The Schrödinger equation

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1 Introduction

In the last chapter we learnt particles have a wave nature, with wave length and frequency related to momentum and energy respectively, by a universal constant h. By universal,it means, all quantum systems are expected to satisfy these relations, with the same h. Wave nature of the particle is expected to be governed by a wave function, which satisfy superposition principle as in Young's double slit slit experiments. The goal of this lecture is to deduce the dynamical (time-dependent) equation of motion the wave function satisfies. This will be followed by obtaining a time-independent equation.The postulates of quantum mechanics, providing the "rules of the game", is explained.

2 Schrodinger equation for free particles

Consider a free particle of mass m in a one-dimensional motion, for simplicity.The dispersion relation relating the energy and momentum is given by $E = \frac{p^2}{2m}$. Recall the wave -particle duality,

$$E = \hbar\omega, p = \hbar k \tag{1}$$

, where ω, k respectively are the angular frequency and the wave number of the corresponding matter wave.Since the proportionality $\hbar$ is an universal constant, we can apply to any system. The dispersion relation,i.e.$\omega(k)$, is a wave property, using (1),

$$E = \frac{p^2}{2m} \tag{2}$$

$$\omega(k) = \frac{\hbar k^2}{2m} \tag{3}$$

Since we are considering free-particle which has constant momentum, and hence uniform wavelength, we can assume the matter wave has a plane wave solution.

The goal is to assume a plane wave solution and deduce the partial differential equation, which gives (3). This must have the following features:

a)It should be linear, as we need superposition principle to hold in agreement with experiments.
b)Being an equation of general validity, i.e. for all momenta and energy, the equation itself should not have ω, k in it and can only have the mass of the particle, m, and fundamental constant $\hbar$.
c)We are on a look out for an equation involving space and time derivatives, which is independent of k or ω, and depends only on $m, \hbar$.
Student Usually, given a differential equation we will find the solution. Are we inverting the procedure?
Teacher Yes, given a solution we are guessing the equation which will give free particle dispersion relation, (3).

To describe a plane wave, we have the following possibilities:

$$\psi_1 = \cos(kx - \omega t) \tag{4}$$

$$\psi_2 = \sin(kx - \omega t) \tag{5}$$

$$\psi_3^{\pm} = \exp \pm i(kx - \omega t) \tag{6}$$

To start with, in the solution above k, ω are unrelated.

We find for (4)

$$\frac{\partial \psi_1}{\partial x} = -\frac{k}{\omega}\frac{\partial \psi_1}{\partial t} \tag{7}$$

Use the required dispersion relation (3), to get

$$\frac{\partial \psi_1}{\partial x} = -\frac{m}{\hbar k}\frac{\partial \psi_1}{\partial t} \tag{8}$$

This cannot be an acceptable wave equation as it depends on k. None of the possibilities involving the real functions, (4) or (5) will lead to an equation independent of $k, \omega(k)$, We will try the exponential form for the plane wave, say ψ_3^+.

$$\frac{1}{i\omega}\frac{\partial \psi_3^+}{\partial t} = \frac{1}{k^2}\frac{\partial^2 \psi_3^+}{\partial x^2} \tag{9}$$

Using the dispersion relation ((3)), we get

$$-i\frac{\partial \psi_3^+}{\partial t} = \frac{\hbar}{2m}\frac{\partial \psi_3^+}{\partial x^2} \tag{10}$$

Bringing it in a form which is useful for latter consideration and the equation has the energy dimension, we get the *celebrated Schrodinger equation for free-particles.*

$$i\hbar\frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial \psi}{\partial x^2} \tag{11}$$

Comments

1. Working the real function, viz; trigonometric function, as a plane wave solution did not yield the Schrodinger equation

2. We need a wave function which is a complex form of plane wave solution alone rendered Schrodinger equation.

3. In classical theory some times we work with Re(complex function) as a convenience. But in quantum mechanics, *complex nature of the wave function is a compulsion, not a convenience.*

   $\boxed{\textit{Student}}$ Can we speculate that even if complex numbers were not known, quantum mechanics would have forced their discovery!?

   $\boxed{\textit{Teacher}}$ Perhaps Yes!. Historically, when Heisenberg formulated, what is now known as "Matrix mechanics", he was not aware of matrices, which he discovered.

