Max Planck's solution:

- Proposed that the energy of harmonic oscillations is quantized in proportion to ν, discretely.

$$E = \underbrace{h\nu}_{\text{"One quanta"}} \cdot n$$

Where $h = 6.626 \times 10^{-34}\ J/s$, planck's constant
n = an integer, $0, 1, 2, 3 \ldots$

- Broke classical physics: $n \neq 1.5$.

Albert Einstein: Photoelectric effect

- Described how UV light ejects electrons

To describe this process, physicists used the relation:

$$E_{light} = \underset{\text{(work)}}{\phi_{e^-}} + \underset{\text{(kinetic energy of electron)}}{KE_{e^-}}$$

In order for an electron to be ejected, $E_{light} > \phi_{e^-}$:

$$KE_{e^-} = E_{light} - \phi_{e^-}$$

Einstein also used Planck's ideas to describe light as traveling in quanta as well:

$$KE_{e^-} = \rho V - \phi$$, and found that his $\rho = h$, planck's constant

Bohr assumed angular momentum, l, was also quantized for his model of the atom.

$$l = m \cdot v \cdot r = \alpha n.$$ Bohr found that $\alpha = \hbar$, or $\frac{h}{2\pi}$.

Louis de Broglie then proposed wave particle duality – if waves can act as particles, then the opposite, that particles act like waves, must also be true:

$$\lambda = \frac{h}{p}$$, where λ = wavelength
p = particle momentum
h = planck's constant

In this course, how particles behave as waves will be the focus.

There are 5 essential postulates for quantum mechanics!

1) The wave function
2) Q.M. operators and measurements
3) Outcome of a single measurement
4) Outcome of many measurements
5) The Schrödinger Equation

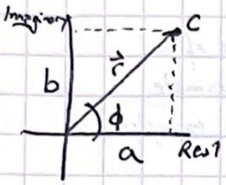
Q.M deals extensively with imaginary numbers. Therefore, a review of concepts is necessary.

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

A complex number is defined as

$$c = a + ib, \text{ where } i^2 = -1$$

$$\therefore c^2 = a^2 - b^2 + 2iab$$



Representing complex numbers in a coordinate plane, we find that

$$r^2 = a^2 + b^2,$$
$$a = r\cos\phi$$
$$b = r\sin\phi$$
$$\underline{c = r\cos\phi + ir\sin\phi}$$

Can be simplified to a trignometric identity:

$$= r\underbrace{(\cos\phi + i\sin\phi)}_{e^{i\phi}} = re^{i\phi}$$ – Contracted to an exponential – very important

We will see that the wave function Ψ is often represented as a complex number.

the complex conjugate of a complex number, c^*, is denoted:

$$c^* = a - ib.$$

When we multiply a complex number by its conjugate, we get a real value, which tells us something practically useful:

$$c^*c = a^2 + b^2.$$ This is accordingly, the magnitude, or $|c|^2$.

Recall the identities:

$$\cos\phi = \frac{e^{i\phi} + e^{-i\phi}}{2}, \quad \sin\phi = \frac{e^{i\phi} - e^{-i\phi}}{2i}$$

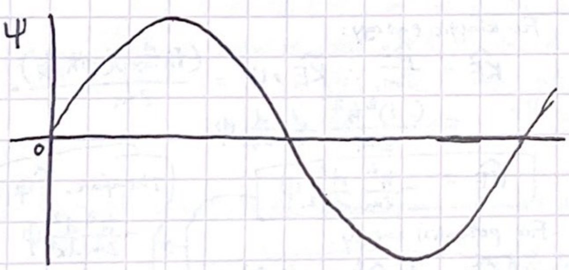
---

① The Wave Function

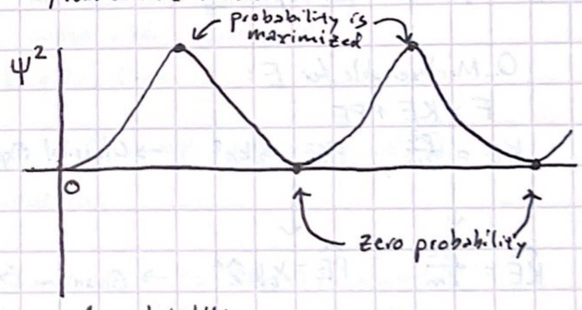
Assuming a particle exists in three dimensions, the wave function is described as: $\Psi(\vec{r}, t)$, where $\vec{r}(\vec{x}, \vec{y}, \vec{z})$.

