MP 8.12.05

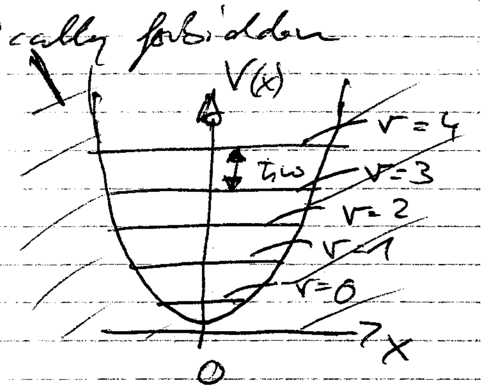
Yesterday: Translational Motion (free, particle in box, tunnel.)

Today: <u>VIBRATIONAL MOTION</u>

harmonic motion $\Leftrightarrow$ $F = -kx$ $\quad$ k = force constant (spring constant)

$$F = -\frac{dV}{dx}$$

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



<u>S.E. for harmonic oscillator</u>

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

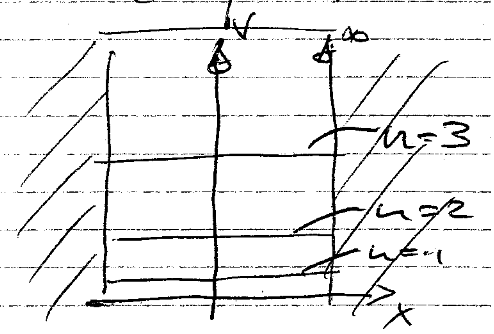
boundary conditions:

$\psi = 0$, $x = \pm\infty$

$\rightarrow$ <u>quantization of energy</u>

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

$$\omega = \sqrt{\frac{k}{m}}, \quad v = 0, 1, 2, 3, \ldots$$



<u>compare to particle in box:</u>

- energies also quantized (boundary cond.)
- $\Delta E = E_{v+1} - E_v = \hbar\omega = \text{const}$ ($\rightarrow 0$ for large m) correspondence principle

  $\Leftrightarrow$ $\Delta E \sim n$ (particle in box)
- non-zero lowest energy state for similar arguments as yesterday (uncertainty principle, ψ has <u>some</u> curvature) here for quantum number $v = 0$ ($\Leftrightarrow n = 1$)

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

<u>the wavefunctions:</u>

- more complex than for particle in a box b/c $V(x)$ rises to infinity more slowly ($\sim x^2$) and in a more complex way

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

is a standard integral in math for physics

Solutions are of the form:

$$\psi_v(x) = N_v H_v(y) e^{-y^2/2} \quad , \quad y = \frac{x}{\alpha} \quad , \quad \alpha = \left(\frac{\hbar^2}{mk}\right)^{1/4}$$

$H_v(y)$ is an Hermite polynomial, very useful properties that simplify handling

$H_0 = 1$, $H_1 = 2y$, $H_2 = 4y^2 - 2$, ...

recursion relation:

$$H_{v+1} - 2yH_v + 2vH_{v-1} = 0$$

important integral:

$$\int_{-\infty}^{\infty} H_{v'} H_v e^{-y^2} dy = \begin{cases} 0 & v' \neq v \\ \pi^{1/2} 2^v v! & v' = v \end{cases}$$

used for normalization:

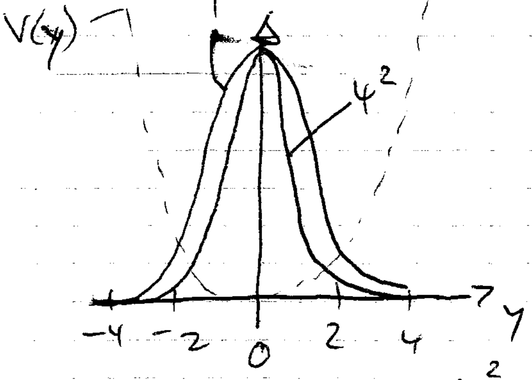
$$\int_{-\infty}^{\infty} \psi_v^* \psi_v \, dx = \alpha \int_{-\infty}^{\infty} \psi_v^* \psi_v \, dy = \alpha N_v^2 \int_{-\infty}^{\infty} H_v^2(y) e^{-y^2} dy =$$