4. This is a linear, homogeneous equation.

Extension of free-particle Schrodinger equation to 3-dimensions is straight forward: $\frac{\partial}{\partial x} \to \nabla$ leading to

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi \tag{12}$$

Plane wave solution extends everywhere and consequently we cannot ask, where is the particle?It is everywhere. If we want to have description of free particle localised in a small region, then we have form a "wave-packet" localised at $t = 0$ around a small region. This can be constructed by superposing waves of different wavelength as we do for any waves.This is allowed as the Schrodinger equation is *linear.*

$$\psi(\mathbf{x}, t) = \int \frac{d^3k}{(2\pi)^3} g(\mathbf{k}) \exp(i\mathbf{x}.\mathbf{x} - \omega(k)t) \tag{13}$$

Choosing $g(\mathbf{k})$ judiciously, wave packets of suitable form can be constructed.

3 "Deriving" Schrodinger equation for general case

Consider a particle moving in an arbitrary potential $V(\mathbf{x}, t)$. Since momentum is now not a constant, the wavelength is not uniform. Hence we cannot assume a plane wave solution to start with. The energy-momentum relation is the sum of kinetic and potential energy:

$$E = \frac{\mathbf{p}^2}{2m} + V(\mathbf{x}, t) \tag{14}$$

We know the Schrodinger equation when $V = 0$, (17). Let us *guess* the Schrodinger equation in the general case to be

$$i\hbar\frac{\partial\psi}{\partial t} = \big(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{x}, t)\big)\psi \tag{15}$$

The above is a linear equation as QM requires.It reduces to $V = 0$ case, which we obtained.

$\boxed{\textit{Student}}$ How do we know this guess of (15) is the right one, in the absence of a derivation?

$\boxed{\textit{Teacher}}$ We do NOT know if the Schrodinger equation is correct. All the predictions obtained by solving this equation, for every system agrees, in detail, with experiments. It is safe to say, so far no experiment has disagreed with the predictions of quantum mechanics. Hence we believe this equation to be the law in quantum world! This is the reason, derivation, in the title was put in quotes.

This Time-Dependent Schrodinger Equation (TDSE), (15), is the fundamental one.

Since from the Hamiltonian formulation of classical mechanics we know $H \equiv \frac{\mathbf{p}^2}{2m} + V$, we can take the Hamiltonian,in quantum theory to be in the same form giving the identification $\mathbf{p}^2 = -\hbar^2\nabla^2$. We choose the relation:

$$\mathbf{p} = -i\hbar\nabla \tag{16}$$

Though we could have chosen the other sign $+i\hbar\nabla$, it is convenient to choose (16). Even when the there is a velocity-dependent potential is present, we can expect the TDSE to be governed by the Hamiltonian H

$$i\hbar\frac{\partial\psi}{\partial t} = H\psi \tag{17}$$

The advantage of this form of the Schrodinger equation, is we can take the classical expression for any system and replace it for a quantum case.

$\boxed{\textit{Student}}$ Is it an unambiguous procedure?

$\boxed{\textit{Teacher}}$ No! Any ambiguity in such a replacement, must be resolved only appealing to experiments, to qualify as the correct quantum Hamiltonian for that system.

Features of the time-dependent Schrödinger equation:

1. (17) is an equation of motion for the wave function for the system governed by the Hamiltonian H. This is a first-order equation in time. Hence knowledge of $\psi(\mathbf{x}, t_0)$ for the whole range of the coordinates at a time t_0 will yield a unique wave function at a later time t. In this sense, quantum mechanics is a deterministic theory, without relating to measurement issues associated, which will be discussed at a later stage.

   We should emphasize the distinction from classical mechanics of particles, where only a finite number $\mathbf{q}_0, \mathbf{p}_0$ at a time t_0 is required to define state of a particle. In quantum mechanics we need for the wave function $\psi(\mathbf{x}, t_0)$

at a time t_0 for the *whole* range of the coordinates. Hence has infinite degrees of freedom.

Student If one has wavefunction for a system for partial range of coordinates only, and no knowledge of the remaining range, can it be considered as a solution to the Schrodinger equation?

Teacher No! One should know the wave function for the full range of coordinates. When we need to integrate over the whole range of coordinates, one requires the function everywhere.

2. (17) is a linear and homogeneous equation. Such equations will have a feature that if ψ is a solution, so is $\psi' = N\psi$ where N is a constant.

   Student This feature of linearity and homogeneity holds for acoustic wave equations too. In what way it is different in QM?

