

Quantum Mechanics

Part 1: Theory

1 The Wave Function

The Schrödinger Equation

In classical mechanics you may get all the info of a 1D particle by getting $x(t)$. [i.e. $v = \frac{dx}{dt}$, etc...]

In quantum mechanics we're looking for:

Wave Function

$$\text{Schrödinger's Equation} \quad i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V \Psi \quad \hbar = \frac{h}{2\pi}$$

The Statistical Interpretation

Born's Statistical Interpretation

$$\int_a^b |\Psi(x, t)|^2 dx = \begin{cases} \text{Probability of finding the particle} \\ \text{between } a \text{ and } b \text{ in time } t. \end{cases}$$



This interpretation brings indeterminacy, even if we have the wave function, we can only get statistical information!

which raises the thought experiment: If I did measure the position of particle, where was the particle just before being measured?

3 schools of thought:

Realist: The particle really was at that point, so quantum mechanics is incomplete (since it only gives probability)!

Orthodox: The particle wasn't anywhere. We made it take a stand by measuring it!

Agnostic: It doesn't matter where it was since we can't measure it.

"... How many angels are able to sit on top of a needle? " - Pauli

Bell discovered it really does matter

When the particle is measured the wave form

collapses



What is a measurement?

Quantum vs Classical? (Bohr) Leaving a record? (Heisenberg)

Probability

Discrete Variables

In QM, the average is usually called expectation value.
(not the most probable, just the mean)

$$\langle j \rangle = \frac{\sum j N(j)}{N} = \sum j p(j)$$

In general the average of a function:

$$\langle f(j) \rangle = \sum_{j=0}^{\infty} f(j) p(j)$$

To know "spread" in distribution with respect to the average:

$$\Delta j = j - \langle j \rangle$$

Value - Average

Now the average of that, but

$$\langle \Delta j \rangle = 0$$



to get around this

$$\langle (\Delta j)^2 \rangle \equiv \sigma^2$$

Variance

and

Standard deviation: σ

Quick way to get the standard deviation

$$\begin{aligned} \sigma^2 &= \langle (\Delta j)^2 \rangle = \sum (\Delta j)^2 p(j) = \sum (j - \langle j \rangle)^2 p(j) = \sum (j^2 - 2\langle j \rangle j + \langle j \rangle^2) p(j) = \sum (j^2 - 2\langle j \rangle j + \langle j \rangle^2) p(j) \\ &= \sum j^2 p(j) - \langle j \rangle^2 \end{aligned}$$

$$\sigma = \sqrt{\langle j^2 \rangle - \langle j \rangle^2}$$

Continuous Variables

We want probabilities over intervals.

Probability density: $p(x) dx = \left\{ \begin{array}{l} \text{Probability that something} \\ \text{lies between } x \text{ and } x+dx \end{array} \right\}$

Probability of x between a and b :

$$P_{ab} = \int_a^b p(x) dx$$

Some rules

$$1 = \int_{-\infty}^{\infty} p(x) dx \quad \langle x \rangle = \int_{-\infty}^{\infty} x p(x) dx \quad \langle f(x) \rangle = \int_{-\infty}^{\infty} f(x) p(x) dx$$

Normalization

Since $|\psi|^2$ is the probability density,

then $\int_{-\infty}^{\infty} |\psi|^2 dx = 1$ must be true.

However this would be imposing a restriction on Ψ (Schrödinger's eq.)

Since

$\frac{1}{\psi} \psi(x, t)$ is also a solution to Schrödinger's.

complex
constant

We shall pick A to ensure the restriction is satisfied.
called:

Normalizing

Non-normalizable ($\psi = 0$ or $\psi = \infty$) are rejected.

But how do we know that a normalized function at $t=0$ will stay normalized?

Well, the Schrödinger eq has that property, ∇
it preserves normalization

To prove, we just check for time independence

$$\frac{d}{dt} \int_{-\infty}^{\infty} |\psi(x,t)|^2 dx = \int_{-\infty}^{\infty} \frac{\partial}{\partial t} |\psi(x,t)|^2 dx = \int_{-\infty}^{\infty} \frac{\partial}{\partial t} (\psi \psi^*) dx = \int_{-\infty}^{\infty} (\psi \frac{\partial \psi^*}{\partial t} + \psi^* \frac{\partial \psi}{\partial t}) dx$$

According to Schrödinger's eq.

$$= \int_{-\infty}^{\infty} \left(\frac{i\hbar}{2m} \left(\psi^* \frac{\partial^2 \psi}{\partial x^2} - \frac{\partial \psi^*}{\partial x} \psi \right) \right) dx = \int_{-\infty}^{\infty} \frac{\partial}{\partial x} \left[\frac{i\hbar}{2m} \left(\psi^* \frac{\partial \psi}{\partial x} - \frac{\partial \psi^*}{\partial x} \psi \right) \right] dx$$

Now

$$= \frac{i\hbar}{2m} \left(\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x} \right) \Big|_{-\infty}^{\infty} = \frac{d}{dt} \int_{-\infty}^{\infty} |\psi(x,t)|^2 dx$$

ψ must be 0 at $\pm \infty$

therefore $\frac{d}{dt} \int_{-\infty}^{\infty} |\psi(x,t)|^2 dx = 0$ TIME INDEPENDENT!

Momentum

For a particle in state ψ , the expected value of x is

$$\langle x \rangle = \int_{-\infty}^{\infty} x |\psi(x,t)|^2 dx$$

[Continuous average]

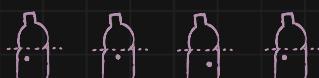
sort of the
average position
a particle with
state ψ will
take
(to make it work
similarly to classical
mechanics?)

