MOLECULAR PHYSICS, WED 7.12.05

last lectures: QM principles + concepts:
- Schrödinger equation
- wavefunction Ψ (interpretation as prob. d[illegible]
- information in wavefunction and extraction by operators (e.g. $\hat{H}\Psi = E\Psi$)
- expectation values ($\langle\Omega\rangle = \int \Psi^* \hat{\Omega} \Psi \, dV$)
- uncertainty principle $\Delta p \cdot \Delta q \geq \frac{1}{2}\hbar$

complementary variables

$$\Delta\Omega_1 \Delta\Omega_2 \geq \frac{1}{2}|\langle[\hat{\Omega}_1, \hat{\Omega}_2]\rangle|$$ (operators don't commute)

Now apply these concepts to describe the behavior of atoms + molecules:

QUANTUM THEORY: TECHNIQUES + APPLICATIONS

Solve S.E. → three basic types of motion (translation, vibration, rotation)

important for molecular physics, b/c molecules can store energy in these modes of motion (gas molecules: ~~E~~ $\approx U = E_{kin}$ (+ $E_{interactions}$)) ideal gas assumpt.

Rotation + vibration can be seen in spectroscopy

Translational motion

$\hat{H}\Psi = E\Psi \qquad \hat{H} = -\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2}$ (free motion of particle)

⇒ have to find solutions to

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} = E\Psi$$ (second order differential equation)

General solutions:

$$\Psi_k = Ae^{ikx} + Be^{-ikx}$$

insert solutions in SE:

$$-\frac{\hbar^2}{2m}\left(-Ak^2 e^{ikx} - Bk^2 e^{-ikx}\right) = E\psi$$

$$\frac{\hbar^2 k^2}{2m}\underbrace{\left(Ae^{ikx} + Be^{ikx}\right)}_{\psi} = E\psi \qquad \text{eigenvalue equation}$$

$$\Rightarrow E_k = \frac{\hbar^2 k^2}{2m}$$

k can have arbitrary values $\Rightarrow$ translational energy of a free particle is not quantized!

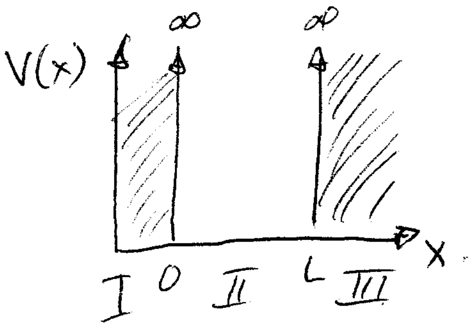
e^{ikx} describes particle with linear momentum $p_x = +\hbar k$
particle moving to $+x$

e^{-ikx} " " to $-x$ w/ $p_x = -\hbar k$
($e^{\pm ikx}$ are eigenfunctions of operator $\hat{p}_x$)

in either case:
$|\psi^2| = e^{-ikx} \cdot e^{ikx} = 1$
probability of finding a particle does not depend on x
$\Rightarrow$ position of particle is unpredictable
Consistent w/ uncertainty principle since $\hat{p}_x$ and $\hat{x}$ don't commute
if momentum is certain $\Rightarrow$ position cannot be specified

The situation changes if we confine the particle to a box

PARTICLE IN A BOX



$$V(x) = \begin{cases} \infty & x < 0 \\ 0 & 0 \le x \le L \\ \infty & x > L \end{cases}$$

- idealization of a gas molecule free to move in 1-dim. container

also used for: - electrons in metals
- conjugate molecules (in 3-4 lectures)
- statistical mechanics for assesing E_{kin} contribution of molecules to thermodynamic properties