To simplify the math, let us consider a particle in only one dimension, x.

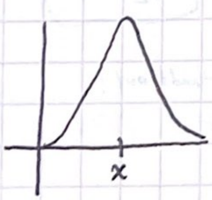
$\Psi(x,t)$:



Probabilistic model:



The description of what happens to the particle is in terms of probabilities.

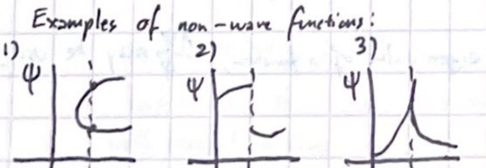


$$\underbrace{P(x,t)\,dx}_{\text{Probability Density Function}} = \Psi(x,t)^2\,dx$$

$$\int_{\text{space}} |\Psi|^2 dx = 1$$

The wave function must be
- Single valued
- Derivative defined

Examples of non-wave functions:



① has 2 probabilities at one point, and ② and ③ have an undefined derivative.

Since Ψ is in terms of complex numbers,

$$P(x,t)\,dx = \Psi(x,t)^2 dx$$
$$P(x,t)\,dx = |\Psi(x,t)|^2 dx.$$

Suppose $\Psi = e^{i\phi}$. What does the probability distribution look like?

If $\Psi = e^{i\phi}$, then

$$P(x,t)\,dx = |e^{i\phi}|^2 = e^{i\phi}(e^{-i\phi}) = e^{-i\phi + i\phi} = 1$$

This means that any wave function, Ψ, multiplied by just $e^{i\phi}$ will have a PDF of $|\Psi|^2$:

$$|\Psi e^{i\phi}|^2 = |\Psi|^2 \underbrace{|e^{i\phi}|^2}_{1} = |\Psi|^2.$$

② The Quantum Mechanical Operators and Measurements

For every observable (anything that can be measured), there is an equivalent Q.M. operator:

$$A \rightarrow \hat{A}$$

An operator is a set of instructions for converting input entities to output entities, and works very similarly to a functione, but on a larger scale

Function: $x \longrightarrow \boxed{f(x)} \longrightarrow y$

Operator: $f(x) \longrightarrow \boxed{\hat{A}} \longrightarrow g(x)$

A summation is an example of an operator. A derivative is an example of an operator. There are many examples.

Properties of operators:

$\hat{A}(\psi+\phi) = \hat{A}\psi + \hat{A}\phi$

$\hat{A}(c\psi) = c\hat{A}\psi$, where c = constant

$\hat{B}(\hat{A}\psi) = \hat{B}\cdot\hat{A}\psi$, but not necessarily $=\hat{A}\cdot\hat{B}\psi$

The operator does not necessarily commute

$\hat{A}\hat{A}\psi = \hat{A}^2\psi$

for $e^x = 1 + x + \frac{1}{2}x^2 + \frac{1}{3}x^3 + \ldots$

then $e^{\hat{A}} = 1 + \hat{A} + \frac{1}{2}\hat{A}^2 + \ldots$

In Q.M., two key operators are defined:

1) $x \rightarrow \hat{x}$, corresponding to coordinate

2) $p \rightarrow \hat{p}$, corresponding to momentum

$$\boxed{\begin{aligned}\hat{x}\psi &= x\psi \\ \hat{p}\psi &= -i\hbar\tfrac{d}{dx}\psi\end{aligned}}$$

All other observables may be represented in these terms. For example, find the Q.M. observable for energy:

Q.M observable for E:

$E = KE + PE$

$KE = \frac{p^2}{2m}$, $PE = \frac{1}{2}kx^2$ → Classical Expressions

↓ ↓

$\hat{KE} = \frac{\hat{p}^2}{2m}$ $\hat{PE} = \frac{1}{2}k\hat{x}^2$ → Quantum Expressions

