c_{2l+3}}{c_{2l+1}} \approx \frac{\alpha}{l}$$

## The one-dimensional harmonic oscillator: Quantum treatment



$$e^z = \sum_{n=0}^{\infty} \frac{z^n}{n!} = 1 + z + \frac{z^2}{2!} + \dots$$

$$e^{\alpha x^2} = 1 + \alpha x^2 + \dots + \frac{\alpha^l x^{2l}}{l!} + \frac{\alpha^{l+1} x^{2l+2}}{(l+1)!} + \dots$$

$$\frac{\alpha^{l+1}}{(l+1)!} \div \frac{\alpha^l}{l!} = \frac{\alpha}{l+1} \sim \frac{\alpha}{l} \quad \text{For large } l$$

## The one-dimensional harmonic oscillator: Quantum treatment



For large x:

Each series goes as  $e^{ax^2} \longrightarrow \Psi$  goes as  $e^{ax^2/2}$

If we could somehow break off the series after a finite number of terms, then the factor  $e^{-ax^2/2}$  would ensure that  $\psi$  went to zero as x became infinite.

How?

If the coefficient for  $c_v$  ( $n=v$ ) become zero, then  $c_{v+2}, c_{v+4}, \dots$  vanishes

$$c_{n+2} = \frac{\alpha + 2\alpha n - 2mE\hbar^{-2}}{(n+1)(n+2)} c_n$$

## The one-dimensional harmonic oscillator: Quantum treatment



$$n=v \quad \alpha + 2\alpha v - 2mE\hbar^{-2} = 0$$

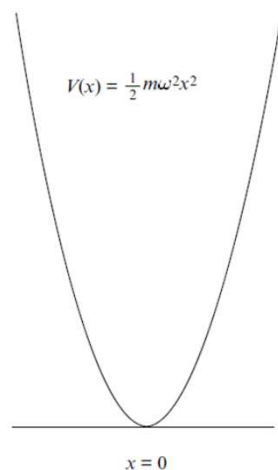
$$2mE\hbar^{-2} = (2v+1)2\pi\nu m\hbar^{-1}$$

$$E = (v + \frac{1}{2})h\nu, \quad v = 0, 1, 2, \dots$$

$$E_n = (n + \frac{1}{2})\hbar\omega, \quad \text{with } n = 0, 1, 2, 3, \dots$$



## The one-dimensional harmonic oscillator: Quantum treatment



$$E_3 = \frac{7}{2} \hbar \omega$$

$$E_2 = \frac{5}{2} \hbar \omega$$

$$E_1 = \frac{3}{2} \hbar \omega$$

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

Zero point energy  $\neq 0$

## The one-dimensional harmonic oscillator: Quantum treatment



$$c_{n+2} = \frac{\alpha + 2\alpha n - 2mE\hbar^{-2}}{(n+1)(n+2)} c_n$$



$$E = (v + \frac{1}{2}) \hbar \nu$$

$$c_{n+2} = \frac{2\alpha(n-v)}{(n+1)(n+2)} c_n$$

$$\psi_v = \begin{cases} e^{-\alpha x^2/2} (c_0 + c_2 x^2 + \dots + c_v x^v) \\ e^{-\alpha x^2/2} (c_1 x + c_3 x^3 + \dots + c_v x^v) \end{cases}$$

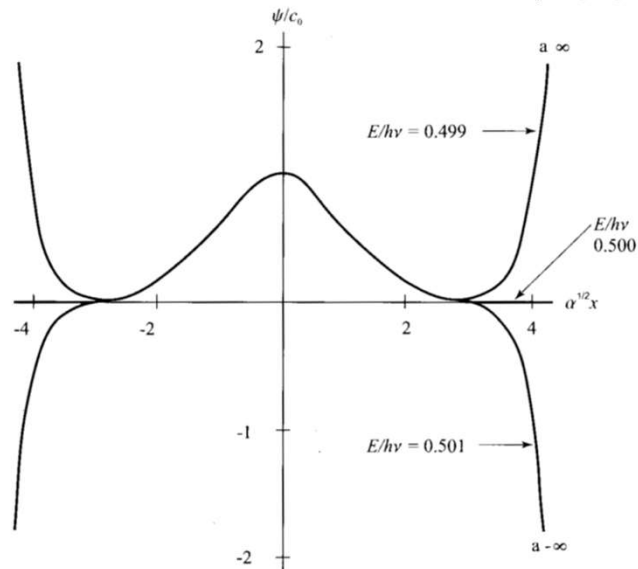
For values of E that differ from above mentioned equation,  $\psi$  is not quadratically integrable

### The one-dimensional harmonic oscillator: Quantum treatment

$$\psi = e^{-\alpha x^2/2} \sum_{l=0}^{\infty} c_{2l} x^{2l}$$



In the region around  $x = 0$ , the three curves nearly coincide. For  $|\alpha^{1/2}x| > 3$ , the  $E/h\nu = 0.500$  curve nearly coincides with the  $x$  axis.