Solutions:

region I and III : $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi = E\psi$

since $V \to \infty$ $\psi \to 0$ (the particle cannot be in these regions)

region II : $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$ (same as free particle)

difference: boundary conditions

$$\psi_I(x=0) = \psi_{II}(x=0) = 0$$

and

$$\psi_{II}(x=L) = \psi_{III}(x=L) = 0$$

$\psi_k(x) = C\sin kx + D\cos kx$, $E_k = \frac{k^2\hbar^2}{2m}$ (as for free particle)

but boundary conditions imply a quantization

④

$$\psi(0) = C\sin k\cdot 0 + D\cos k\cdot 0 = D = 0$$

$$\Rightarrow \psi_k(x) = C\sin kx$$

$$\psi(L) = C\sin kL = 0 \Leftrightarrow kL = n\pi \quad , n = 1, 2, \ldots$$

(Why can't $C = 0$? The particle has to be somewhere)

Same reason why $n \neq 0 \Leftrightarrow k \neq 0 \Leftrightarrow \psi \neq 0$

$$\Rightarrow \psi_n(x) = C\sin\left(\frac{n\pi x}{L}\right) \qquad n = 1, 2, 3, \ldots$$

and

$$E_n = \cancel{\frac{n^2h^2}{8mL^2}} \frac{k^2\hbar^2}{2m} = \frac{n^2\pi^2}{L^2\cdot 2\cdot m}\frac{h^2}{(2\pi)^2} = \frac{n^2h^2}{8mL^2}$$

The energy of the particle is quantized!
(comes from boundary conditions)
which makes only certain wavefunctions acceptable. (very general conclusion!)
Here, only E is quantized, but other observables can be quantized as well.

Still needed: $C \Rightarrow$ by normalization

$$\int_0^L \psi^2 dx = C^2 \int_0^L \sin^2\frac{n\pi x}{L}\,dx$$

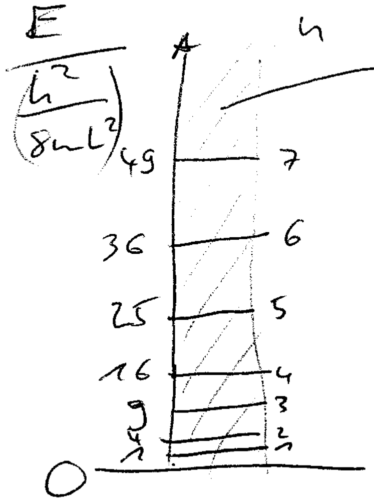
$$= C^2 \frac{L}{2} \Rightarrow C = \sqrt{\frac{2}{L}} \quad (\neq n)$$

$$\int \sin^2 ax\,dx = \frac{1}{2}x - \frac{1}{4a}\sin 2ax + \text{Const}$$

$$\boxed{E_n = \frac{n^2h^2}{8mL^2}, \quad n = 1, 2, 3, \ldots \qquad \psi_n(x) = \left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{n\pi x}{L}\right); \quad 0 \leq x \leq L}$$

Properties of the solutions.

n is called quantum number (in other cases also half-integers)
specifies state of a system



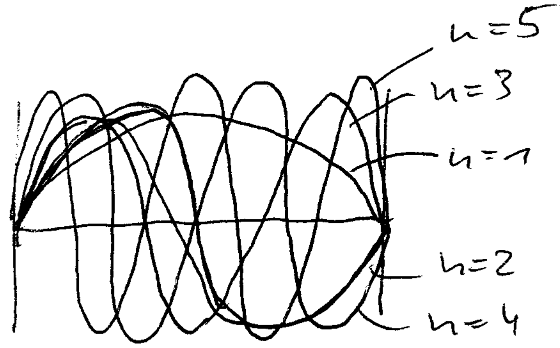
classically allowed energies

$E \sim n^2$ • $\Delta E \approx (n+1)^2 - n^2 = 2n+1 \sim n$

ΔE increases w/ n

$\Delta E = \frac{(2n+1)\, h^2}{8mL^2} \to 0$ for $L \to \infty$

continuous E for ~~CoS~~ sized dim.



