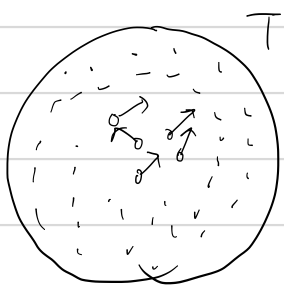
History of Quantum mechanics

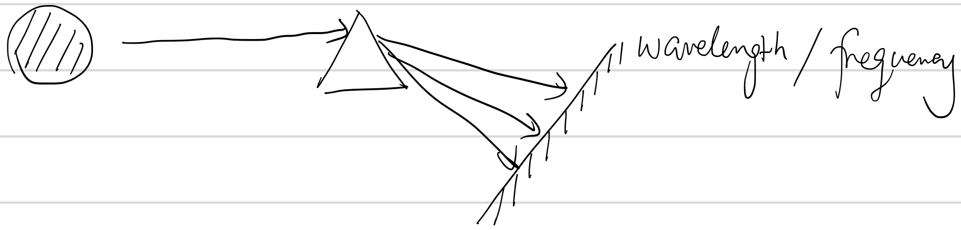
1. First "Quanta" : Black body radiation.

Black-body radiation is the thermal electromagnetic radiation.

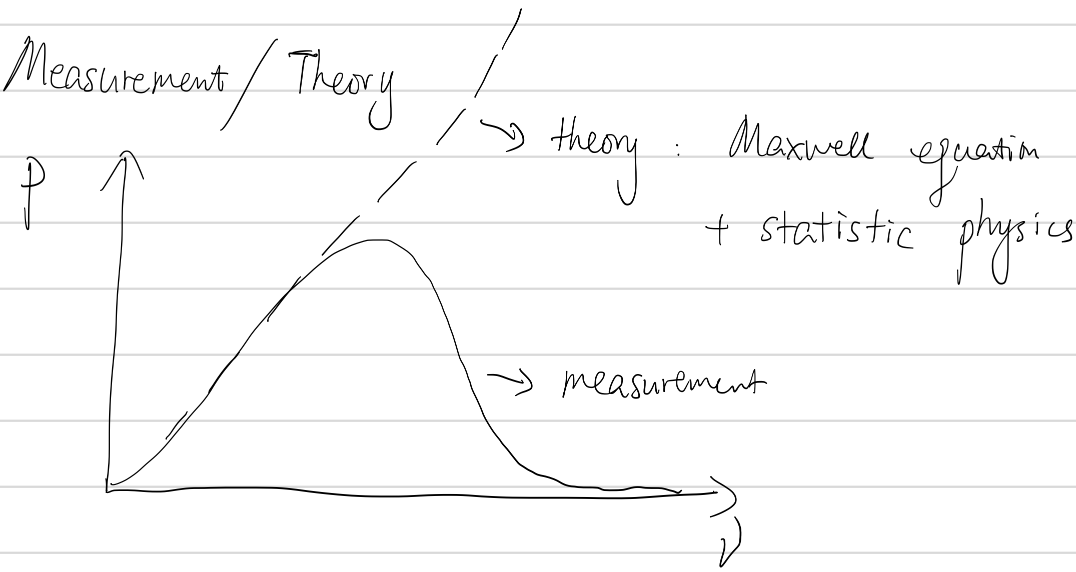


origin: molecules/atoms moves when temperature is not absolutely zero.
Some of them carries charge, or dipoles, and the motion of charged particles emit EM-wave.
The more movement, the more radiation.

Example: Lava (show movie), sun, Incandescent light bulb, ...



Measurement / Theory



The problem is, at high frequency, the emission doesn't come down.

Planck approached this problem in an very interesting way.

He knows statistic physics very well. He knows that for molecules in air,
The probability of the molecule having a kinetic energy of $E_1 = \frac{1}{2} m v_1^2$ is:

$$P(E_1) \propto e^{-E_1/kT} \rightarrow P(E_1) = \frac{e^{-E_1/kT}}{\sum_{i=1}^{\infty} e^{-E_i/kT}}$$ (it's actual more complicated than this)

T is temperature in Kelvin, k is Boltzmann constant

$$k = 1.38 \times 10^{-23} \ m^2 \cdot kg \cdot s^{-2} \cdot K^{-1}$$

He noticed something; at $E_1 \rightarrow \infty$, $P(E_1) \rightarrow 0$.

Meaning there's almost no particle at extremely high speed/energy.

And the measurement of blackbody radiation shows no emission at higher frequency.

So he says: the emission is somewhat like the energy of molecules, each emission carries certain energy $E_1 = \hbar\omega_1$
$= h\nu$

So naturally, emission at higher frequency drops.