### The one-dimensional harmonic oscillator: Quantum treatment



why is  $E_0 \neq 0$  ?

## Even and odd functions



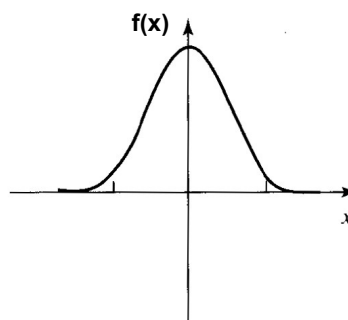
### Even functions:

**Definition:**  $f(-x) = f(x)$

**Example:**  $x^2$ ,  $e^{-bx^2}$

$$(-x)^2 = x^2$$

$$e^{-b(-x)^2} = e^{-bx^2}$$



$$\int_{-a}^{+a} f(x) dx = 2 \int_0^a f(x) dx$$

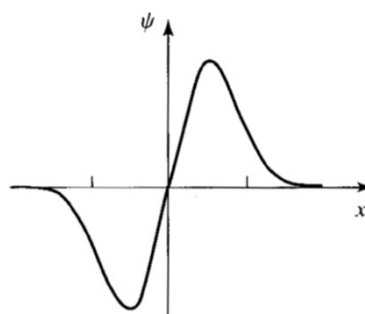
## Even and odd functions



### Odd functions:

**Definition:**  $g(-x) = -g(x)$

**Example:**  $x$ ,  $1/x$ ,  $xe^{x^2}$ .



$$\int_{-a}^{+a} g(x) dx = 0$$

## The Harmonic-Oscillator Wave Functions



$$\psi_v = \begin{cases} \overset{\text{even}}{e^{-\alpha x^2/2}} \overset{\text{even}}{(c_0 + c_2 x^2 + \dots + c_v x^v)} \longrightarrow \text{even} \\ \overset{\text{even}}{e^{-\alpha x^2/2}} \overset{\text{odd}}{(c_1 x + c_3 x^3 + \dots + c_v x^v)} \longrightarrow \text{odd} \end{cases}$$

$$\psi_0 = c_0 e^{-\alpha x^2/2} \quad \text{even}$$

**Normalization:**  $1 = \int_{-\infty}^{\infty} |c_0|^2 e^{-\alpha x^2} dx = 2|c_0|^2 \int_0^{\infty} e^{-\alpha x^2} dx$

$$\psi_0 = (\alpha/\pi)^{1/4} e^{-\alpha x^2/2}$$

Exercise: complete the normalization of  $\psi_0$  wave function.

## The Harmonic-Oscillator Wave Functions



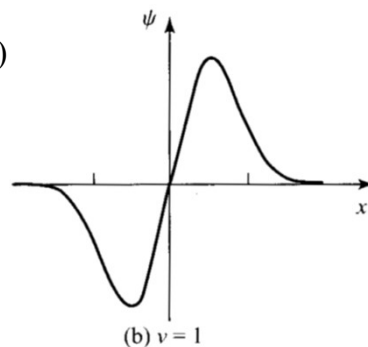
$$\psi_v = e^{-\alpha x^2/2} (c_1 x + c_3 x^3 + \dots + c_v x^v)$$

$$\downarrow$$

$$\psi_1 = c_1 x e^{-\alpha x^2/2}$$

$$\downarrow \text{normalization}$$

$$\psi_1 = (4\alpha^3/\pi)^{1/4} x e^{-\alpha x^2/2}$$



## The Harmonic-Oscillator Wave Functions

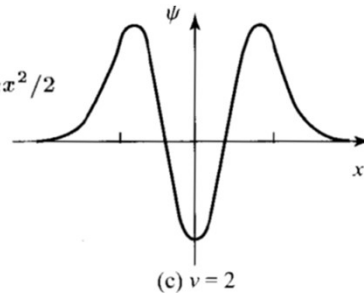


$$\psi_v = e^{-\alpha x^2/2} (c_0 + c_2 x^2 + \dots + c_v x^v) \quad c_{n+2} = \frac{2\alpha(n-v)}{(n+1)(n+2)} c_n$$

