Lec 2: Modern Quantum Mechanics.

Ref: Bransden book
Griffith, Cohen-Tanauji

From the previous discussions, we learn the following ideas, which work for both electromagnetic wave (as a matter of fact any wave) as well as "particles."

(i) Phase space quantization (Bohr-Sommerfeld quantization).

Energy is quantized in unit of inverse time period: $E = \hbar\omega = h/T$.
Momentum is " " " " inverse wave length: $p = \hbar k = h/\lambda$.
Ang. momentum is " " " " inverse 2π rotation: $L = \hbar m = hm/2\pi$.
Cleary this relation can be generalized to all phase space variables.

(ii) Probability description:

A trajectory of classical particle can be decomposed into the plane wave basis (Fourier transformation), which make it clear that a classical trajectory is actually made of short-wavelength waves ($\lambda \sim 10^{-10}$ m). Once we go to such small length scale, we observe the wave nature of particles and vice versa. Such a trajectory will be defined by a mathematical complex function $\Psi(\vec{r},t)$. Its amplitude $P(\vec{r},t) = |\Psi(\vec{r},t)|^2$ denotes the probability density of finding the particle at $\vec{r}$ at t.

(iii) Superposition Principles:

When a particle has finite probabilities of taking multiple states (like two states in a double slit experiment) where the two states are accesible within its wavelength ($\lambda \sim h/p$) and period ($T \sim h/E$), then the particle actually access all these states (infact all possible states in the universe but the probability of accessing other states outside this range is infinitely small and hence we can neglect them).

This is the linear superposition principle:

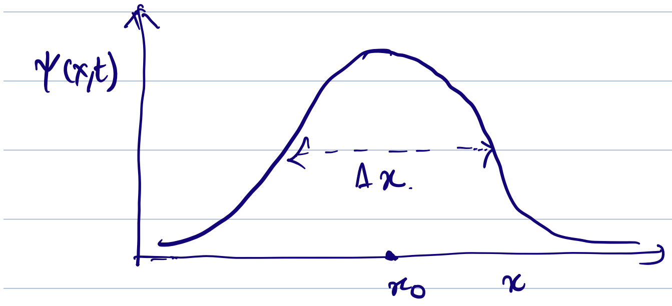
$$\Psi(\vec{r},t) = \sum_i \underset{\uparrow\ \text{coefficients.}}{\phi_i}\ \underset{\uparrow\ \text{basis.}}{\chi_i(\vec{r},t)} \qquad --(1)$$

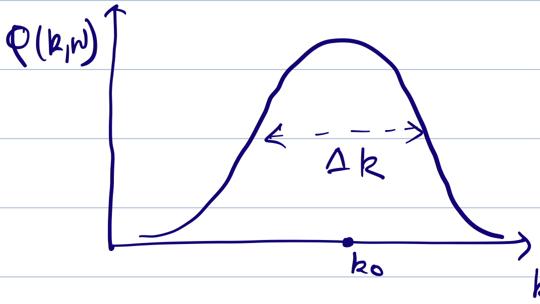
where $|c_i|^2$ is the probability density of accessing the i^{th} state $\varphi_i(\vec{r},t)$ if no other states are accesible, and $|c_i|^2$ is the probability of accessing i^{th} state when all other states are also accesible ($\because \sum_i |c_i|^2 = 1$)

(This linear superposition principle is not so surprising for light since the plane waves are the solutions of the linear 2nd order PDE. As the above superposition principle is also valid for general particle wave function, so, the corresponding equation of motion is expected to be linear differential equations – c.f. Schrödinger equation).

Wave Packet & Heisenberg Uncertainty Principle

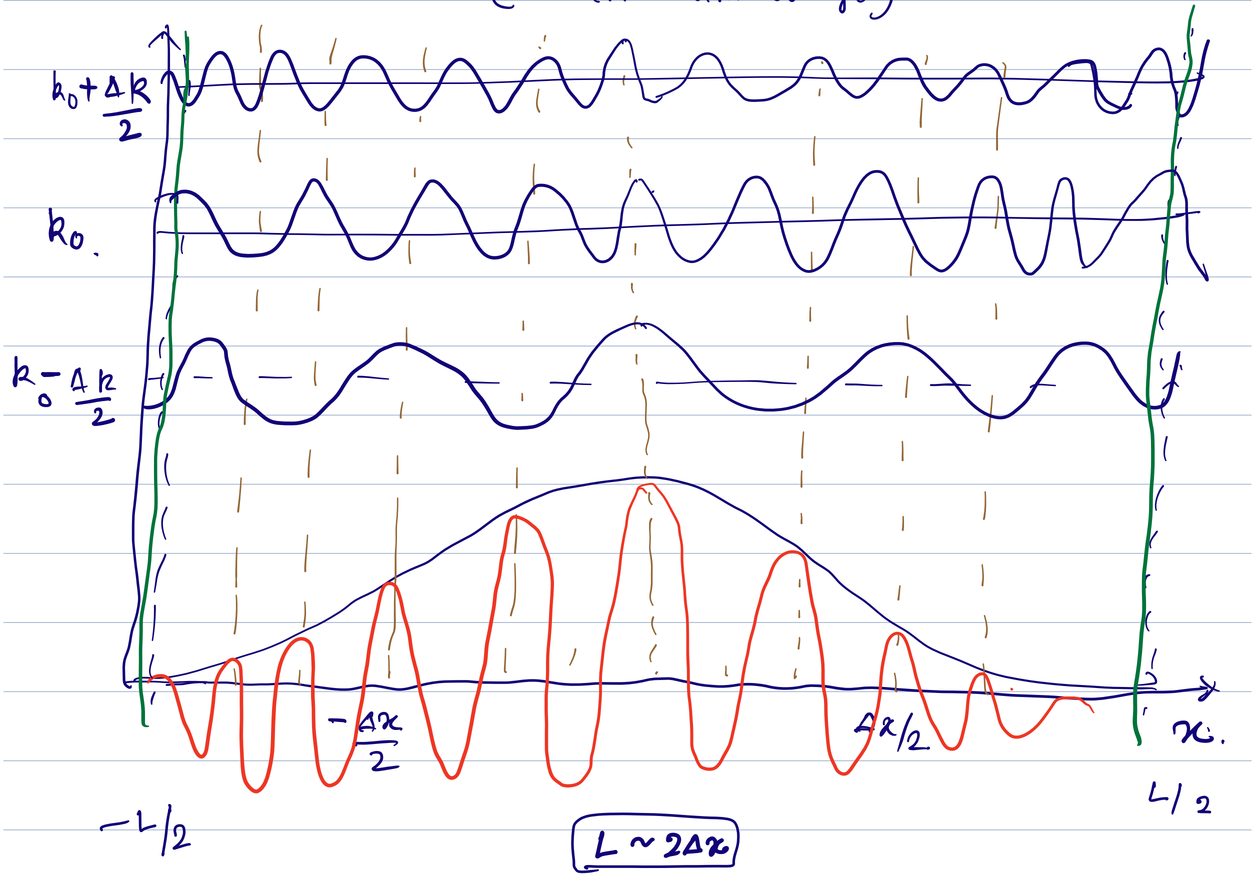
Now we want to create those wavefunctions which are in between the δ-function and plane waves, such that these functions can have finite width and finite range of wavenumbers, ie, finite uncertaities in both position and momentum. How much uncertainty in each coordinate do we acquire? That we will see to be linked to the lowest energy possible which we will call the ground state energy. A plane wave corresponds to free particles, i.e. particles with only kinetic energy, and without any potential energy or rest mass (relativistic). On the otherhand, a δ-function wavefunction is fully localized and hence no kinetic energy. Therefore, a general wave packet corresponds to systems with both K.E. & P.E. K.E. depends on $\vec{p}$ and hence delocalize the wave & P.E. generally depends on x and hence tend to localize (confine it, and we hence need a wave packet as a compromize between them which will also minimize (and in certain cases quantize) the total energy. Therefore, we anticipate a connection between wave packet, uncertainty principles, and ground state energy.



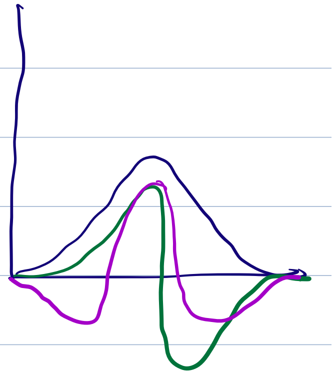


This means, we are talking about wavefunctions of the above shapes, which is confined in some Δx such that as we fourier transform to the momentum space, we also get a finite width Δk, with $\Delta p \Delta x \gtrsim \hbar$. The state acquires minimum/ground state energy when $\Delta p \Delta x \sim \hbar$, as we will prove below.

- We can construct the above wave packet as a collection of plane waves spread across Δk, around k_0. We have seen one example, for a Gaussian wave packet, where $\Delta x \sim \sigma$ & $\Delta k \sim 1/\sigma$.
  (Cohen-Tannoudji)



The above picture demonstrates that a wave packet can be constructed with a linear combination (superposition) of several plane waves in the width Δk around k_0. It can be also viewed as standing wave of plane waves reflected from the potential barrier near the boundary at $x_0 \pm \Delta x_0$ where the reflected waves loose (gain momentum $\Delta p = \hbar \Delta k$ and the reflected waves interfere with the original one to give wave packet. There are more wave packets possible with nodes in between as shown in the adjacent figure in different colors, but we will show later that any wave packet with nodes (ie, shorter wavelength) will have higher energy than the wavepacket with largest wavelength and no node.



(In modern language, a wavepacket is often referred as a "mixed state", since it's a collection of many well defined momentum states).

- The spread of the wave packet in the real space Δx looks like inversely proportional to the spread of the wavefunction in the momentum space Δk. To establish that, lets only consider three waves as shown in the above figure which are spread over in the range of Δk. This momentum spread between the three waves determines when a destructive interference will occur, and the distance between the two nearest destructive interference points determines the spread of the wave packet in real space Δx. Mathematically, we take a linear superposition of three such waves, with the wave at k_0 has heighest weight, $\phi(k_0)$, whereas the other two waves have $\phi(k_0 \pm \Delta k) \sim \phi(k_0)/2$. So, we get.

$$\psi(x) = \phi(k_0)\left[e^{ik_0 x} + \frac{1}{2} e^{i\left(k_0+\frac{\Delta k}{2}\right)x} + \frac{1}{2} e^{-i\left(k_0-\frac{\Delta k}{2}\right)x}\right]$$

$$= e^{ik_0 x}\left[1 + \cos\left(\frac{\Delta k}{2} x\right)\right] \quad --- (1).$$

Therefore, the wave function vanishes at $\frac{\Delta k}{2} x = \pi n$, $n = \pm 1, \pm 2, \ldots$

Therefore, the shortest distance between them is $\Delta k \Delta x = 4\pi$.

This can be written as

$$\Delta p \, \Delta x = \frac{h}{2} \geq \hbar \quad --- (2)$$

This formula relates the spread in position as inversely proportional to the number of momentum states required to produce a wave packet.

(H.W) Consider the above wave function and compute Δx, Δp as the standard deviation from the average value of the position and momentum measured for this wave function. Then we can reproduce the above relation in eqn (2). Therefore, the spread in position & momentum in the wave function tells us about the variance in the measurement in the position and momentum values. It's clear now that they are inversely proportional to each other and hence both uncertainty can not be made arbitrarily small. In fact, if we try to make one small, then the other one grows. So, both position and momentum cannot be measured simultaneously with arbitrarily small precision. Their bound in the smallest possible phase space area as,

$$\boxed{\Delta p \Delta x \gtrsim \hbar}$$

The same is true for all pairs of phase space variables such as $\Delta E \Delta t \gtrsim \hbar$, $\Delta L \Delta \theta \gtrsim \hbar$, etc.

