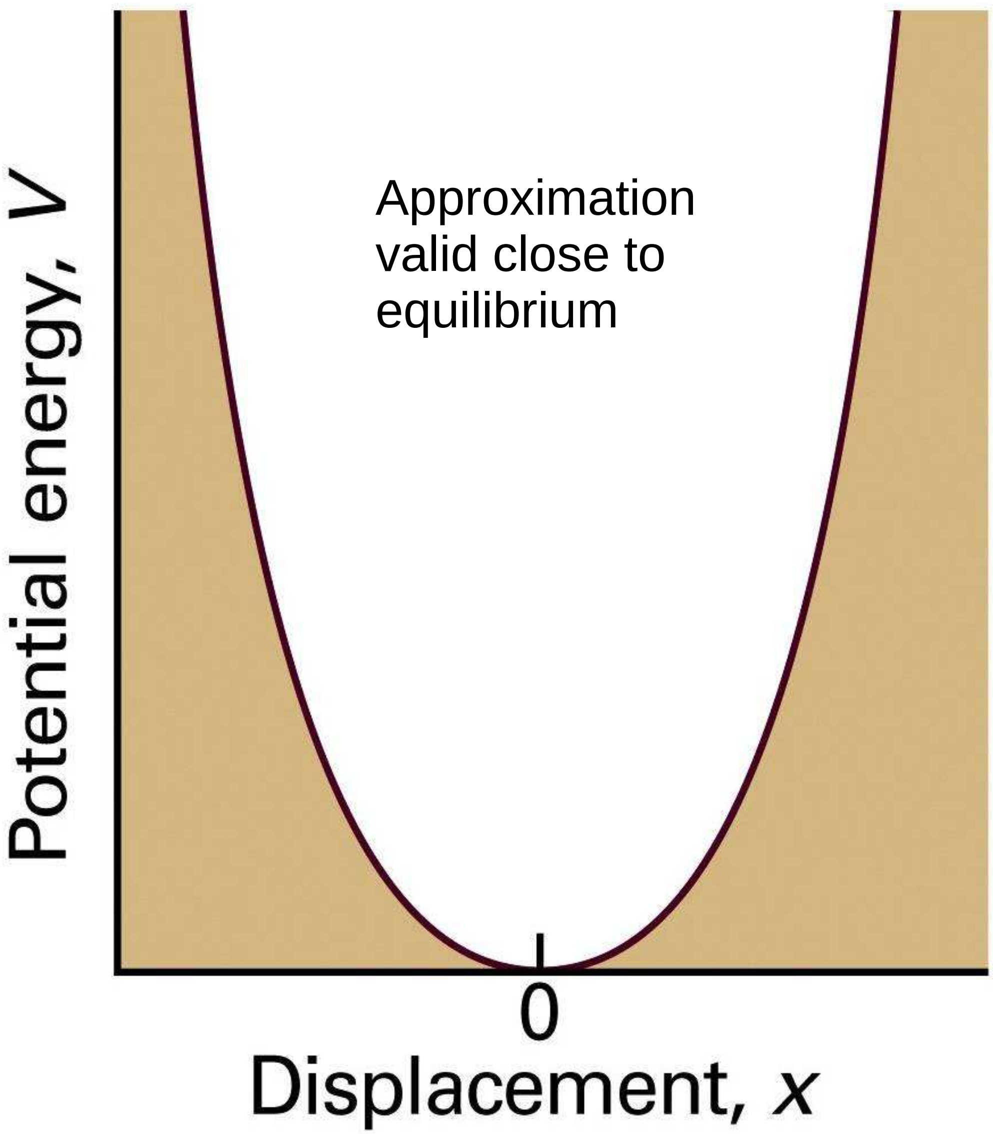
Vibration of a diatomic molecule - Harmonic oscillator