• all the same amplitude
b/c $C = \sqrt{\frac{2}{L}} \neq n$

gas in container arbitrary E_{kin}

• all sine waves w/ decreasing wavelength ~~and~~ and increasing wavenumber $k = \frac{2\pi}{\lambda} = \frac{n\pi}{L}$, $\lambda = \frac{2L}{n}$

• Shorter λ → higher mean curvature

$\lambda \downarrow \;\to\; \frac{d^2\psi}{dx^2} \uparrow \;\to$ higher kinetic energy

$\left(\cancel{p = \frac{h}{\lambda},\ E = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2}}\right)$

• # of nodes (passes through 0) $= n-1$

# of nodes $\uparrow \to \lambda \downarrow \to E_{kin} \uparrow$

• linear momentum of particle in a box?

$\sin kx$ = standing wave => not well defined

$p_x \psi = \frac{d}{dx} \sin kx = -k \cos kx$ => not an eigenvalue equation

ψ is not an eigenfunction of momentum operator, but)

$\psi(x) = \cancel{\sin kx}$ can be seen as a superposition of eigenfunctions of the p_x-operator:

$$\psi_n = \sqrt{\frac{2}{L}} \sin\frac{n\pi x}{L} = \frac{1}{2i}\sqrt{\frac{2}{L}}\left(e^{ikx} - e^{-ikx}\right) \qquad k = \frac{n\pi}{L}$$

50% of measurements $\rightarrow +k\hbar$
50% of measurements $\rightarrow -k\hbar$

classically: particle rattles from left to right and back

$$\langle p \rangle = \int \psi^* \frac{d}{dx} \psi \, dx$$

$$= \cancel{\S} + \frac{1}{4}\frac{2}{L} \int_0^L \left(e^{-ikx} - e^{ikx}\right)\left(ike^{ikx} + ike^{-ikx}\right) dx$$

$$= \frac{ik}{2L} \int_0^L \left(1 + e^{-2ikx} - e^{2ikx} - 1\right) dx$$

$$= \frac{ik}{2L}\left[\frac{-1}{2ik}\left(e^{-2ikL} - 1\right) - \frac{1}{2ik}\left(e^{2ikL} - 1\right)\right]$$

$$= -\frac{2}{4L}\left(e^{-2i\frac{n\pi}{L}L} - 1\right) = \underline{\underline{0}}$$

$$\langle p^2 \rangle = (\ldots) = \frac{n^2 h^2}{4L^2}$$

$\rightarrow$ Self-test!?

$n \neq 0 \Rightarrow E_1 = \frac{h^2}{8mL^2}$ is lowest possible energy $\Leftrightarrow$ classical mechanics

"zero-point energy"

2 physical explanations?

1.) uncertainty principle:

particle confined to finite region $\Rightarrow \Delta X \not\to \infty$

$\Rightarrow \Delta p \not\to 0 \Leftrightarrow p = 0$ not possible

$\Leftrightarrow E_{kin} = 0$ not possible

2.) $\psi(x=0) = \psi(x=L) = 0$

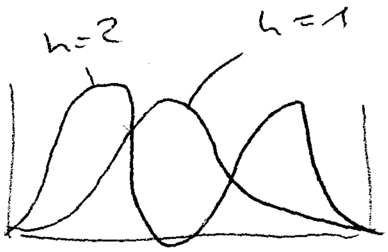
since it can also not be zero everywhere but smooth + continuous

$\psi(x)$ has to have some curvature

$\Leftrightarrow$ particle has some kinetic energy

<u>probability density</u>

$$\psi^2(x) = \frac{2}{L} \sin^2 \frac{n\pi x}{L}\, dx$$



<u>very large n</u> $\Rightarrow$ continuous (except for rapid osc.)

$\Rightarrow$ approaches classical limit (on average anywhere) equal times at all points

"<u>correspondence principle</u>"

<u>illustration of "orthogonality"</u>

two ψ are orthogonal if $\int \psi_n^* \psi_{n'}\, dV = 0$

$$\int_0^L \psi_n^* \psi_{n'}\, dx = \frac{2}{L} \int_0^L \sin \frac{n\pi}{L} x \sin \frac{n'\pi}{L} x$$

$$= \frac{2}{L} \left[\frac{\sin (n-n')\pi x}{2\pi (n-n')} - \frac{\sin (n+n')\pi x}{2\pi (n+n')} \right]_0^L$$

(valid for $n^2 \neq n'^2$)

