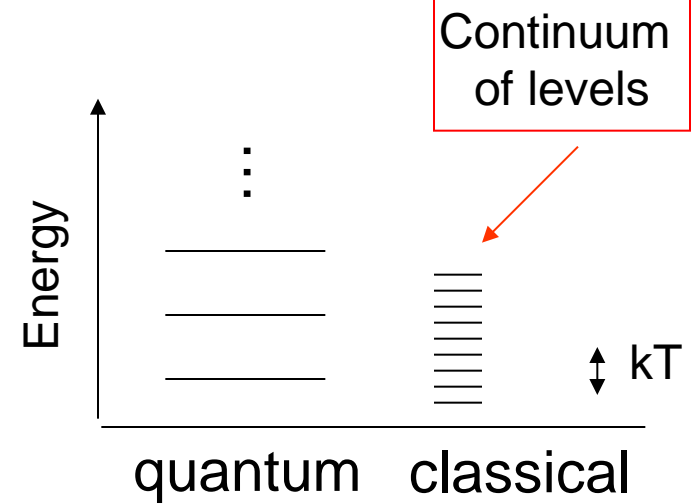


Chapter 2

When do we need to use QM?

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



Boltzmann eq.

$$\frac{n_i}{n_0} = \frac{g_i}{g_0} e^{-\varepsilon_i/kT}$$

relative population



Energy of lowest level (0) taken to be 0

n_0 = # in ground state

n_i = # in excited state

g_i = degeneracy of level i

(# of arrangements that give the same energy)

Classical waves

$$\psi(x, t) = A \sin 2\pi \left(\frac{x}{\lambda} - \frac{t}{T} \right)$$

Can also write as

$$\Psi(x, t) = A \sin(kx - \omega t)$$

(corresponds to wave travelling to right)

More generally,

$$\psi(x, t) = A \sin(kx - \omega t + \phi)$$

↑ phase

$$\text{freq} \sim \nu = \frac{1}{T}; T = \text{period}$$

$$\nu = \nu \lambda$$

ν = velocity

λ = wavelength

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

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

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)

The waves obey the following partial differential equation

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

This is shown by substituting

Let $\psi(x, t) = A \sin(kx - \omega t)$

$$\frac{\partial^2}{\partial x^2} [A \sin(kx - \omega t)] = \frac{1}{v^2} \frac{\partial^2}{\partial t^2} [A \sin(kx - \omega t)]$$

$$-Ak^2 = -\frac{A\omega^2}{v^2}$$

$$k^2 = \frac{\omega^2}{v^2} \rightarrow v = \omega / k = v\lambda$$

Complex representation

$$\Psi = Ae^{i(kx - \omega t + \phi)}$$

(wave equation)

Euler:

$$e^{ix} = \cos x + i \sin x$$

$$e^{-ix} = \cos x - i \sin x$$

$$\cos x = (1/2)(e^{ix} + e^{-ix})$$

$$\sin x = (1/2i)(e^{ix} - e^{-ix})$$

$$i = \sqrt{-1}$$

Some properties of complex numbers

$$z = a + bi \quad \text{a complex \# where } i = \sqrt{-1}$$

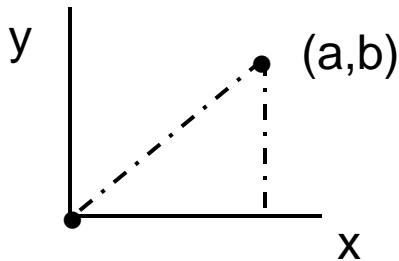
$$zz^* = (a + bi)(a - bi) = a^2 + b^2 \quad (\text{real})$$



complex conjugate

$$z = re^{i\theta} \quad \Bigg| \quad zz^* = a^2 + b^2$$

$$r = \sqrt{a^2 + b^2}, \quad \theta = \sin^{-1}\left(\frac{b}{r}\right); \quad b = r \sin \theta$$



$$z = re^{i\theta} = r[\cos \theta + i \sin \theta] = a + bi$$

$$|z| = \sqrt{z^* z} = r$$

Standing Waves

In the use of standing waves, we can write

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

Substituting this into the wave equation $\frac{\partial^2 \Psi}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 \Psi}{\partial t^2}$

$$\cos \omega t \frac{d^2 \psi(x)}{dx^2} = -\frac{\omega^2}{v^2} \psi(x) \cos \omega t$$

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

In the case of a standing wave we end up with a differential equation that depends only on x (i.e., no t dependence)

Derivation of the Schrödinger eq.

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



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



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



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

Let $\lambda = h/p$ (de Broglie)

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

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

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.

$\psi(x)$ is a soln. of the time-indep. SE

In QM, all observables (position, momentum, energy, angular momentum, etc.) 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

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

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

H is the Hamiltonian operator $\frac{-\hbar^2}{2m} \frac{d^2}{dx^2} + V$

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

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

No

is it an eigenfunction 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

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

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

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

Kronecker
delta
function



The *, means "take the complex conjugate, i.e., "i" replaced by "-i"

Suppose

$\psi = e^{ix}$, then $\psi^* \psi$ becomes

$$e^{-ix} e^{ix} = e^0 = 1$$

Note that the probability of say
finding an electron
somewhere is given by $\Psi^* \Psi$,
and probabilities are
necessarily real

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**

If both orthogonal and normalized, then called **orthonormal**

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

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

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

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

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

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

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

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

2. Integrate over both sides

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

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

b_n is the projection of f onto ψ_n

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 $-L \leq x \leq L$

see page
462 of
text

Key ideas:

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

One way of proving the standing wave result from early in the chapter

$$\sin(a + b) = \frac{1}{2i} \left(e^{i(a+b)} - e^{-i(a+b)} \right)$$

$$\sin(a - b) = \frac{1}{2i} \left(e^{i(a-b)} - e^{-i(a-b)} \right)$$

$$\sin(a + b) + \sin(a - b) = \frac{1}{2i} \left[e^{ia} e^{ib} + e^{ia} e^{-ib} - e^{-ia} e^{-ib} - e^{ia} e^{ib} \right]$$

$$= \frac{1}{2i} \left\{ e^{ia} (e^{ib} + e^{-ib}) - e^{-ia} (e^{ib} + e^{-ib}) \right\}$$

$$= \frac{1}{i} \left\{ e^{ia} \cos b - e^{-ia} \cos b \right\}$$

$$= \frac{1}{i} (e^{ia} - e^{-ia}) \cos b = 2 \sin a \cos b$$