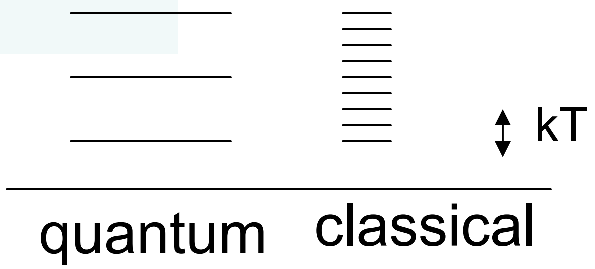
Chapter 1

When do we need to use QM?

1) Wavelength λ ≈ dimensions of the system

2) Energy level spacing >> kT



Boltzmann eq.

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

populations

Degeneracies (two or more levels with the same energy)

Can treat the system classically if energy spectrum ≈ continuous

Classical waves

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

(wave equation)

v = velocity

Ψ(x,t) = A sin(kx – ωt)
(show that this satisfies the wave eq.)

$$k = \frac{2\pi}{\lambda}$$ = 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)

Complex representation

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

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

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

Derivation of the Schrödinger eq.

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

$$\downarrow$$

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

$$\downarrow$$

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

$$\downarrow$$

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

$$\downarrow$$

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

time independent S. E.

Substitute:

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

for classical standing wave

$$\boxed{\mathrm{v} = \nu\,\lambda}$$

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 <u>observables</u> are associated with <u>operators</u>

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

eigenfunction

operator eigenvalue

Eigenvalue eq.

In QM the eigenvalues correspond to the observables and are real

z= x +iy, i =√(-1)

Example of a complex number

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

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

H is the Hamiltonian operator

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

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

Yes

Orthogonality

Kronecker
delta
function

vector space

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

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

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

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

function space

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

$$\Rightarrow \quad 1 \quad \mathrm{i = j}$$

$$\neq 0 \quad \mathrm{i \neq j}$$

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 **normalized**

Normalize a(a – x) on 0 ≤ x ≤ a

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

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

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

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

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Orthonormal set of functions: orthogonal and normalized

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

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

b_n is the projection of f onto ψ_n

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

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 $-L \leq x \leq L$

Key ideas:

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

1. **State of QM system completely specified by wavefunction Ψ(x,t)**

$$P(x_0,t_0) = \Psi(x_0,t_0)^*\Psi(x_0,t_0)dx = \left|\Psi(x_0,t_0)\right|^2 dx$$

probability of finding the particle within dx of x_0 at time t_0

$$\int_{-\infty}^{\infty} \left|\Psi(x,t)\right|^2 dx = 1$$

probability of finding the particle somewhere

$\Rightarrow$ Ψ is single valued

Ψ and $\dfrac{d\Psi}{dx}$ are continuous

Ψ cannot be ∞ over a finite interval

2. Each observable is associated with a QM operator

position: $\hat{x} = x$

momentum: $\hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x}$

KE: $\hat{E}_{kin} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} = \frac{\widehat{p}^2}{2m}$

PE: $\hat{E}_{pot} = V(x)$

total E: $\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$

angular momentum: $\hat{l}_x = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$

. . . .

All operators for QM observables are Hermitian

As discussed below, Hermitian operators have real eigenvalues

Dirac bra-ket nomenclature

$$\left\langle m \middle| \hat{\Omega} \middle| n \right\rangle = \int \psi_m^* \hat{\Omega} \psi_n d\tau$$

* $\Rightarrow$ complex conjugate
i.e., i → -i

Definition of a Hermitian operator

$$\int \psi_m^* \hat{\Omega} \psi_n d\tau = \left\{ \int \psi_n^* \hat{\Omega} \psi_m d\tau \right\}^*$$

or

$$\left\langle m \middle| \hat{\Omega} \middle| n \right\rangle = \left\langle n \middle| \hat{\Omega} \middle| m \right\rangle^*$$

Quantum mechanical observables correspond to Hermitian operators

Eigenvalues of Hermitian operators are real

Show $\frac{\hbar}{i}\frac{\partial}{\partial x}$ is Hermetian

$$\int \psi_m^* \frac{\hbar}{i}\frac{\partial}{\partial x}\psi_n dx \overset{?}{=} \left[\int \psi_n^* \left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)\psi_m dx\right]^*$$

$$\int udv = uv\,| - \int vdu$$ (Integration by parts)

$$\int \psi_m^* \frac{\hbar}{i}\frac{\partial}{\partial x}\psi_n dx = \frac{\hbar}{i}\int \psi_m^* \frac{\partial}{\partial x}\psi_n dx$$

$$= \frac{\hbar}{i}\left[\psi_m^*\psi_n\,|_{-\infty}^{\infty} - \int \psi_n \frac{\partial}{\partial x}\psi_m^* dx\right]$$

A well-behaved wavefunction
→ 0 as x → ± ∞

$$-\frac{\hbar}{i}\int \psi_n \frac{\partial}{\partial x}\psi_m^* dx$$

But $\left[\int \psi_n^* \frac{\partial}{\partial x}\psi_m dx\right]^* = \int \psi_n \frac{\partial}{\partial x}\psi_m^* dx$

$$\left(\frac{\hbar}{i}\right)^* = -\frac{\hbar}{i}$$

which completes the proof.