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

$$\frac{dy}{dx} = \frac{1}{\alpha}$$

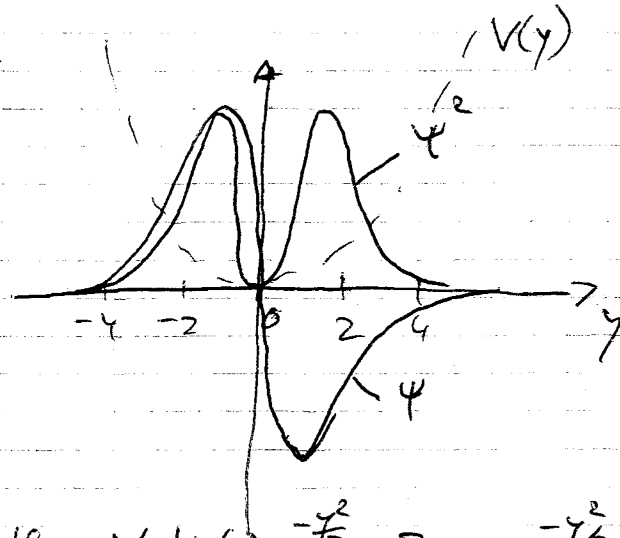
$$= \alpha N_v^2 \sqrt{\pi}\, 2^v v!$$

$$\rightarrow N_v = \left(\frac{1}{\alpha\sqrt{\pi}\, 2^v v!}\right)^{1/2}$$



Gaussian

$$\psi_0 = N_0 H_0(y) e^{-y^2/2} = N_0 e^{-y^2/2}$$



$$\psi_1 = N_1 H_1(y) e^{-y^2/2} = 2N_1 y e^{-y^2/2}$$

Properties of harmonic oscillators

calculating expectation values of observables Ω

$$\langle \Omega \rangle = \int_{-\infty}^{\infty} \psi_v^* \hat{\Omega} \psi_v \, dx = \langle v^* | \hat{\Omega} | v \rangle$$

Dirac bracket notation

- this bracket is also called a matrix element of the operator $\hat{\Omega}$, written Ω_{vv}
- operator btw. bra and ket in place of the "c"

  $\langle bra | c | ket \rangle$
- integration is implicit for complete bracket
- notation is simple, full integrals look fearsome but can be dealt w/ by properties of H.P. given

example:

$$\langle x \rangle = \langle v | \hat{x} | v \rangle = \int_{-\infty}^{\infty} \psi_v^* x \psi_v \, dx = N_v^2 \int_{-\infty}^{\infty} (H_v e^{-y^2/2}) x (H_v e^{-y^2/2}) dx$$

$$= N_v^2 \alpha^2 \int_{-\infty}^{\infty} (H_v e^{-y^2/2}) y (H_v e^{-y^2/2}) dy$$

$$= N_v^2 \alpha^2 \int_{-\infty}^{\infty} H_v y H_v e^{-y^2} dy$$

$$\left[\begin{array}{l} \text{recursion relation:} \\ y H_v = v H_{v-1} + \frac{1}{2} H_{v+1} \end{array} \right]$$

$$= N_v^2 \alpha^2 \left[v \underbrace{\int_{-\infty}^{\infty} H_{v-1} H_v e^{-y^2} dy}_{=0} + \frac{1}{2} \underbrace{\int_{-\infty}^{\infty} H_{v+1} H_v e^{-y^2} dy}_{=0} \right]$$

$\langle x \rangle = 0$ on average in the center

$$\langle x^2 \rangle = (\ldots) = \left(v + \frac{1}{2}\right) \frac{\hbar}{(mk)^{1/2}}$$ (recursion relation twice)

<u>mean potential energy of harmonic oscillator</u>

$$\langle V \rangle = \langle \tfrac{1}{2} k x^2 \rangle = \tfrac{1}{2} k \langle x^2 \rangle = \tfrac{1}{2}(v+1)\hbar \left(\tfrac{k}{m}\right)^{1/2}$$