- This is the Heisenberg Uncertainty Principle.

(The above derivation is done with a specific example, but the uncertainty relation is completely fundamental.)

Ground state energy from uncertainy principles

We consider the general wavefunction in plane wave basis:

$$\psi(\vec{r},t) = V\int \frac{d^3k}{(2\pi)^3}\frac{d\omega}{2\pi} e^{i(\vec{k}\cdot\vec{r}-\omega t)}\,\phi(\vec{k},\omega) \quad ---(3)$$

$$\phi(\vec{k},\omega) = \int d^3r\,dt\;\psi(\vec{r},t)\,e^{-i(\vec{k}\cdot\vec{r}-\omega t)} \quad --(4)$$

- Particle: For $\phi(k) = 1$, $\psi(\vec{r}) = \delta(\vec{r})$ $\Rightarrow \Delta x = 0,\ \Delta p \to \infty$
- Wave : For $\phi(k) = \delta(k-k_0)$, $\psi(\vec{r}) = Ve^{i\vec{k}\cdot\vec{r}}$ $\Rightarrow \Delta x \to \infty,\ \Delta p = 0.$
- Wave packet: In general $\phi(k)$, & $\psi(\vec{r})$ have finite spread in momentum & position space related by $\Delta p\,\Delta x \geq \hbar$.

Q. Then the question is how much position and momentum spread or uncertainity a particle/wave takes? What does it depend on? Which uncertainty is preferable for a given system.

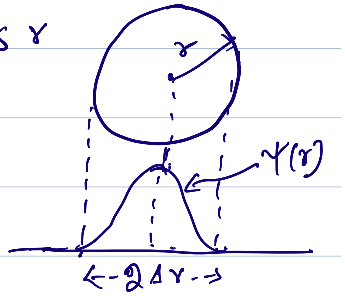
Ans: It turns out, based on the boundary condition, the system tries to optimize the two uncertainties to achieve the lowest energy state (ie, the ground state).

Lets put this hypothesis on test.

(1) Bohr's Atom: Let us consider what is the uncertainty in the ground state energy of the Bohr Atom or by

optimizing the position & momentum uncertainty do we get the Hydrogen Atom's ground state energy ?

→ An electron orbiting in a circle of radius r can have the maximum uncertainty in radius is $\Delta r \sim r$. Then the uncertainty in momentum is bounded to be $\Delta p \sim \hbar/\Delta r \sim \frac{\hbar}{r}$. --- (5)



Then energy (operator) is $\hat{E} = \frac{\hat{p}^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r}$. The average value of energy is

$$\langle \hat{E} \rangle = \frac{\langle \hat{p}^2 \rangle}{2m} - \frac{Ze^2}{4\pi\epsilon_0}\left\langle \frac{1}{r} \right\rangle . \quad ---(6)$$

Now how is Δp related to $\langle \hat{p}^2 \rangle$?

$\Delta p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2}$ = which measures the variation of momentum across its mean value. Now, the average momentum $\langle p \rangle = 0$ in an orbit, otherwise the particle will move away from the orbit. So, $\langle p^2 \rangle = (\Delta p)^2 \sim \frac{\hbar^2}{r^2}$. --(7)

So, substituting eq (7) in (6), we get,

$$\langle \hat{E} \rangle \approx \frac{\hbar^2}{2m}\frac{1}{r^2} - \frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r}.$$

Minimizing the average energy w.r.to r gives

$$\left.\frac{d\langle \hat{E} \rangle}{dr}\right|_{r=r_0} = 0 \Rightarrow -\frac{\hbar^2}{m r_0^3} + \frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r_0^2} = 0$$

$$\Rightarrow \boxed{r_0 = \frac{4\pi\epsilon_0 \hbar^2}{m Z e^2}} = a_0 = \underline{\text{Bohr radius}} \ (\text{for } Z=1)$$

The energy at the Bohr radius is

$$E = \frac{\hbar^2}{2\pi r_0^2} - \frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r_0} = -\frac{Ze^2}{4\pi\epsilon_0 \, 2a_0} = -13.6 \text{ ev.}$$

as Bohr estimated for $n = 1$.

- H.W. : (i) Reproduce the above result by using the uncertainty principle in $\Delta L \, \Delta\theta \geq \hbar$. Can we also obtain the same result with $\Delta E \, \Delta t \geq \hbar$ relations?

(ii) Estimate the Ground state energy of an harmonic oscillator: $H = p^2/2m + \frac{1}{2} m\omega^2 x^2$.

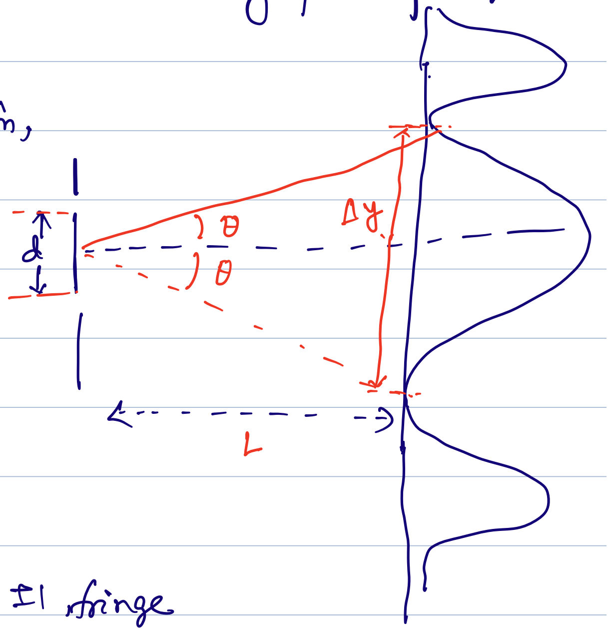
(iii) Estimate the Ground state energy for a particle trapped in a box of length L. The particle in a box has the potential profile of $V(x) = 0$ for $|x| < L$ & $V(x) = \infty$ for $x \geq L$.

② Can we predict the diffraction pattern of the double slit experiment via uncertainty principle?

- If we do a full calculation, we get the condition for diffraction as

$$2d \sin\theta = n\lambda \quad -(8)$$

where $n = \pm 1, \pm 2, \ldots$ correspond to the minima.



- We want to show that $n = \pm 1$ fringe corresponding to the minimum uncertainty. We can do it for position & momentum (H-W), but lets focus on the angular momentum & angle uncertainty: $\Delta L_z \Delta\theta = \hbar$.

- The spread of the wave packet Δy between the nearest two minima is the uncertainty in position. For small angle, this corresponds to the uncertainty in the angle θ as $\Delta\theta$ $\left(\sim \frac{\Delta y}{2L}\right)$

- The corresponding spread in momentum $\Delta p_y \sim \hbar/\Delta y$. For radial wave, the spread of the wave in $\Delta\theta$ is restricted to the spread of the Fourier mode in the values of angular momentum ΔL_z (we will learn more about it later).

- Now, $L_z = x p_y - y p_x = -y p_x$ (since the particle has no momentum along y).

So, $\Delta L_z = d \Delta p_x = d p_x$, since $y = d =$ fixed,

$\Delta p_x \sim \sqrt{\langle p_x^2 \rangle - \langle p_x \rangle^2}$

$\sim \sqrt{\langle p_x^2 \rangle} \sim p_x$.

$p_x \sim h/\lambda$.

Since $\Delta L_z \Delta \theta = \hbar$.

So, $d \Delta \theta = \frac{\hbar}{2 p_x} \sim \lambda/2$.

$$\Rightarrow \boxed{2 d \Delta \theta = \lambda} \quad \text{--- (9)}$$

This proves that the angular spread of the diffraction for a particle/wave of de Broglie wavelength $\lambda \sim h/p$ for a double slit distance d is determined by the uncertainty principle indeed.

(3) "Time packet" or pulse & lifetime or decay rate of a state

Much like the uncertainty relation between x & p is understood via the Fourier transformation of the wavefunction, a similar argument for the Fourier transformation of the time to frequency can be given to derive $\Delta E\,\Delta t \gtrsim \hbar$.

Focussing only on the time part, we have (not considering the position)

$$\psi(t) = \int \frac{d\omega}{2\pi}\,\phi(\omega)\,e^{-i\omega t} \quad --(10)$$

$$\& \quad \phi(\omega) = \int dt\,\psi(t)\,e^{i\omega t} \quad --(11)$$

Therefore, $\psi(t)$ denotes a "time-packet" or pulse which is negligibly small outside the time spread Δt. Then this time-packet can be expressed as a superposition of monochromatic waves $\phi(\omega)$ within the angular frequency spread of $\Delta\omega$, such that $\Delta\omega\,\Delta t \gtrsim 1 \Rightarrow \Delta E\,\Delta t \gtrsim \hbar$. This says if the time packet exists in the time-interval Δt, then the energy of this packet cannot be measured below the precision $h/\Delta t$. In other words, if we consider an ensemble of identically prepared systems/particles described by the wavefunction ψ, then the measurement of an energy on each member of an ensemble will produce a range of values spread over an interval ΔE of extent greater than or of the order of $h/\Delta t$.

- Another interpretation of the energy-time uncertainty is the decay time of the particle. If we say the energy of a particle is completely fixed such that the variance in energy $\Delta E = 0$, then the time interval to find the particle in this energy state is infinity. This means, the lifetime of the particle in this state is infinite. Otherwise, if the energy variance of a given energy state is finite, then the uncertainty principle suggests that the time-interval to find the particle in this spread of energy state is also finite $\Delta t \sim \hbar/\Delta E$. Therefore, the particle has the finite probability to leave this state and make a transition to another state. The spread in energy ΔE is called the natural energy width of that state, and $\Delta t \sim \tau \sim \hbar/\Delta E$ is called the lifetime of a particle in this energy state. The ground state is the lowest possible energy level of a system. A particle in the ground state can not loose energy to go to any other lower energy states. Therefore, the liftime of a ground state is infinity and the natural energy width is zero. A particle in the ground state is the most stable configuration.

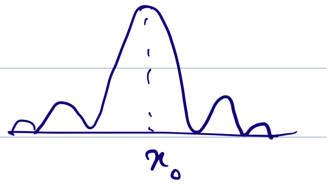
- In most of our description in QM-I, and also in QM-II, we like to use the wavefunction for which energy/frequency is completely known and lifetime is infinity for convenience. This is called energy eigenstate.

- Is the wave packet moving or stationary?

$$\Psi(x,t) = \int \frac{dk}{2\pi}\,\frac{d\omega}{2\pi}\;\phi(k,\omega)\;\underbrace{e^{i(kx-\omega t)}}_{\text{(plane wave basis)}} \qquad -(1)$$

Where is the center of this wave packet at t?

- The center of the wave packet is where the probability density $\rho(x,t) = |\Psi(x,t)|^2$ is maximum.



- A single plane wave's velocity is obtained from frequency & wave length relation $c = \nu\lambda = \omega/k$ which is called phase velocity.
- But now we have a wave packet. It propagates with a group velocity. A group velocity differs from the phase velocity, mainly when the frequency-wavelength relation $\omega(k)$, or the energy-momentum relation $E(p)$ differs from the simple linear dependence of a plane wave. Such a relation $\omega(k)$ or $E(p)$ is called the dispersion relation.