3. **In a <u>single</u> measurement of an observable associated with Â, only an eigenvalue of Â can be measured.**

4. **Expectation value:**

$$<\hat{A}>=\frac{\int_{-\infty}^{\infty}\Psi^{*}\hat{A}\Psi dx}{\int_{-\infty}^{\infty}\Psi^{*}\Psi dx}$$

← For normalization

Average of the observable A, if many measurements are done

If Ψ is an eigenfunction of Â, all measurements
give the same result

If Ψ is <u>not</u> an eigenfunction of Â

$$\Psi=\sum b_n\phi_n$$

eigenfunctions of Â with eigenvalues a_n

$$<\hat{A}>=\sum\left|b_m\right|^2 a_m \ ,$$

assuming Ψ is normalized

In this case, different measurements give different results

Suppose $\psi(x) = \frac{1}{2}\phi_1(x) + \frac{\sqrt{3}}{2}\phi_2(x)$, where $\phi_1,\ \phi_2$ are eigenfunctions of Â

$$\hat{A}\phi_1 = a_1\phi_1, \quad \hat{A}\phi_2 = a_2\phi_2$$

How frequently do we measure a_1? a_2?

5. The time evolution of a QM system is given by

$$i\hbar\frac{\partial\Psi}{\partial t}(x,t) = \hat{H}\ \Psi(x,t)$$

If ψ is a solution of the time-independent SE

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

$$\hat{H}\Psi = -\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + V(x)\Psi = i\hbar\frac{d\Psi}{dt}$$

Can we separate x, t $\Psi(x,t) = \psi(x)\theta(t)?$

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

now multiply by $\frac{1}{\theta\psi}$

$$-\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2} + V(x) = i\hbar\frac{1}{\theta}\frac{d\theta}{dt}$$

$$-\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2}+V(x)=i\hbar\frac{1}{\theta}\frac{d\theta}{dt}$$

Left-hand side is independent of *t* and right-hand side is independent of *x*

- Both sides must be equal to a constant, E
- Separates into two ordinary differential equations:

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

which may be written in this form

(2) $i\hbar\frac{d\theta}{dt}=E\theta$

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

Simultaneous Observables

The values of two different observables, *A* and *B*, can be simultaneously determined (precisely) only if the measurement does not change the state of the system.

$$a \leftrightarrow \hat{A} \qquad\qquad b \leftrightarrow \hat{B}$$

$$\hat{B}\hat{A}\psi_n(x) = \hat{B}\alpha_n\psi_b(x), \quad \text{if } \ \psi_n \text{ an e.f. of } \hat{A} \qquad (A\psi_n = \alpha_n\psi_n)$$

$$= \beta_n\alpha_n\psi_n, \qquad \text{if } \psi_n \text{ also an e.f. of } \hat{B} \qquad \left(B\psi_n = \beta_n\psi_n\right)$$

$$\Rightarrow \qquad \hat{B}\hat{A}\psi_n = \hat{A}\hat{B}\psi_n \qquad \Rightarrow$$

Two operators commute

$\Updownarrow$

simultaneous observables

$$(\hat{A}\hat{B} - \hat{B}\hat{A}) = \underbrace{[\hat{A}, \hat{B}]}_{\text{commutator}} = 0$$

p_x, x cannot be known exactly

p_x, H cannot be known exactly unless V = constant)

Uncertainty principle (Heisenberg)

$$\Delta p \bullet \Delta x \geq \frac{\hbar}{2}$$

≠ 0 because $\hat{p}_x$ and $\hat{x}$ do not commute

Δp and Δx can be associated with standard deviations

$$\Delta x = \sqrt{\left\langle x^2 \right\rangle - \left\langle x \right\rangle^2}$$

$$\Delta p = \sqrt{\left\langle p^2 \right\rangle - \left\langle p \right\rangle^2}$$

$$\delta x = \Delta x$$

$$\delta p_x = \Delta p_x$$

$$\Delta x = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(x_i - \left\langle x \right\rangle)^2} = \sqrt{\left\langle x^2 \right\rangle - \left\langle x \right\rangle^2}$$

spread in x

In general

If two operators obey

[A, B] = iC

$$\Rightarrow \Delta A \Delta B \geq \frac{1}{2}\left|C\right|$$

If A, B commute, C = 0

If Ω does not depend on time, the time evolution of its average is given by

$$\frac{d\Omega}{dt} = \frac{i}{\hbar}\left[H, \Omega\right]$$

If [H, Ω] = 0, Ω is called a constant of the motion

$$\sum_s |s >< s| = 1$$

Completeness relation (closure relation)

$$\langle r|AB|c\rangle = \sum_s \langle r|A|s\rangle\langle s|B|c\rangle$$

$$H|\psi > \ = E|\psi >$$

$$H\sum_n c_n\,|n> \ = E\sum_n c_n\,|n>$$

Here we expand the wave function in the basis set $|n\rangle$

$$\sum_n c_n \langle m|\,H\,|n\rangle = \sum E\,c_n \langle m|n\rangle$$

$$\sum_n H_{mn} c_n = E\,c_m$$

$$H_{m1}c_1 + H_{m2}c_2 + \ldots + H_{mn}c_n = Ec_m$$

$$\begin{pmatrix} H_{11} & H_{12} & - & - \\ H_{21} & H_{22} & - & - \\ - & - & - & - \\ H_{n1} & H_{n2} & - & - \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \\ \cdot \\ c_n \end{pmatrix} = E\begin{pmatrix} c_1 \\ c_2 \\ \cdot \\ c_n \end{pmatrix}$$