What does this mean?

It is NOT the average position of a single particle measured over and over



It is the average position of a whole ensemble of particles in state ψ .



Bottles with particles in
state ψ

If we measure the position at
the same time, it will match

$$|\psi|^2$$

and $\langle x \rangle$ should be the average.

Average of repeated measurements on an ensemble of identically prepared systems

NOT the average of repeated measurements on one and the same system

With time $\langle x \rangle$ will change ($\psi(x, t)$), how fast does it move?

how fast the average changes over time compared to next average
(kinda comparing snapshots)

$$\frac{d}{dt} \langle x \rangle = \int x \frac{\partial}{\partial t} |\psi|^2 dx = \frac{i\hbar}{2m} \int x \frac{\partial}{\partial x} \left(\psi + \frac{\partial \psi}{\partial x} - \frac{\partial \psi^*}{\partial x} \psi \right) dx = -\frac{i\hbar}{2m} \int \left(\psi \frac{\partial \psi}{\partial x} - \frac{\partial \psi^*}{\partial x} \psi \right) dx$$

$$\langle v \rangle = \frac{d}{dt} \langle x \rangle = -\frac{i\hbar}{m} \int \psi^* \frac{\partial \psi}{\partial x} dx$$

The expectation value of the velocity is equal to time derivative of expectation value of position

This is NOT the velocity of the particle (that doesn't exist since we don't know where it used to be)

We usually work with momentum

$$\langle p \rangle = m \frac{d \langle x \rangle}{dt} = -i\hbar \int \left(\psi^* \frac{\partial \psi}{\partial x} \right) dx$$

We can rewrite $\langle x \rangle$ and $\langle p \rangle$

$$\begin{aligned} \langle x \rangle &= \int \psi^*(x) \psi dx && \text{Operator } (x) \text{ represents position} \\ \langle p \rangle &= \int \psi^* \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) \psi dx && \text{Operator } \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) \text{ represents momentum} \end{aligned}$$

We can write physical quantities with operators

$$\langle Q(x, p) \rangle = \int \psi^* \left(Q(x, \frac{\hbar}{i} \frac{\partial}{\partial x}) \right) \psi dx$$

Expectation value of any dynamical quantity, for particle in state ψ .

for example

Kinetic energy : $T = \frac{1}{2} mv^2 = \frac{p^2}{2m}$

"Quantum" K.E. : $\langle T \rangle = \int \psi^* \left(\frac{1}{2m} \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right)^2 \right) \psi dx$

The Uncertainty Principle



Where is the wave? I do know
What is its wavelength? I do know



Where is the wave? I do know
What is its wavelength? I do know

Inescapable trade-off: The more precise the position, the less precise wavelength

De Broglie Formula

$$p = \frac{\hbar}{\lambda} = \frac{2\pi\hbar}{\lambda}$$

This reflects the inherent particle-wave complementarity?

Heisenberg's Uncertainty Principle

$$\sigma_x \sigma_p \geq \frac{\hbar}{2}$$

(standard deviation x) (standard deviation p)

ψ with precise position yields imprecise momentum.

2 Time - Independent Schrödinger equation

Stationary States

We know some quantities of ψ , but how do you get ψ itself?

We solve $i\hbar \frac{d\psi}{dt} = -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi$ for some V .

Assuming V is independent of t

by separation of variables $\psi(x,t) = \psi(x)\psi(t)$ we get

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

Both sides must be a constant

Both sides depend on different variables

Left side

$$\frac{d\psi}{dt} = -\frac{iE}{\hbar}\psi$$

with general solution

$$\psi(t) = e^{-\frac{iEt}{\hbar}}$$

Right side

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

Time independent Schrödinger equation

To get ψ we must have V first.

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

Interpretation:

1 Stationary States

Although $\psi(x,t)$ depends on time

$$|\psi(x,t)|^2 = \psi^*\psi = \psi^* e^{\frac{iEt}{\hbar}} \psi e^{-\frac{iEt}{\hbar}} = |\psi(x)|^2$$

does not depend on time!

for any dynamical value

$$\langle Q(x,p) \rangle = \int \psi^* Q(x, \frac{\hbar}{i} \frac{d}{dx}) \psi dx$$

Every expectation value is constant in time !

The Infinite Square Well

Suppose $V(x) = \begin{cases} 0, & \text{if } 0 \leq x \leq a \\ \infty, & \text{otherwise} \end{cases}$



Outside $\psi = 0$ ∵ (0 probability)

Inside $V = 0$ ∵ $-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi$

Or $\frac{d^2\psi}{dx^2} = -k^2\psi^2$ where $k = \frac{\sqrt{2mE}}{\hbar}$ [$E \geq 0$]

This (simple harmonic oscillator) has solution

$$\psi(x) = A \sin(kx) + B \cos(kx)$$

With boundary conditions

$$\psi(0) = A \sin 0 + B \cos 0 = B = 0$$

$$B = 0$$

$$\psi(x) = A \sin(kx)$$

$$\psi(a) = A \sin(ka) + B \cos(ka) = A \sin(ka) = 0 \quad (\text{trivial})$$

$$\sin(ka) = 0$$

$$ka = 0, \pm\pi, \pm 2\pi, \dots \quad (\text{trivial})$$

$$k = \frac{n\pi}{a} \quad n = 1, 2, 3$$

Now, with this constant

$$k = \frac{\sqrt{2mE}}{\hbar} \Rightarrow \frac{k^2 \hbar^2}{2m} = E$$

$$\Rightarrow E_n = \left(\frac{n\pi}{a}\right)^2 \frac{\hbar^2}{2m}$$

Cannot have any energy, must have an allowed value

(Due to n)

