Chpt. 2.

When do we need to use QM?

1) when $\lambda \approx$ dimensions of the problem
2) energy level spacing $\gg kT$

Boltzmann: $$\frac{n_i}{n_j} = \frac{g_i}{g_j} e^{-(\varepsilon_i-\varepsilon_j)/kT}$$

populations ↑ ↑ degeneracies

can treat the system classically if energy spectrum $\approx$ continuous

Classical waves $$\frac{\partial^2 \Psi(x,t)}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 \Psi(x,t)}{\partial t^2}$$

$\Psi(x,t) = A\sin(kx - \omega t)$
(show this satifies the wave eq)

$k = \frac{2\pi}{\lambda}$ = wave vector
$\omega = 2\pi\nu$ = angular freq.

Add two waves of same freq. and amplitude, opposite direction

$$\Psi = A[\sin(kx - \omega t) + \sin(kx + \omega t)]$$
$$= 2A\sin kx\cos\omega t = \psi(x)\cos\omega t$$

↑ Standing wave (fixed nodes)

Complex representation

$$\Psi = Ae^{i(kx - \omega t + \phi')}$$

Euler: $e^{i\alpha} = \cos\alpha + i\sin\alpha$

Cl. wave eq. → Schrodinger eq.

$$\frac{\partial^2\Psi}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2\Psi}{\partial t^2}$$

$\Psi(x,t) = \psi(x)\cos\omega t$ for cl. standing wave

↓

$$\frac{d^2\psi(x)}{dx^2} + \frac{\omega^2}{v^2}\psi(x) = 0$$

↓

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2}{\lambda^2}\psi = 0$$

$\lambda = \frac{h}{p}$

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2 p^2}{h^2}\psi = 0$$

$$E = \underbrace{\frac{p^2}{2m}}_{KE} + \underbrace{V(x)}_{PE}$$

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

time-indep. S.E.

$\hbar = \frac{h}{2\pi}$

$$\boxed{-\frac{\hbar^2}{2m}\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V\Psi}$$

time-dependent S.E.

↓

$$i\hbar\frac{\partial\Psi}{\partial t} = E\Psi, \quad \Psi(x,t) = \psi(x)e^{-iEt/\hbar}$$

for stationary states

In QM all observables are associated with operators

$$\hat{O}\psi_n = a_n\psi_n$$

eigenvalue eq.

↑ operator ↑ eigenvalue ← eigenfunction

↑ in QM these are real

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

$$\downarrow$$

$\hat{H}\psi = E\psi$ $\qquad\qquad$ $\hat{H}$ = Hamiltonian operator

is $\psi = Ae^{ikx} + Be^{-ikx}$ an e.f. of $\frac{d}{dx}$?

$\frac{d}{dx}\psi = ikA\,e^{ikx} - ikBe^{-ikx} \neq \text{const}\cdot\psi$ | No

is it an e.f. of $\frac{d^2}{dx^2}$?

$\frac{d^2}{dx^2}\psi = -k^2Ae^{ikx} - k^2Be^{-ikx} = -k^2\left[Ae^{ikx} + Be^{-ikx}\right]$ | yes

<u>orthogonality</u>

vector space

$x\cdot y = 0$
$x\cdot z = 0$
$y\cdot z = 0$

function space

$$\int_{-\infty}^{\infty}\psi_i^*(x)\,\psi_j(x)\,dx = \delta_{ij}$$

$\Rightarrow\ 0 \quad i \neq j$
$\neq 0 \quad i = j$

The different eigenfunctions of a QM operator are orthogonal (degenerate eigenfunctions are a special case).

If $\int_{-\infty}^{\infty}\psi_i^*\psi_i\,dx = 1$, the functions are <u>normalized</u>

Normalize $a(a-x)$ on $0 \leq x \leq a$

let $\psi = Na(a-x)$: $\int_0^a N^2a^2(a-x)^2\,dx = N^2a^2\int_0^a(a^2-2ax+x^2)dx$

$$= N^2a^2\left[a^2x - ax^2 + \frac{x^3}{3}\right]_0^a = N^2a^2\frac{a^3}{3} = \frac{N^2a^5}{3}$$

set $N^2 \frac{a^5}{3} = 1 \Rightarrow N = \sqrt{3/a^5}$

$\psi = \sqrt{\frac{3}{a^5}}\, a(a-x)$ is normalized on $0 \leq x \leq a$

<u>orthonormal set</u> : orthogonal and normalized.

The ef's of a QM operator form a <u>complete set</u>

$\Rightarrow$ any function in that space can be written in terms of the eigenfunctions

$$f(x) = \sum_{n=1}^{\infty} b_n \psi_n(x) \quad \Bigg| \quad b_n = \int_{-\infty}^{\infty} f(x)\psi_n(x)\,dx$$

---

fourier series $f(x) = \frac{1}{2} b_0 + \sum_n b_n \cos\frac{n\pi x}{L} + \sum_n \sin\frac{n\pi x}{L}$ for a function periodic over $-L \leq x \leq L$ | see page 454 of text.

Summary :

- time indep + time dependent Schrodinger eq's
- operators
- eigenvalue equations
- orthogonal functions and complete sets.