For kinetic energy:

$\hat{KE} = \frac{\hat{p}^2}{2m}$, $\therefore \hat{KE}\cdot\psi = \frac{(-i\hbar\frac{d}{dx})(-i\hbar\frac{d}{dx})}{2m}\cdot\psi$

$= \frac{(-i)^2\hbar^2}{2m}\frac{d}{dx}\frac{d}{dx}\psi$

$\boxed{\hat{KE} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi}$

For potential energy:

$\boxed{\hat{PE} = \frac{k}{2}\hat{x}^2 = \frac{k}{2}\hat{x}^2\psi}$

Therefore, $\hat{E}\psi = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi + \frac{k}{2}\hat{x}^2\psi$

Ex.) Consider $\psi = kx$, where k = constant.

Then for $x \rightarrow \hat{x}$, $\boxed{\hat{x}\psi = kx^2 = x\psi}$

for $p \rightarrow \hat{p}$, $\boxed{\hat{p}\psi = -i\hbar k = -i\hbar\left(\frac{\psi}{x}\right)}$

Now consider $\psi = e^{ikx}$, where k = constant

Then for $x \rightarrow \hat{x}$, $\boxed{\hat{x}\psi = xe^{ikx} = x\psi}$

for $p \rightarrow \hat{p}$, $\boxed{\hat{p}\psi = -i\hbar ike^{ikx} = \hbar k\psi}$

Practice: Is the derivative of $\psi = 7\sin bx$ an eigenfunction?

Compare these four results. Which one stands out?

- $x\psi$
- $-i\hbar\left(\frac{\psi}{x}\right)$
- $x\psi$
- $\hbar k\psi$ ← This one does: it is simply the original wave function, ψ, multiplied by a constant.

If $\hat{A}\psi = a\psi$, where a = constant, then it is an eigenfunction: "eigenvalue equation"

To find the eigen value of a function, $\frac{\hat{A}\psi}{\psi}$ may be used

③ <u>The Outcome of a Single Measurement</u>

The outcome of a single physical measurement depends on its eigenvalue. (We will elaborate later)

$$\hat{A}\Psi = a\Psi$$

④ <u>The Outcome of Many Measurements</u>

Measuring a wave function many times destroys it. We can model the average value using:

$$\langle A \rangle = \frac{\int \Psi^* \hat{A}\Psi \, dx}{\underbrace{\int |\Psi|^2 \, dx}_{=1, \text{ as it is a probability density}}}$$

Average value of many measurements

Consider $\hat{A}\Psi = a\Psi$, a "pure state" wave function. Then if we try to apply this measurement,

$$\langle A \rangle = a \frac{\int |\Psi|^2 dx}{\int |\Psi|^2 dx} = a, \text{ shown in ③.}$$

Therefore, if and only if $\hat{A}\Psi = \phi$ then the $\langle A \rangle$ formula applies:

$$\langle A \rangle = \frac{\int \Psi^* \phi \, dx}{\int |\Psi|^2 dx}.$$

When $\hat{A}\Psi = \phi$, this is known as the <u>superposition</u> state.

⑤ <u>The Schrödinger Equation</u>

The Schrödinger Equation comes in a time dependent form and a time-independent form.

TDSE:

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

where $\hat{E} = \hat{H}$, or the hamiltonian operator. $\hat{E}$ is also known as the energy operator.

TISE:

$\hat{H}\Psi = E\Psi$, where <u>E is a constant</u>. What is the import of this?