Now, to find A

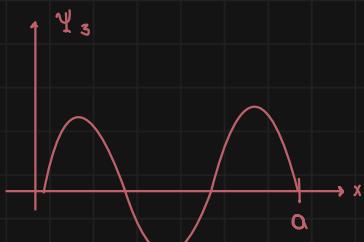
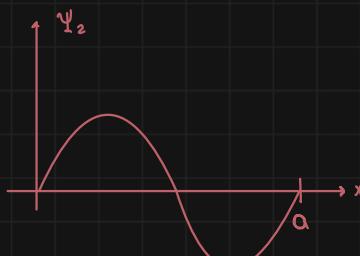
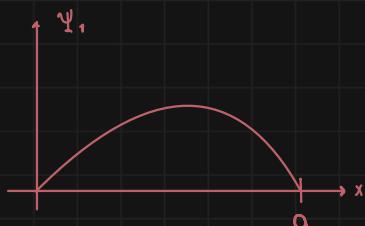
Normalize

$$\int_0^a |A|^2 \sin^2(kx) dx = |A|^2 \frac{a}{2} = 1 \quad A = \sqrt{\frac{2}{a}}$$

Final solutions

$$\psi(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} x\right)$$

Infinite solutions (n)



The Free Particle

i.e. no potential, $V(x) = 0$ everywhere

Free Particle Schrödinger Equation

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

$$\frac{d^2\psi}{dx^2} = -K^2\psi \quad \text{with} \quad K = \frac{\sqrt{2mE}}{\hbar}$$

with solution

$$\psi(x) = A e^{ikx} + B e^{-ikx}$$

The same as inside the infinite square well.

Now we don't have boundary conditions to restrict.

It can have any positive energy.

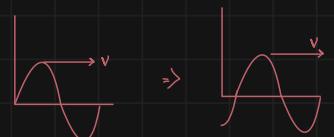
Adding time dependence ($e^{-i\frac{Et}{\hbar}}$, $E = \frac{K^2\hbar^2}{2m}$)

$$\Psi(x,t) = A e^{iK(x - \frac{\hbar K}{2m}t)} + B e^{-iK(x + \frac{\hbar K}{2m}t)}$$

Any function with form $(x \pm vt)$

represents a wave of fixed profile

travelling to $\mp x$ at speed v



$$\Psi(x,t) = \underbrace{A e^{iK(x - \frac{\hbar K}{2m}t)}}_{\text{Wave to the right}} + \underbrace{B e^{-iK(x + \frac{\hbar K}{2m}t)}}_{\text{Some energy wave to the left}}$$

Rewriting with K dependence

$$\Psi_K(x,t) = A e^{i(Kx - \frac{\hbar K^2}{2m}t)} \quad \text{with} \quad K \equiv \pm \frac{\sqrt{2mE}}{\hbar} \quad \begin{cases} K > 0, \text{ to the right} \\ K < 0, \text{ to the left} \end{cases}$$

Stationary states are propagating waves

$$\text{with wavelength} \quad \lambda = \frac{2\pi}{|K|}$$

$$\text{with momentum} \quad p = \hbar K$$

$$\text{with speed} \quad v_{\text{quantum}} = \frac{\hbar |K|}{2m} = \sqrt{\frac{E}{2m}}$$

De Broglie $\lambda = \frac{\hbar}{p} \Rightarrow K = \frac{\hbar}{\lambda}$

This wave function is not normalizable

$$\int_{-\infty}^{\infty} \Psi_K \Psi_K^* dx = |A|^2 \int_{-\infty}^{\infty} dx = |A|^2 (\infty)$$

Which means there is no such thing as free particle with definite energy

The general solution is a linear combination as integral over K (instead of sum over n)

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(K) e^{i(Kx - \frac{\hbar K^2}{2m}t)} dK$$

$$(C_n \text{ is } \frac{1}{\sqrt{2\pi}} \phi(K) dK)$$

This CAN be normalized, but it carries a range of K 's (diff energies / speeds)

Therefore, we call it wave packet

The Delta-Function Well

Quick Dirac Delta remainder:

Infinitely high, infinitely narrow spike at the origin with area 1.



$$\delta(x) = \begin{cases} 0, & \text{if } x \neq 0 \\ \infty, & \text{if } x = 0 \end{cases}, \quad \int_{-\infty}^{\infty} \delta(x) dx = 1$$

It's a generalized function

$$f(x) \delta(x-a) = f(a) \delta(x-a) \quad \therefore \quad \int_{-\infty}^{\infty} f(x) \delta(x-a) dx = \int_{-\infty}^{\infty} f(a) \delta(x-a) dx = f(a)$$

Let's consider the potential

$$V(x) = -\propto \delta(x) \quad \text{with } \propto: \text{constant}$$



This is an artificial potential, but kinda cute little math clutter

The Schrödinger eq. becomes

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} - \propto \delta(x) \psi = E \psi$$

Returns bound states ($E > 0$)
scattering states ($E < 0$)

$E < 0$ For bound states

In region $x < 0$, $V(x) = 0$

$$\frac{d^2\psi}{dx^2} = -\frac{2m}{\hbar^2} E \psi = K^2 \psi \quad \text{with} \quad K = \frac{\sqrt{-2mE}}{\hbar} \quad [E \text{ is } < 0]$$

With solution: $\psi = A e^{-Kx} + B e^{Kx}$ $A=0$
 \downarrow
 \downarrow
Blows up
at $x = -\infty$