So the intensity of emission at frequency ω is:

$$I(\omega) \propto \underset{\substack{\swarrow \\ \text{each emission} \\ \text{energy}}}{\hbar\omega} \cdot \underset{\substack{\downarrow \\ \text{total emission} \\ \text{number}}}{N_{tot}} \cdot \underset{\substack{\downarrow \\ \text{probability at} \\ \text{frequency } \omega}}{\frac{e^{-\hbar\omega/kT}}{\sum_{\omega} e^{-\hbar\omega/kT}}}$$

(This is not the actual equation Planck wrote down, his one is more complicated)

$$I(\nu, T) = \frac{2h\nu^3}{c^2} \frac{1}{e^{h\nu/kT} - 1}$$

He fit the h-constant, and $I(\omega)$ agrees perfectly with the experiment. $h = 6.626 \times 10^{-34}$ J·s.

Bonus: You can use Planck equation to calculate the temperature of the sun. (peak emission near 500 nm).

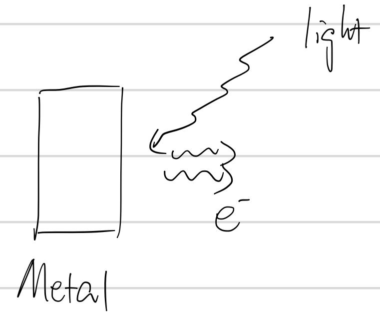
Will be in homework

This is the first time, people think of radiation of energy E_{tot} as $E_{tot} = N \cdot h\nu$; identical energy packet.

Planck himself does not like his theory, but he won Nobel Prize for this anyway.

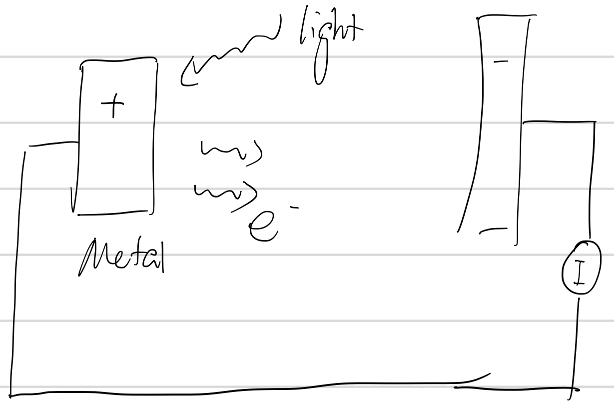
If you think a little deeper on his theory, he is suggesting energy and mass (particle) are connected in someway, as they are all discontinued. Later: $E = mc^2$.

2. 1906. Photoelectric effect.



Shine light on metal, transferred some energy to electrons, they escape the metal.

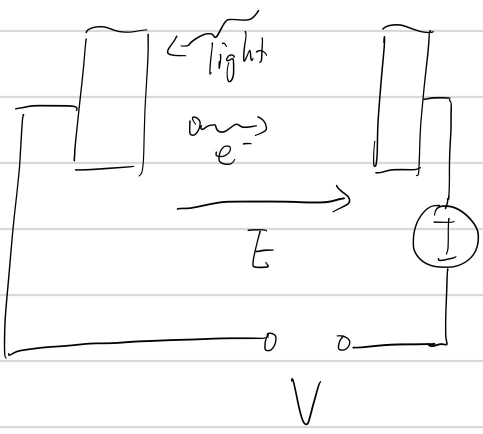
Now, one obvious question is: light intensity/frequency vs. electron number/energy



Current $\propto$ number of electrons.

Should be proportional to light energy

What about the electron kinetic energy/speed?



When the electrical potential:

$q \cdot V$, is larger than kinetic energy of the electron, the direction of the current will be reversed.

So at critical voltage, where current is zero. $E_{kinetic} = q|V_c|$

For light: Intensity $\sim E^2 + B^2$, independent of frequency. (from Maxwell equation).

So what can we predict $|V_c|$ vs. light intensity/frequency?

Intuitively, $|V_c| \nearrow$ with intensity $\nearrow$; independent of frequency.

It's like smash something with a hammer, stronger you hit, the more energy you use, then things coming off will have greater speed.

Experiment results: (1) $|V_c|$, independent of light intensity.

(2) $|V_c| \nearrow$ linearly with light frequency.