$$\psi_2 = (c_0 + c_2 x^2) e^{-\alpha x^2/2} \quad c_2 = \frac{2\alpha(-2)}{1 \cdot 2} c_0 = -2\alpha c_0$$

$$\psi_2 = c_0 (1 - 2\alpha x^2) e^{-\alpha x^2/2}$$

$$\psi_2 = (\alpha/4\pi)^{1/4} (2\alpha x^2 - 1) e^{-\alpha x^2/2}$$



## The one-dimensional harmonic oscillator: Quantum treatment



### 2) The ladder operator procedure

$$\psi_v(x) = (2^v v!)^{-1/2} \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} H_v(\alpha^{1/2} x)$$

$$H_n(z) = (-1)^n e^{z^2} \frac{d^n e^{-z^2}}{dz^n}$$

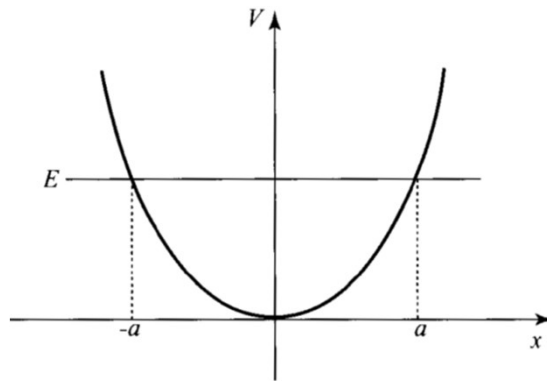
$$z H_n(z) = n H_{n-1}(z) + \frac{1}{2} H_{n+1}(z)$$

**Example:**

Obtain the the Hermite polynomials for  $n=0$  to  $n=10$ , and normalized  $\psi_1$  to  $\psi_5$

$$H_0 = 1, \quad H_1 = 2z, \quad H_2 = 4z^2 - 2, \quad H_3 = 8z^3 - 12z$$

## The Harmonic-Oscillator Wave Functions



Classically:

$$E = T + V$$

$$T \geq 0$$

$$E - V = T \geq 0$$

$$E \geq V$$

The classically allowed ( $-a \leq x \leq a$ ) and forbidden ( $x < -a$  and  $x > a$ ) regions for the harmonic oscillator.

## The Harmonic-Oscillator Wave Functions



In quantum mechanics:

$$\hat{T}\Psi \neq \text{cte}\Psi$$

$$\hat{V}\Psi \neq \text{cte}\Psi$$

Stationary state wave functions

We can not assign definite values to T and V

Classical equations:  $E = T + V$  and  $V \geq 0$

Quantum mechanics:  $E = \langle T \rangle + \langle V \rangle$  and  $\langle V \rangle \geq 0$

So, in quantum mechanics  $\langle V \rangle \leq E$ , but we can not write  $V \leq E$

A particle has some probability to be found in classically forbidden regions where  $V > E$

## The Harmonic-Oscillator Wave Functions



For a harmonic oscillator stationary state

$$E = (v + \frac{1}{2})h\nu$$

$$V = \frac{1}{2}kx^2 = 2\pi^2\nu^2mx^2$$

$$V \leq E$$

$$2\pi^2\nu^2mx^2 \leq (v + \frac{1}{2})h\nu$$

$$x^2 \leq (v + \frac{1}{2})h/2\pi^2\nu m = (2v + 1)/\alpha, \quad \alpha \equiv 2\pi\nu m/\hbar$$

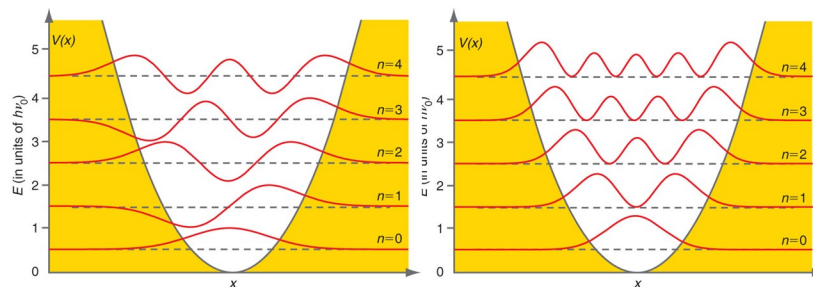
$$-(2v + 1)^{1/2} \leq \alpha^{1/2}x \leq (2v + 1)^{1/2}$$