In region $x > 0$, $V(x) = 0$

Same Schrödinger eq., with solution:

$$\psi = F e^{-Kx} + G e^{Kx} \quad \text{with } G=0 \quad = F e^{-Kx} \quad (x > 0)$$

\downarrow
Blows up
at $x = \infty$

Standard Boundary Conditions for ψ

- 1. ψ is always continuous
- 2. $d\psi/dx$ is continuous except where the potential is infinite

From condition 1, we know $F=B$

$$\psi(x) = \begin{cases} B e^{-Kx} & \text{for } x \leq 0 \\ B e^{Kx} & \text{for } x \geq 0 \end{cases}$$



From condition 2 (nothing immediate, our function has no $V=\infty$), but we can analyze:

Integrate Schrödinger eq. and take the limit

$$\int_{-\varepsilon}^{\varepsilon} \text{Schrödinger eq. } dx \Rightarrow -\frac{\hbar^2}{2m} \int_{-\varepsilon}^{\varepsilon} \frac{d^2\psi}{dx^2} dx + \int_{-\varepsilon}^{\varepsilon} V(x) \psi(x) dx = E \int_{-\varepsilon}^{\varepsilon} \psi(x) dx$$

$$\lim_{x \rightarrow 0} \left(-\frac{\hbar^2}{2m} \frac{d\psi}{dx} \Big|_{-\varepsilon}^{\varepsilon} + \int_{-\varepsilon}^{\varepsilon} V(x) \psi(x) dx \right) = E \int_{-\varepsilon}^{\varepsilon} \psi(x) dx$$

$$\Delta \left(\frac{d\psi}{dx} \right) = \frac{2m}{\hbar^2} \lim_{x \rightarrow 0} \int_{-\varepsilon}^{\varepsilon} V(x) \psi(x) dx$$

Usually ψ (continuous) except $V(x) = \infty$

Finite Square Well

let's consider the finite square well potential

$$V(x) = \begin{cases} -V_0, & \text{for } -a \leq x \leq a \\ 0, & \text{for } |x| > a \end{cases}$$



Like the infinite well, we have both

• bound states ($E > 0$)

• scattering states ($E < 0$)

For bound states $E > 0$

• Region $x < -a$, $V(x) = 0$

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi \Rightarrow \frac{d^2\psi}{dx^2} = \frac{E}{\hbar^2} \psi \quad \text{with} \quad k = \frac{\sqrt{-2mE}}{\hbar} \quad \begin{cases} \text{Real,} \\ E \text{ is positive} \end{cases}$$

solution: $\psi(x) = A e^{-kx} + B e^{kx} \Rightarrow B e^{kx}, \text{ for } x < a$

• Region $x > a$, $V(x) = 0$

Same eq. with solution: $\psi(x) = F e^{-kx} + G e^{kx} \Rightarrow F e^{-kx}, \text{ for } x > a$

• Region $-a < x < a$, $V(x) = -V_0$

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} - V_0 \psi = E\psi \Rightarrow \frac{d^2\psi}{dx^2} = -\frac{E}{\hbar^2} \psi \quad \text{with} \quad l \equiv \frac{\sqrt{2m(E+V_0)}}{\hbar} \quad \begin{cases} \text{Even the } E \text{ is} \\ \text{negative,} \\ E > -V_0 \\ \text{So, real and positive} \end{cases}$$

solution: $\psi = C \sin(lx) + D \cos(lx) \quad \text{for } -a < x < a$

Continuity at $a, -a$. But since function is even, we can just get a , the other is automatic

For even solutions:

$$\psi(x) = \begin{cases} Fe^{-kx} & x > a \\ 0 \cos(lx) & 0 < x < a \\ \psi(-x) & x < 0 \end{cases}$$

Continuity at $x=a$:

$$Fe^{-ka} = D \cos(ka)$$

Continuity $\frac{d\psi}{dx}$ at $x=a$:

$$-kF e^{-ka} = -l(D \sin(ka))$$

Dividing both:

$$k = l \tan(ka)$$

Formula for allowed energies

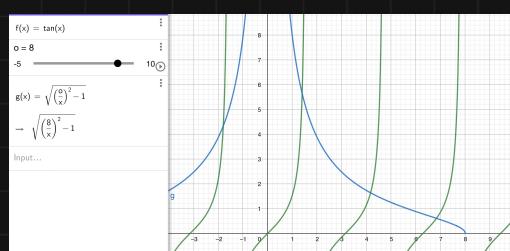
For fun: $z = ka$, $z_0 \equiv \frac{a}{\hbar} \sqrt{2mV_0}$

so $(K + l^2) = \frac{2mV_0}{\hbar^2}$, $Ka = \sqrt{z_0^2 - z^2}$

Rewriting

$$\tan z = \sqrt{\left(\frac{z_0}{z}\right)^2 - 1}$$

z_0 : "size" of the well



Transcendental,
just graph it lol

There are odd solutions, just change cos to sin and calculate,

3 Formalism

Hilbert Spaces

We have seen some interesting properties in quantum systems, we will now prove and generalize the theory in a powerful form.

Quantum Theory is based on

Wave functions :	State of a system	(abstract vectors)
operators :	Observables	(linear transformations)

Vector

$$|\alpha\rangle \longrightarrow \vec{a} = \begin{pmatrix} a_1 \\ a_2 \\ \dots \\ a_N \end{pmatrix}$$

tuple of N components with respect to
a specified orthonormal basis

Inner Product

$$\langle \alpha | \beta \rangle = a_1^* b_1 + a_2^* b_2 + \dots + a_N^* b_N$$

remember, generalized DOT product
(useful to see as amount of α in β)

Matrices (linear combinations etc)

$$|\beta\rangle = T|\alpha\rangle \longrightarrow \vec{b} = \vec{T}\vec{a} = \begin{pmatrix} t_{11} & t_{12} & \dots & t_{1N} \\ \dots & \dots & \dots & \dots \\ t_{N1} & t_{N2} & \dots & t_{NN} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ \dots \\ a_N \end{pmatrix}$$

Vectors in quantum mechanics are usually functions in infinite-dimensional spaces.
They act weird.