Approximation valid close to equilibrium

Figure 9-20
Atkins Physical Chemistry, Eighth Edition

Real molecule

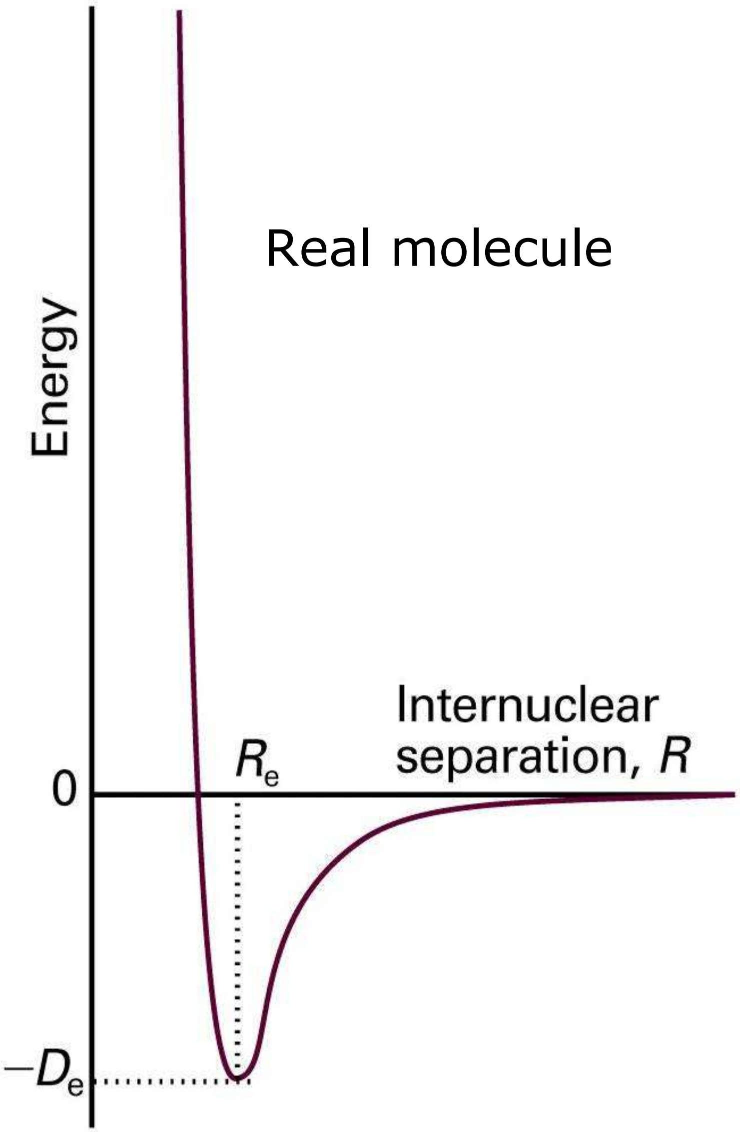


Figure 11-1
Atkins Physical Chemistry, Eighth Edition

Note Title 02-02-2011

$$\left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2\right)\psi = E\psi$$

1) $x \to \infty$ $\quad \psi \sim e^{-\alpha x^2/2}$ $\quad \alpha = \sqrt{\frac{\mu k}{\hbar^2}}$