## The Harmonic-Oscillator Wave Functions

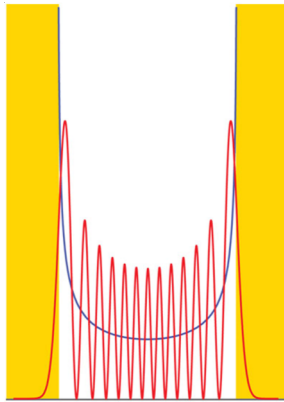


There are 2 different phenomenon to classical H.O

- 1) energy of ground state is not zero : ZPE
- 2) particle can be found in the classical forbidden region



## The Harmonic-Oscillator Wave Functions



Probability density of 12<sup>th</sup> state of H.O

## The Harmonic-Oscillator Wave Functions



As we go to higher energy states  $\psi$ ,  $|\psi|^2$  tend to have maxima farther from origin

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

$$\langle V \rangle = \int_{-\infty}^{\infty} |\psi|^2 V dx$$

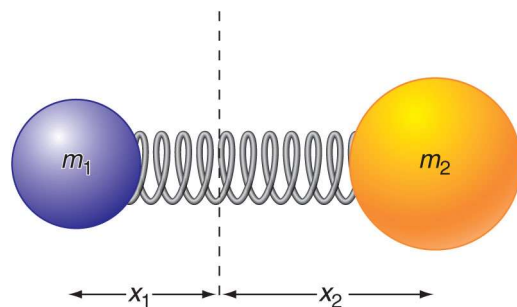
$$\langle T \rangle = -(\hbar^2/2m) \int_{-\infty}^{\infty} \psi^* \psi'' dx$$

↓ Integration by parts

$$\langle T \rangle = (\hbar^2/2m) \int_{-\infty}^{\infty} |d\psi/dx|^2 dx$$



## Vibration of molecules

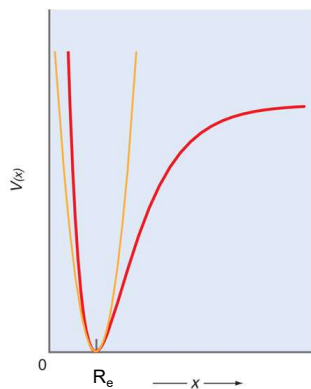


$$\mu = \frac{m_1 + m_2}{m_1 + m_2}$$

$$U = U(R)$$

Internal motion of diatomic molecule  $\equiv$  vibration + rotation

## Vibration of molecules



$$x \equiv R - R_e$$

$R_e \equiv$  equilibrium distance

$$k = d^2V/dx^2$$

$$k = d^2U/dR^2|_{R=R_e}$$

$$\nu_e = \frac{1}{2\pi} \left( \frac{k}{\mu} \right)^{1/2}, \quad \mu = \frac{m_1 m_2}{m_1 + m_2}, \quad k = \left. \frac{d^2U}{dR^2} \right|_{R=R_e}$$

Equilibrium vibrational frequency

## Vibration of molecules



$$E_{\text{vib}} = (v + \frac{1}{2})h\nu_e - (v + \frac{1}{2})^2 h\nu_e x_e$$

Unharmonicity constant  $\equiv \nu_e x_e > 0$

Selection rule  $\Delta v = 1$

For absorption or emission of electromagnetic radiation to occur, the vibration must change the molecule's dipole moment.

$$\begin{aligned} \nu_{\text{light}} &= (E_2 - E_1)/h \approx [(v_2 + \frac{1}{2})h\nu_e - (v_1 + \frac{1}{2})h\nu_e]/h \\ &= (v_2 - v_1)\nu_e = \nu_e \end{aligned}$$

$\Delta v = 2, 3, \dots$  **overtones**, much weaker than  $\Delta v = 1$

## Vibration of molecules



$$\nu_{\text{light}} = \nu_e - 2\nu_e x_e (v_1 + 1)$$

$$\frac{N_i}{N_j} = \frac{g_i}{g_j} e^{-(E_i - E_j)/kT} \quad \text{Boltzmann distribution law}$$

$E_i$  and  $E_j$  are the energies of levels  $i$  and  $j$ ,  $g_i$  and  $g_j$  are the degeneracies of levels  $i$  and  $j$ ,  $N_i$  and  $N_j$  are the populations of levels  $i$  and  $j$ .

$g_i = 1$  for a nondegenerate level

$$v = 0 \rightarrow 1$$

$(v = 0 \rightarrow 2, 0 \rightarrow 3, \dots)$  Overton bands

$v = 1 \rightarrow 2, 2 \rightarrow 3$  Hot bands

## Vibration of molecules



$$\tilde{\nu} \equiv 1/\lambda = \nu/c$$

$$E_{\text{vib}} = \sum_i (v_i + \frac{1}{2}) h \nu_i$$

**For a polyatomic molecule**