If E is constant, and Ψ depends on x and t only, then

$$i\hbar \frac{\partial \Psi}{\partial t} = E\Psi \longrightarrow i\hbar \frac{d\Psi}{dt} = E\Psi.$$

Isolating $\frac{d\Psi}{dt}$, we get $\frac{d\Psi}{dt} = \underbrace{-\frac{i}{\hbar}E}_{\text{A constant} = k}\Psi$, $\frac{d\Psi}{dt} = k\Psi$ (An eigenfunction)

To find the eigenfunction, we do some mental gymnastics:

let $\Psi = f$, then

$$\frac{d}{dt}(f) = kf$$

$$\frac{\frac{d}{dt}(f)}{f} = k \longrightarrow \int \frac{d}{dt} \ln(f) dt = \int k \, dt$$

$$\ln(f) = kt + B$$

$$f = e^{kt+B} = e^{kt} \cdot f(B)$$

Translating to the original Ψ,

$$\Psi(t) = \underbrace{\Psi_{t=0}}_{f(B)} \underbrace{\left(e^{-\frac{i}{\hbar}Et}\right)}_{e^{kt}}$$

<u>Time ~~is~~ independence</u>

$$\Psi(t,x) = \Psi(x,t=0) \underbrace{e^{-\frac{i}{\hbar}Et}}_{\cos(\frac{E}{\hbar}t) - i\sin(\frac{E}{\hbar}t)}$$

$\longrightarrow$ The frequency of oscillation is $\frac{E}{\hbar}$, or ω.

Then it follows that $e^{-i\omega t}$, and since $\omega = \frac{E}{\hbar}$, then

$$E = \hbar\omega \equiv E = h\nu$$

Recall that: $\omega = 2\pi\nu$ and $\hbar = \frac{h}{2\pi}$

Therefore, the probability of density of the wave function is:

$$PDF = \Psi^*\Psi \, dx = \Psi^*(x,t=0)^{i\omega t}\left[\Psi(x,t=0)e^{-i\omega t}\right] = |\Psi(x,t=0)|^2 \underbrace{e^{\frac{i\omega t - i\omega t}{t=0}}}_{=1} = |\Psi(x,t=0)|^2$$

Importantly, this means that the probability <u>does not change</u> with respect to time.

Addendum to 4th Postulate:

Recall that

$$\langle A\rangle = \frac{\int \psi^* \hat{A}(\psi)\,dx}{\int |\psi|^2\,dx}$$ is the average value of many measurements of the wave function.

It is generally the case that when applying an operator to a wave function, another function is returned:

$$\hat{A}\psi = \phi \leftarrow \text{(Another function)}$$

Assume however, that we have a set of eigen functions, $\{\phi_1, \phi_2, \phi_3, \ldots, \phi_n\}$ each with their own corresponding eigenvalues, $\{a_1, a_2, a_3, \ldots, a_n\}$ Such that $\hat{A}\phi_n = a_n\phi_n$.

How can we use this information to help with the case that $\hat{A}\psi = \phi$?

We must therefore explore the properties of eigenfunctions:

- Eigenfunctions must be normalized, such that

$$\int \phi_1^* \phi_1\,dx = 1$$

- Eigenfunctions demonstrate orthogonality when their dot products are taken:

$$\int \phi_i \cdot \phi_j\,dx = 0 \quad \text{if} \quad i \neq j$$

Recall that $\vec{a}\cdot\vec{b} = |\vec{a}||\vec{b}|\cos\phi$ ~~∡φ~~ if $\phi = 90°$, then $\vec{a}\cdot\vec{b} = 0$ due to orthogonality.

$$\underbrace{\int \phi_i \cdot \phi_j\,dx}_{\text{replaces } \vec{a}\cdot\vec{b}} = 1 \quad \text{if} \quad i = j$$

- If the dot product of two vectors equals 1, and the vectors are both normalized, they must be the same vector.

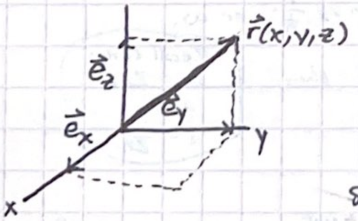
The eigenfunctions of an operator from the complete set - that is, any other function which depends on the same coordinates, can be represented as a linear combination of the eigen functions; known as "superposition" state

$$\psi = \underbrace{b_1\phi_1 + b_2\phi_2 + b_3\phi_3 + \ldots}_{\text{Projections of vectors onto individual coordinate vectors.}} = \sum b_i\phi_i$$