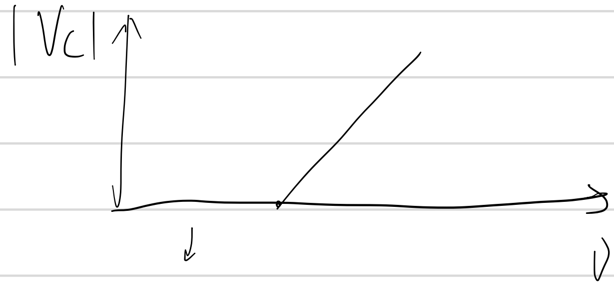
In 1905, Einstein proposed a simple idea: similar to Planck's idea:

Light comes in as separate packets, each packet has energy of $h\nu$; the total energy of the light is

$$\underbrace{N}_{\#\text{ of chunks}} \cdot h\nu$$

So: $\underbrace{E_{kinetic}}_{\text{electron}} = \underbrace{h\nu}_{\text{absorb energy from one packet}} - \underbrace{W}_{\text{work done to escape metal.}}$

So: $E_{kinetic} \propto V_c \propto h\nu$



$h\nu < W$, no electrons.

Perfect with experiment data.

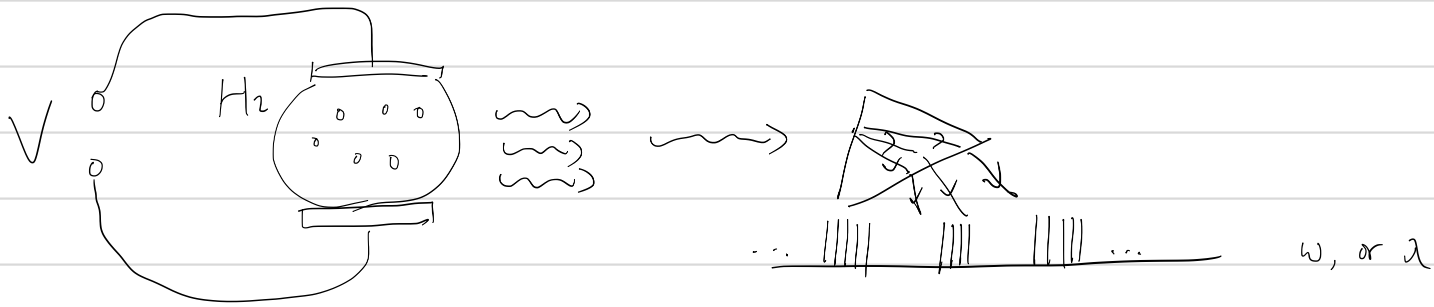
1°. Light behaves like particles... : localized, no interferenced
also .... waves. : not-localized, interference

2°. From EM-wave, you can derive: $E = c \cdot P$; (momentum)
also we know: $\lambda = c/\nu$;

So: $E = h\nu \Rightarrow p = \frac{h}{\lambda}$ (Widely used).

This is such bold assumptions, and Planck is really against it...

3. Spectrum of Hydrogen atoms



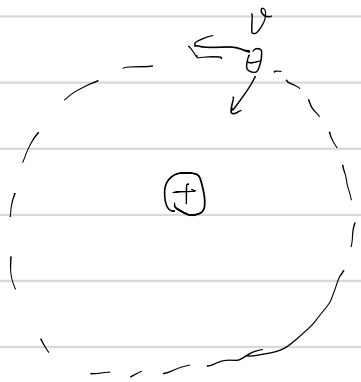
$$\frac{1}{\lambda} \propto f = R_0 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right); \quad n_1, n_2 \text{ are intergers.}$$

$$n_2 > n_1 \geq 1$$

This is inconsistent with almost everything we learned about atoms / electrons...
(Since we just review wave's and boundary conditions, you might think there's a connection between the integer number of the frequency of a piano string vs. the interger number in hydrogen atom spectrum.

In reality, it took physicists 20 years (1900, Planck first quantum to 1920, De Broglie) to make this connection.

Let's look at a classical atom model



$$F = \frac{k q_1 q_2}{r^2}$$ (Coulomb Law)

$$= ma = \frac{mv^2}{r}$$ (Centripetal force)

$$\Rightarrow \frac{k \cdot e^2}{r} = mv^2$$

Each velocity $\rightarrow$ a radius (just like our solar system)

The energy of the atom is:

$$E = \underbrace{\frac{1}{2} mv^2}_{\text{kinetic energy}} - \underbrace{\frac{ke^2}{r}}_{\text{Coulomb potential energy}}$$

$E = -\dfrac{ke^2}{2r}$; So the electron has a continuous energy spectrum.

When it moves from $r_1 \rightarrow r_2$, its energy change, and emit a photon

This is the best you can do with classical atom model

$$\hbar\omega = E(r_1) - E(r_2)$$

Two major issues:

1°. Spectrum is continous, nothing like the experiment.

2°. Electron with accelatation ($a \neq 0$) means radiation of EM-field; electron is always loosing energy.

They will move closer and closer to the nuclear and the model is not stable.