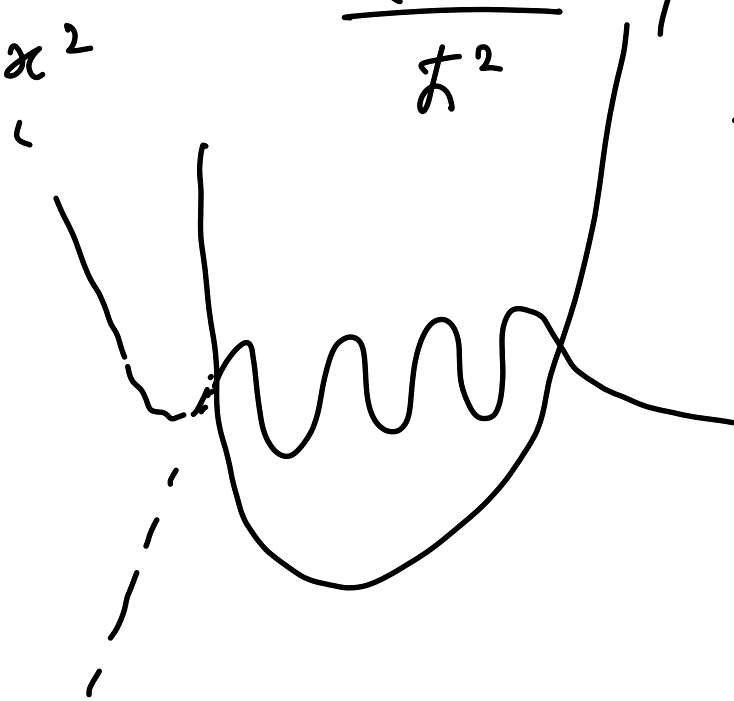
$\cancel{\alpha}$ $\frac{1}{L^2}$

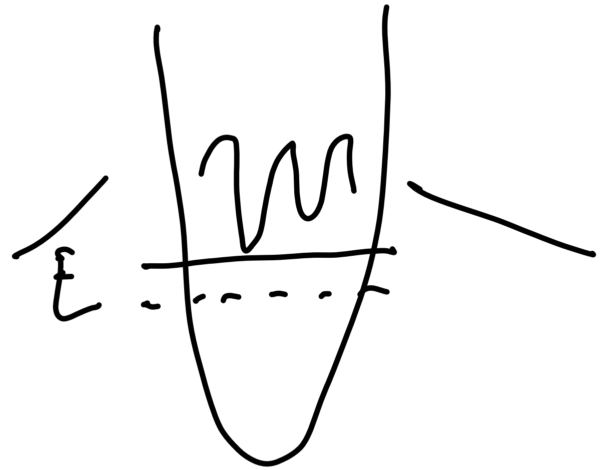
2) For all x

$$\psi = \underbrace{g(x)}_{\text{state - dependent}} \times e^{-\alpha x^2/2}$$

Note Title 02-02-2011

$$\frac{d^2\psi}{dx^2} = -\frac{2m(V-E)}{\hbar^2}\psi$$





$$E_v = \left(v + \tfrac{1}{2}\right)\hbar\omega$$

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