Assuming a general form of $E(p)$ we obtain the phase of wave as $e^{i\beta(p)/\hbar}$ where

$$\beta(p) = px - E(p)\,t \qquad --(1)$$

Assuming that the phase $\beta(p)$ is a smooth, differentiabl function around the wave packet center, then we can expand $\beta(p)$ around the momentum p_0 in a Taylor's series

$$\beta(p) \approx \beta(p_0) + (p-p_0)\frac{\partial\beta}{\partial p}\Big|_{p_0} + \mathcal{O}\left[(p-p_0)^2\right]. \quad \text{--- (2)}$$

(When $\frac{\partial\beta}{\partial p} = 0$, we have $\beta(p) = \beta(p_0) = \text{Constant}$ which makes the dispersion $E(p_0)$ to be a fixed function of p and hence as we showed above, the center of the wave packet becomes stationary at $x=0$. This condition $\frac{\partial\beta}{\partial p} = 0$ is called the stationary phase condition).

We can now rewrite the wave packet as

$$\psi(x,t) = e^{i\beta(k_0)/\hbar}\int_{-\infty}^{\infty}\frac{dk}{2\pi}\frac{d\omega}{2\pi}\,\phi(k,\omega)\,e^{i(k-k_0)(x-x_0)}\,e^{i\omega t} \quad \text{--- (3)}$$

where

$$\boxed{x_0(t) = -\frac{\partial\beta}{\partial p}\Big|_{k=0.}} \quad \text{--- (4).}$$

Therefore, the wave packet is actually moving, because of the energy-momentum relation.

(When we have potential energy term $E = p^2/2m + V(x)$, $x_0(t)$ can be complicated.)

- What is the velocity (group velocity) $v_g = \frac{\partial x_0}{\partial t}$?

$$v_g = \frac{\partial x_0}{\partial t} = -\left[\frac{\partial}{\partial t}\left(\frac{\partial \beta}{\partial p}\right)_{p_0}\right]$$

$$= \frac{\partial}{\partial t}\left[\frac{\partial}{\partial p}\left(p_0 x - E(p)t\right)\right]$$

$$= \left.\frac{\partial E}{\partial p}\right|_{p_0}.$$

$$\Rightarrow \boxed{\begin{aligned} v_g &= \left.\frac{\partial E}{\partial p}\right|_{p_0} \\ &= \left.\frac{\partial \omega}{\partial k}\right|_{k_0} \end{aligned}} \quad — (5).$$

(This "group" velocity differ from the "phase velocity" which is the velocity of an individual plane wave $v_{ph} = \omega/k$.)

- Denoting the "group momentum" as p, i.e., $v_g = p/m$, we obtain the Newton's equation

$$\frac{\partial E}{\partial p} = p/m.$$

$$\Rightarrow E = \frac{p^2}{2m} + \text{constant} \quad (\text{we set constant} = 0)$$

(This proves the correspondence principle).

H.W. (i) How about a relativistic particle's dispersion $E = pc$?

(ii) Consider the Gaussian wavepacket introduced in previous chapter and obtain the uncertainty and group velocity.

(iii) Consider a 3D plane wave $e^{i(\vec{k}\cdot\vec{x} - \omega t)}$ and obtain group velocity, dispersion relation.

Measurables, Operators, Expectation / Averge Values

- We have so far introduced two sort of wavefunctions, namely a delta function and a plane wave (for light). These are two extreme limits of all possible wavefunctions that we can build, because, the delta function wavefunction is fully localized in position and completely undetermined wavenumber / momentum. On the other hand, a plane wave is a completely oscillatory / delocalized in position, but have a well defined, single wavevector / momentum. But none of them good wavefunctions for non-relativistic particles and we need to construct wave packet.

- To figure out the position, momentum, energy, and any physically measurable quantity of a wavefunction, we need a prescription on how to compute such quantity. For that we will resort to the probability description, but modification is required because of complex wavefunction. For a probability distribution of $\rho(\vec{x},t) = P(\vec{x},t)$, any physical quantity is obtained as an averge value of many many measurements and defined by

$$\langle O \rangle = \int O \, \rho(x,t) \, dx. = \int O \, |\psi(x,t)|^2 \, dx. \quad \text{--- ②}$$

The above description does not however depend on the phase of the wave function and can be incomplete in many cases. Therefore, a more general average or expectation value is defined for wave mechanics as

$$\boxed{\langle o\rangle = \int \psi^*(x,t)\; o\; \psi(x,t)\; d^3x} \quad \cdots \textcircled{3}$$

The above definition is sort of an ansatz, but we will see that it works and does not lead to inconsistency.

- The above prescription does not yet define what is the quantity 'o' on the right hand side which would correspond to the physical quantity that we are measuring on the L.H.S. We actually have to define them. We call them operator and often denote by a hat $\hat{o}$. We don't measure an operator, but we measure its expectation value $\langle\hat{o}\rangle$. Lets take some examples first.
- Lets start with the plane wave case

$$\psi_{k,\omega}(\vec{r},t) = A\, e^{i(\vec{k}\cdot\vec{r}-\omega t)} \quad \cdots (4).$$

we know that this is the solution of the wave equation and its energy & momentum are

$E = \hbar\omega$ & $\vec{p} = \hbar\vec{k}$ --- (5).

⟹ From eq (3), we want the energy to be.

$$\hbar\omega = E = \langle \hat{E} \rangle = \int \psi^*(\vec{r},t)\, \hat{E}\, \psi(\vec{r},t)\, d^3r.$$

By inspection, we see that

$$\boxed{\hat{E} = i\hbar \frac{\partial}{\partial t}} \quad \cdots \quad (5).$$

Therefore, the energy operator, what we call the Hamiltonian operator, is defined by the derivative of the "conjugate" variable, i.e, time. This makes sense, become time derivative $\frac{\partial \psi}{\partial t} \approx \frac{\psi(t+\delta t) - \psi(t)}{\delta t}$, gives time-translation from $\psi(t)$ to $\psi(t+\delta t)$ which can be determined from the phone space if we know the energy & vice versa.

⟹ Similarly, the momentum operator is obtained to be

$$\hbar\vec{k} = \vec{p} = \langle \hat{\vec{p}} \rangle = \int \psi^*(\vec{r},t)\, \hat{\vec{p}}\, \psi(\vec{r},t)\, d^3r.$$

$$\boxed{\hat{\vec{p}} = -i\hbar \frac{\partial}{\partial \vec{x}}} \quad \cdots \quad (6).$$

- So, similarly, the momentum operator is defined by the $(-i\hbar)$ times derivative w.r.to its conjugate variable.

⟹ Since, $\psi(x,t)$ is defined in the x & t space, the position and time operarators are simply $\hat{x}$ & $\hat{t}$.

$$\left.\begin{aligned} \vec{x} = \langle \hat{\vec{x}} \rangle &= \int \psi^*(x,t)\, \hat{\vec{x}}\, \psi(x,t)\, d^3x. \\ t = \langle \hat{t} \rangle &= \int \psi^*(x,t)\, \hat{t}\, \psi(x,t)\, d^3x. \end{aligned}\right\} \text{—}(7)$$

(first definition).

- The operator $\hat{x}, \hat{t}$ are some mathematical notations for the wavefunction defined in the (x,t) space. In some sense we are saying the position & time associated with this wavefunction at a given $\bar{x}, t$ are well defined [we will find that $\Psi(x,t)$ is the eigenfunction ("eigen" means "proper") of the position & time operators.]

To elaborate the above statement, we can go to the momentum & energy space and define these operators again. The wavefunction in the momentum & frequency space is nothing but the inverse Fourier transformation of $\Psi(x,t)$ as

$$\Psi(\vec{r},t) = V\int \frac{d^3k}{(2\pi)^3}\frac{d\omega}{2\pi} e^{i(\bar{k}\cdot\bar{r}-\omega t)} \phi(\vec{k},\omega)$$

$$\Rightarrow \quad \phi(\vec{k},\omega) = \int d^3r\,dt\ \Psi(\vec{r},t)\ e^{-i(\vec{k}\cdot\vec{r}-\omega t)}$$

— (8).

So, $\phi(k,\omega)$ are the momentum & energy space wavefunction corresponding to $\Psi(x,t)$. Now.

$$\rightarrow \hbar\vec{k} = \vec{p} = \langle\hat{\vec{p}}\rangle = \int \phi^*(k,\omega)\ \hat{\vec{p}}\ \phi(k,\omega)\ \frac{d^3k}{(2\pi)^3}$$

$$\rightarrow \hbar\omega = E = \langle\hat{E}\rangle = \int \phi^*(k,\omega)\ \hat{E}\ \phi(k,\omega)\ \frac{d^3k}{(2\pi)^3}$$

$$\rightarrow \quad \vec{r} = \langle \vec{r} \rangle = \int \varphi^*(k,w)\left(-i\frac{\partial}{\partial \vec{k}}\right)\varphi(k,w)\frac{d^3k}{(2\pi)^3}$$

$$\rightarrow \quad t = \langle \hat{t} \rangle = \int \varphi^*(k,w)\left(i\frac{\partial}{\partial w}\right)\varphi(k,w)\frac{d^3k}{(2\pi)^3}$$

$$\Rightarrow \boxed{\begin{aligned} \hat{\vec{x}} &= -i\frac{\partial}{\partial \vec{k}} = -i\hbar\frac{\partial}{\partial \vec{p}}, \\ \hat{t} &= i\frac{\partial}{\partial w} = i\hbar\frac{\partial}{\partial E} \end{aligned}} \quad \text{---} (9).$$

- We can very much define the rest of the operators such as angular momentum etc from these operators.

- **H.W. 1** : (i) Evaluate position for the wave function $\delta(\vec{x}-\vec{a})$, Evalue its momentum. Then evaluate the uncertainty in their corresponding values.

  (ii) Repeat the same for a the plane wave $\psi(x,t) = Ae^{i(k\cdot\vec{r}-wt)}$.

H.W. 2. Express the continuity equation $\frac{\partial \rho}{\partial t} + \vec{\nabla}\cdot\vec{J} = 0$ in terms of the operators.

$\rho = |\psi|^2 = \psi^*\psi$, $\vec{J} = \rho\vec{v} = \rho\frac{\vec{p}}{m}$ in position space

Schrödinger Equation

- For a classical particle we want to know $x(t)$ and this comes from a solution of the (Newton's) equation of motion in the time-domain.
- In quantum mechanics, we have a complex function $\psi(x,t)$ whose equation of motion has to be generalized in space and time. (In some sense $\psi(x,t)$ encodes a mapping of the trajectory of the particle into a functional space of both space & time to incorporate the wave nature / uncertainty of the particle not being fixed at (x,t) / ie the probabilistic approach rather than a deterministic approach to the particle's trajectory.)

- Once we start with an initial wavepacket at some initial condition (x_0, t_0), the job of the equation of motion is to predict the wavefunction $\psi(x,t)$ at a different position & later time. We just saw in the previous section that if we know the group velocity, we can predict the center of the wavepacket at a later time. That is true. But, in general, the energy is not a simple function of p only, but complicated function of momentum and space as $E = \frac{p^2}{2m} + V(x)$.

- So, we need a proper equation of motion in both space & time to predict $\psi(x,t)$. What is the equation of motion?

Hint: For a photon which is also the quantum particle of the electromagnetic wave, we know the equation of motion. That was the wave equation

$$\frac{\partial^2\psi}{\partial t^2} = c^2\frac{\partial^2\psi}{\partial x^2} \quad \text{(in 1D)} \quad --(1)$$

This equation, if we write in the energy and momentum operator form, looks like

$$\hat{E}^2\psi(x,t) = c^2\hat{p}^2\psi(x,t) \qquad \left[\begin{array}{l} \hat{E} = i\hbar\frac{\partial}{\partial t} \\ \hat{p} = -i\hbar\frac{\partial}{\partial t} \end{array}\right].$$

Then multiply $\psi^*(x,t)$ from left and integrate in space to obtain

$$\int \psi^*\hat{E}^2\psi\, dx = c^2\int \psi^*\hat{p}^2\psi(x,t)\, dx$$

$$\Rightarrow \langle E\rangle^2 = c^2\langle p\rangle^2$$ [using the definition of expectation value].

$$\Rightarrow E = \pm cp$$ [We often don't use ⟨ ⟩ for an expectation value].