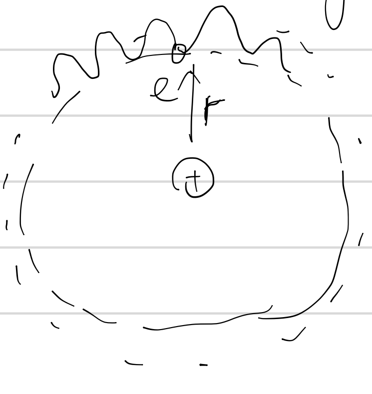
1920. De Broglie :

De Broglie saw the connection of the integer number and the wave solution.
So he thought by "assuming" electrons are waves, we might get the correct spectrum.

How can you go from waves $\rightarrow$ integer number?

Boundary condition.

For waves going in circle: the boundary condition is:



electron is the same at 0 and 2π

$\Rightarrow$

$$2\pi r = N \cdot \lambda$$

So the question becomes: what is the wavelength?

De Broglie knew Einstein's paper really well.

Einstein's paper derived a result for photon:

$$E = \hbar\omega; \quad E = p \cdot c; \quad \Rightarrow p = \hbar k = \frac{h}{\lambda}$$

De Broglie just assumed that the same result, will hold for electron:

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

So now we have: $mv = \dfrac{h}{\lambda} = \dfrac{h}{\frac{2\pi r}{N}} \Rightarrow mv = \dfrac{h \cdot N}{2\pi r}$.

We know: $\dfrac{mv^2}{r} = \dfrac{ke^2}{r^2}$; $E = \dfrac{1}{2}mv^2 - \dfrac{ke^2}{r} = -\dfrac{ke^2}{2r}$

$$v^2 = \frac{ke^2}{mr} = \left(\frac{h \cdot N}{2\pi r m}\right)^2 \Rightarrow \frac{ke^2 \cdot m.}{\hbar^2 \cdot N^2} = \frac{1}{r}$$

$$E = \frac{-ke^2}{2r} = \frac{-m \cdot k^2 e^4}{2\hbar^2} \cdot \frac{1}{N^2}$$

photon: $\hbar\omega = E_1 - E_2 = \dfrac{-mk^2e^4}{2\hbar^2}\left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right)$;

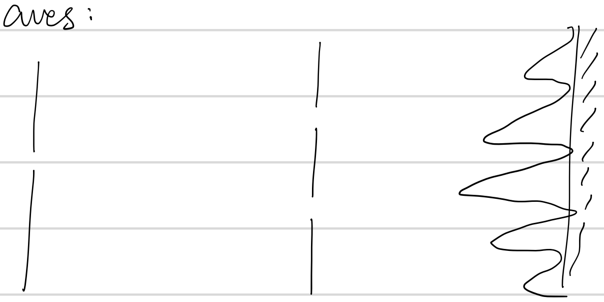
This model works, but is quiet ugly.

Electron is a particle when you calculate force and energy,

then Electron is wave when you need boundary condition.

So what is electron?

Waves:



Non-localized
Interference

particles

Localized
no interference.

Here comes Schordinger:

To this point, we know everything Schordinger knew, except he is much better in physics than use.

He was a research scientist (not a professor) in the group of Peter Debye (later Nobel prize in 1936)

Debye saw De Brogile's thesis, not sure what it is, but seems interesting.

He gave it to Schordinger and said: if electron is wave, then what's the wave equation?

Schordinger worked for six weeks, and came up with the Schordinger equation.

(He actually came up with two equations, but the first one doesn't agree with Hydrogen atom spectrum. So he didn't publish it.

Later the equation was rediscovered by Klein and Gordon, it turns out to be the relativity wave equation for boson.

Klein, Gordon were not awarded for Nobel prize.)

Now let's try to get Schordinger equation:

✩ Side Note

Before we go into the wave equation, I want to introduce a famous inequality equation to build the idea that probability in quantum mechanics is far more complicated than classical probability.

Bell inequality:

$$N(\text{Virgina}, M) + N(F, EE) \geq N(\text{Virgina}, EE)$$

$$\begin{array}{ccc} \| & \| & \| \\ N(\text{Vir}, M, EE) & + N(\text{Vir}, F, EE) & N(\text{Vir}, M, EE) \\ + N(\text{Vir}, M, \text{Not } EE) & + N(\text{not Vir}, F, EE) & + N(\text{Vir}, F, EE) \end{array}$$

This is very trivial. It uses the fact that the number of students of a certain catagory must be ≥ 0.

If you devide the total number of student, $N \to$ Probability.

We can generalize this statement. For binary state A, B, C.

$$N(A, B) + N(\bar{B}, C) \geq N(A, C)$$

This simple inequality equation, does not hold for quantum mechanics.