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

$$E = (v+\tfrac{1}{2})\hbar\omega \quad \Rightarrow \quad \underline{\langle V \rangle = \frac{E_v}{2}}$$

$$E = V + E_{kin} \quad \Rightarrow \quad \underline{\langle E_{kin} \rangle = \frac{E_v}{2}}$$

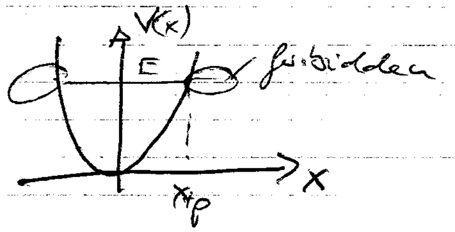
Special case of <u>virial theorem</u>:

If the potential energy of a particle has the form $V = a x^b$, then its mean potential and kinetic energies are related by

$$2\langle E_{kin} \rangle = b \langle V \rangle$$

In QM harmonic oscillator can be be found where $V > E$, which is classically forbidden (corresponds to negative E_{kin})

$$E = V + E_{kin} \qquad E_{kin} = E - V < 0$$



turning point classically:

$$E = V = \tfrac{1}{2} k x_{tp}^2 \qquad (\text{no } E_{kin})$$

$$x_{tp} = \pm \sqrt{\frac{2E}{k}}$$

$$P = \int_{x_p}^{\infty} \psi_v^2 \, dx$$ probability of finding "outside" pot. well

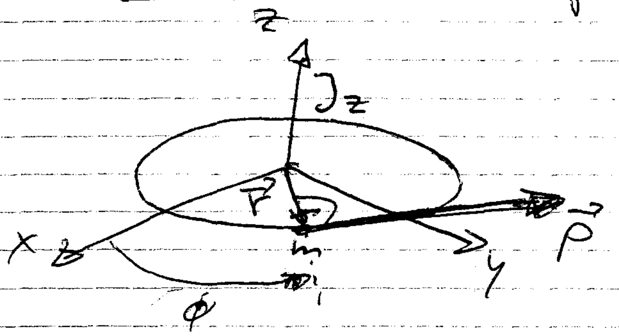
$$y_{tp} = \frac{x_{tp}}{\alpha} = \left\{ \frac{2(v+\tfrac{1}{2})\hbar\omega}{\alpha^2 k} \right\}^{1/2} = (2v+1)^{1/2}$$

$$P_{v=0} = \int_{x_p}^{\infty} \psi_0^2 dx = \alpha N_0^2 \int_{1}^{\infty} e^{-y^2} dy = (\underset{\text{erf}(z)}{\ldots}) = 0.079$$

Total: 16% probability of finding in forbidden "zone"

ROTATIONAL MOTION

Rotation in 2D: particle on a ring



$V = 0$

$E = E_{kin} = \frac{p^2}{2m}$

angular momentum $\vec{J}$

$\vec{J} = \vec{r} \times \vec{p}$

If motion is in x,y-plane $\Rightarrow$ $J_z = \pm rp$ (two possible directions)

$E = \frac{J_z^2}{2mr^2}$

moment of inertia: $I = mr^2$

$E = \frac{J_z^2}{2I}$ $\left(\leftrightarrow \frac{p^2}{2m} \text{ (linear motion)}, \; J_z \hat{=} p, \; I \hat{=} m \right)$

Quantization of angular momentum:

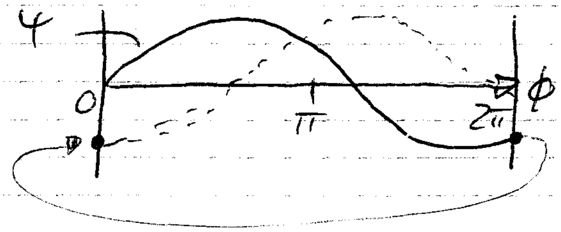
$J_z = \pm pr$ and $p = \frac{h}{\lambda}$ (de Broglie)

$J_z = \pm \frac{hr}{\lambda}$ (the shorter λ, the larger J_z)

where does quantization come in?