   Teacher There is a fundamental difference between the sound wave equation for displacement in the medium $y(x,t)$ and the Schrodinger equation for ψ. In the case of sound waves, $y' = Ny$ and y represent *different* states. The amplitude and energy associated with y' and y will be different. But, as we will discuss in detail later, $\psi' = N\psi$ and ψ represents the same state, with no change in the observable properties.

   Another difference is, in acoustics, $y = 0$ represents the equilibrium configuration, whereas $\psi = 0$ has no such meaning.

4 Stationary state

The system we want to study is, generally, described by the potential, which in general can be time-dependent. But for the time-independent potentials, a special class of solutions are possible, which are called as *stationary state solution.*

We consider

$$H = \frac{1}{2m}\nabla^2 + V(\mathbf{x}) \tag{18}$$

We need to find $\psi(\mathbf{x}, t)$ as the solution to ((17))

Stationary state solutions are the class when the solution factories into space -dependent part and time-dependent part:

$$\psi(\mathbf{x}, t) = \phi(\mathbf{x}) f(t) \tag{19}$$

Assume the solution of the above form in the (17), we get

$$i\hbar \frac{df}{f} = \frac{1}{\phi} H\phi \tag{20}$$

Since the LHS is only a function of t and independent of $\mathbf{x}$, and the RHS is only of function of $\mathbf{x}$ and independent of t, each must be constant (independent of $\mathbf{x}$ and t). LHS is t-independent only when V in the Hamiltonian is time independent. Note of the above expression is energy.Hence we can call,E the separation constant

$$i\hbar\frac{df}{f} = \frac{1}{\phi}H\phi = E \tag{21}$$

Solving for $f(t)$ we have $f(t) = e^{\frac{-iEt}{\hbar}}$. ϕ is the solution of the equation

$$H\phi(\mathbf{x}) = E\phi(\mathbf{x}) \tag{22}$$

The above is time-independent Schrodinger equation. We obtained it a a special case of TDSE ((17)). This also gives,

$$i\hbar\frac{\partial\psi}{\partial t} = H\psi = E\psi \tag{23}$$

Hence the latter is fundamental equation.

$\boxed{Student}$ Does it mean the identification $\frac{\partial}{\partial t} \to E$, is valid only of stationary states, whereas the corresponding identification for the momentum is always valid?

$\boxed{Teacher}$ Yes

4.1 Admissibility conditions on the wave function

Consider a particle in a one-dimensional motion, (for simplicity), in a potential $V(x)$, governed by the Schrodinger equation:

$$\frac{-\hbar^2}{2m}\frac{d^2\phi}{dx^2} + V(x) = E\phi(x) \tag{24}$$

The *differential equation* must continuous at all range of x; any discontinuity at a given point ,say x_0 point due to any term must be compensated at that point by other terms.

$\boxed{Student}$ Is this a physical requirement or mathematical one?

$\boxed{Teacher}$ This is a mathematical requirement.Even Maxwell‘s equations in different regions must obey such continuity property.

From (24), we have by integrating the Schrodinger equation, from $-\epsilon$ to $+\epsilon$ about any point, say $x = 0$ and let $\epsilon \to 0$ after integration.

$$\frac{-\hbar^2}{2m}\int_{-\epsilon}^{+\epsilon} dx\frac{d^2\phi}{dx^2} + \int_{-\epsilon}^{+\epsilon} dxV(x)\phi(x) = E\int_{-\epsilon}^{+\epsilon} dx\phi(x) \tag{25}$$

The first term easily integrates to $\frac{d\phi}{dx}|_{-\epsilon}^{+\epsilon}$. We require ϕ to be continuous every where as its modulus is the probability.

$$\frac{-\hbar^2}{2m}[\frac{d\phi}{dx}|_{+\epsilon} - \frac{d\phi}{dx}|_{-\epsilon}] + \int_{-\epsilon}^{+\epsilon} dxV(x)\phi(x) = 0 \tag{26}$$

We consider the following cases separately: a)$V(x)$ is continuous at all points,b) it is discontinuous with a *finite* discontinuity, at say, $x = 0$. c) it is discontinuous with a *infinite* discontinuity at $x = 0$.

a) The second term vanishes for continuous functions, forcing the first term also to be zero, leading to continuity of the first derivative.