So, it works for relativistic, massless particles.

We need an equation for non-relativistic one which follows $E = p^2/2m + V(x)$.

- Can we think of the continuity equation

$$\frac{\partial \rho}{\partial t} + \vec{\nabla}\cdot\vec{J} = 0 \qquad -- (2)$$

as a possible equation of motion? It does not involve the phase of the wave function (at least not in an obvious way). So, it looses a lot of information about the phase of the wave function. But this equation is a valid equation, so whatever a proper equation of motion be, its solution must reproduce the continuity equation. So, we have to do this sanity check.

- **Schrödinger Equation:**

Schrödinger equation is an equation of motion for non-relativistic particle. It should be an equation such that the expectation value of $\langle\hat{E}\rangle$, $\langle\hat{p}^2\rangle$ & $\langle\hat{V}\rangle$ should follow the energy-momentum relation $\langle\hat{E}\rangle = \left\langle\frac{\hat{p}^2}{2m}\right\rangle + \langle\hat{V}\rangle$ --(3). Using the definition of the expectation value, we get

$$\int dx \left[\psi^*(x,t)\ \hat{E}\ \psi(x,t)\right] = \int dx \left\{\psi^*(x,t)\left[\frac{\hat{p}^2}{2m} + \hat{V}(\hat{x})\right] + \psi(x,t)\right\}.$$

where $\hat{E}$ & $\hat{p}^2$ operators are defined above as $\hat{E} = i\hbar\frac{\partial}{\partial t}$ & $\frac{\hat{p}^2}{2m} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$. The potential operator is deduced by replacing x with $\hat{x}$ operator in its variable, i.e, $V(x) \to \hat{V}(\hat{x})$.

Then the above integral is valid for any general function and is equal at all points in position. Therefore, we get

$$\cancel{\psi^*}\,\hat{E}\,\psi = \cancel{\psi^*}\left[\frac{\hat{p}^2}{2m} + \hat{V}(x)\right]\psi$$

[Since these operators are hermitian, and hence has real expectation / eigenvalues, so, we can assume that they act on ψ on the right hand side. This is actually a general general result that we can see from linear algebra. Therefore, we can eliminate the $\psi^*(x,t)$ state from the left.]

Then substituting the operators, we get

$$\boxed{i\hbar\frac{\partial}{\partial t}\psi(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x,t) + \hat{V}(x)\,\psi(x,t)} \quad \text{---}(4)$$

This is our Schrödinger's equation of motion. In 3D, $\frac{\partial^2}{\partial x^2} \to \nabla^2$ & $\hat{V}(x) \to \hat{V}(\vec{r})$, $\psi(x,t) \to \psi(\vec{r},t)$.

[H.W. (i) What will be the schrödinger equation for the $\psi^*(x,t)$ state?

(ii) Show that the wave packet

$$\psi(x,t) = \int \frac{dk}{2\pi}\frac{d\omega}{2\pi}\,\phi(k,t)\,e^{i(kx-\omega t)}$$

is a solution of the schrödinger equation, where $p = \hbar k$ & $E(p) = \hbar\omega(p)$.]

- Properties of the Schrödinger equation.

(i) Superposition principle.

Its linear and homogeneous. Therefore, if Ψ_1 & Ψ_2 are two solutions of eq(4) and $\Psi = c_1 \Psi_1 + c_2 \Psi_2$ is also a solution of the same equation for c_1 & c_2 being constants. Therefore, the equation allows the linear superposition principle.

(ii) Boundary Condition.

The PDE is first order in time, but 2nd order in position. This is because the energy is quadratic in momentum. (This is in contrast with relativistic photons where both position & time derivatives are 2nd order. Hence we had a linear energy momentum relation).

A first order PDE solution has one unknown and a 2nd order PDE has two unknowns. Therefore, to know the full solution $\Psi(x,t)$ of eq(4), we need one boundary condition in time and two boundary conditions in position. In some occations, the solutions and the physical interpretations of the wavefunction can vary drastically based on the boundary condition. Therefore, boundary conditions are extremely important.

Since, its a 2nd order PDE in position, Ψ should be continuous, and its first derivative should exist and continuous.

- In another words, if the wave function $\Psi(x,t)$ is known at a given time t_0 (ie the boundary condition), its known at all later time $t > t_0$ at the same position.

- Similarly, if the wavefunction $\Psi(x,t)$ and its first spatial derivatives are known at a given position, or the wavefunction is known at two different positions at the same time (two boundary condition are hence provided), then the wavefunction is known at all other points in space at the same time.

(iii) Conservation of Probability:

As we mentioned earlier, and showed explicety for the electromagnetic field, that the wavefunction associated with a particle in quantum mechanics has a statistical interpretation, in which $\rho(x,t) = |\Psi(x,t)|^2$ denote the probability density of finding the particle at x & t. This puts two more restrictions

(a) The total probability of finding the particle within the entire space is 1 at all time. ie,

$$\int_{-\infty}^{\infty} dx \, \underbrace{|\Psi(x,t)|^2}_{\rho(x,t)} = 1 \quad \text{--(5)}.$$

(This is also because, the Schrödinger equation is homogeneous and does not have any source term. Therefore, the particle creation or destruction at any time is not possible within the Schrödinger equation).

Eq (5) also indicates that while the L.H.S. has time argument, but the R.H.S is constant. This means, under the Schrödinger equation the $\Psi(x,t)$ should always have a time-dependence such that $|\Psi|^2 = \Psi^*(x,t)\,\Psi(x,t)$ becomes time-independent. One simple, and quite general, example solution is $\Psi(x,t) = \Psi(x,0)\, e^{-iEt}$. This condition is also called a $\boxed{\text{Unitary condition or unitarity}}$, which we may learn later. Eq (5) is also called normalization condition by which we can fix one of the free parameters of the PDE equation.

(b) We also saw from Maxwell's equations that a charge particle (like electron) follows the continuity equation. This is true for all particles, and related to the above condition. The continuity eq is

$$\frac{\partial \rho}{\partial t} + \vec{\nabla}\cdot\vec{J} = 0. \qquad \text{at a given } \underline{\underline{x,t}}. \quad \cdots (6)$$

where $\rho = |\Psi|^2$ and $\vec{J}$ is yet to be determined. The $\frac{\partial \rho}{\partial t}$ term appears to contradict the condition (5), where we said ρ does not have any time-dependence. What we actually mean ρ does not explicitly depend on time, But it can change in time due to the time dependence of its variables $\vec{x}$, but its change in time at a given position is equal to the flow of probability density away from it, which is the probability current density $\vec{J}$.

So, let us see whether schrödinger equation satisfies these two conditions. Considering a small volume / length L with in the entire space in which $\int_V dV |\psi|^2 \neq 1$, we differentiate with time,

$$\frac{\partial}{\partial t}\int_V dV\, |\psi|^2 = \int_V dV \left[\psi^*\left(\frac{\partial \psi}{\partial t}\right) + \left(\frac{\partial \psi^*}{\partial t}\right)\psi\right] \qquad --- (7).$$

Now, we replace $\frac{\partial \psi}{\partial t}$, $\frac{\partial \psi^*}{\partial t}$ from the schrödinger equation to obtain

$$\text{R.H.S} = \int_V dV\, \frac{i\hbar}{2m}\left[\psi^*(\nabla^2\psi) - (\nabla^2\psi^*)\psi\right]$$

[The potential term cancels out]

Performing integration by parts we get

$$\int_V dV\, \underbrace{\frac{i\hbar}{2m}\vec{\nabla}\cdot\left[\psi^*\vec{\nabla}\psi - (\vec{\nabla}\psi^*)\psi\right]}_{-\vec{\nabla}\cdot\vec{J}}$$

Therefore, we obtain the probability current density as

$$\vec{J} = -\frac{i\hbar}{2m}\left[\psi^*\vec{\nabla}\psi - (\vec{\nabla}\psi^*)\psi\right]$$

$$= \frac{1}{2m}\left[\psi^*\left\{\underbrace{\left(-i\hbar\vec{\nabla}\right)}_{\vec{p}}\psi\right\} + \left\{\underbrace{\left(-i\hbar\nabla\right)^*}_{\vec{p}^*}\psi^*\right\}\psi\right]$$

$$= \mathrm{Re}\left[\psi^*\left(-i\frac{\hbar}{m}\nabla\right)\psi\right].$$

[Notice that $\hat{\vec{p}}$ operator acts on ψ whereas its complex conjugate $\hat{\vec{p}}^*$ acts on ψ^*.].

$$\Rightarrow \quad \vec{J} = \underbrace{\psi^*\left(\frac{\hat{\vec{p}}}{2m}\psi\right)}_{\vec{v}} + \underbrace{\left(\frac{\hat{\vec{p}}^*\psi^*}{2m}\right)\psi}_{\vec{v}^*}$$

This expression looks like $J = nev$ with charge $e=1$ and density $\rho = \psi^*\psi$.

Since the volume v is chosen arbitrarily, so, the integrands are equal. Hence we prove that the schrödinger equation satisfy the continuity equation of its probability.

(c) The above unitary condition of the probability in eq(5) is also a manifestation of the fact that the energy functional $\hat{E} = \frac{\hat{P}^2}{2m} + \hat{V}$ is Hermition. This energy functional operator $\hat{E}$ is called the Hamiltonian operator (in analogy with the Hamiltonian defined in classical mechanics).

$$\boxed{\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}(\vec{x})} \quad \text{---} (8).$$

Then the schrödinger equation is written in a concise form:

$$\boxed{i\hbar\frac{\partial}{\partial t}\Psi(x,t) = \hat{H}\Psi(x,t)} \quad — (9).$$

(c) Taking complex conjugate on both sides, we get

$$\Rightarrow -i\hbar\frac{\partial}{\partial t}\Psi^*(x,t) = (\hat{H}\Psi)^* = \Psi^*\hat{H}^* \quad \text{--} (10).$$

Then starting from equation (7) with $V \to \infty$ (the entire space), we hence.

$$\frac{\partial}{\partial t}\int_{-\infty}^{\infty} dv\, |\psi|^2 = 0 = \int dv \left[\psi^*\left(\frac{\partial \psi}{\partial t}\right) + \left(\frac{\partial \psi^*}{\partial t}\right)\psi\right].$$

from eq (9), (10) $$= \int_{-\infty}^{\infty} dv \left(-\frac{i}{\hbar}\right)\left[\left(\psi^* H \psi\right) - \left(\psi^* H^* \psi\right)\right]$$

$$= \left(-\frac{i}{\hbar}\right)\int_{-\infty}^{\infty} dv\ \psi^* \left(H - H^*\right)\psi .$$

Since this result is valid irrespective of the form of H, so, the integrand must be zero. This proves that
$$\boxed{\hat{H} = \hat{H}^*} = \text{Real (or Hermitian for a matrix operator).}$$

Therefore, the time evolution of a wave function under a Hermitian Hamiltonian is always unitary, i.e., the probability is conserved. Hermitian operator also ensures that its expectation value is real (H-W). Later on as we will convert eq (8) into an eigenvalue equation where the eigenvalue of the Hamiltonian will be identified with the total energy, we will claim that the energy eigenvalue of a Hermitian Hamiltonian is always real.