$= 0$

$$\int \sin ax \sin bx\, dx = \frac{\sin (a-b) x}{2(a-b)} - \frac{\sin (a+b) x}{2(a+b)} + \text{const.}$$

$\int_0^L \psi_n^* \psi_{n'} \, dx$ is often written $\langle n | n' \rangle = 0 \quad (n \neq n')$

Dirac bracket notation

ψ_n^* $\langle n|$ bra

$\psi_{n'}$ $|n'\rangle$ ket

$\langle n|n'\rangle$ bra-c-ket

integration over all space is understood

$\langle n|n\rangle = 1$ normalization condition

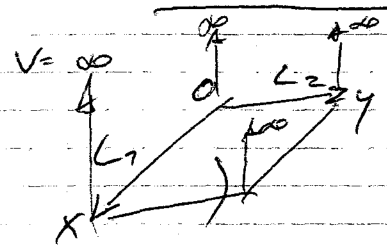
together:

$\langle n|n'\rangle = \delta_{nn'}$ (Kronecker delta)

$$\delta_{nn'} = \begin{cases} 0 & \text{if } n' \neq n \\ 1 & \text{if } n = n \end{cases}$$

orthonormal = orthogonal + normalized

MOTION IN TWO AND MORE DIMENSIONS



particle confined to surface

infinitely high walls

S.E.

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2}\right) = E\psi$$

2nd order partial differential eqn.

Separation of variables

- important technique
- later also used for hydrogen atom

Ansatz: $\psi(x,y) = X(x)\cdot Y(y)$

$$\frac{\partial^2\psi}{\partial x^2} = \frac{\partial^2 XY}{\partial x^2} = Y\frac{d^2X}{dx^2} \qquad \frac{\partial^2\psi}{\partial y^2} = \frac{\partial^2 XY}{\partial y^2} = X\frac{d^2Y}{dy^2}$$

only show if not known already

$$-\frac{\hbar^2}{2m}\left(Y\frac{d^2X}{dx^2} + X\frac{d^2Y}{dy^2}\right) = EXY \quad \Big| :XY$$

$$\underbrace{\frac{1}{X}\frac{d^2X}{dx^2}}_{\neq y} + \underbrace{\frac{1}{Y}\frac{d^2Y}{dy^2}}_{\neq x} = -\frac{2mE}{\hbar^2} = \text{constant}$$

$$\frac{1}{X}\frac{d^2X}{dx^2} = -\frac{2mE_x}{\hbar^2} \qquad \frac{1}{Y}\frac{d^2Y}{dy^2} = -\frac{2mE_y}{\hbar^2}$$

$$E = E_x + E_y$$

$$-\frac{\hbar^2}{2m}\frac{d^2X}{dx^2} = E_x X \qquad -\frac{\hbar^2}{2m}\frac{d^2Y}{dy^2} = E_y Y$$

Separation of variables:

<u>1</u> 2nd order <u>partial</u> DE $\Rightarrow$ <u>2</u> 2nd order <u>ordinary</u> DE

We know the solutions to these already!

$$X_{n_1}(x) = \sqrt{\frac{2}{L_1}}\sin\frac{n_1\pi x}{L_1} \qquad Y_{n_2}(y) = \sqrt{\frac{2}{L_2}}\sin\frac{n_2\pi x}{L_2}$$

$$\Rightarrow \boxed{\begin{array}{l} \psi_{n_1 n_2}(x,y) = \dfrac{2}{\sqrt{L_1 L_2}}\sin\dfrac{n_1\pi x}{L_1}\sin\dfrac{n_2\pi x}{L_2} \\ \qquad\qquad 0 \le x \le L_1, \quad 0 \le y \le L_2 \\ E_{n_1,n_2} = \left(\dfrac{n_1^2}{L_1^2} + \dfrac{n_2^2}{L_2^2}\right)\dfrac{h^2}{8m} \end{array}}$$

Dirac notation: $\psi_{n_1,n_2}(x,y) = |n_1,n_2\rangle$

n_1 and n_2 are independent!