b)When the potential is discontinuous with *finite* discontinuity, the integral being area under the curve, will have a finite height and vanishing width, when $\epsilon \to 0$, leading to zero area under the curve. Thus for finite discontinuity , the second integral is zero. Thus again continuity of the first derivative of the wave function.

c) When $V(x)$ has an infinite discontinuity then $\lim \epsilon \to 0 \int_{-\epsilon}^{+\epsilon} dx V(x)\phi(x)$ represents the area under integral as a product with infinite height and zero width, leading to a *finite* answer. The derivative term $\left[\frac{d\phi}{dx}|_{+\epsilon} - \frac{d\phi}{dx}|_{-\epsilon}\right]$ must cancel this finite term, for the equation to be continuous.

To summarize, :

1)When the potential is continuous or has a finite discontinuity, then both $\phi(x), \frac{d\phi}{dx}$ will be continuous.

2)When $V(x)$ has an infinite discontinuity at a point x_0, like a delta function potential, then $\phi(x)$ will be continuous, but the first derivative has tobe discontinuous at that point

4.2 Features of stationary states

Stationary states are characterized by the two properties:

$$\psi(\mathbf{x}, t) = \phi(\mathbf{x}) \exp\left\{\frac{-iEt}{\hbar}\right\} \tag{27}$$

$$H\phi(\mathbf{x}) = E\phi(\mathbf{x}) \tag{28}$$

These two leads to the following features:

1. Probability density is time -independent:

$$|\psi(\mathbf{x}, t)|^2 = |\phi(\mathbf{x})|^2. \tag{29}$$

2. The total wave function $\psi(\mathbf{x}, t)$ is the eigenstate of the Hamiltonian

$$H\psi(\mathbf{x}, t) = E\psi(\mathbf{x}, t)|. \tag{30}$$

3. Only for stationary states, we can have energy operator as

$$E \to i\hbar\frac{\partial}{\partial t} \tag{31}$$

When stationary states for a given H are superposed, the resulting are non-stationary states.

Non-stationary states Let ϕ_1, ϕ_2, say are the energy eigen states of the Hamiltonian with the eigen values E_1, E_2 : $H\phi_1(\phi_2) = E_1(E_2)\phi_1(\phi_2)$ Let us consider wave function which is a superposition of these two states:

$$\psi(\mathbf{x}, t) = c_1\phi_1(\mathbf{x}) \exp\left\{-i\frac{E_1 t}{\hbar}\right\} + c_2\phi_2(\mathbf{x}) \exp\left\{-i\frac{E_2 t}{\hbar}\right\} \tag{32}$$

where c_1, c_2 are arbitrary coefficients, whose meaning and restrictions will be stated later. The two features associated with stationary states are now absent:

1. $|\psi(\mathbf{x}, t)|^2$, given by (32) will have a time -dependence from the cross-terms with $c_1 c_2^*, c_1^* c_2$ as coefficients. Probability density is hence *time -dependent*

2. (32) is not an eigenfunction of the Hamiltonian:

$$H\psi = c_1 E_1 \phi_1(\mathbf{x}) \exp\left\{-i\frac{E_1 t}{\hbar}\right\} + c_2 E_2 \phi_1(\mathbf{x}) \exp\left\{-i\frac{E_2 t}{\hbar}\right\}$$

   is not proportional to ψ.

$\boxed{\textit{Student}}$ Does the time-dependent potential problem also classify as a non-stationary state?
$\boxed{\textit{Teacher}}$ Yes.

Normalisation Since the Schrodinger equation (24) is homogeneous,as for any such equations, ψ and $\mathcal{N}\psi$, where $\mathcal{N}$ an arbitrary constant is also a solution.

The physical interpretation of $|\psi(\mathbf{x}, t)|^2$, as the probability density requires the $\int |\psi(\mathbf{x}, t)|^2 d^3x$, represents the total probability for the particle anywhere within the space. This can be ensured by normalisation

We have two cases to consider:

1. $\int_\infty^\infty dx \psi^*(x)\psi(x) < \infty$, the corresponding ψ is called as square-integrable functions. In case cases , we can normalise ψ.

$$\int_\infty^\infty \psi^*(\mathbf{x}, t)\psi(\mathbf{x}, t) = \mathcal{N} \tag{33}$$

$$\psi' \equiv \frac{1}{\sqrt{\mathcal{N}}}\psi \tag{34}$$

$$\int_\infty^\infty dx \psi'^* \psi' = 1 \tag{35}$$

   Such functions ψ' are called normalized ones.