(d) For the 2nd derivative of ψ to exist, ψ and its first derivative in space should be continuous, finite, and single valued (analytic) at all x.

Observables ≡ Expectation values of operators

Anything measurable in quantum mechanics has a corresponding operator whose expectation value is what we measure. Since the measurables are real numbers, so the operators are Hermitian. The expectation value is a quantum mechanical analog of the statistical average value, with the difference that

$$\langle \hat{F} \rangle = \int dx \;\; \psi^*(x,t) \; \hat{F}(x,t) \, \psi(x,t) \quad \text{--(11)}.$$

where $\hat{F}$ is a Hermitian operator which acts on ψ on the right (Being its Hermitian, it also acts on the left except the momentum operator that $\hat{p}$ acts on ψ, while $\hat{p}^*$ acts on ψ^* on the left. So, I sometimes prefer to call the momentum operator as non-Hermitian operator which happen to have real eigenvalues. But most books denote $\hat{p}$ as a Hermitian operator with the above property.)

We have already encountered most of the operators we need to discuss, w, $\hat{x}$, $\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$, $\hat{E} = -i\hbar \frac{\partial}{\partial t}$,
$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x = i\hbar\left(x \frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$, $\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}(\hat{x})$.
$= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \hat{V}(\hat{x})$, and so on.

H.W . Generalize all these operators to 3D and also in the spherical and cylindrical coordinates.

⊛ Equation (11) actually denote $\hat{F}$ as an operator in the position space since its acting on the ψ states in the position space only. The operator in the Fourier or momentum space changes. They can be derived from the position space operator by Fourier transforming in the R-H-S in eq 11.
The measured quantity on the L-H-S does not depend on whether one is using position or momentum space.

$$\langle \hat{F} \rangle = \int dx \; \psi^*(x,t) \; \hat{F}(x,t) \; \psi(x,t)$$

$$= \int dx \int \frac{dk}{2\pi} e^{-ikx} \varphi^*(k,t) \int \frac{dk'}{2\pi} e^{ik'x} \hat{\tilde{F}}(k',t) \int \frac{dk''}{2\pi} e^{ik''x} \varphi(k'',t)$$

$$= \int \frac{dk}{(2\pi)} \frac{dk'}{(2\pi)} \frac{dk''}{2\pi} \varphi^*(k,t) \hat{\tilde{F}}(k',t) \varphi(k'',t) \underbrace{\int dx \; e^{-i(k-k'-k'')x}}_{\delta(k-k'-k'')}$$

$$= \int \frac{dk}{(2\pi)} \frac{dk'}{(2\pi)} \varphi^*(k,t) \hat{\tilde{F}}(k-k',t) \varphi(k',t)$$

Show the operators in the momentum space becomes.
$\hat{x} \to -i\hbar \frac{\partial}{\partial p}$, $\hat{p}$, $\hat{E} = -i\hbar \frac{\partial}{\partial t}$, $L_z = x p_y - y p_x = -i\hbar\left(\frac{\partial}{\partial_y} p_y - y \frac{\partial}{\partial x}\right)$
$\hat{H} = \frac{p^2}{2m} + V\left(-i\hbar \frac{\partial}{\partial p}\right)$ and so on.

More in chapter 4:

- Commutator between two operators:

Unlike in classical mechanics or statical mechanics, where the ordering between two operators, say, $\hat{A}\hat{B}$ do not matter, but in quantum mechanics, the result may change depending on which operator acts on the wavefunction on the right. The difference between the product of two operators is denoted by a bracket, called, commutator, defined as

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}.$$

This commutator is clearly a new operator. If the expectation value of this operator is zero, then we say the two operators commute, otherwise they don't commute.

E.g. $\hat{A} = \hat{x}, \quad \hat{B} = \hat{p}_x.$

$$\langle \hat{x}\hat{p}_x \rangle = \int dx \; \psi^* x\left(-i\hbar \frac{\partial}{\partial x}\right)\psi$$

$$\langle \hat{p}_x \hat{x} \rangle = \int dx \; \psi^* \left(-i\hbar\frac{\partial}{\partial x}\right)(x\psi)$$

$$= \int dx \; \psi^* \left\{\left[\left(-i\hbar\frac{\partial}{\partial x}x\right)\psi + x\left(-i\hbar\frac{\partial \psi}{\partial x}\right)\right]\right\}$$

[using the chain rule].

So, $\langle [\hat{x}, \hat{p}_x] \rangle = \langle (x p_x - p_x x) \rangle$

$$= \int dx \, (i\hbar)\, \psi^* \psi = i\hbar \int \psi^* \psi \, dx$$

$$= i\hbar$$

Since this result is general for all states $\psi(x)$, so, the equality can be deduced at the operator level as

$$\boxed{[\hat{x}, \hat{p}_x] = i\hbar\hat{I}} \quad --- (12)$$

where the R.H.S represents a constant operator.

In fact one can go ahead and connect this commutator with the uncertainty principle, i.e,

$$\boxed{\Delta p_x \Delta x \geqslant -i\langle\psi|[\hat{x}, \hat{p}_x]|\psi\rangle} \quad -- (13).$$

Where the average on RHS is taken over any w.f $\psi(x)$.
We will prove this identity later. The result suggests that all variables and their canonical conjugate variables, which cannot be measured simultaneously, due to Heisenberg's uncertainty principle, their corresponding operators do not commute. It can be said in the reverse way that, if two operators do not commute, then these two operators' expectation values cannot be measured simultaneously, i.e, their variations are restricted by the Heisenberg uncertainty principle.

- $[\hat{x}, \hat{p}_x] = [\hat{y}, \hat{p}_y] = [\hat{z}, \hat{p}_z] = i\hbar$

  $[\hat{x}, \hat{p}_y] = [\hat{y}, \hat{p}_x] = 0$ for all such combinations.

  $[\hat{p}_x, \hat{p}_y] = [\hat{x}, \hat{y}] = 0$. " " " .

- $[\hat{\theta}, \hat{L}_z] = [\hat{\phi}, \hat{L}_x] = [\hat{\chi}, \hat{L}_y] = i\hbar$ where θ is the angular operator for a rotation around the z-axis and so on.

- We know that $\Delta E \Delta t \geq h/2$, but there is no such canonical relation between $[\hat{t}, \hat{E}]$.

- The non vanishing commutator between position and cannonical conjugate variable is analogous with the non vanishing Poisson bracket in classical mechanics. The definition of commutator and Poisson bracket are completely different and there is no relation between them.

H.W. (i) Is $\hat{x}\hat{p}_x$ an Hermitian operator?

(ii) How about $(\hat{x}\hat{p}_x + \hat{p}_x\hat{x})/2$?

[To be discussed again in chapter 4.

Correspondence Principle : QM → CM (Ehrenfest Theorem)

As Bohr suggested, any good quantum mechanical theory should reproduce the classical mechanics result at the limit $\hbar \to 0$. Lets see that for the Schrödinger equation, which was done by Ehrenfest. He suggested that the expectation value of E, p, x etc should satisfy the classical (Newton's eq). We actually started with the $E = p^2/2m + V(x)$ relation to derive the Schrödinger equation. Now let us see if the $\dot{\vec{p}} = -\vec{\nabla} V$ equation is also satisfied for the expectation values.

(In deriving the Ehrenfest theorem, you always have to keep in mind that unlike in CM, where a stationary / least action path in the action exist which gives our equation of motion, in QM, the action $S \sim h$ does not have such a stationary path, rather it is allowed to fluctuate in order of h. This is called quantum fluctuation which govern uncertainty in the expectation value of all quantities.)

The derivation of the Newton's law is slightly lengthy but straight forward and can be seen from Bransden's book (sec 3.4). Below, I sketch the solution.

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

- $$\frac{d\langle p_x \rangle}{dt} = -i\hbar \frac{d}{dt}\left[\int dx \; \psi^* \frac{\partial}{\partial x}\psi\right]$$

$$= -i\hbar \int dx \frac{\partial}{\partial t}\left(\psi^* \frac{\partial \psi}{\partial x}\right)$$

$$= -i\hbar \int dx \left[\left(\frac{\partial}{\partial t}\psi^*\right)\left(\frac{\partial \psi}{\partial x}\right) + \psi^* \underbrace{\frac{\partial}{\partial t}\Big(}\frac{\partial \psi}{\partial x}\Big)\right]$$

[A total derivative, when it passes into the integration becomes a partial derivative]

These two derivative commute so, we can write $\frac{\partial}{\partial x}\left(\frac{\partial \psi}{\partial t}\right)$.

Then we substitute the schrödinger eq and replace $\frac{\partial \psi}{\partial t} = -i/\hbar\left[-\frac{\hbar^2}{2m}\nabla^2 + V(x)\right]$, $\frac{\partial \psi^*}{\partial t} = i/\hbar\left[-\frac{\hbar^2}{2m}\nabla^2 + V(x)\right]$.

then we Green's integral formula to obtain on the R.H.S $= -\left\langle \frac{\partial V}{\partial x} \right\rangle$.

and we derive the Newton's law

$$\frac{d\langle p_x \rangle}{dt} = -\left\langle \frac{\partial V}{\partial x} \right\rangle.$$

We have chapter 6 entirely for higher dimensions.

Schrödinger Equation in Higher Dimension

The form of the Schrödinger equation remains the same and only the Laplacian operator ∇^2 increases its dimension: as

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}.$$

Then the equation becomes

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\Psi(\vec{r},t) = i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t) \quad -(1)$$

- Its now clear that all the variables are in the kinetic energy term are separable. If the variables in the potential energy are also separable, then we can use separation of variable method for the solution $\Psi(\vec{r},t)$. Assuming this is the case, then the general solution can be written in the form

$$\Psi(\vec{r},t) = \Psi_1(x,t)\,\Psi_2(y,t)\,\Psi_3(z,t) \quad -(2)$$

In the Fourier space:

$$\Psi(\vec{r},t) = L^3\int \frac{dk_x}{(2\pi)}\frac{dk_y}{(2\pi)}\frac{dk_z}{(2\pi)}\frac{d\omega}{(2\pi)} e^{i(k_x x + k_y y + k_z z - \omega t)} \phi_1(k_x,\omega)\,\phi_2(k_y,\omega)\,\phi_3(k_z,\omega)$$

$$= L^3\int \frac{d^3k}{(2\pi)^3}\frac{d\omega}{2\pi} e^{i(\vec{k}\cdot\vec{r} - \omega t)}\,\phi(\vec{k},\omega).$$

H.W. Write ∇^2 in the spherical and cylindrical coordinates and express $e^{i\vec{k}\cdot\vec{r}}$ in terms of Bessel & spherical Harmonics.

⊛ Time-independent Schrödinger equation

- Any explicit time dependence is not there in the kinetic energy term $-\frac{\hbar^2\nabla^2}{2m}$.
- If the potential energy $V(\vec{r})$ is also time-independent, we can employ separation of variable between position and time and obtain a time-independent Schrödinger equation. (Although the separation of variable will still work even if the potential is time-dependent, but time variable is separated from space variable, but in this course we will not consider any explicit time dependence in V. So, the total energy is a constant of motion).
- So, we have

$$i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t) = \underset{\overset{\downarrow}{\left[-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r})\right].}}{\hat{H}(\vec{r})}\,\Psi(r,t) \qquad -(1)$$

We use the separation of variable

$$\Psi(\vec{r},t) = \psi(\vec{r})\,f(t). \qquad --(2)$$

This gives,

$$\frac{i\hbar}{f(t)}\frac{df(t)}{dt} = \frac{1}{\psi(r)}H\psi(r) \qquad ---(3).$$

$$= E$$

(some constant (independent of time & space) which we will identify with total energy eigenvalue.