<u>3-dim accordingly (...)</u>

Degeneracy

If $L_1 = L_2 = L$

$$\psi_{1,2} = \frac{2}{L}\sin\frac{\pi x}{L}\sin\frac{2\pi y}{L} \qquad E_{1,2} = \frac{5h^2}{8mL^2}$$

$$\psi_{2,1} = \frac{2}{L}\sin\frac{2\pi x}{L}\sin\frac{\pi y}{L} \qquad E_{2,1} = \frac{5h^2}{8mL^2}$$

The wave functions are different but the energies are the same.

$\Rightarrow$ $\psi_{1,2}$ and $\psi_{2,1}$ ($|1,2\rangle$ and $|2,1\rangle$) are <u>degenerate</u>

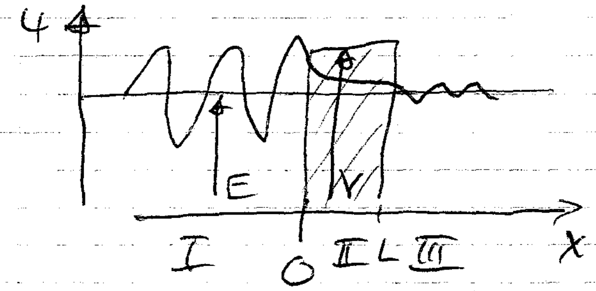
the energy level $\frac{5h^2}{8mL^2}$ is "doubly degenerate"

3D: $|1,1,2\rangle$, $|1,2,1\rangle$, and $|2,1,1\rangle$

$\frac{6h^2}{8mL^2}$ is triply degenerate

TUNNELING

QM phenomenon of penetration of particle through classically forbidden zones



particle incident from left w/ mass m

Region I: free particle

$$\psi = Ae^{ikx} + Be^{-ikx}$$

$$k\hbar = (2mE)^{1/2}$$

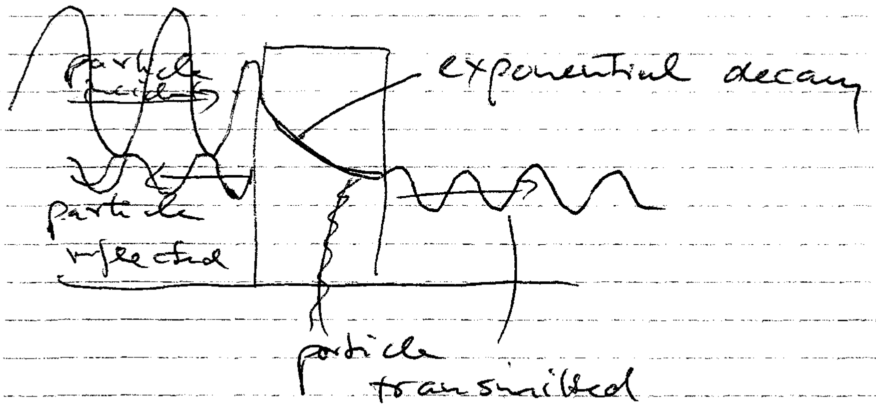
Region II: SE: $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi = E\psi$ $\qquad V = \text{const.}$

$V > E$

$$\Rightarrow \psi = Ce^{\kappa x} + De^{-\kappa x},\ \kappa\hbar = \{2m(V-E)\}^{1/2} \quad (E - V < 0)$$

in region II : $\psi(x)$ consists of real functions
in region I : $\psi(x)$ " of complex, oscillating functions

Region III: $\psi = A' e^{ikx} + B' e^{-ikx}$, k is the same as in region I but amplitudes are smaller



use boundary conditions to specify 6 coefficients:

$\psi_I(0) = \psi_{II}(0)$: $A + B = C + D$

$\psi_{II}(L) = \psi_{III}(L)$: $Ce^{\kappa L} + De^{-\kappa L} = A' e^{ikL} + B' e^{-ikL}$

also

$\psi'_I(0) = \psi'_{II}(0)$: $ikA - ikB = \kappa C - \kappa D$

$\psi'_{II}(L) = \psi'_{III}(L)$: $\kappa Ce^{\kappa L} - \kappa De^{-\kappa L} = ikA' e^{ikL} - ikB' e^{-ikL}$