Applying this knowledge: Suppose that $\psi = b_1\phi_1 + b_2\phi_2$, and an operator $\hat{A}$ acts on ψ to produce:

$$\hat{A}\psi = a_1 b_1 \phi_1 + a_2 b_2 \phi_2$$

- We can exploit the property that eigenfunctions are a linear combination of its coordinates:



$\vec{r}(x,y,z) = x\vec{e}_x + y\vec{e}_y + z\vec{e}_z$. If we dot product the result to the vector $\vec{e}_y$ for example, we find:

$$\vec{e}_y \cdot \vec{r}(x,y,z) = x\underbrace{\vec{e}_x\cdot\vec{e}_y}_{0} + y\underbrace{\vec{e}_y\cdot\vec{e}_y}_{1} + z\underbrace{\vec{e}_z\cdot\vec{e}_y}_{0} = y$$

Such that $\int \phi_2^* \cdot \psi\,dx$ replaces the original to give:

$$b_1\int \underbrace{\phi_2^*\phi_1}_{=0}\,dx + b_2\int \underbrace{\phi_2^*\phi_2}_{=1}\,dx + b_3\int \underbrace{\phi_2^*\phi_3}_{=0}\,dx + \ldots$$

to equal just b_2.

Since $\int \phi_2^* \psi \, dx = b_1 \int \phi_2^* \phi_1 \, dx + b_2 \int \phi_2^* \phi_2 \, dx + b_3 \int \phi_2^* \phi_3 \, dx + \dots = b_2$,

This means that b_2, or the projection of the wave function onto the individual eigenfunction of a vector, is the only solution to the case in which $\psi \cdot \phi_2^*$.

Applying this to $\psi = b_1\phi_1 + b_2\phi_2$:

We know that $\hat{A}\psi = a_1 b_1 \phi_1 + a_2 b_2 \phi_2$. Then using the property discussed above, we can multiply this wave function by a conjugate then integrate it:

$$\int_{space} (b_1^*\phi_1^* + b_2^*\phi_2^*)(a_1 b_1 \phi_1 + a_2 b_2 \phi_2)\, dx$$

$\downarrow$ FOIL

$$a_1 b_1^* b_1 \int \underbrace{\phi_1^* \phi_1}_{=1} dx + a_2 b_2 b_1^* \int \underbrace{\phi_1^* \phi_2}_{=0} dx + \dots (0) + (1)$$

(Expanded form)

$$a_1 b_1^* b_1 \int \underbrace{\phi_1^* \phi_1}_{=1} dx + a_2 b_2 b_1^* \int \cancel{\phi_1^* \phi_2}^{\,0} dx + a_1 b_2^* b_1 \int \cancel{\phi_2^* \phi_1}^{\,0} dx + a_2 b_2^* b_2 \int \underbrace{\phi_2^* \phi_2}_{=1} dx$$

$$= a_1 b_1^* b_1 + a_2 b_2^* b_2 = a_1 |b_1|^2 + a_2 |b_2|^2 = \int \psi^* \hat{A} \psi \, dx$$

Referring back to $\langle A \rangle = \dfrac{\int \psi^* \hat{A} \psi \, dx}{\int |\psi|^2 dx}$, we see that we can substitute to get

$$\boxed{\langle A \rangle = a_1 \frac{|b_1|^2}{|b_1|^2 + |b_2|^2} + a_2 \frac{|b_2|^2}{|b_1|^2 + |b_2|^2}}$$

What does this form of the expression mean?

Suppose N is a measurement in superposition with 2 possible outcomes:

$N_1 \rightarrow a_1$
$N_2 \rightarrow a_2$.

then $\langle A \rangle = \dfrac{a_1 N_1 + a_2 N_2}{N} = a_1 P_1 + a_2 P_2$

$P_1 = N_1/N$ Probability of N_1

$P_2 = N_2/N$ Probability of N_2

If we compare $\langle A \rangle = a_1 \underbrace{\dfrac{|b_1|^2}{|b_1|^2 + |b_2|^2}}_{= P_1} + a_2 \underbrace{\dfrac{|b_2|^2}{|b_1|^2 + |b_2|^2}}_{P_2}$

Therefore, we have expressed our average of measurements in terms of probabilities.