(Even tho a sum for the inner product ALWays exist, the integral might not (diverge))

All functions of x form a vector space.

But to have a possible physical state, Ψ must be normalized.

$$\int |\Psi|^2 dx = 1 \quad \text{why?}$$

If a wave function cannot
be normalized it doesn't
have a real physical probability



[probability / area has to be 1, there
aren't any 0.6 or 1.5 total probabilities]

This wave function can't be
normalized and therefore isn't "real"

The set of all square integrable functions, on specified interval

$$f(x) \text{ such that } \int_0^b |f(x)|^2 dx < \infty$$

make up a (smaller) vector space, called Hilbert Space (or $L_2(a, b)$)

Wave functions live in Hilbert Space why?

Because if a wave function
 $f(x) = \Psi(x)$ is square-integrable
i.e. $\int_{-\infty}^{\infty} |\Psi(x)|^2 dx < \infty$



it constitutes a physically possible (normalizable) probability function !

Inner product of two functions

$$\langle f | g \rangle = \int_a^b f(x)^* g(x) dx$$

sort of dot product
of functions

If f and g are square-integrable (in Hilbert Space)
the inner product is guaranteed to exist.

From the integral Schwarz inequality

$$\left| \int_a^b f(x)^* g(x) dx \right| = \sqrt{\int_a^b |f(x)|^2 dx} \sqrt{\int_a^b |g(x)|^2 dx}$$

$(< \infty)$ $(< \infty)$
converge ✓

Note that $\langle g | f \rangle = \langle f | g \rangle^*$

Inner product with itself

$$\langle f | f \rangle = \int_a^b |f(x)|^2 dx$$

- is real and non-negative

If

Easy to understand as dot product
 $f \cdot f = 1$ normalized
 $f \cdot g = 0$ or orthogonal

- $\langle f | f \rangle = 1$ means f it's normalized

- $\langle f | g \rangle = 0$ means the functions are orthogonal

- A set of functions $\{f_n\}$ is orthonormal if its both normalized and orthogonal

$$\langle f_m | f_n \rangle = \delta_{mn}$$

$$\delta_{mn} = \begin{cases} 1, & m=n, \text{ normalized} \\ 0, & m \neq n, \text{ orthogonal} \end{cases}$$

- A set of functions $\{f_n\}$ is complete if any other function (in Hilbert Space of course) can be expressed as a linear combination of them

$$f(x) = \sum_{n=1}^{\infty} c_n f_n(x)$$

Remember completeness from linear algebra

if $\{f_n(x)\}$ are orthonormal, the coefficients are given by Fourier's Trick

?

Remember Fourier's Trick for a function $f(x)$

Multiply f by ψ_m^* and integrate Using the fact that it is complete They are orthonormal

$$\int \psi_m(x)^* [f(x)] dx = \sum_{n=1}^{\infty} c_n \int \psi_m^* [\psi_n] dx = \sum_{n=1}^{\infty} c_n \delta_{mn} = c_m$$

$$= \langle \psi_n | \psi_m \rangle = \delta_{mn}$$

by orthonormality

$$\int \psi_m(x)^* f(x) dx = \langle \psi_m | f \rangle = c_m$$

Exercise 1 and 2

1a) Show all square integrable functions is a vector space.

Most requirements are trivial (commutative $|f\rangle + |g\rangle = |g\rangle + |f\rangle$, etc.)

The only hard one

$$\int |h|^2 dx = \int (f+g)^* (f+g) dx = \int f^* f + f^* g + g^* f + g^* g dx$$

$\|h\|^2$ is square integrable

$\Rightarrow \int f^* f + g^* g dx$ has to be square integrable ✓

h is therefore square-integrable

square integrable

$\sqrt{\int f^* f dx} + \sqrt{\int g^* g dx}$ by Schwarz

- 1b) Show the integral satisfies conditions for inner product.
- Conditions for inner product:
- $\langle g|f \rangle = \langle f|g^* \rangle^*$
 - $\langle f|f \rangle \geq 0$ only if $f=0$ ✓
 - $\langle h|(Af + Bg) \rangle = A\langle h|f \rangle + B\langle h|g \rangle$
 - simply expand $\int h^* Af + h^* Bg \, dx$ ✓

2a) Range for $f(x) = x^v$ is in Hilbert space on $[1, 0]$, v is real.

To be in Hilbert space, it must be square-integrable

$$\text{so normalizing } \langle f|f \rangle = \int_0^1 x^{2v} \, dx = \frac{1}{2v+1} x^{2v+1} \Big|_0^1 = \frac{1}{2v+1} (1 - 0^{2v+1})$$

if $2v+1$ is negative, all blows up $(\frac{1}{0}, \frac{1}{0^2}, \dots)$

$$\text{so } 2v+1 > 0 \\ v > -\frac{1}{2}$$

Observables

Hermitian Operators

Expectation value expressed with inner notation

$$\langle Q \rangle = \int \Psi^* \hat{Q} \Psi \, dx = \langle \Psi | \hat{Q} \Psi \rangle$$

(\hat{Q} is Q but all p replaced by $\hat{p} = \frac{\hbar}{i} \frac{d}{dx}$)

The result of a measurement must be real, therefore the average is real

$$\langle Q \rangle = \langle Q \rangle^*$$

But the complex conjugate reverses the order $\langle g|f \rangle^* = \langle f|g \rangle$ from

$$\langle \Psi | \hat{Q} \Psi \rangle = \langle \hat{Q} \Psi | \Psi \rangle \quad \text{true for any } \Psi.$$

thus, operators that represent observables have the property:

$$\langle f | \hat{Q} f \rangle = \langle \hat{Q} f | f \rangle \quad \text{for all } f(x)$$

these operators are called hermitian.

