STUDY MATERIAL

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Topic: Postulates of Wave Mechanics

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Postulates of Wave Mechanics

Any formalism in science starts with some basic assumptions. Quantum mechanics is no exception. What we are going to study is, to be precise, Wave Mechanics, which was developed by Erwin Schrödinger, which involves adaptation of wave equations used classically in various branches of physics. Another representation was developed by Werner Heisenberg using matrices, called the Matrix Mechanics. They were combined in a single entity by P. A. M. Dirac as Quantum Mechanics.
All these formalisms are equivalent regarding physical interpretation, differing only in the mathematics used.

There are five basic postulates of wave mechanics, the last one being the Time-Dependent Schrödinger Equation (TDSE), which is the new master equation of motion, instead of Newton's equations which could predict trajectories of particles in motion quite well in the macroscopic scale, but failed in the subatomic scale.

➢ Postulate 1: Representation of the System

The 'State function' or 'Wave function'

The "state" or configuration of a dynamical system (evolving in space and time) is represented by a function Ψ, which is a function of the space coordinates (the state variables) and time.

Ψ is a complex function (in general) and it contains all information about the system under consideration. It is called a 'state function', or 'wave function' or 'probability amplitude function'. For example, for a single particle executing motion in one dimensional space, Ψ will depend on *x and t* (time). For a single particle in 3-dimensional space, it will depend on *x, y, z and t*. For two particle system Ψ will depend on x_1, y_1, z_1, x_2, y_2, z_2 and *t*, where (x_1, y_1, z_1) and (x_2, y_2, z_2) are the space coordinates of particles 1 and 2 respectively.

We shall come back for a detailed discussion on wave functions. For now, let us accept that the wave function needs to satisfy certain criteria to be acceptable. The wave function as such cannot have any physical significance as it is a complex function. But we can still associate a physical significance with it, by multiplying it with it's complex conjugate, to remove the complex part.

➢ Postulate 2: Representation of Observables

‘Hermitian Operators’

Each measurable quantity of a system (observable) is represented by a certain type of linear operator, called Hermitian operator.

An operator is a mathematical entity that tells us how to change the function or number that follows it. Summation, multiplication, differentiation *etc* are common operators that we use. Linear operators are those which satisfy the following property:

Suppose $\hat{A}$ is a linear operator operating on functions Ψ and Φ

Then it will satisfy the equation

$$\hat{A}\,(C_1\,\Psi + C_2\,\Phi) = C_1\,\hat{A}\,\Psi + C_2\,\hat{A}\,\Phi$$

where C_1 and C_2 **are two constants. We shall discuss later, in detail, about Hermitian operators which are a subset of linear operators. Basic operators are defined for the space coordinates, conjugate momentum coordinates and total energy. Quantum mechanical operators for all the other measurable properties can be constructed using these basic operators in the following way.**

The classical expression for the measurable quantity is written down in terms of the space (position) coordinates and momenta coordinates. Then the relevant quantum mechanical operators are applied to replace the classical variables.

➢ Postulate 3: Measurement of Observables give 'Eigenvalues' ('Good values') only.

In any measurement of a measurable property A, (which is represented by the quantum mechanical operator Â) of a system in the state Ψ, only those values will be observed which are the eigenvalues α_i.

The state Ψ can be expressed as a linear combination of a 'complete set' of eigenfunctions of Â

$$\Psi = \Sigma C_i \Psi_i$$

C_i are constants and Ψ_i are 'eigenfunctions' or 'eigenstates' of the operator Â. The summation may even go to an infinite number of states.

Eigenvalues are those which satisfy the 'eigenvalue equation':

$\hat{A}\,\Psi_i = \alpha_i\,\Psi_i$ where α_is are constants, called 'eigenvalues'.

Ψ_i is an eigenfunction (or eigenstate) of Â, belonging to the eigenvalue α_i.

We know that on measurement, we shall get one of the eigenvalues. The question is, which one? We do not know. However, we know that the probability of obtaining a particular value α_i is given by $|C_i|^2$.

Even if the initial state is not an eigenstate, as a result of measurement, it will collapse into a 'nearby' eigenstate.

➢ Postulate 4: Average value of Observables

If we have an 'ensemble' of states of the system represented by Ψ, and measurement of property A is done on each of them at the same instant, then the average (expectation) value of those measurements will be

$$\langle \hat{A} \rangle = \int \Psi_i{}^* \hat{A} \Psi_i \, \partial\tau \;\; / \;\; \int \Psi_i{}^* \Psi_i \, \partial\tau$$

$\Psi_i{}^*$ is the complex conjugate of Ψ_i.

The integral is over all space relevant to the system. It can be from +∞ to -∞, 0 to ∞, 0 to any constant value, any limit depending on the system under consideration. $\partial\tau$ is the relevant hypervolume element. For example, for a single particle executing motion in one dimensional space, $\partial\tau$ will be dx. For single particle in 3-dimensional space, it will be $\partial x \partial y \partial z$. For two particle system Ψ will be $\partial x_1 \partial y_1 \partial z_1 \partial x_2 \partial y_2 \partial z_2$, where (x_1, y_1, z_1) and (x_2, y_2, z_2) are the space coordinates of particles 1 and 2 respectively.

The denominator will be unity if the wave function is 'normalized'. If the state function Ψ happens to be an eigenstate of Â, the expectation value becomes the eigenvalue α. That means we can predict the exact value α.

$$\langle \hat{A} \rangle = \int \Psi^* \hat{A} \Psi \, \partial\tau \;/\; \int \Psi^* \Psi_i \, \partial\tau = \int \Psi^* \alpha \Psi \, \partial\tau = \alpha$$

➢ Postulate 5: Evolution of the state in time

The evolution of the system in time is given by the evolution of the wavefunction, according to the Time-dependent Schrödinger Equation (TDSE), an adopted wave equation, similar to the classical wave equations used in electromagnetic theory of light, with somewhat different interpretation.

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

Where $\hat{H}$ is the Hamiltonian operator (representing the total energy of a system). For a single particle executing motion in one dimensional space, $\hat{H}$ will be $-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + v(x)$

Here, m is the mass of the particle and $V(x)$ is the potential energy of the particle, a function of space coordinate *x*. The first term is the kinetic energy of the particle.

This is a second order partial differential equation. We can have special solutions for them, for which the space and the time part are separable as $\psi(x)\ \phi(t)$. For these special solutions we can have a separate time-independent equation, which is nothing but the eigenvalue equation corresponding the total energy of a system (E is the energy eigenvalue):

$$\hat{H}\ \psi(x) = E\ \psi(x)$$