2. The functions $\int_\infty^\infty dx \psi^*(x)\psi(x) \to \infty$, are NOT square-integrable. The plane wave solution $e^{i(kx-\omega t)}$ belongs to this class.

   Such solutions have to be *box-normalized*, which will be discussed later.

5 Probability conservation

$\boxed{\textit{Student}}$: Since $\mathcal{N} = \int |\psi(\mathbf{x}, t)|^2 d^3x$, has only integral over space, should not $\mathcal{N}$ be time-dependent?

$\boxed{\textit{Teacher}}$: If we normalise the wave function at a particle time $t = t_0$, how do we know it remains normalised at a later time? The onus is on us,to verify that $\mathcal{N}$, is indeed a constant in time.

It is better, to recall the conservation of charge Q, which holds in classical electrodynamics: $Q = \int d^3x \rho_e(\mathbf{x}, t)$ is conserved i.e. $\frac{dQ}{dt} = 0$ through the continuity equation. If $\rho_e, \mathbf{J}_e$, represent the charge density and the charge current, then $\frac{\partial \rho_e}{\partial t} + \nabla.\mathbf{J}_e = 0$ should always be satisfied. Similar feature takes place for probability density.

$$\frac{\partial \rho}{\partial t} = \psi^* \frac{\partial \psi}{\partial t} + \frac{\partial \psi^*}{\partial t}\psi \tag{36}$$

$$= \psi^* \frac{1}{i\hbar}\left(\frac{-\hbar^2}{2m}\nabla^2 + V\right)\psi + [\frac{-1}{i\hbar}(\frac{-\hbar^2}{2m}\nabla^2 + V)\psi^*]\psi \tag{37}$$

$$== \frac{-\hbar}{i2m}[\psi^*\nabla^2\psi - \psi(\nabla^2\psi^*)] \tag{38}$$

$$= \frac{-\hbar}{2im}\nabla.[\psi^*\nabla\psi - \psi\nabla\psi^*] \tag{39}$$

Here in the second line use of (17) for time-derivative of ψ and the complex conjugate of (17) for that of ψ^*.In the third line, since $V(x)$, is real, it cancels. The last line is re-expressing the penultimate one: Operating ∇ on each term, $\nabla.\psi^*\nabla\psi$, term drops out. Define

$$\mathbf{S} \equiv \frac{\hbar}{2im}(\psi^*\nabla\psi - \psi\nabla\psi^*) \tag{40}$$

Then (39), with (40), is

$$\frac{\partial \rho}{\partial t} + \nabla.\mathbf{S} = 0 \tag{41}$$

This is the continuity equation for probability density and $\mathbf{S}$ is called probability current density, in analogy to charge current density in electrodynamics.

Integrating (41) over a volume V, enclosed by a surface S,

$$\frac{\partial}{\partial t}\int_V d^3x\rho = -\int_V d^3x\nabla.\mathbf{S} \tag{42}$$

$$= -\int_S \mathbf{S.dA} \tag{43}$$

In the last step, Gauss theorem was used to convert the volume integral to the surface integral, bounding the volume. In the case of normalisable wave functions, the surface integral is evidently zero as the surface S extends to infinity, V extends to the whole space. The way the probability continuity equation is satisfied, is different for different kinds of states:

1. When $\phi = \phi^*$, the probability current $\mathbf{J}$ is zero and ρ is time-independent. These are for bound stationary states.
2. For standing waves, $\nabla.\mathbf{J} = 0$ and ρ is time-independent
3. For non-stationary states, contribution from $\frac{\partial \rho}{\partial t}$ cancels with $\nabla.\mathbf{J}$.

$\boxed{Student}$ Why are stationary states called so?

$\boxed{Teacher}$ This name could have been taken from classical electrodynamics, where for stationary or steady currents, charge density is time-independent. Similarly, for stationary states, probability density is time-independent.