Hermitian operators complete condition: $\langle f | \hat{Q} g \rangle = \langle \hat{Q} f | g \rangle$ for all $g(x)$ and $f(x)$

Quick recap:

Operators that represent observables are hermitian and have real expectation values.

Observables are represented by hermitian operators

Is momentum hermitian?

$$\langle f | \hat{p} g \rangle = \int_{-\infty}^{\infty} f^* \left(\frac{\hbar}{i} \frac{d}{dx} g \right) \, dx = \frac{\hbar}{i} f^* g \Big|_{-\infty}^{\infty} - \int g \left(\frac{\hbar}{i} \frac{df}{dx} \right)^* \, dx = \int \frac{\hbar}{i} \frac{df^*}{dx} g \, dx = \langle \hat{p} f | g \rangle \quad \begin{matrix} \text{Goes to zero at } \infty \\ \text{because square-integrable} \end{matrix}$$

$\begin{matrix} \text{equivalent} \\ \curvearrowleft \curvearrowright \end{matrix}$

Exercise

5a) Get hermitian conjugate \hat{Q}^+ $\left[\langle f | \hat{Q} g \rangle = \langle \hat{Q}^+ f | g \rangle \right]$

$$\langle f | \frac{d}{dx} g \rangle = \int f^* \frac{d}{dx} g \, dx = f^* g - \int \frac{d}{dx} f^* g \, dx = -\langle \frac{d}{dx} f | g \rangle \Rightarrow \left(\frac{d}{dx} \right)^+ = -\frac{d}{dx}$$

$$\langle f | ig \rangle = \int f^* (ig) \, dx = \int (-if)^* g \, dx = \langle -if | g \rangle \Rightarrow i^+ = -i$$

$$\langle f | xg \rangle = \int f^* (xg) \, dx = \int (xf)^* g \, dx = \langle xf | g \rangle \Rightarrow x^+ = x$$

Determinate States

Normally when you measure an observable Q on a lot of identically prepared systems you get a different result each time (quantum indeterminacy etc)

Would it be possible to have a state such that every measurement of Q returned the same value q ?

This would be a determinate state.

(stationary states are determinate states of the Q Hamiltonian, a Ψ_n will always return E_n)

The standard deviation would be zero (no spread)

$$\sigma^2 = \langle (\hat{Q} - \langle Q \rangle)^2 \rangle = \langle \Psi | (\hat{Q} - q)^2 \Psi \rangle = \langle (\hat{Q} - q) \Psi | (\hat{Q} - q) \Psi \rangle = 0$$

avg. value
 $\langle Q \rangle = q$

?

so, $\hat{Q} \Psi = q \Psi \longrightarrow \vec{A} \vec{v} = \lambda \vec{v}$

Eigenvalue equation for \hat{Q} !

Ψ is the eigenfunction of \hat{Q}

q is the eigenvalue

Determinate states are eigenfunctions of \hat{Q}

A measurement of Q in this Ψ state will yield eigenvalue q

Spectrum

The collection of all eigenvalues of an operator.

Sometimes two + linearly independent eigenfunctions share eigenvalues, if that's the case the spectrum is called degenerate.

For example, $\hat{H} \Psi = E \Psi$
 transformation \nearrow eigenfunction \downarrow eigenvalue

we can multiply by $e^{-iE\hat{t}}$ it would be the same eigenvalues.

Example

$\hat{Q} = i \frac{d}{d\phi}$, ϕ : 2D Polar coordinates. Is \hat{Q} hermitian? Find eigenfunction and eigenvalues

We know $0 \leq \phi \leq 2\pi$, $f(\phi + 2\pi) = f(\phi)$ [periodical]

$$\text{Hermitian: } \langle f | \hat{Q} g \rangle = \int_0^{2\pi} f^* \left(i \frac{d}{d\phi} g \right) d\phi = i \int_0^{2\pi} f^* \frac{dg}{d\phi} d\phi = i \int_0^{2\pi} f^* g \frac{d}{d\phi} d\phi = \langle \hat{Q} f | g \rangle$$

$u = f^*$ $du = \frac{df}{d\phi} d\phi$
 $dV = \frac{dg}{d\phi}$ $V = g$

Eigenvalue eq: $i \frac{d}{d\phi} f(\phi) = q f(\phi)$

with solution: $f(\phi) = A e^{-iq\phi}$

restriction: $f(0) = f(0 + 2\pi) \Rightarrow e^{-iq(2\pi)} = 1 \quad q = 0, \pm 1, \pm 2, \dots$

Spectrum is all integers, non-degenerate.

