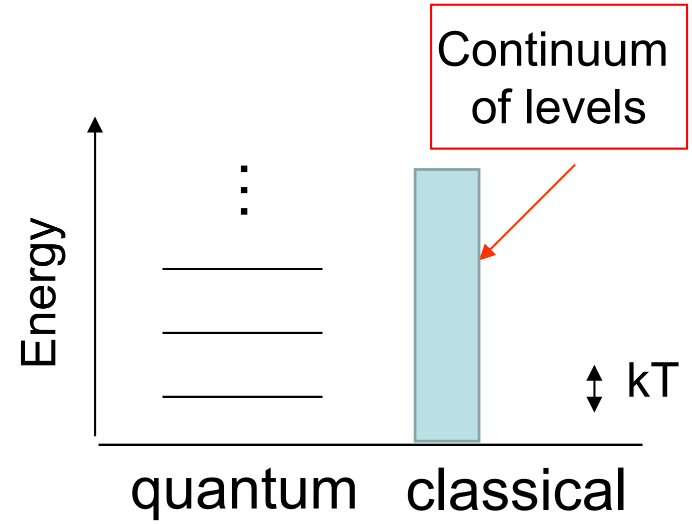
Chapter 2

When do we need to use QM?

1) λ ≈ dimensions of the system

2) Energy level spacing >> 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

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

$$v = \upsilon\lambda$$

v = velocity
λ = wavelength

$k = \dfrac{2\pi}{\lambda}$ = wave vector

$\omega = 2\pi\upsilon$ = 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

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

This is shown by substituting

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

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

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

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

Complex representation

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

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

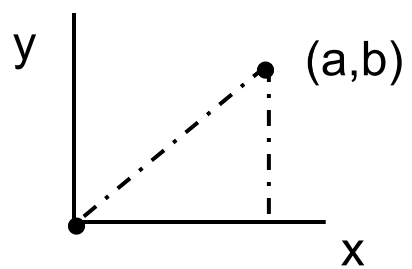
$z = a + bi$ a complex # where $i = \sqrt{-1}$

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

complex conjugate

$$z = e^{i\theta}$$

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



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

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

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

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

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

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

There is a separate differential equation for te t dependence.

Separation of variables

Derivation of the time-independent Schrödinger eq.

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

Let λ = h/p (de Broglie)

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

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

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

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

Schrodinger Eq.

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

In QM, all observables (position, momentum, energy, angular momentum, etc.) are associated with operators

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

operator — eigenvalue — eigenfunction

Eigenvalue eq.

In QM the eigenvalues correspond to the observables and are real

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

$$\downarrow$$

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

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

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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 $\frac{d^2}{dx^2}$?

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

Yes

Orthogonality

Kronecker delta function

vector space

x • **y** = 0

x • **z** = 0

y • **z** = 0

where **x**, **y**, **z** are vectors in the x, y, z directions

function space

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

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

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

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 Ψ* Ψ, 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 ≤ x ≤ a

$$\text{let} \quad \psi = Na(a-x): \quad \int_0^a N^2 a^2 (a-x)^2 dx = N^2 a^2 \int_0^a \left(a^2 - 2ax + x^2\right) dx$$

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

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

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

The EF's of a QM operator form a **complete set** **(basis 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: ***v*** = *a**i*** +*b**j*** +*c**k***

where ***i***, ***j***, ***k*** are unit vectors in the ***x***, ***y***, ***z*** directions

b_n is the projection of f onto ψ_n

Fourier series

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

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

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

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

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

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

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

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