No particles in Region III traveling to the left
$\Rightarrow B' = 0$

In barrier (region II) exponential decay
$\Rightarrow C = 0$

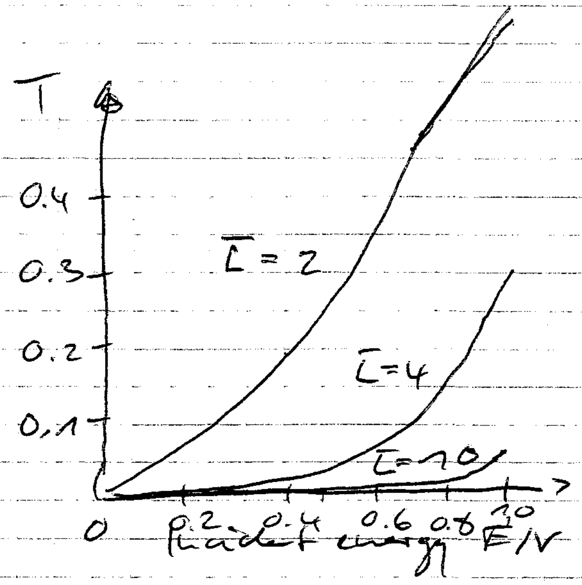
$\Rightarrow$ 4 equations and 4 unknowns
$\rightarrow$ can be solved

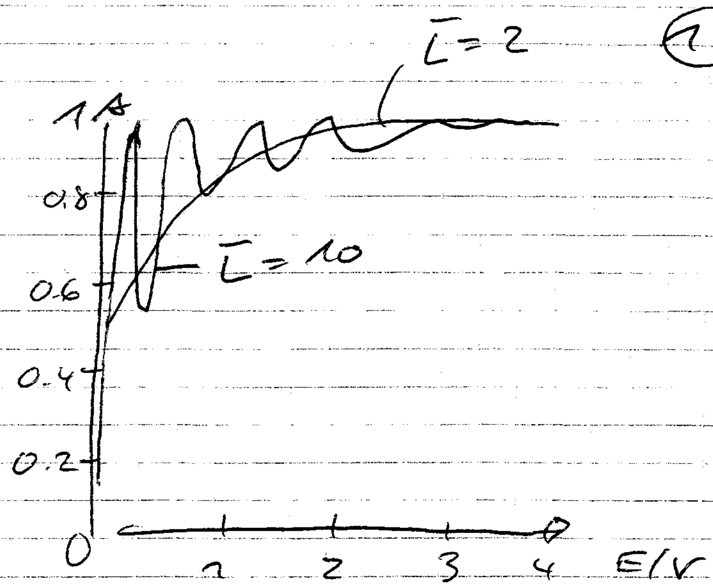
Transmission probability:

prob. particle traveling right in RI : $|A|^2$
" " " right in RIII : $|A'|^2$

$$T = \frac{|A'|^2}{|A|^2} = (\ldots) = \left\{ 1 + \frac{(e^{\kappa L} - e^{-\kappa L})^2}{16\,\varepsilon(1-\varepsilon)} \right\}^{-1}$$

$$\varepsilon = \frac{E}{V}$$





$$\bar{L} = \frac{L(2mV)^{1/2}}{\hbar}$$

normalized barrier width

Classically: $T = 0$ $(E<V)$ $\qquad T = 1$ $(E>V)$

For high, wide barriers $(\kappa L \gg 1)$

$$T = 16\,\varepsilon(1-\varepsilon)\,e^{-2\kappa L}$$

decreases exponentially w/ L and $\sqrt{m}$

$(\kappa = \{2m(V-E)\}^{1/2}$

- Tunneling important for smaller particles e^-, μ but also important in α-decay of nuclei

- Scanning tunneling microscopy (STM)

piezo

tip

e^- tunneling

- move tip to keep current constant
- stay at certain height and monitor current

$\Rightarrow$ Scan over surface to get atomically fine resolution of topography