Some generalities on the energy spectrum

1. In classical theories, orbits of motion can be closed or open; bound or unbound. In both cases, the energy will always take only continuous values. In contrast, depending on the form of the potential, energy in the quantum case, can take continuous or discrete values or can have both continuous and discrete values, depending on the energy E. Bound states in quantum theories always have discrete energy spectra, whereas scattering states take continuous values.
2. Wave function associated with bound state energy will vanish at spatial infinity. This is in accordance with the probability interpretation of the wave function, a particle bound in a finite region, must have zero-probability of being found at infinity. Square-integrable wave functions belong to this class. Bound state wave function
$$\phi(\mathbf{x}) \rightarrow 0 \quad \text{as} |\mathbf{x}| \rightarrow 0 \tag{44}$$
3. Since the lowest energy is when kinetic part is zero, E has a lower bound $E > V_{min}$.
4. When $V(x) \rightarrow \infty$, particle bound inside it will have a *positive* discrete bound state energy.
5. When $V(x) \rightarrow 0$, bound state energy will be negative discrete.
6. There are scattering states, which are in contrast to bound state, has *continuous* energy. They are NOT square-integrable. Physically it means there is a non-vanishing probability for being found at spatial infinity.

6 Postulates of quantum mechanics

Quantum mechanics is based on three structures even at a kinematic level: State (wave function), Observable (operator) and real number (eigenvalue). These three structures viz; *State, Observable, measurement value* are very different. One should be careful not to use these terms interchangeably.In contrast, classical mechanics these three are identified as one. Not being conscious of this difference, is partly a reason for students to find QM difficult In the Hamiltonian formulation, for n degree of freedom system, is described by points in a phase space $q_i, p_i, i = 1..n$.The $2n$ values system takes at a time $t = 0$ gives its state . Any real function of the phase space variables is an observable, $F(q_i, p_i)$. Measuring it amounts to giving a (real) numerical value of the function F for the given phase space variable. We have thus, state, observable and a real numerical value of it for the given state all coalesce into one, as functions on the phase space space.

The rules for applying quantum mechanics to any system can be framed as postulates, which is arrived by study of several systems which turn out to be in agreement with the following results in quantitative study. .

$\boxed{Student}$ Why historically do we refer Newton's laws as "Laws", whereas to QM as "Postulates"?

$\boxed{Teacher}$ Newtons laws are based directly on everyday experiences and hence we can state as laws. But for quantum systems, we have only indirect information on the system, through spectral lines, line intensities, cross-sections. We should have rules of the game such that the formalism proposed agrees with the experiments. Once can only postulate some rules to relate with the experimentally measurable quantities. If it agrees with all known cases, we gain confidence that these rules are correct. This has happened with quantum mechanics.

The postulates proposes how to relate physical properties of the system to mathematical structures of quantum mechanics. The four postulates stated below, relate the three structures of quantum theory above, which are kinematic in nature, to the mathematical structures, hold at particular time. The fourth one to dynamics, i.e. equation of motion.

6.1 State of the system

State of the system is represented completely by a complex function , called *wave function* $\psi(\mathbf{x}, t)$. If ψ_i, ψ_2, represent possible states of the system, then so will be any arbitrary linear combination:$a\psi_1 + b\psi_2$.

Probability of finding a particle associated with ψ between $\mathbf{x} + d\mathbf{x}$ and $\mathbf{x}$ is given by

$$\rho(\mathbf{x})d^3x = \psi^*(\mathbf{x}, t)\psi(\mathbf{x}, t)d^3x \tag{45}$$

Where $\rho(\mathbf{x})$ is the probability density. This interpretation is due to Max Born.

$\boxed{Student}$ How did Born arrive at this interpretation?

$\boxed{Teacher}$ He took a cue from Einstein who used photon duality to make EM wave comprehensible to associate the intensity (square of the amplitude of EM wave) as a measure of the number of photons. Recall, that is how he could explain photo-electric effect. Born studied scattering problems, after realising that only with bound state studies interpretation of the wave function may not be straightforward. In the scattering studies, one needs to define the intensity of the scattered particles, which turned out to be proportional to $|\psi|^2$. This he associated with the probability density of finding a particle.

$\boxed{Student}$Is the probability interpretation of the wave function, the first instance of an intrinsic probability feature introduced, apart from classical statistical mechanics?

$\boxed{\textit{Teacher}}$ No! Even in a decay of a collection of radioactive atoms, given N such atoms, one cannot say with certainty, which among these N will decay at which moment. That is also purely a quantum effect.

Observables

Observables are represented by operators, obeying property of linearity and Hermitian nature. The definition of it will be taken up later. Linear operator obeys :$\hat{O}(a\psi_1 + b\psi_2) = a\hat{O}\psi_1 + b\hat{O}\psi_2$ All operators in QM, whether it is represents an observable or not, obey the linear nature. Among the operators, a subset which are hermitian alone represent observables. Among the operators, there are three classes which occur frequently in quantum mechanics: which are a)Hermitian b) Unitary c) Projection operators.