Exercise

$$\hat{Q} = \frac{d^2}{d\phi^2} \quad \text{some conditions.}$$

$$\text{Hermitian: } \langle f | \hat{Q} g \rangle = \int_0^{2\pi} f^* \left(\frac{d^2}{d\phi^2} g \right) d\phi = f^* \frac{d}{d\phi} g \Big|_0^{2\pi} - \int_0^{2\pi} \frac{d}{d\phi} f^* \frac{d}{d\phi} g d\phi = \int_0^{2\pi} \frac{d^2 f^*}{d\phi^2} g d\phi - \int_0^{2\pi} \frac{d^2 g}{d\phi^2} f d\phi$$

$$\text{Eigenval eq.: } \frac{d^2}{dx^2} f = q f \quad ; \quad \text{Solution: } \lambda^2 = q \quad \lambda = \sqrt{q} \quad f(\emptyset) = A e^{q\emptyset} + B e^{-q\emptyset}$$

for $f_1 = A e^{q\emptyset}$, with boundary cond.

$$e^{2nq} = 1 \quad q = -n^2, \quad n = 0, 1, 2, \dots$$

$$e^{-2nq} = 1$$

Eigenfunctions of a Hermitian Operator

Now we study eigenfunctions of hermitian operators (determinate states of observables)
if measured, always the same REAL result

2 categories:

1. Discrete

Eigenfunc in Hilbert space, realizable states [Harmonic oscillator]

2. Continuous

Eigenfunc not normalizable, not-realizable states [Free particle]
but linear combinations may be normalizable

• Discrete spectra

The normalizable eigenfunc of hermitian operator
have 2 properties.

Reality 1. Their eigenvalues are real

if you measure
an observable
of particle in
determinate state,
you get a real number

$$\hat{Q}f = qf \Rightarrow q \langle f | f \rangle = q^* \langle f | f \rangle$$

\downarrow plug into integral form

Orthogonality 2. Eigenfunctions of distinct eigenvalues are orthogonal

$$\begin{aligned} \hat{Q}f &= qf \\ \hat{Q}g &= q'g \end{aligned} \Rightarrow \langle f | \hat{Q}g \rangle = \langle \hat{Q}f | g \rangle \Rightarrow q \langle f | g \rangle = q^* \langle f | g \rangle$$

\downarrow it is hermitian

q is real and if $q \neq q'$: $\langle f | g \rangle = 0$ dot product is zero

if $q = q'$ (degenerate) any linear combination
is a new eigenfunc with some eigenval, then
we can construct orthogonal eigenfunctions (Graham-Schmidt)

That's why the harmonic oscillator states are orthogonal!

Eigenfunctions with distinct eigenvalues

$$\hat{H}f = hf \quad \hat{H}g = h'g \quad \dots$$

Completeness Axiom. The Eigenfunctions of an observable operator are complete
(Any function can be expressed as a linear combination of them)

Quantum Mechanics in 3 Dimensions

Schrödinger Equation in Spherical Coordinates

Quite simple

$$i\hbar \frac{\partial \Psi}{\partial t} = \left[\frac{1}{2m} \left(p_x^2 + p_y^2 + p_z^2 \right) + V \right] \Psi$$

$$p_x \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial x} \quad p_y \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial y} \dots \Rightarrow \vec{p} = \frac{\hbar}{i} \nabla$$

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

Now $V(\vec{r})$, $\Psi(\vec{r}, t)$

Probability of finding a particle in infinitesimal volume $d^3r = dx dy dz$
is $|\Psi(\vec{r}, t)|^2 d^3r$

$$\int_V |\Psi|^2 d^3r = 1$$

If potential is independent of time (as before), the stationary states are

$$\Psi(\vec{r}, t) = \psi_n(\vec{r}) e^{-\frac{iEt}{\hbar}}$$

where ψ satisfies the T I Schrödinger eq.

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

with general solution (T I)

$$\Psi(\vec{r}, t) = \sum C_n \psi_n(\vec{r}) e^{-\frac{iEt}{\hbar}}$$

↓
Determined
by $\psi(\vec{r}, 0)$

Becomes an integral for
continuum states

Separation of Variables

Typically the potential depends only on distance from the origin, $V(r, \theta, \phi)$
We use spherical coordinates (r, θ, ϕ)

T I Schrödinger eq in spherical :

$$-\frac{\hbar^2}{2m} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \left(\frac{\partial^2 \psi}{\partial \phi^2} \right) \right] + V \psi = E \psi$$

We look for solutions with form $\psi(r, \theta, \phi) = R(r) Y(\theta, \phi)$

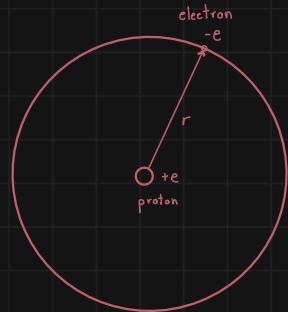
Simplifying:

$$\underbrace{\left\{ \frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2} [V(r) - E] \right\}}_{= \ell(\ell+1)} + \underbrace{\frac{1}{Y} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right\}}_{= -\ell(\ell+1)} = 0$$

only r
Radial Equation

only θ, ϕ
Angular Equation

The Hydrogen Atom



From Coulomb's Law, we know the potential energy

$$V(r) = -\frac{e^2}{4\pi \epsilon_0} \frac{1}{r}$$

So, the radial eq. becomes

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left[-\frac{e^2}{4\pi \epsilon_0} \frac{1}{r} + \frac{\hbar^2 l(l+1)}{2m r^2} \right] u = E u$$

Solve for u and determine E .