- Then we have $\displaystyle\int_{f(t_0)}^{f(t)} \frac{df}{f} = -i/\hbar\, E \int_{t_0}^{t} dt.$

$$f(t) = f(t_0)\, e^{-i/\hbar\, E\,(t-t_0)}. \quad -(4)$$

where $f(t_0)$ is to be evaluated with the boundary condition. We set $t_0 = 0$ for simplicity. Then we have ($f(0)$ is absorbed in $\psi(\vec{r})$ below)

$$\Psi(\vec{r},t) = \psi(\vec{r})\, e^{-i/\hbar\, E t} \quad -(5).$$

So, we see that the time part is purely a phase, and disappears from the probability density $\rho(\vec{r},t)$, since E is real and $\hat{H}$ is Hermitian. So, $\frac{\partial\rho}{\partial t} = 0 \Rightarrow \vec{\nabla}\cdot\vec{J} = 0.$ (H-W)

- Then we have from the R.H.S

$$\boxed{\hat{H}\psi(\vec{r}) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi(\vec{r}) = E\,\psi(\vec{r})} \; -(6)$$

This is the time-independent Schrödinger equation.

- $\underline{E}$ is the expectation value of energy operator, ie, the Hamiltonian $\hat{H}$ and we have

$$E = \langle\hat{H}\rangle = \int d^3r\; \psi^*(\vec{r})\, \hat{H}\, \psi(\vec{r}) \quad -(7).$$

- <u>Eigenvalue</u>: In fact E is not just the expectation value of the Hamiltonian, but according to eq(6), it's also the energy eigenvalue of the Hamiltonian operator. We have studied eigen values in both classical mechanics and mathematical physics, which gives normal modes.

In general, an operator, say $\hat{H}$, acting on a function ψ, gives another function $\hat{H}\psi = \varphi(\vec{r})$. Eigenvalue and eigendirection is one special solution in which the operator maps the function onto itself, ie,

$$\hat{H}\psi_E(\vec{r}) = E\,\psi_E(\vec{r}).$$

at all variable $\vec{r}$. This means E does not depend on $\vec{r}$, ie, E is a constant of motion. Since E is a constant of motion, this means E does not fluctuate, and it has no uncertainty associated with its constant value. This means E is completely <u>determined</u>. This can be proved easily by the fact that any n^{th} power of E is determined by n^{th} power of the H operator:

$$E^n = \langle \hat{H}^n \rangle = \langle \hat{H} \rangle^n = \int dx\ \psi^* \hat{H}^n \psi = \left(\int dx\ \psi^* \hat{H} \psi\right)^n.$$

Therefore, the variance $\Delta E = \sqrt{\langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2} = 0$. In other words, the lifetime of particles being in the energy eigenstates is infinite. This is precisely what is happening in the Bohr's orbits in atoms. All the orbits with different 'n = 1, 2, ...' corresponds to different eigenvalues of the corresponding Hamiltonian. Each energy levels E_n corresponds to different energy eigenvalues and the corresponding eigenfunctions $\psi_n(\vec{r})$, are the solution of the time independent Schrödinger equation

$$H \psi_n(\vec{r}) = E_n \psi_n(\vec{r}) \quad \text{---} (8).$$

- $n = 1, 2, \ldots$ is called a <u>quantum number</u>. A quantum number is associated with the discrete eigenvalues of an operator. Here the operator is the Hamiltonian, and n are thus the called the energy quantum number.

- One can have more operators for which the wavefunction may become the simultaneous eigenfunction. E.g., the energy eigenfunctions $\psi_n(\vec{r})$ may also be a simultaneous eigenfunction of momentum $\vec{p}$, and/or angular momentum $\vec{L}$ and so on. For each such operator, say the angular momentum as an example, there will be a discrete eigenvalues and an associated quantum numbes, say

$[\hat{H}, \hat{L}] = 0.$

$$L_z \psi_{n,m}(\vec{r}) = m\hbar \, \psi_{n,m}(\vec{r}) \, . \quad \text{--} (9)$$

Then the wavefunction will have both the quantum numbers $\psi_{n,m}(\vec{r})$. Then on each level, both energy and the angular momentum are known. It can now be shown that when $\psi(\vec{r})$ is a simultaneous eigenfunction of two operators then these two operators commute, and hence these two quantities can be simultaneously measured without any uncertainties. Another great advantage of having quantities sharing the same eigenstates with the Hamiltonian is that sometimes solving eigenvalue problem of that quantity might be easier than solving the Hamiltonian.

- Therefore what Bohr postulated that the energies of the atomic orbits in an Hydrogen atom are quantized, and they are quantized in quantum unit of the quantized angular momentum can now be identified by the simultaneous eigenfunction of the Hamiltonian operator and the angular momentum operator. We can now actually solve the time-independent Schrödinger equation for an hydrogen atom and reproduce the energy of the Bohr's energy levels. We will see that not only a single angular momentum that is quantized, but the total angular momentum is also quantized and one have three quantum numbers $E_{n\ell m}$ associated with each orbit. We will actually solve the hydrogen atom problem in details in this course.

- In the Hamiltonian $\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}(\hat{x}) = \hat{K} + \hat{V}$, the kinetic $(\hat{K})$ & potential $(\hat{V})$ energies often do not commute, because often kinetic energy is a function of momentum while potential energy is often a function of position and since momentum and position do not commute, hence $\hat{K}$ and $\hat{V}$ do not commute. Therefore, even though the total energy is conserved, but the kinetic & potential energies are not individually conserved. In other words, the energy eigenfunctions $\psi_n(\bar{r})$ are not a simultaneous eigenfunction of the kinetic & potential energies. Plane wave solution $e^{i\bar{k}\cdot\bar{r}}$ is an eigenstate of the momentum operator and hence is an eigenstate of the kinetic energy term $\hat{K} = \hat{p}^2/2m$, but as a potential energy is turned on, one obtains wave packet which is not an eigenstate of the kinetic energy anymore, while a wave packet is an eigenstate of the Hamiltonian.

(• Wave packet ψ_E has $\Delta p \, \Delta x \sim \hbar$, $\Delta E = 0$, $\Delta t \sim \hbar/\Delta E \to \infty$, $\Delta L = 0$, $\Delta\theta \to \infty$.

This will be discussed in chapter 4.

(*) More on energy eigen functions:

$$\hat{H}\psi_n(\vec{r}) = E_n\psi_n(\vec{r}) \quad \text{---} (1).$$

- Its a property of the generic eigenvalue problem that we have encountered in Mathematical Physics Course that all the eigenfunctions are normalizable (ie, square integrable) and are orthogonal to each other (for Hermitian operator/ matrix which is what the Hamiltonian is).

ie. $$\int_{-\infty}^{\infty} dx \; \psi_n^*(x)\,\psi_m(x) = \delta_{nm}. \quad \text{--} (2).$$

- So, the eigenfunctions of an Hermitian operator forms an Hilbert space. Since $\psi_n(x)$ are linearly independent and complete, any general function $\chi(x)$ be expanded in this Complete Hilbert space

$$\chi(\vec{r},t) = \sum_{n=-\infty}^{\infty} c_n(t)\psi_n(\vec{r}) \quad \text{--} (3).$$

$E = \int dx \; \chi^* \hat{H} \chi$

where $C_n(t)$ are Complex numbers, constant in space. ψ_n corresponds to quantized energy eigenvalues. If a particle has energy exactly matches with one of the eigenenergy, then the particle will go to that state and stay there forever. But if a particle has any arbitrary energy, then the particle will not go to any particular eigenstate, but remain in a superposition state with finite probability $|c_n|^2$ of being in all eigenstates. The values of c_n are determined by the boundary conditions as well as the average energy of the particle

$$E = \int dx \; \chi^*(x) H(x) \chi(x) = \int dx \Big(\sum_n \overset{\uparrow}{c_n^*} \psi_n^*\Big) \hat{H} \Big(\sum_m \overset{\uparrow}{c_m} \chi_m\Big)$$

numbers and commute with $\hat{H}$.

$$= \int dx \sum_{m,n} c_n^* c_m \underbrace{\left(\psi_n^* H \psi_m\right)}_{E_m \psi_n^* \psi_m}$$

from eq (1).

$$= \sum_{n,m} c_n^* c_m E_m \int dx \underbrace{\psi_n^* \psi_m}_{\delta_{mn}}$$

from eq 3.

$$= \sum_n |c_n|^2 E_n .$$

- To determine the time dependence of $c_n(t)$, we have to solve the time-dependent Schrödinger equation. It's clear that the time dependence should only be in the phase of $c_n(t) = |c_n| e^{i E_n t/\hbar}$ such that $|c_n|$ remains time independent in the above expectation value. We will learn more about it in QM-II course.

- **Classical particle vs Quantum/Elementary particle:** When an particle has the energy which matches the eigenenergy of a quantum system, it goes to that level and stays forever. They then posses quantum of energy and exhibit quantum behavior. Usually the elementary particles have those small, quantum energy scales and exhibit quantum behavior. On the other hand when a large body, consisting of many many elementary particles ($\sim 10^{23}$), then their energy & momentum becomes large ($10^{23} \times h$) compared to the quantum of energy and momentum, so we don't see the quantum nature.

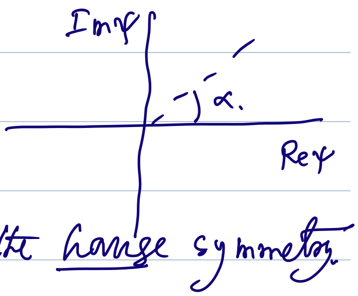
Properties of time-independent Schrödinger eq. & Solutions

⊛ Rewriting the time-independent schrödinger eq as.

$$\nabla^2 \psi = \frac{2m}{\hbar^2}\left[V(x) - E\right]\psi(x) \quad - - (1).$$

- This is a linear, homogeneous 2nd order PDE.
- As long as $V(x)$ is finite everywhere, $\nabla^2\psi$ is also finite. Therefore, $\psi(x)$, $\partial\psi/\partial x$ are all continuous, finite, and analytic functions of x.
- Since the Hamiltonian is Hermitian, so, if $\psi(x)$ is an eigenstate of H, then $\psi^*(x)$ is also its eigenstate of $\hat{H}$

- The Schrödinger equation and the probability density, and all expectation values remain invariant if we multiply the wavefunction by a constant phase. This means, if we multiply $\psi(x) \to \psi(x)\, e^{i\alpha}$, where α is real and arbitrary, then $\psi^*(x) \to \psi^*(x)\, e^{-i\alpha}$, and eq (1) does not change and also $\rho(x) = \psi^*\psi$ and expectation value $\langle \hat{O} \rangle = \int dx\, \psi^* \hat{O}\, \psi$ remain invariant. This is like a rotation in the complex wavefunctional space. This is a symmetry (like rotational symmetry we studied in CM) and called the gauge symmetry.



Therefore, the Schrödinger equation uniquely determines the amplitude of the wavefunction, but the phase of the wavefunction remains arbitrary. If we fix the phase at a given point, say at the boundary condition points, then the phase is fixed and well defined at all x. However, one can only multiply a constant phase $e^{i\alpha}$ to the wavefunction but the phase α cannot be x dependent. Because, otherwise the derivative term will acquire a new term $\frac{d\alpha}{dx}$ which will change the Hamiltonian. Therefore, the quantum theory has a global gauge symmetry (α = constant in space and time), but not always a local gauge symmetry (local means $\alpha(x,t)$ dependent).