In general, an operator $\hat{O}$ acting on a function will make it a different one:

$$\hat{O}\psi(\mathbf{x}) = \phi(\mathbf{x}) \tag{46}$$

. For a given operator , there are class of functions, which are called eigen functions, which gives back the same one:

$$\hat{O}\ \psi(\mathbf{x}) = \lambda\psi(\mathbf{x}) \tag{47}$$

An example could be $\frac{d}{dx}$ acting on say $\sin x$, will give $\cos x$. But when it acts on $\exp\{\alpha x\}$, gives back $\exp\{\alpha x\}$. Hence the latter is an eigen function for $\frac{d}{dx}$. Here $\psi(\mathbf{x}), \lambda$ respectively are eigenfucntion and eigenvalue, for this operator.In general, λ, will be complex. We will see later, Hermitian operators, will have real eigenvalues.

If the hermitian, unitary and projection operator respectively are represented as H, U, P. Then their eigen values have the following nature:

$$\begin{aligned} H\psi &= \lambda\psi \quad \lambda\text{real} \qquad (48)\\ U\psi &= \exp\{i\theta\}\theta\text{real} \qquad (49)\\ P\psi &= \pm 1\psi \qquad (50) \end{aligned}$$

Unitary operators appear, mostly, in the form $U = \exp\{i\theta H\}$, where H is Hermitian. We will see later, these operators have a realisation. We have already seen, that momentum operator $\hat{p}$ is represented as a differential operator.

6.2 Measurement of observable

Consider any observable $\hat{O}$, which has spectrum of eigenvalues, $\lambda_1, ...\lambda_n$, with eigenfunctions $\Lambda_1, ...\Lambda_n$. If we measure $\hat{O}$ on any quantum system in a general state ψ, the only possible outcome of the result will be *one* of the n eigenvalues only. This statement holds for any state of the system.

Consider a normalized state ψ, which is *not*, one of the eigenfunctions of $\hat{O}$. Suppose we subject the system in the state ψ to the apparatus measuring the observable $\hat{O}$ and we get the result of the measurement to be λ_1. Suppose we subject the same system through the apparatus measuring the same observable.We are NOT guaranteed to get the same λ_1 as eigenvalue.

This feature is the heart of quantum mechanics.

$\boxed{Student}$ Is it the same as the uncertainty principle?

$\boxed{Teacher}$ No. The uncertainty principle is associated with the measurement of two observables.

For the given state ψ, we can only give probability p_i a given eigenvalue λ_i results. Since the result is one of the n eigenvalues, we should expect $\sum_i p_i = 1$. If after measurement, λ_i eigenvalue results, the state which was ψ before measurement, will become the eigenfunction ϕ_i after it. This is stated as ψ "collapses " to Λ_i.

This is presently understood as the act of measurement by an apparatus disturbs the system in an unpredictable way and collapses it to one of the eigenfunctions Λ_i with a probability p_i and gives as the outcome of measurement λ_i. This is referred to as the Copenhagen interpretation. This was discussed in the earlier chapter.

What was the value, system had, for the observable $\hat{O}$, before measurement? After all we are interested in that objective quantity, which measurement should give. Quantum mechanics, forbids us from asking that question as they do not have an objective reality associated.

If ψ happens to be one the eigenfunctions Λ_i then the outcome will λ_i with probability $p_i = 1$.

Now the recipe for computing the probability p_i is: (proof later)

$$\boxed{p_i = |\int d^3x \Lambda_i(\mathbf{x})^* \psi(\mathbf{x})|^2} \tag{51}$$

Expectation values With only probabilistic outcome of experimental results, the next best we can aspire for is a mean value, or referred to as expectation value. This requires us to imagine a large collection of identical system, measure the frequency with which each eigenvalue occurs. Out of N trials , if $n_1, n_2..$ times $\lambda_1, \lambda_2..$ occurs then the expectation value is:

$$< O >= \frac{n_1\lambda_1 + n_2\lambda_2 + ..}{N} \tag{52}$$

Identifying the frequency of occurrence, with the probability p_i of λ_i,

$$< O >= \sum_i p_i \lambda_i \tag{53}$$

The following will be shown later (normalisable states):

$$< O >= \int d^3x \psi^* \hat{O} \psi \tag{54}$$

If the state is not normalised, the above expression has to be divided by $\int d^3x \psi^* \psi$.