For example, electron has angular momentum along $\vec{x}, \vec{y}, \vec{z}$ axis. It's either $\frac{h}{2}$, or $-\frac{h}{2}$ (binary, 1 or -1)

If you do this measurement:

$$N(\uparrow_x, \uparrow_y) + N(\downarrow_y, \uparrow_z) < N(\uparrow_x, \uparrow_z)$$

It doesn't satisfy Bell inequality.

The probability in quantum mechanics doesn't work the same way as probability in Vegas.

Probability wave and operator.

In history, Schordinger derived Schordinger equation before he knew anything about the meaning of the wave equation. (Genius)

I once tried to introduce Schordinger equation without talking about probability wave, but it didn't work very well...

So let's try a different route, and talk about wave-function first.

Double Slit experiment for single electrons

$\boxed{\text{(See movie)}}$

1°. It seems random where individual electron will hit the screen.

2°. But accumulate individual electron measurements, we see interference petern.

This is the best experiment to propose some postulates (rules) for quantum mechanics.

Classical physics: $\{\vec{x}, \vec{p}\}$, complete knowledge of measurable property

Energy $= V(\vec{x}) + \frac{\vec{p}^2}{2m}$; angular momentum: $\vec{L} = \vec{p} \times \vec{x}$.

Does it work for quantum system?

No.

1°. From the electron / box thought experiment in the first lecture, we know there's an uncertainty principle in the real world (will talk in details more).

We can't know the exact value of $\vec{x}$ and $\vec{p}$

(color / orientation of the electron)

So doesn't work.

2°. We know there's interference effect, so $(\vec{x}, \vec{p})$ that describes particle would not work.

Postulate 1: The state of a quantum object (or system) is completely specified by a wave function. $\psi(\vec{r}, t)$. (complex function)

Postulate 2: The probability of the electron (or other object) showing up at position $\vec{r} \to \vec{r} + d\vec{r}$ is $|\psi(\vec{r}, t)|^2 d\vec{r}$ (always positive)

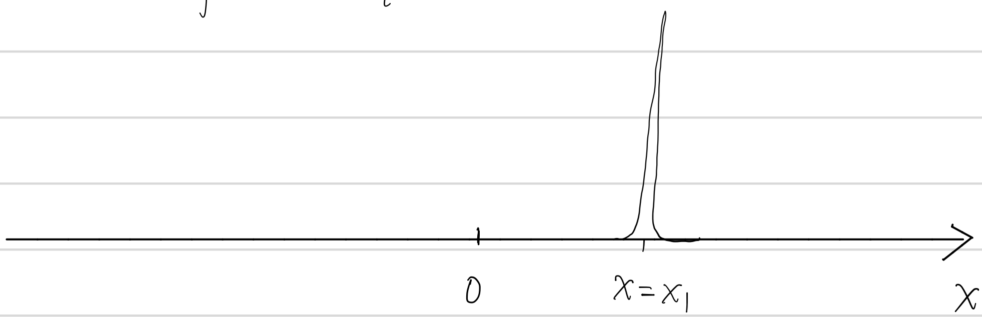
We can expand this a little bit: the probability of electron showing up in regime $x \in (a, b)$ is:

$$P_{a,b} = \int_a^b |\psi(x,t)|^2 \cdot dx$$

2.1 Because it's probability, electron appears in $(-\infty, +\infty)$ must be 1, so:

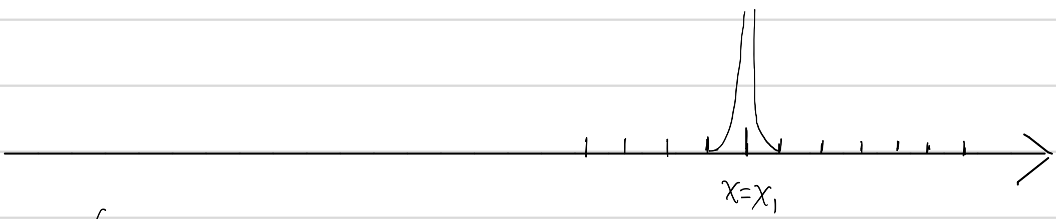
$$\int_{-\infty}^{\infty} |\psi(x,t)|^2 dx = 1. \quad \text{Normalization of wave-function.}$$

Example 1: An electron is at position x_1 (very precise), what is the wavefunction $\psi(x)$?



If $\Delta x \to 0$ (we know electron is exactly at x_1), then we get a special function: delta-function.

Think about this: we zoom in at area near $x = x_1$



at $\left(x_1 - \frac{\Delta x}{2}, x_1 + \frac{\Delta x}{2}\right)$, $\psi(x)$ is very large;

at $x_1 \pm \frac{3\Delta x}{2}$, $x_1 \pm \frac{5}{2}\Delta x$, ... ; $\psi(x) = 0$.

