

Chapter 2

When do we need to use QM?

- 1) $\lambda \approx$ dimensions of the system
- 2) Energy level spacing $\gg kT$

Boltzmann eq. $\frac{n_i}{n_j} = \frac{g_i}{g_j} e^{-(\epsilon_i - \epsilon_j)/kT}$

populations \uparrow n_j

Degeneracies (two or more levels with the same energy) \uparrow g_j

quantum classical

Can treat the system classically if energy spectrum \approx continuous

Classical waves

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

(wave equation)

$v =$
velocity

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

$$k = \frac{2\pi}{\lambda} = \text{wave vector}$$

$$\omega = 2\pi\nu = \text{angular freq.}$$

Add two travelling 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

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

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

Derivation of the Schrödinger eq.

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

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

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

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

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

time independent S. E.

Substitute:

$$\Psi(x, t) = \psi(x) \cos \omega t$$

for classical standing wave

$$v = \nu \lambda$$

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

Substitute: $\hbar = \frac{h}{2\pi}$ and

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

Classical expression for total energy

time-dependent S. E.

$$i\hbar \frac{\partial \Psi}{\partial t} = E\Psi$$

$$\Psi(x, t) = \psi(x)e^{-iEt/\hbar}$$

Form of wavefunction for a stationary state

Energy is constant over time.

Ψ is a soln. of the time-indep. SE

In QM, all observables are associated with operators

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

operator eigenvalue eigenfunction

Eigenvalue eq.

In QM the eigenvalues correspond to the observables and are real

$z = x + iy, i = \sqrt{-1}$
Example of a complex number

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

$$\hat{H}\psi = E\psi$$

H is the Hamiltonian operator

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

$$\frac{d}{dx}\psi = ikAe^{ikx} - ikBe^{-ikx} \neq \text{const. } \psi$$

No

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

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

Yes

Orthogonality

vector space

$$\mathbf{x} \cdot \mathbf{y} = 0$$

$$\mathbf{x} \cdot \mathbf{z} = 0$$

$$\mathbf{y} \cdot \mathbf{z} = 0$$

where \mathbf{x} , \mathbf{y} , \mathbf{z} are vectors
in the x , y , z directions

function space

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

$$\Rightarrow 1 \quad i \neq j$$

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

Kronecker
delta
function

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 **normalized**

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

$$\begin{aligned} \text{let } \psi = Na(a - x): \int_0^a N^2 a^2 (a - x)^2 dx &= N^2 a^2 \int_0^a (a^2 - 2ax + x^2) dx \\ &= N^2 a^2 \left[a^2 x - ax^2 + \frac{x^3}{3} \right]_0^a = N^2 a^2 \frac{a^3}{3} = \frac{N^2 a^5}{3} \end{aligned}$$

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

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

Orthonormal set of functions: orthogonal and normalized

The EF's of a QM operator form a **complete set**

⇒ any function in that space can be written in terms of the eigenfunctions

$$f(x) = \sum_{n=1}^{\infty} b_n \psi_n(x)$$

1. $f(x)\psi_m(x) = \psi_m(x) \sum_{n=1}^{\infty} b_n \psi_n(x)$

2. Integrate over both sides

$$b_n = \int_{-\infty}^{\infty} f(x)\psi_n(x)dx$$

b_n is the projection of f onto ψ_n

The analogue in vector spaces is: $\mathbf{v} = a\mathbf{i} + b\mathbf{j} + c\mathbf{k}$

where $\mathbf{i}, \mathbf{j}, \mathbf{k}$ are unit vectors in the $\mathbf{x}, \mathbf{y}, \mathbf{z}$ directions

Fourier series

$$f(x) = \frac{1}{2}b_0 + \sum_n b_n \cos \frac{n\pi x}{L} + \sum_n a_n \sin \frac{n\pi x}{L}$$

for a function periodic over $-L \leq x \leq L$

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Key ideas:

- time independent and time dependent Schrödinger equations
- operators
- eigenvalue equations
- orthogonal functions and complete basis sets