- As mentioned earlier, we need two boundary conditions in space and one boundary condition in time to uniquely determine $\psi(x)$.

- Every system prefers to be in its lowest energy configuration. Therefore, for a generic potential, the probability of finding a particle at the potential minimum (with constant total energy E) is highest for the ground state energy. This gives an intuition on how the real part of the wavefunction should look like in a given potential profile.

- The normalization (i.e, the square integrability) condition on the wavefunction puts constraints on the asymptotic behavior of the wavefunction.

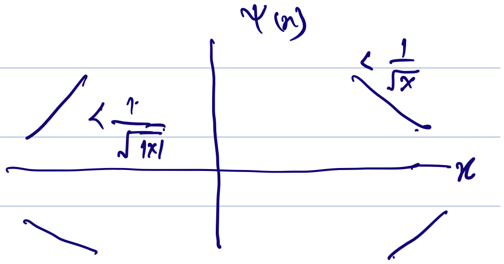
<u>In 1D</u>

$$\int_{-\infty}^{\infty} dx \; \psi^*(x)\,\psi(x) = 1.$$

For this integral to converge as $x \to \pm\infty$, the wave function must fall off faster than $1/\sqrt{|x|}$ in 1D (or $1/|x|^{d/2}$ in d-dimensions). Because, the 'dx' part grows linearly with x (in 1D) and hence the integrand part has to decay faster than $|x|$ and hence

$$\psi(x) \leq 1/\sqrt{|x|}.$$

as $x \to \pm\infty$.



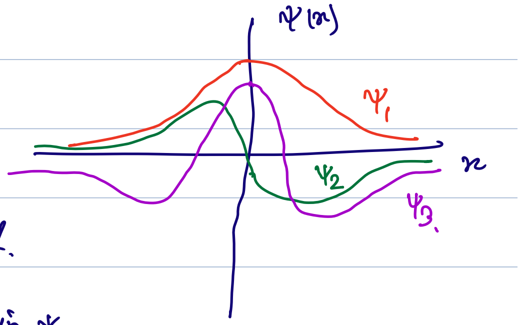
Therefore, any potential energy which makes the solution of the Schrödinger equation with wavefunction $\psi(\pm\infty) > 1/\sqrt{x}$ in 1D is not a physical and stable solution. In this case, the particle will have increasing probability density as $x \to \pm\infty$ and the particle will never be bounded. One of the example where such an unstable solution arise is when $V \to -\infty$ as $x \to \pm\infty$, so that the particle goes to lower energy ($V = -\infty$) as $x \to \pm\infty$, and it will never be bounded and the energy will not be quantized.

Therefore, the normalization condition already makes the system bounded, which has implications on the quantization of energy.

- The above condition that the wavefunction must decays as $x \to \pm\infty$ suggests that the wavefunction has to have at least one extremum in between where $\frac{d\psi}{dx} = 0$ and $\left|\frac{d^2\psi}{dx^2}\right| \geqslant 0$. (Interestingly, at the point where $d\psi/dx = 0$, the momentum operator $-i\hbar\frac{d}{dx}$ also goes to zero. But the momentum is not necessarily zero there unless ψ is also an eigenstate of the momentum operator.) From the schrödinger equation, $\frac{d^2\psi}{dx^2}$ and ψ have same & opposite sign when $(V(x)-E) > 0$ & < 0, respectively.

- Therefore, what we are seeing as solution of the equation of motion in quantum mechanics is very different from the solution of equations of motions in classical or electromagnetism or statistical mechanics. Here, the solution of an equation of motion is an eigenvalue equation and not all solutions are allowed or physical. One of the features of the eigenvalue problem is that there are discrete eigenvalues E_n with corresponding eigenfunctions ψ_n, and all the eigenfunctions are linearly independent. What this physically mean is that, lets take two energy eigenvalues E_1 & E_2 with corresponding eigenfunctions ψ_1 &

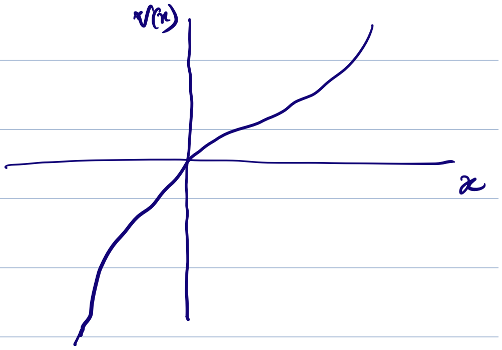
ψ_2. One cannot continuously deform an eigenfunction $\psi_1(x)$ to obtain $\psi_2(x)$. Its like two orthogonal unit vectors in a coordinate system (indeed the eigenstates form Hilbert space). This also implies that one cannot continuously go from E_1 to E_2. Therefore, all the solutions ψ_n and E_n are discrete and there is no continuous path to go from one to another. As we said above, all eigenstates must be normalizable, and hence have atleast one extremum. Two functions with one extremum can be smothly deform one into another and thus they are linearly dependent. Since Schrödinger equation is linear in ψ, then all wavefunctions are linearly dependent (smothly connected to) to a given eigenfunction ψ_1 have the same energy eigenvalues and they correspond to the same state. For example, multiplying $\psi_1(x)$ by a constant number or a phase do not change the schrödinger eq and as long as they are normalizable, they correspond to the same state. On the otherhand, for example, the three states ψ_1, ψ_2, ψ_3 having 1, 2, 3 extrema, as shown in the above figure, are linearly independent. If they correspond to the solutions of the same schrödinger equation, then their energy eigenvalues must be distinct and not to be connected with a small deformation of the wave functions.



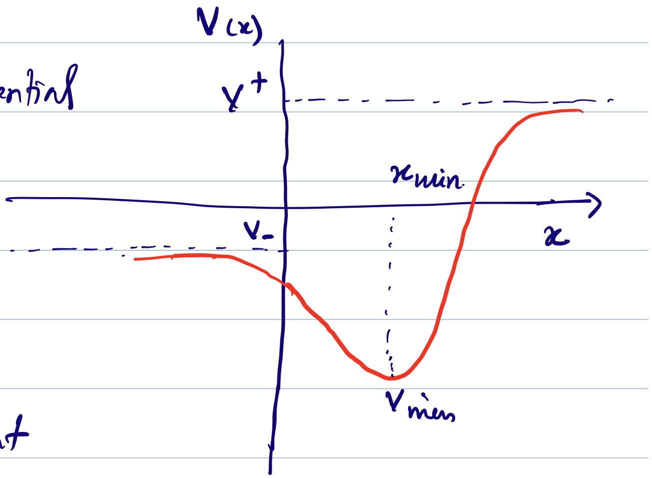
So, what we have just learned is that the solution of the Schrödinger equation of motion, being an eigenvalue equation, have discrete energies which are unique, but their eigenfunctions are not unique but linearly independent and must be normalizable. (This makes it completely different from the classical solution $x(t)$ of Newton's eq which is unique).

(A loose analogy between $\Psi(x,t)$ and $\vec{x}(t)$ as the solutions of QM & CM, respectively can be drawn as follows. The classical solution $\vec{x}(t)$ can be written as a linear combination of three linearly independent basis/unit vectors in 3D. The solutions of the QM is a function $\Psi(x,t)$. The eigenstates are similarly the basis (like unit vectors) of the vector space/ Hilbert space. Each eigenbasis are linearly independent and corresponds to discrete energy eigenvalue. A general solution then can be written as a linear superposition of all the eigenbasis states in the Hilbert space corresponding to a Hamiltonian).

⊛ Generic potentials and Stability conditions:



- Since the potential goes to $-\infty$ as $x \to -\infty$ in this example, the energy is also $-\infty$ and the particle will roll down to $-\infty$. Then the probability and hence the real part of the wave function keeps on growing as $x \to -\infty$. This is not a normalizable wave function, and the energy is also not finite. This is an unbounded, unstable system. We will not consider such systems.



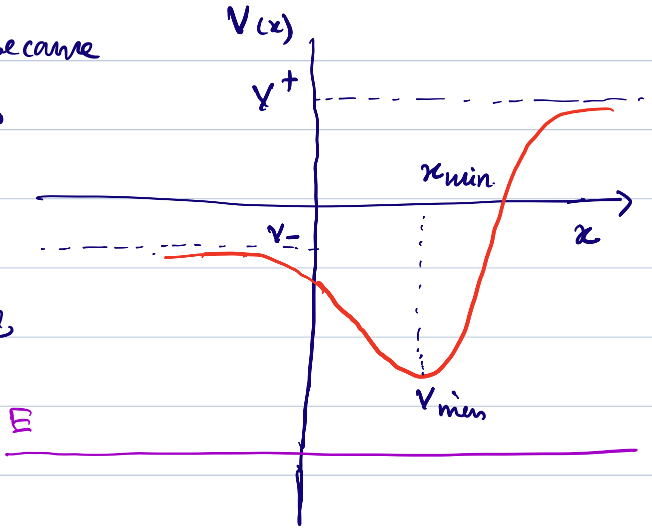
- This is a generic finite potential profile with one minima at x_{min} is what we will consider now for different values of E. (Remember that any constant energy added to the potential will not change the eigenvalue & eigenfunction spectrum, it will only give a constant shift to all eigenvalues.).

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

Case I : $E < V_{min} < 0$.

- No classical solution exists because kinetic energy is negative.
- Quantum solution ?

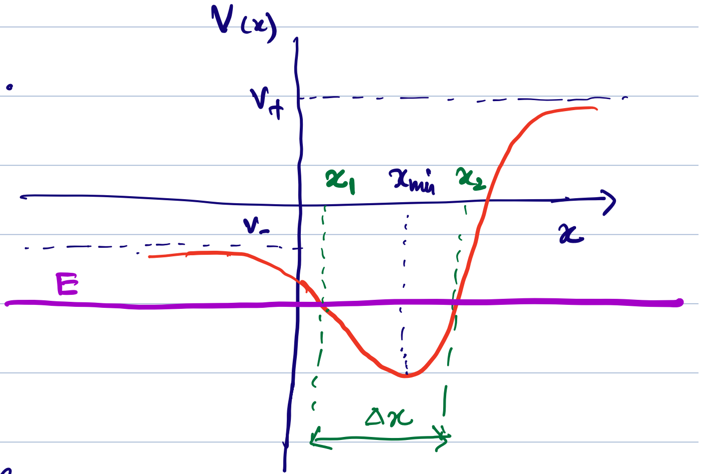
Therefore, $(V(x) - E) > 0$ at all values of x. Therefore, the extremum of ψ does not exist at any finite value of x (because $(V(x) - E)\psi = ()\frac{d^2\psi}{dx^2} > 0$ as x increases except when $\psi(x) = 0$ which corresponds to an inflection point). Therefore, no normalizable, i.e, physically acceptable quantum solution also exists. This is an unstable solution.



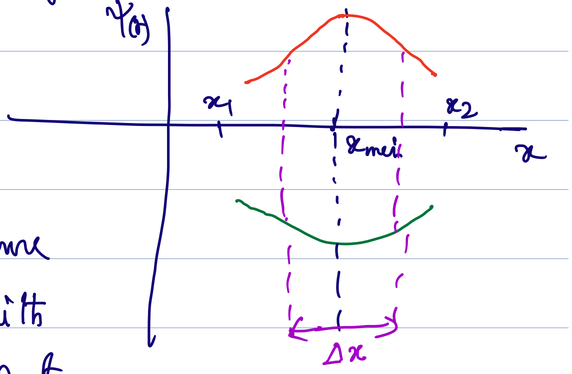
Case II $V_{min} < E < V_-$

- $x_1 < x < x_2$: classical region.