This is the meaning of very precise at x_1.

And also we need to let $\Delta x \to 0$.

How large is $\psi(x)$ at $x = x_1$? Use:

$$\int_{-\infty}^{+\infty} |\psi(x)|^2 dx = 1 \Rightarrow \sum_{N=-\infty}^{+\infty} |\psi(x_1 + N\cdot\Delta x)|^2 \cdot \Delta x$$

$$= |\psi(x=x_1)|^2 \cdot \Delta x = 1 \Rightarrow |\psi(x=x_1)|^2 = \frac{1}{\Delta x}$$

Also we know $\Delta x \to 0$; $\therefore |\psi(x=x_1)|^2 = \frac{1}{0} \to \infty$.

It's infinity.

So the simplest case in classical physics: particle at location x_1, is not simple at all in quantum mechanics.

The corresponding wave-function:

$$\begin{cases} |\psi(x=x_1)|^2 = \infty \\ |\psi(x)|^2 = 0, \quad x \neq x_1 \\ \int_{-\infty}^{+\infty} |\psi(x)|^2 = 1 \end{cases}$$

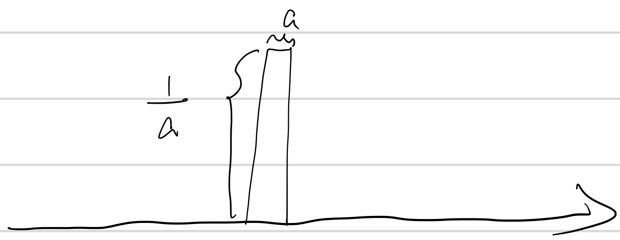
And there's a name for this function: Dirac delta function.

$$\begin{cases} \delta(x-x_1) = \infty, \quad x = x_1 \\ \delta(x-x_1) = 0, \quad x \neq x_1 \\ \int_{-\infty}^{+\infty} \delta(x-x_1)\, dx = 1. \end{cases}$$

There are many interesting properties about this δ-function, and we will cover them in the future.

In case this is too conceptual, we give an example of δ-function.

$$\begin{cases} f(x) = \dfrac{1}{a} \ ; & x \in (-\frac{a}{2}, \frac{a}{2}) \\ f(x) = 0 \ ; & x \notin (-\frac{a}{2}, \frac{a}{2}) \\ a \to 0. \end{cases}$$



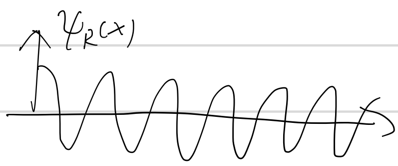
Homework: Use this dirac-function to show $\int_{-\infty}^{+\infty} f(x)\,\delta(x)\,dx = f(x=0)$

Practise: Homework: If an electron is either at $x=x_1$, or $x=x_2$ (very precise), and the probability at $x=x_1$, $x=x_2$ is identical, what is $|\psi(x)|^2$?
Write your answer use δ-function.

Example 2: another extreme case is, it's a plane wave (just like light). The electron can be anywhere.

$$\psi(x) = \alpha e^{ikx}, \text{ or } \psi(x,t) = \alpha e^{-i\omega t + ikx}.$$

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



So: $\psi(x) = \alpha e^{ikx}$ is just a linear combination of $\cos kx$ and $\sin kx$.

What's special about this function? The probability at any position is identical.

$$|\psi(x,t)|^2 = |\alpha|^2 .$$

Again, this is tough mathematically, because we need:

$$\int_{-\infty}^{+\infty} |\psi(x,t)|^2 dx = 1 = |\alpha|^2 \int_{-\infty}^{+\infty} dx = |\alpha|^2 \cdot \infty , \Rightarrow |\alpha|^2 \to 0.$$

This wave-function means $\Delta x \to \infty$ (No idea of where the particle is)

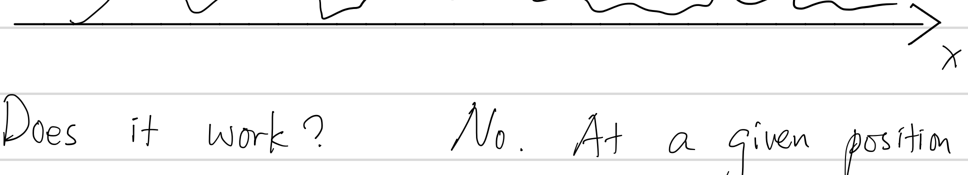
Is the wave-function useful?

From De Broglie: $p = \hbar k = \frac{h}{\lambda}$

This wave-function, has a well-defined momentum! $p = \hbar k$.

$\Delta p \to 0$; $\Delta x \to \infty$; $\Delta x \cdot \Delta p$ might be anything.