Can we find functions that diagonalize the Hamiltonian matrix

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Diagonalizing a 2 x 2 Hamiltonian

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

$$\begin{pmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

$\Rightarrow$ c_1, c_2, etc. = 0, trivial solution
or

$$\begin{vmatrix} H_{11}-E & H_{12} \\ H_{21} & H_{22}-E \end{vmatrix} = 0 \Rightarrow$$

$$(H_{11}-E)(H_{22}-E)-H_{12}^{2}=0$$

$$E^{2}-E(H_{11}+H_{22})+H_{11}H_{22}-H_{12}^{2}=0$$

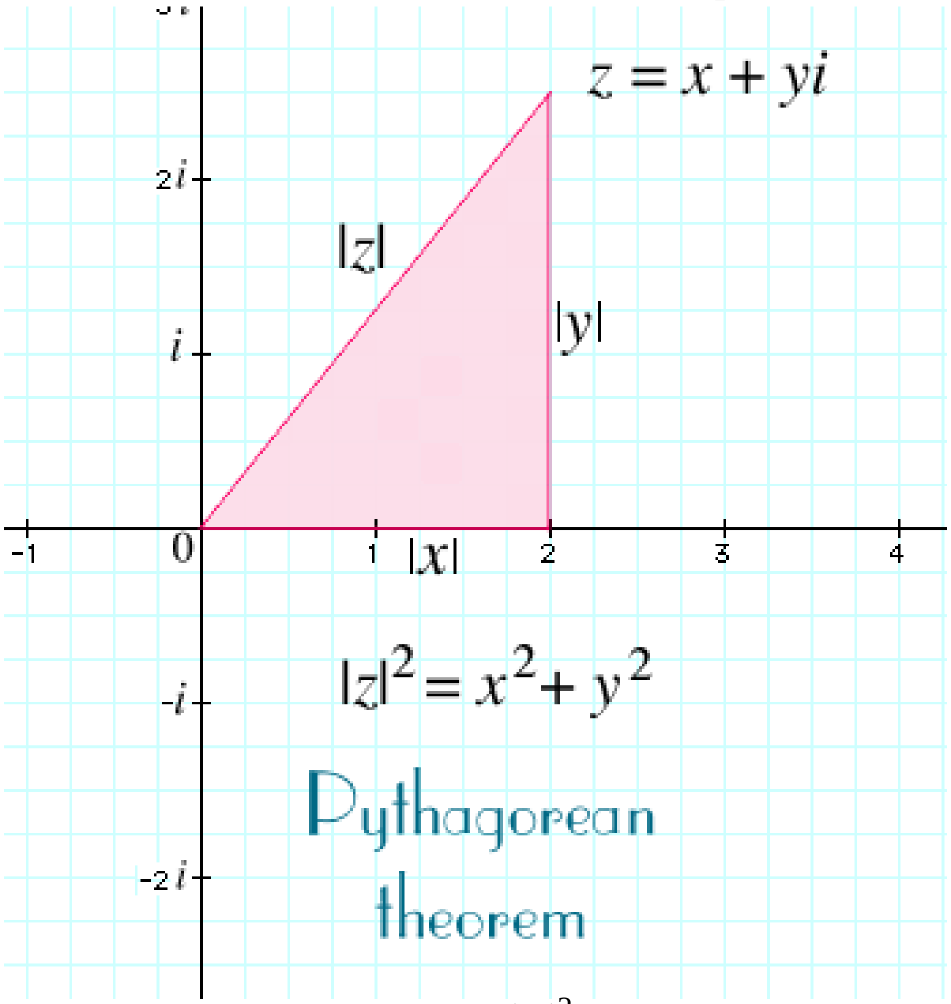
Assuming $H_{12} = H_{21}$

$$E_{\pm}=\frac{H_{11}+H_{22}}{2}\pm\frac{1}{2}\sqrt{(H_{11}-H_{22})^{2}+4H_{12}^{2}}$$

Plug E_+ into the system of equations → c_1^+, c_2^+

Plug E_- into the system of equations → c_1^-, c_2^-

Complex numbers



- |*z*| = distance from *z* to 0 in the complex plane:

$$|z| = \sqrt{x^2 + y^2}$$

- For a real number x,

  |*x*| = distance from *x* to 0 on the real number line.

$$|z|^2 = z * z = (x + iy)(x - iy) = x^2 + y^2$$

$$|z| = \sqrt{|z|^2} = \sqrt{x^2 + y^2}$$