For example, assume that $\psi = 3\phi_1 + 4\phi_2$. What is the probability that the particle is in either state?

$$\langle A \rangle = a_1 \frac{|b_1|^2}{|b_1|^2 + |b_2|^2} + a_2 \frac{|b_2|^2}{|b_1|^2 + |b_2|^2}, \quad \therefore \langle A \rangle = \frac{9}{9+16} = 9/25 \ (36\%) \text{ for } \phi_1$$

$$\langle A \rangle = \frac{16}{9+16} = 16/25 \ (64\%) \text{ for } \phi_2$$

"God does not play dice"

Suppose $\Psi = 2\phi_1 + 3i\phi_2 - 4\phi_3$
$\underbrace{\quad a_1 \qquad a_2 \qquad a_3 \quad}_{\text{Eigenvalues}}$

Probabilistically,
$$P = \frac{2^2}{2^2+3^2+4^2} + \frac{3^2}{2^2+3^2+4^2} + \frac{4^2}{2^2+3^2+4^2} = \langle A \rangle$$
This can also be solved using expectation value, but it is much more complicated.
$$\langle A \rangle = \frac{\int \Psi^* \hat{A} \Psi \, dx}{\int |\Psi|^2 dx}$$

All wave functions we've been dealing with have been assumed to be normalized: $\int |\Psi|^2 dx = 1$
If $\int |\Psi|^2 dx = c$, where $c \neq 1$, how can we normalize the wave function?

Use algebra: $\int |\Psi|^2 dx = c$, then $\int \frac{|\Psi|^2}{c} dx = 1$
$$\therefore \int \frac{\Psi^* \Psi}{\sqrt{c}\sqrt{c}} dx = 1$$

$\boxed{\tilde{\Psi} \text{ is the normalized wave function: } \int |\tilde{\Psi}|^2 dx = 1}$

$$\boxed{\tilde{\Psi} = \frac{\Psi}{\sqrt{\int |\Psi|^2 dx}}}$$

Note that this does not effect Schrödinger's equation:
$$i\hbar \frac{\partial}{\partial t} \frac{\Psi}{\sqrt{c}} = \hat{H} \frac{\Psi}{\sqrt{c}}, \quad \hat{A} \frac{\Psi}{\sqrt{c}} = a \frac{\Psi}{\sqrt{c}}, \quad \hat{A}\tilde{\Psi} = a\tilde{\Psi}$$

Ex.) Suppose our wave function is $\Psi = e^{ikx}$ (the eigenfunction of the momentum operator)
Our system is defined as $0 \longleftarrow x \longrightarrow L$. The probability to find the particle anywhere within this range is 1 (i.e., the particle can only exist in this range): $\int_0^L |\Psi|^2 dx = 1$.
To find the normalized wave function, $\tilde{\Psi}$, we apply $\tilde{\Psi} = \frac{\Psi}{\sqrt{\int |\Psi|^2 dx}}$
Solving for the denominator,
$$\int_0^L |\Psi|^2 dx = 1; \quad |e^{ikx}|^2 = e^{-ikx} \cdot e^{ikx} = e^{-ikx+ikx} = e^0 = 1$$
So $\int_0^L dx = L$. Therefore,
$$\tilde{\Psi} = \frac{\Psi}{\sqrt{\int |\Psi|^2 dx}} = \boxed{\frac{e^{ikx}}{\sqrt{L}}} = \tilde{\Psi}$$
Normalized

The Ultimate Recipe for Solving Any Quantum Mechanical System:

1) Define/Write the Hamiltonian Operator
   $E = K + U$
   $\hat{H} = \hat{K} + \hat{U}$
2) Write the Schrödinger Equation
   $\hat{H}\Psi = E\Psi$
3) Define Boundary Conditions
   - Is the function normalized?
   - Is the particle's wave function continuous?
   - Is the particle bound in space?
4) Solve Schrödinger's Equation, accounting for boundary conditions
   - Ψ and E will be solved for simultaneously
5) Ask crazy questions