2.2. Can any function $f(x)$ be a wave-function?



Does it work? No. At a given position x, there exists two or more probability.

Postulate 3: Given <u>Two</u> possible configurations on a quantum system corresponding to Two distinct wave function;

$\psi_1(x)$ and $\psi_2(x)$. The system could also be at a superposition of $\psi_1(x)$ and $\psi_2(x)$

$$\psi(x) = \alpha \psi_1(x) + \beta \psi_2(x) \; ; \quad \alpha, \beta \text{ are complex number.}$$

$\psi_1(x)$, $\psi_2(x)$ can be particle at two different spot, can be two waves with different momentum, ...
(From a mathematical point of view, it's very similar to the classical wave equations, where the sum of wave solutions are still solutions. Later, we will see it's much more that that..)

You can naturally expand this postulate to N possible configurations

$$\psi(x) = \alpha_1 \psi_1(x) + \alpha_2 \psi_2(x) + \cdots\cdots$$

How this leads to interference effect?

Example: Our wave-function, is in superposition of e^{ik_1x} and e^{ik_2x}.

$$\psi(x) = \alpha e^{ik_1x} + \beta e^{ik_2x}$$; for simplicity, let $\alpha = \beta = 1$, and neglect the normalization factor

From previous example, we know that individually,

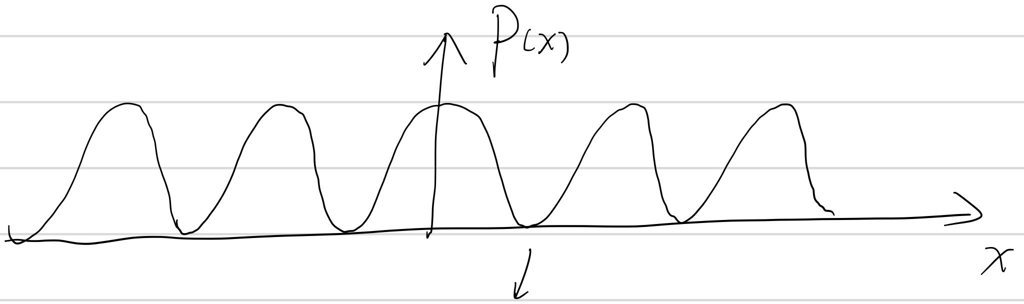
$\psi_1 = e^{ik_1x}$ and $\psi_2 = e^{ik_2x}$ both have uniform probability distribution (namely, same everywhere)

$|\psi_1|^2 = 1$; $|\psi_2|^2 = 1$.

However: $|\psi|^2 = |\psi_1 + \psi_2|^2 = |e^{ik_1x} + e^{ik_2x}|^2$

$= (e^{ik_1x} + e^{ik_2x})(e^{-ik_1x} + e^{-ik_2x}) = 1 + 1 + e^{i(k_1-k_2)x} + e^{-i(k_1-k_2)x}$

$= 2 + 2\cos(k_1-k_2)x$; (Use $e^{ix} = \cos x + i\sin x$)



If you're looking at this spot:
two electron flux, combine, give you zero electron!

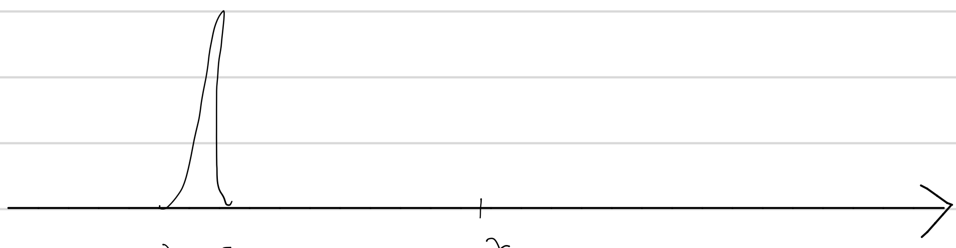
In general: $P(x) = |\alpha\psi_1 + \beta\psi_2|^2$

$= |\alpha|^2|\psi_1|^2 + |\beta|^2|\psi_2|^2 + \underbrace{\alpha\psi_1 \cdot \beta^*\psi_2^* + \alpha^*\psi_1^*\beta\psi_2}_{\text{always real}}$

$\neq |\alpha|^2 P_1(x) + |\beta|^2|\psi_2|^2$.

You can't add probability. You add wave-function.

A deeper look at position and momentum.



What is its momentum? $p = \hbar k = \frac{h}{\lambda}$

It's a wave, can you tell its wavelength?
No, it's not periodic in any way.

If it doesn't have a well defined wavelength, it doesn't have a well-defined momentum.

$\Delta p \to \infty$; $\Delta x \to 0$; $\Delta x \cdot \Delta p$: can be anything.