$v = 0, 1, 2, ---$

$v = 0$, ground state

Zero point energy

$$E = T + V$$

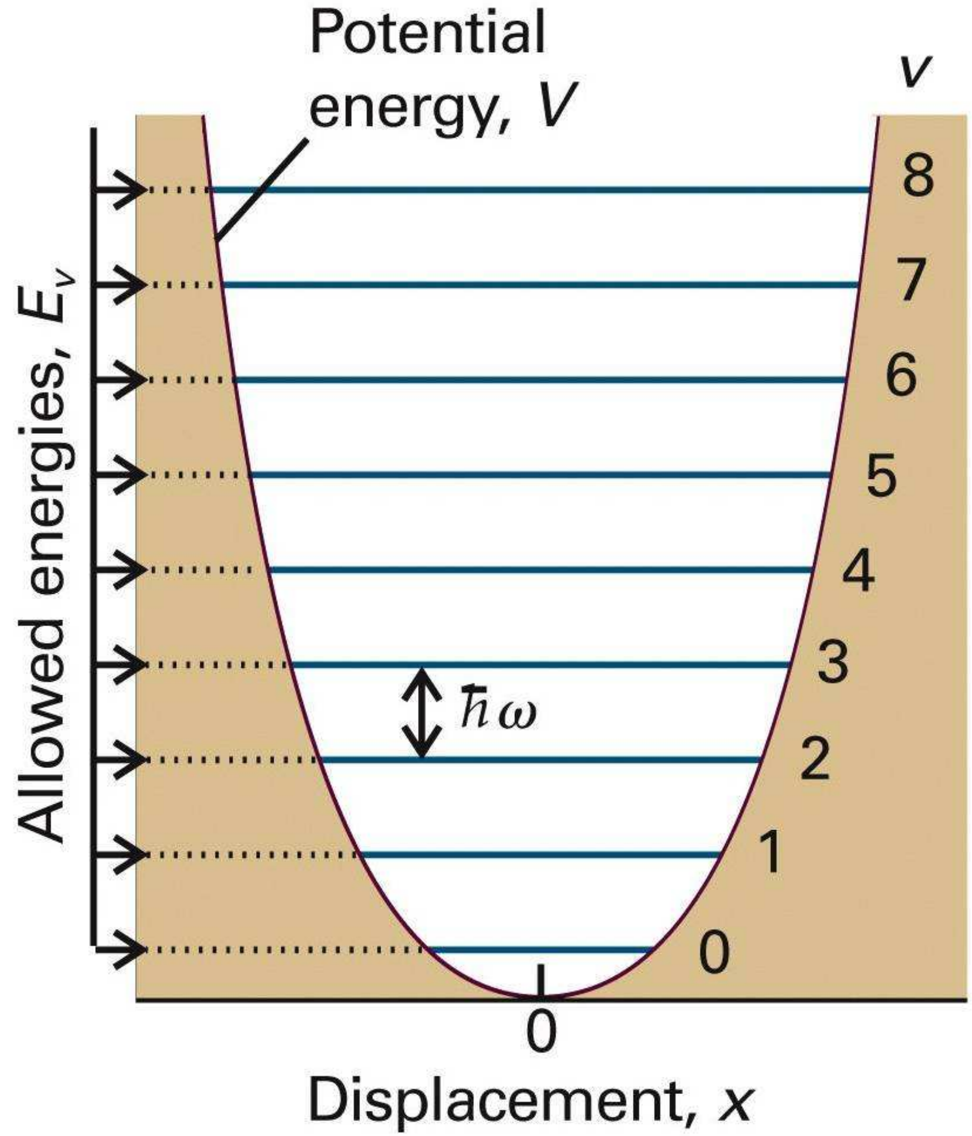


Figure 9-21
Atkins Physical Chemistry, Eighth Edition

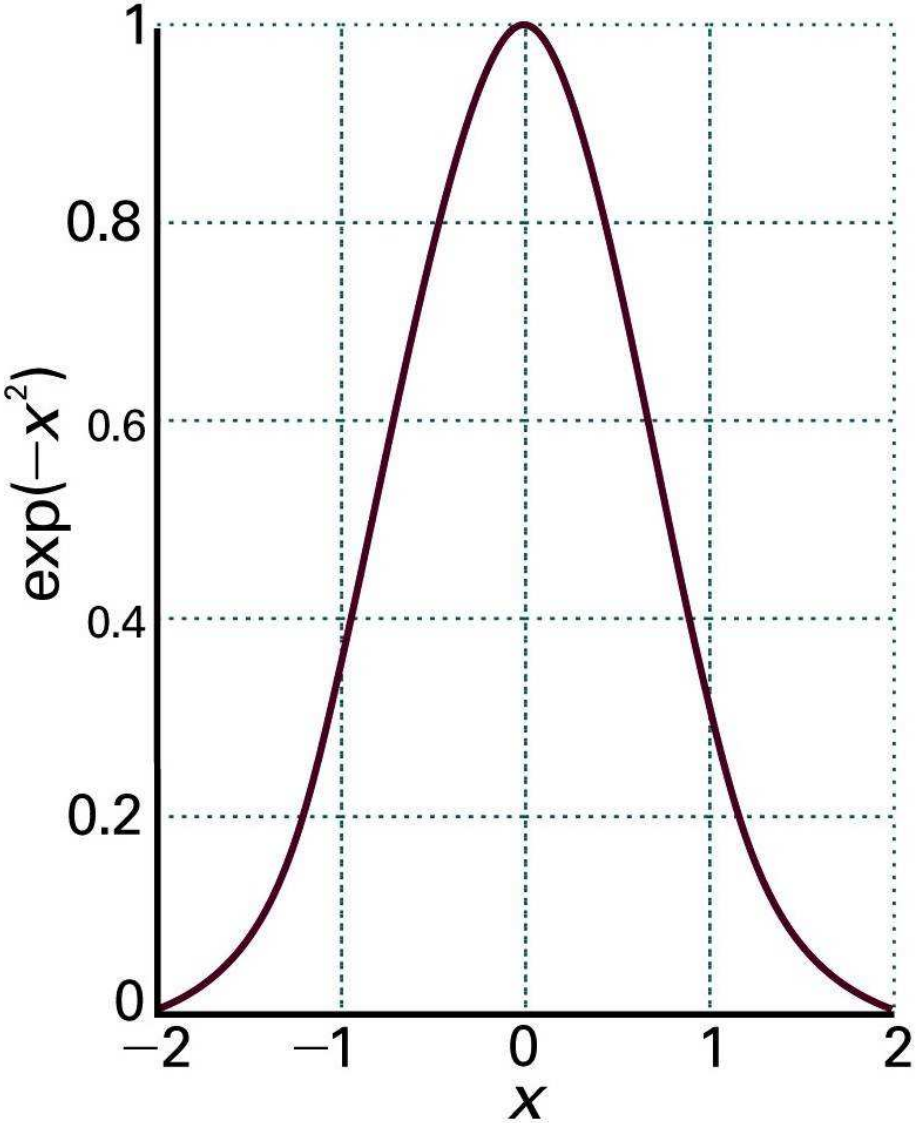


Figure 9-22
Atkins Physical Chemistry, Eighth Edition

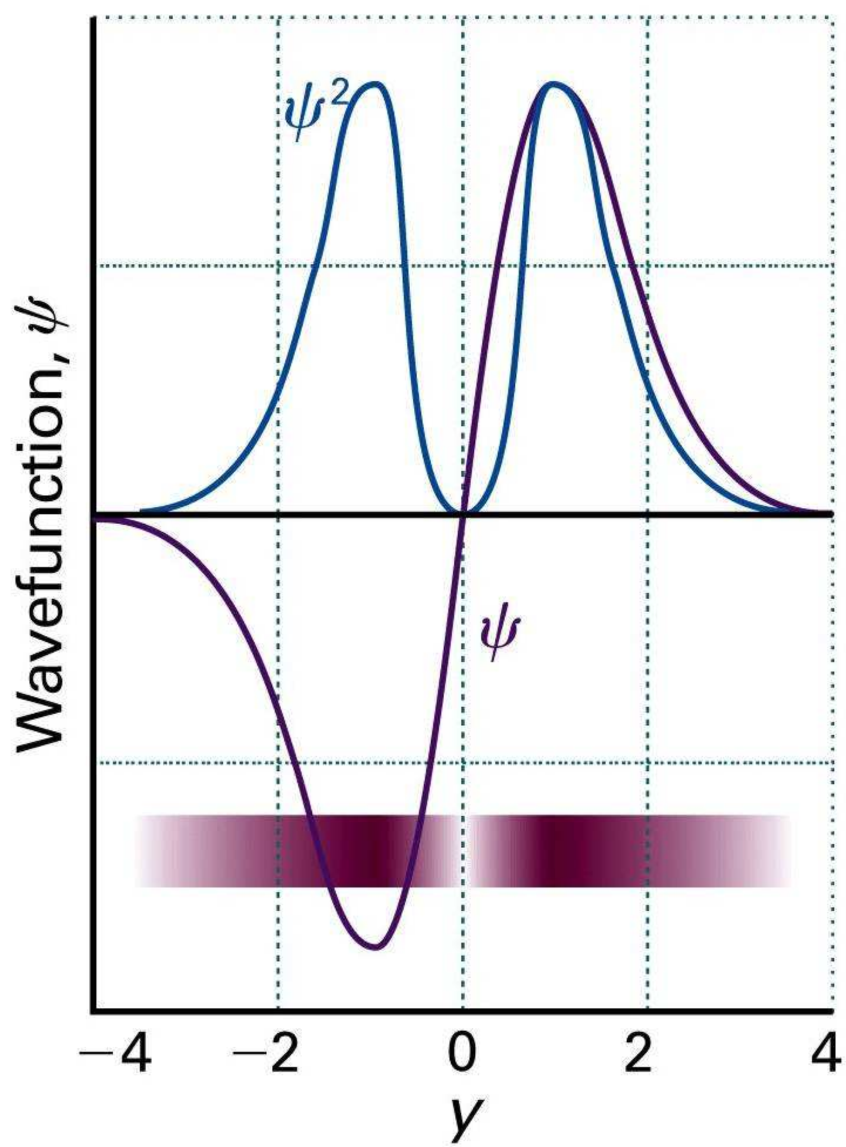


Figure 9-24
Atkins Physical Chemistry, Eighth Edition

$$\psi_v(x) = e^{-\alpha x^2/2} \times H_v(x)$$

$$H_0(x) = \underline{1}$$

$$H_1(x) = 2x \qquad ax^2 + b$$

$H_2(x) =$ quadratic (with no linear term)

$$H_3(x) = cx^3 - dx$$

Note Title

02-02-2011

Table 9.1 The Hermite polynomials $H_v(y)$

V	$H_1(y)$
0	1
1	$2y$
2	$4y^2 - 2$
3	$8y^3 - 12y$
4	$16y^4 - 48y^2 + 12$
5	$32y^5 - 160y^3 + 120y$
6	$64y^6 - 480y^4 + 720y^2 - 120$