In this region, the kinetic energy $E - V(x)$ is positive and hence a classical solution exist. x_1 & x_2 are called the classical turning points which bound the classical region. In this region, quantum solutions also exist and will be a discrete set of linearly

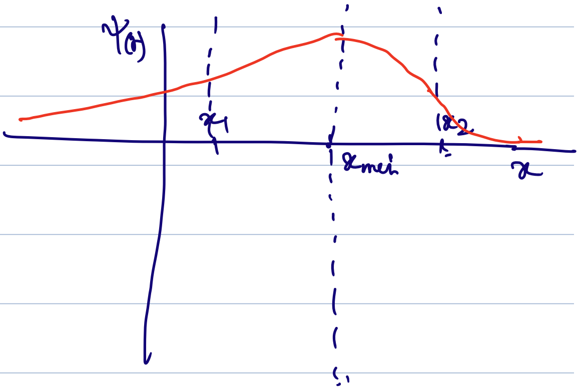


independent solutions ψ_n with discrete energy levels E_n. In the lowest possible energy E_1, which we call ground state, the particle will have higher probability to be at the minimum potential energy position, i.e, at x_{min}. Hence $S_1(x) = |\psi_1(x)|^2$ is expected to have a maxima at x_{min}, which means $\psi_1(x)$ will either have a maximum and minimum at x_{min}. Now, at x_{min}, $V-E<0$, so from the schrödinger equation, $\frac{d^2\psi}{dx^2}$ & ψ have opposite sign. So, if $\psi(x)<0$, then $\frac{d^2\psi}{dx^2}>0$, so it has a minima and vice versa. The ground state is also when the uncertainty $\Delta p \Delta x \sim \hbar$ has the least value. This means it has the largest wave packet with least momentum uncertainty. The wave function/wave packet with one extremum satisfy this condition. So, we can roughly sketch the expected wave function as shown here.



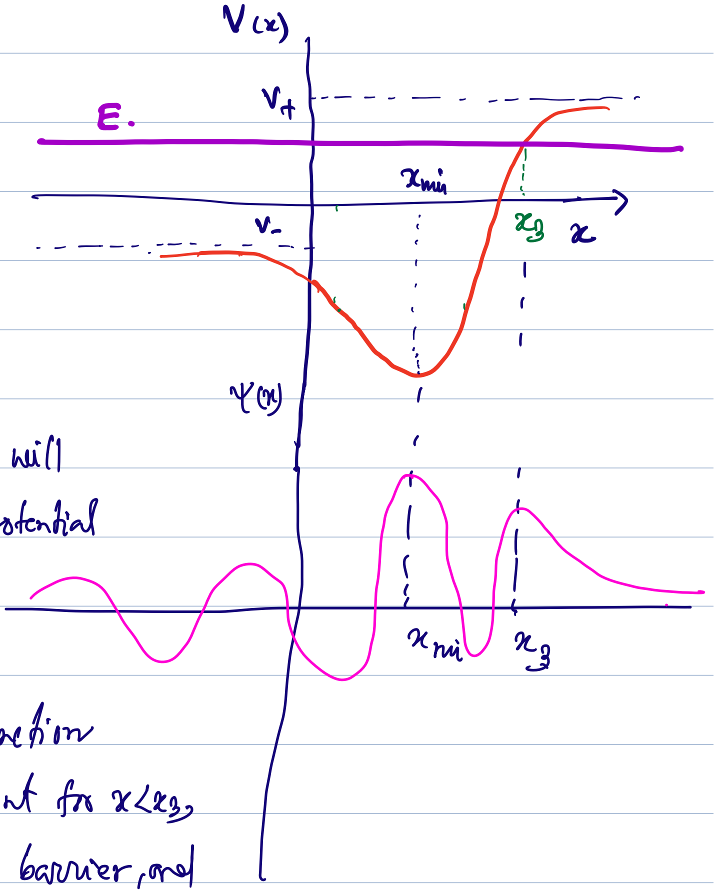
Now we see the two functions in red and green have a maximum or minimum, but they are linearly dependent. Because we can multiply the red one with -1 to obtain the green one. But a constant multiplication does not change the schrödinger eq and probability density. So, they both are the 'same' solutions as far as quantum mechanics goes. We usually choose one of them. (Within the classical turning point, we can have wavefunctions with more nodes, i.e, oscillatory/scattering states with different energy)

- For $x < x_1$ & $x > x_2$: In this region, a classical solution is forbidden since momentum becomes imaginary. But, the Schrödinger equation has a valid solution with decaying wavepacket. Also, since the wave function is continuous across the two regions, so a possible solution is like as shown in the figure. Therefore, the particle has finite probability to tunnel to the classically forbidden region, although usually with much reduced probability density. In fact the wave function will tail further in the $x<x_1$ region than in the $x>x_2$ since the potential barrier is lower in the former direction than in the later one. This is called quantum tunneling.



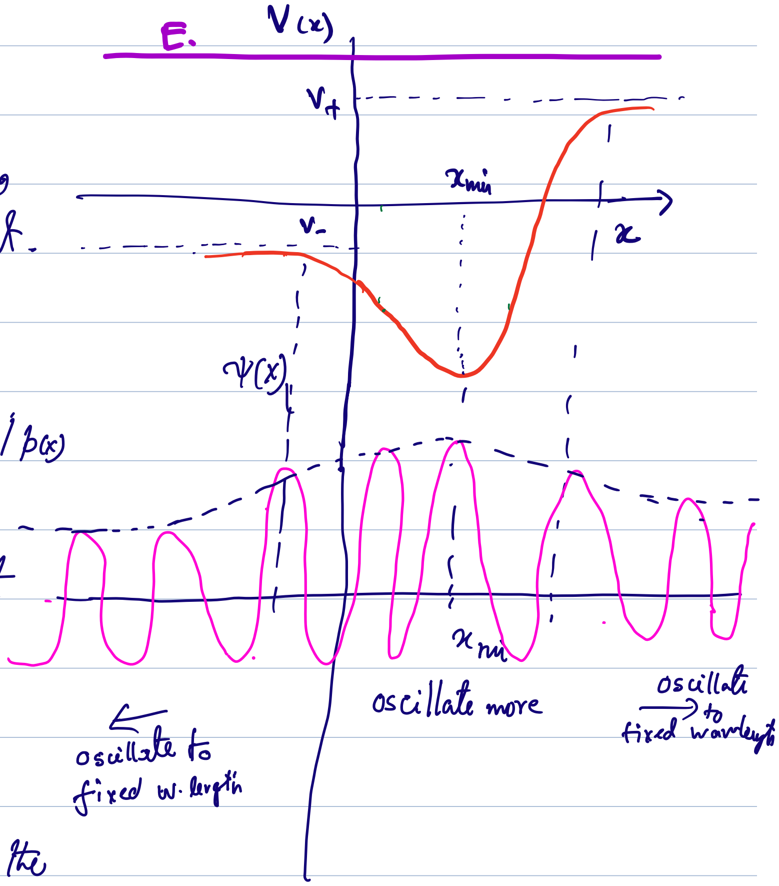
There will be more possible energy levels and wavefunctions $\psi_2, \psi_3 \ldots$ all normalizable and orthogonal to ψ_1, and we will discuss them with specific example.

Case III : $V_- < E < V_+$



In this case, there is only one classical turning point at $x = x_3$. For $x > x_3$, no classical solution is possible. Therefore, in this region the particle will be reflected back from the potential wall at x_3, and some part will be transmitted beyond x_3 but the wavefunction will decay rapidly. But for $x < x_3$, there is now no potential barrier, and hence the particle is like a free particle (plane wave) with with a slightly x-dependent potential V(x). Therefore, it will be an damped oscillatory wavefunction with a larger peak at x_{min} where the probability of finding the particle will be higher since the energy is minimum. Such wavefunction which has $E > V$, i.e, positive kinetic energy are called scattering wave.

Case IV : $E > V_+$



In this case, the kinetic energy is always positive, but its position dependent. Therefore, the corresponding momentum $p(x)$ and hence the wavelength $\lambda(x) \sim h/p(x)$ are position dependent. Therefore, although we get a "plane wave" like solution every where but there is not fixed wave length, and hence the wave function is a superposition of several plane waves with different wavelengths and hence momentum (Fourier modes). The spread in momentum will be determined by the spread in position according to the uncertainty principle ($\Delta p \Delta x \sim \hbar$). So, we do get a wave packet here which is however moving forever and not normalizable. (we will learn in next chapter how to normalize such plane waves).

Summary

In summary, we have essentially found two sorts of solutions of the time-independent schrödinger equation:

$$\nabla^2 \psi(x) = \frac{2m}{\hbar^2}\left(V(x) - E\right)\psi(x) \quad --- (1).$$

The two possible solutions come from the "sign" of the R.H.S. Notice that the dimension of the R.H.S. is $[L^{-2}]$, i.e, the R.H.S gives a $(\text{lengthscale})^2$ to the system. We can use the lengthscale to associate it to the wavelength of the wavefunction, and/or to the uncertainty in the position, which turns out to be the decay length scale of the wavefunction. Let us see that.

We have two signs of the R.H.S.

(A) $E > V(x)$: Classically allowed solutions, Scattering / oscillatory waves.

In this case, the K.E. of the free particle is reduced by the potential energy, but remains positive. So, for the residual K.E., we can associate a residual momentum as

$$E - V(x) = \overset{\text{mom. of free particle}}{\frac{p^2}{2m}} - V(x) = \underset{\text{residual momentum,}}{\frac{p'^2(x)}{2m}} = \frac{\hbar^2 k^2}{2m}.$$

The particle with residual momentum is associated with an wave vector k & hence wavelength λ which depends on x. Then from eq (1)

$$\nabla^2\psi = -\frac{\hbar^2 k(x)^2}{2m}\psi \qquad ---(2).$$

The solution of this equation is roughly like a plane wave / free particle one except k is position dependent. If we take the Fourier transformation of $\psi(x)$ we will find a bunch of wavevectors with spread $\Delta k \sim h/\Delta x$ for the ground state. This is precisely what happens in Case IV above.

(B) $E < V(x)$: Classically forbidden region, decaying solutions

For $E < V(x)$, the residual K.E. is negative and residual "momentum" is imaginary. Therefore, this is a classically forbidden region. But due to uncertainty principles, the quantum particle can tunnel into this region. Because, k is imaginary, we can define a real number K as

$$k = iK.$$

Then we get from eq (2) $$\nabla^2\psi = \frac{\hbar^2 K^2}{2m}\psi(x) \qquad ---(3)$$

This has two solutions $\psi(x) \sim e^{\pm Kx}$ for $x > 0$. Clearly, e^{Kx} blows up as $x \to \infty$, and hence we ignore. Then we have a decaying solution $\psi(x) \sim e^{-\kappa x}$ for $x > 0$. Therefore, κ which has the dimension of inverse length, gives the decay constant of the wavefunction in this classically forbidden region. In fact, κ can be found to be related to $1/\Delta x$.

This is what we saw in Case III on the right hand side. We see that a wavefunction can tunnel to the classically forbidden region from the classically allowed region. But if we have a situation, as in Case I, where $E < V(x)$ at all x, i.e., the entire space is classically forbidden, then there is essentially no positive momentum to begin with and hence the wavefunction will simply decays everywhere, i.e. ceases to exist. This gives an unstable solution. Finally, Case II, was the only case where both sides had classically forbidden regions surrounding a classically allowed region in the middle. Therefore the wavefunction decays on both sides but oscillatory in the middle and hence the wavefunction is properly normalizable. However, the oscillatory (scattering) plane wave by itself is not normalizable and we will start our next chapter by this discussion.