Mathematical Theorem.
Fourier Transform:
Any smooth, well-behaved waveform $f(x)$, can be expressed as linear combination of plane-waves.

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \tilde{f}(k)\, e^{ikx}\, dk$$

$e^{ikx} = \cos kx + i \sin kx$; $\hbar k = p = \frac{h}{\lambda}$

$\tilde{f}(k)$ is the amplitude and phase of plane-wave e^{ikx};

Reverse Fourier transform:

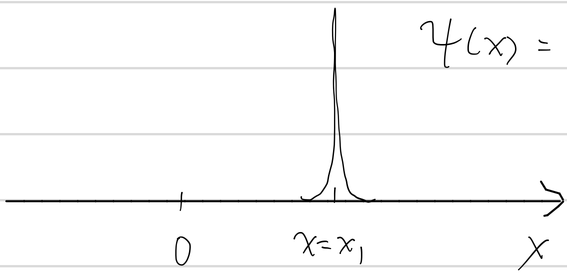
$$\tilde{f}(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} f(x)\, e^{-ikx}\, dx.$$

$f(x)$ and $\tilde{f}(k)$ are equivilent. If you know one, you can know the other.

Physics Version: Any wavefunction $\psi(x)$ can be expressed as superposition of plain waves.

$$\psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \tilde{\psi}(k)\, e^{ikx}\, dk$$

Example 1:



$\psi(x) = \delta(x-x_1)$ (Not normalized...)

What is its momentum?

$$\psi(x) = \delta(x-x_1) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \tilde{\psi}(k)\, e^{ikx}\, dk;$$

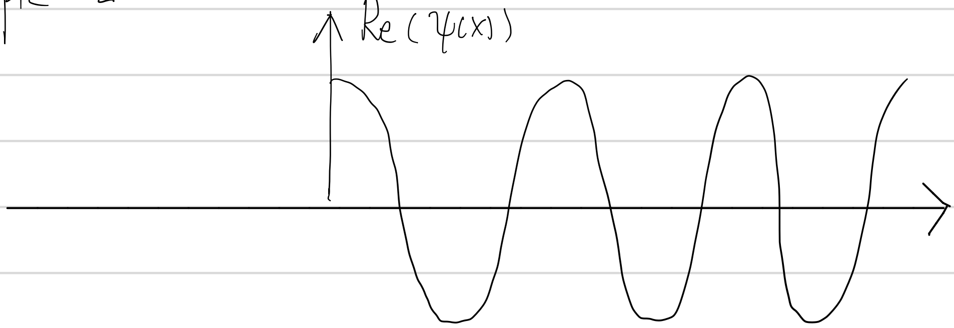
$$\tilde{\psi}(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \delta(x-x_1)\, e^{-ikx}\, dx = \frac{1}{\sqrt{2\pi}} e^{-ikx_1}$$

So the amplitude of wave e^{ikx} is $\left|\frac{1}{\sqrt{2\pi}} e^{-ikx_1}\right| = \frac{1}{\sqrt{2\pi}}$

Same for all k (wavelength, momentum)

So momentum is completely unknown. $\Delta p \to \infty$.

Example 2:



$$\psi(x) = e^{ik_1 x}$$

$$\Rightarrow \quad \tilde{\psi}(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} e^{ik_1 x} \cdot e^{-ikx} \, dx = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} e^{i(k_1 - k)x} \, dx.$$

What is this integral? Notice previously, we have:

$$\psi(x) = \delta(x - x_1) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \tilde{\psi}(k) e^{ikx} dk = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-ikx_1} \cdot e^{ikx} dk$$

$$= \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{ik(x - x_1)} dk = \delta(x - x_1)$$

Similar here: $\sqrt{2\pi} \cdot \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{i(k_1 - k)x} dx = \delta(k_1 - k)$.

$$\tilde{\psi}(k) = \delta(k_1 - k)$$

Only when $k = k_1$, the wave has non-zero amplitude. So $\Delta p \to 0$.

Bonus: with Fourier transform, $p = \hbar k$; and the definition of Δx, Δp:

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} \quad ; \quad \Delta p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2}$$

(Same as standard deviation)

You can derive $\Delta x \cdot \Delta p \geq \frac{\hbar}{2}$ for any wavefunction

But, we will later do it in an easier way.

SideNote: $\Delta x \equiv \sqrt{\frac{\sum_{i=1}^{N} (x_i - \bar{x})^2}{N}} = \sqrt{\sum_{i=1}^{N} \left(\frac{x_i^2}{N} - \frac{2x_i\bar{x}}{N} + \frac{\bar{x}^2}{N} \right)}$

$= \sqrt{\overline{x^2} - \bar{x}^2} = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$.