The Radial Wave Function

For notation let

$$k = \frac{\sqrt{2mE}}{\hbar} \quad \rho = kr \quad \rho_0 = \frac{me^2}{2\pi \epsilon_0 \hbar^2 k}$$

So the radial eq. becomes

$$\frac{d^2 u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2} \right] u$$

Check asymptotic form of solutions

$\bullet \rho \rightarrow \infty$ (large)

$$\frac{d^2 u}{d\rho^2} = u$$

solution $u \approx A e^{-\rho} + B e^\rho$ blows up

$\bullet \rho \rightarrow 0$ (small)

$$\frac{d^2 u}{d\rho^2} = \frac{l(l+1)}{\rho^2} u$$

solution $u \approx C \rho^{l+1} + D \rho^{-l}$ blows up

(Join and add $v(\rho)$ to get rid
of asymptotic behavior)

$$u(\rho) = e^{-\rho} \rho^{l+1} v(\rho)$$

In terms of $v(\rho)$ (just get $\frac{du}{d\rho}$, $\frac{d^2 u}{d\rho^2}$ and substitute)
the radial eq.

$$\rho \frac{d^2 v}{d\rho^2} + 2(l+1 - \rho) \frac{dv}{d\rho} + [\rho_0 - 2(l+1)] v = 0$$

Now assume v is a power series

$$v(\rho) = \sum_{j=0}^{\infty} C_j \rho^j \quad \text{then} \quad \frac{dv}{d\rho} = \sum_{j=0}^{\infty} C_j j \rho^{j-1} = \sum_{j=0}^{\infty} (j+1) C_{j+1} \rho^j$$

$j = j-1$

Plugging back into radial eq. (and getting $\frac{d^2 v}{d\rho^2}$):

$$2(l+1) \sum_{j=0}^{\infty} (j+1) C_{j+1} \rho^j + \sum_{j=0}^{\infty} j(j+1) C_{j+1} \rho^j - 2 \sum_{j=0}^{\infty} j C_j \rho^j + [\rho_0 - 2(l+1)] \sum_{j=0}^{\infty} C_j \rho^j = 0$$

Like powers:

$$C_{j+1} = \left\{ \frac{2(j+l+1) - \rho_0}{(j+1)(j+2l+2)} \right\} C_j$$

Recursion formula for coefficients of $v(\rho)$

For an arbitrary n , the possible values of l
 $l = 0, 1, 2, \dots, n-1$

Due to $n = j_{\max} + l + 1$

for each l there are $(2l+1)$ values of m

$$m = 0, (-1, 0, 1), \dots$$

Total degeneracy of energy level

$$d(n) = \sum_{l=0}^{n-1} (2l+1) = n^2$$

We can write

$$V(p) = \sum_{n-l-1}^{2l+1} (2p)$$

↓

where $L_{q-p}^p(x) = (-1)^p \left(\frac{d}{dx}\right)^p L_q(x)$ is the Associated Laguerre Polynomial

↓

where $L_q(x) = e^x \left(\frac{d}{dx}\right)^q (e^{-x} x^q)$ is the q th Laguerre Polynomial

The Normalized Hydrogen Wave Functions

$$\psi_{nlm} = \left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3} e^{-\frac{r}{na}} \left(\frac{2r}{na}\right)^l \left[L_{n-l-1}^{2l+1} \left(\frac{2r}{na}\right) \right] Y_l^m(\theta, \phi)$$

Trust this normalized. I did.

The wave functions are mutually orthogonal (follows from spherical harmonics)

The Spectrum of Hydrogen

if you put a hydrogen atom into some stationary state Ψ_{nlm}
it should stay there forever.

However, if you tickle it slightly, the electron may undergo
a transition to other stationary state, either by

- Absorbing energy \rightarrow moving up \uparrow
- Giving off energy \rightarrow moving down \downarrow

Also called quantum jumps

These result in H giving off an electron
with energy:

$$E_\gamma = E_i - E_f = -13.6 \text{ eV} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

Difference in energy between initial and final states

According to Planck Formula ($E_y = h\nu$) and $\lambda = \frac{c}{\nu}$:

$$\frac{1}{\lambda} = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad \text{Rydberg Formula}$$

where $R = \frac{m}{8\pi c \hbar^3} \left(\frac{e^2}{8\pi \epsilon_0} \right)^2 = 1.097 \times 10^7 \text{ m}^{-1}$
 Rydberg constant

Add graphs

Angular Momentum

We know stationary states of H atom depend on n, l, m .
 n determines the energy
 l, m are related to angular momentum

Classically, angular momentum is:

$$L = r \times p$$

$$L_x = y p_z - z p_y \quad L_y = z p_x - x p_z \quad L_z = x p_y - y p_x$$

quantum operators

$$p_x \rightarrow -i\hbar \frac{\partial}{\partial x} \quad p_y \rightarrow -i\hbar \frac{\partial}{\partial y} \quad p_z \rightarrow -i\hbar \frac{\partial}{\partial z}$$

Eigenvalues

Operators L_x and L_y do not commute

$$\begin{aligned} [L_x, L_y] &= [y p_z - z p_y, z p_x - x p_z] \\ &= \cancel{[y p_z, z p_x]} - \cancel{[y p_z, x p_z]} + \cancel{[z p_y, z p_x]} + \cancel{[z p_y, x p_z]} \\ &= y p_x [p_z, z] + x p_y [z, p_z] \\ &= -y p_x [z, p_z] + x p_y [z, p_z] \\ &= [z, p_z] (x p_y - y p_x) \\ &= i\hbar (x p_y - y p_x) \end{aligned}$$

Because of commutation relations, only $[r_i, p_i]$ survive

Fundamental Commutation relations for angular momentum

$$[L_x, L_y] = i\hbar L_z ; \quad [L_y, L_z] = i\hbar L_x ; \quad [L_z, L_x] = i\hbar L_y$$

They're incompatible observables

By generalized uncertainty principle:

$$\sigma_{L_x}^2 \sigma_{L_y}^2 \geq \left(\frac{1}{2i} \langle i\hbar L_z \rangle \right)^2 = \frac{\hbar^2}{4} \langle L_z \rangle^2$$

Any measurement on L_i makes the other less precise