Comments:

a) Though outcome of a *single* experiment will be one of the eigenvalues, the expectation values which is a mean value, can be any (real) number.

b) The mean value depends on the wave function. But outcome of single experiment, being any one of the eigenvalues, holds for any wave function.

c)When ψ happens to be an eigenfunction for the observable, then the mean-value and eigenvalue coincide.

6.3 Measurement of two observables

We extend the analysis of measuring a single observable to two observables $\hat{O}_1, \hat{O}_1$. For the case of single observable, if measurement is made on its eigen state, then it does affect the state, and it continues to be in its eigen state.

If they do not commute as operators, i.e. $\left[\hat{O}_1, \hat{O}_1\right] \neq 0$, then it implies, as can be shown, there does not exist any common eigen state.Hence one can never know, both the observables to an arbitrary accuracy. These considerations lead to the celebrated "uncertainty principle", which will discussed in detail later.

6.4 Measurement of subsystems

Consider system which is composed of two sub-systems; like two-electron system in a single state, having total spin $s = 0$ and $s_z = 0$. Measurement on one-subsystem will effect other subsystem, independent of the spatial separation. Such states are "entangled states". We will discuss this further, towards the end.

7 Equation of motion

Next postulate, is the dynamical equation, which we have already motivated.

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi \tag{55}$$

Where H is defined as the Hamiltonian of the system There are three features in the above: 1)first order in time 2)linear equation 3) generated by H. Since the first postulate says, $\psi(\mathbf{x}, t_0)$ defines the state at t_0, the equation of motion must be first-order in time. Linearity of the equation is demanded by the superposition principle, which is the heart of quantum world. In classical mechanics, time-development is generated by the Hamiltonian. Hence we can expect the feature to old to quantum case. The Hamiltonian defines the system, requiring specification of the degrees of freedom, the forces between them etc. The above equation can be used even for time-dependent Hamiltonian.

What one is after is how the system evolves given a state at t_0. This is given by the solution of the equation 55. There are three cases based on H.

1. When H is time-independent,

$$\psi(\mathbf{x}, t) = e^{\frac{-i}{\hbar} H(t-t_0)} \psi(\mathbf{x}, t_0) \tag{56}$$

2. When $H(t)$, but $[H(t_1), H(t_2)] = 0$,

$$\psi(\mathbf{x},t) = e^{\frac{-i}{\hbar}\int_{t_0}^{t} H(t')dt'}\psi(\mathbf{x},t_0) \tag{57}$$

3. The case, $[H(t_1), H(t_2)] \neq 0$, is beyond the scope of the book.

To summarise the postulates are given below.
Postulates of quantum mechanics

1. The state of a quantum system is described by a complex function $\psi(\mathbf{x},\mathbf{t})$.

2. The dynamical variables are represented by a hermitian operator.

3. The outcome of measuring the value of an observable O, having an operator realization $\hat{O}$, in a single experiment is one of its eigenvalues. If the wave function is known, then the corresponding probability can be known. The mean value of the result of several measurements on the same wave function is given by the expectation value

$$< \hat{O} > = \frac{\int d^3x\psi^* O\psi}{\int d^3x\psi^*\psi} \tag{58}$$

4. The dynamical equation is

$$i\hbar\frac{\partial\psi}{\partial t} = H\psi \tag{59}$$

8 Problems

1. In a test, there was one question "Given that a dynamical variable represented by an operator has eigenvalues $1, 0, -1$, what are the possible outcomes of a measurement of it? and what is its expectation values".

   A student objects that without the information of the state vector, both the questions cannot be answered.

   Do you agree with the student? Explain your answer.

2. Check if $x\frac{d}{dx}$ is a linear operator? Show x^α, is its eigenfunction, and find the eigenvalue.

3. Check among $(\frac{d\phi}{dx})^2, \frac{d^2\phi}{dx^2}$, which is a linear operator? Construct an eigenfunction for the linear one, and find its eigenvalue.

4. Does $< x >$ and $\psi^*\psi dx$ represent the same physical quantity? Discuss the similarities and differences.

5. Distinguish between probability, probability density, and total probability for $\psi(x,t)$.