suppose no restriction on λ

$\Rightarrow$



(wave function has to be continuous)

$\Rightarrow$ ψ has different values at each point

$\Rightarrow$ two (random) different possibilities of finding a particle in a certain location

$\Rightarrow$ unacceptable

$\Rightarrow$ the wave function has to reproduce itself on each successive circle

$$\Rightarrow \quad \lambda = \frac{2\pi r}{m_l} \quad , \text{ quantum number } m_l = 0, \pm 1, \pm 2, \ldots$$

$$J_z = \pm \frac{hr}{\lambda} = \frac{m_l h r}{2\pi r} = m_l \frac{h}{2\pi}$$

$$\boxed{J_z = m_l \hbar \quad , \; m_l = 0, \pm 1, \pm 2, \ldots} \quad \left.\begin{matrix} + \text{ clockwise} \\ - \text{ counter''} \end{matrix}\right\} \text{rotation}$$

$m_l = 0 \Rightarrow$ no angular momentum, $\lambda \to \infty$, $\psi = \text{const}$ around circle

($\psi = \text{const}$ is possible, it just cannot be zero everywhere)

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

<u>angular momentum and energy are quantized!</u>

<u>Wavefunction</u>

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) \quad \text{(same as particle on 2D-surface)}$$

choose coordinates appropriate for symmetry of the problem (always good idea!)

$$x = r\cos\phi \qquad y = r\sin\phi$$

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}$$

$r = $ const. in this case $\Rightarrow$ can drop $\frac{\partial}{\partial r}$ terms

$$\hat{H} = -\frac{\hbar^2}{2mr^2}\frac{d^2}{d\phi^2} = -\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2}$$

$$\frac{d^2\psi}{d\phi^2} = -\frac{2IE}{\hbar^2}\psi$$

Solutions are:

$$\psi_{m_l}(\phi) = \frac{e^{i m_l \phi}}{(2\pi)^{1/2}} \qquad m_l = \pm \frac{(2IE)^{1/2}}{\hbar} \quad \text{(no dimension)}$$

here E is not quantized yet

m_l is any number

boundary condition: cyclic

$\Leftrightarrow$ ψ has to be single-valued

$$\psi(\phi + 2\pi) = \psi(\phi)$$

$$\psi_{m_l}(\phi + 2\pi) = \frac{e^{i m_l (\phi + 2\pi)}}{\sqrt{2\pi}} = \frac{e^{i m_l \phi} e^{2\pi i m_l}}{\sqrt{2\pi}} = \psi_{m_l}(\phi) e^{2\pi i m_l}$$

$$= (-1)^{2 m_l} \psi(0) \qquad \left[e^{i\pi} = -1 \right]$$

Since $(-1)^{2m_l} \stackrel{!}{=} 1 \Leftrightarrow m_l = 0, \pm 1, \pm 2, \ldots$

<u>Summary:</u>

- energy quantized
- $E \sim m_l^2 \Rightarrow$ energy independent of rotation direction (as expected)

  $\Rightarrow$ states w/ given $|m_l|$ are doubly degenerate (except for $m_l = 0$)

- angular momentum quantized $L_z = m_l \hbar$

<u>Formal derivation of angular momentum quantization:</u>

$\vec{L} = \vec{r} \times \vec{p}$ (classically), $L_z = x p_y - y p_x$

$\hat{L} = \hat{r} \times \hat{p}$ (QM), $\hat{L}_z = \frac{\hbar}{i} \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$

$(\ldots)$ $\hat{L}_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi}$

$$\hat{L}_z \psi_{m_l} = \frac{\hbar}{i} \frac{d\psi_{m_l}}{d\phi} = i m \frac{\hbar}{i} e^{i m \phi} = m_l \hbar \psi_{m_l}$$

$$\psi_{m_l}^* \psi_{m_l} = \frac{e^{-i m_l \phi}}{\sqrt{2\pi}} \frac{e^{i m_l \phi}}{\sqrt{2\pi}} = \frac{1}{2\pi} \not\propto \phi$$

$\Delta\phi = \infty \Leftrightarrow \Delta L_z = 0$ $(L_z = m_l \hbar)$ complementary variables