$v = 0$, even

$v = 1$, odd

$v = 2$, even

$v = 3$, odd

Table 9-1
Atkins Physical Chemistry, Eighth Edition

Note Title 02-02-2011

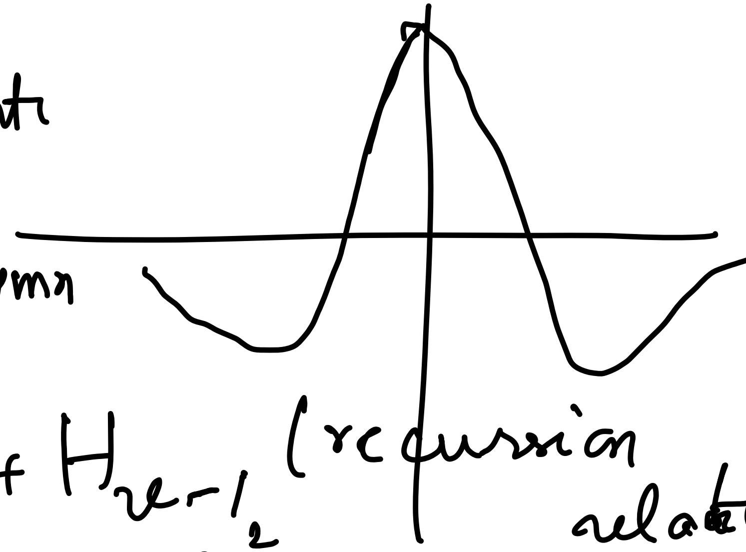
$$\Psi_v = e^{-\alpha x^2/2} (\text{even}) \times H_v(x)$$

$\Downarrow$ even / odd

g.S — no nodes — sym

1st excited — one node — anti

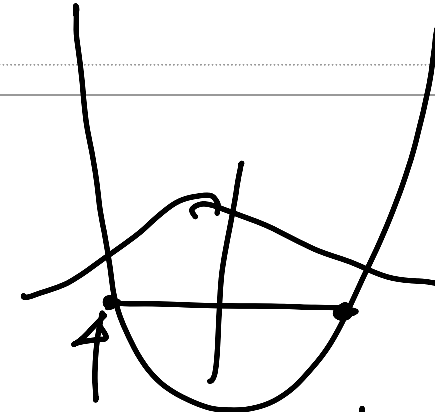
2nd — 2 nodes — Symm



$$2x H_v = H_{v+1} + H_{v-1} \quad \text{(recursion relation)}$$

$$H_v(x) = (-1)^n e^{+x^2} \frac{d^n}{dx^n} e^{-x^2}$$

$$\langle p_x \rangle =$$



classical turning point

For a h.o. in the g.s, write the expression for the prob of finding it in the classically forbidden region.

$$E_0 = \frac{\hbar\omega}{2} = \frac{1}{2} k x^2$$

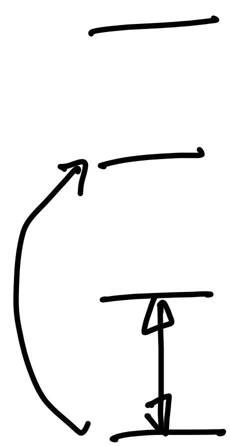
$$\text{Prob} = \frac{2\int_{x_{tp}}^{\infty} e^{-\alpha x^2}\,dx}{\int_{-\infty}^{\infty} e^{-\alpha x^2}\,dx}$$

$$\int \psi_v^* \, \psi_v \, d\tau = 1 \qquad N_v = \frac{1}{\sqrt{2^v v!}} \left(\frac{\alpha}{\pi}\right)^{1/4}$$

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

$\mathrm{Ti}\,{}^{16}\mathrm{O} \rightarrow$

$\mathrm{Ti}\,{}^{18}\mathrm{O} \rightarrow$

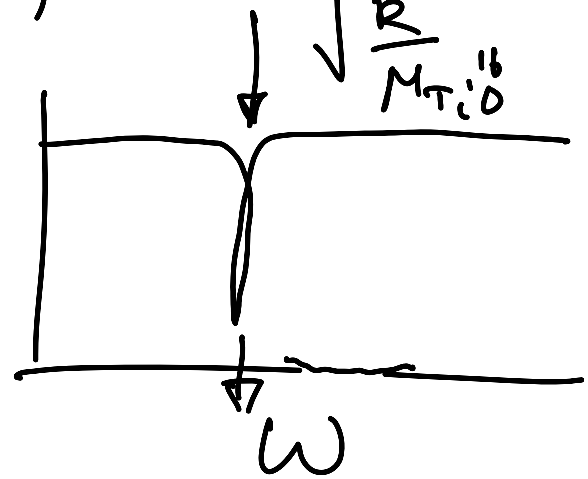


$(v + 1/2)\hbar\omega$

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

Note Title 02-02-2011

$\Delta v = \pm 1$ $\xrightarrow{h\nu}$ $\boxed{Ti\,O^{16}}$ $\longrightarrow$ $\sqrt{\frac{k}{M_{TiO^{16}}}}$



$\vec{\mu} = e\vec{r}$

$\vec{\mu}\cdot\vec{E} = E_x\left(\frac{x}{4}\right) - H_{v-1}\,]$

$2xH_v = H_{v+1}$