CHAPTER 1

Quantum Mechanics – I

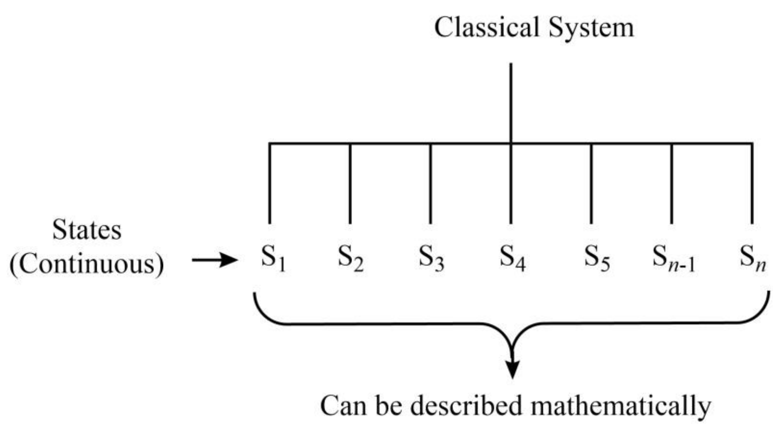
❖ Postulates of Quantum Mechanics

In modern quantum theory, the postulates of quantum mechanics are simply the step-to-step procedure to solve a simple quantum mechanical problem. In other words, it is like the manual that must be followed to retrieve the information about various states of any quantum mechanical system. We will first learn about the nature and the significance of these postulates, and then we will apply them to some real problems like the particle in a one-dimensional box or the harmonic oscillator.

➢ *The First Postulate*

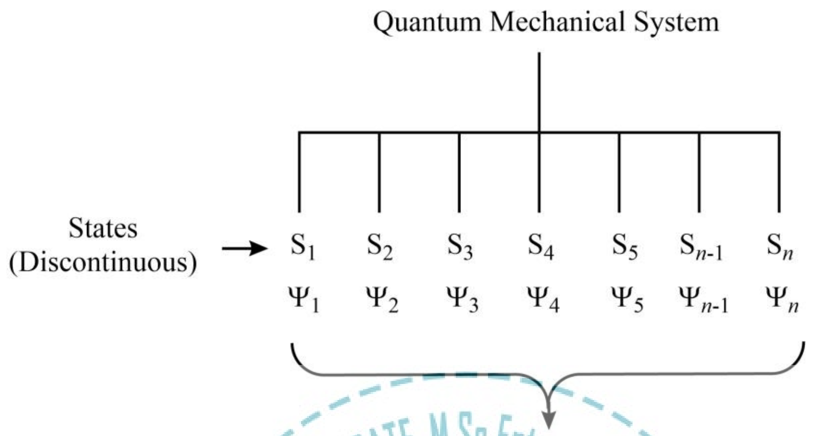
All time-independent states of any quantum mechanical system can be described mathematically as long as the function used is single-valued, continuous and finite.

Explanation: The systems around us can be broadly classified into two categories; the first is classical and the other one as quantum mechanical. The classical systems simply refer to the systems which are governed by the classical or the Newtonian mechanics. Now because all the macroscopic objects follow Newton's laws of motion, they fall in the category of classical systems; for example, a rotating gym dumbbell, the vibrating spring of steel, or an athlete running in the playground. Every classical system can possess many states which belong to a continuous domain, and each state can be described mathematically.



However, if the rotating gym dumbbell is replaced by the rotating diatomic molecule, the system would not remain classical anymore and would start violating classical laws. The states of such microscopic systems (here it just means the extremely small) belong to a discontinuous domain and can also be described mathematically. These mathematical descriptions are labeled as ψ_1, ψ_2, ψ_3 ….. ψ_n and generally called as the "wave functions". The term "wave function" is used because as we go from the macroscopic to the microscopic world i.e. from classical to the quantum mechanical world, things start behaving like waves rather particle. All of the states are wave-like; and because every wave we see around us is continuous, single-valued and finite;

only continuous, single-valued and finite expressions can represent those states. For instance, when you drop a stone in a standstill pond, the waves are generated which travel from the center to the boundary of the pond; and you don't see any discontinuity in it.



Ψ_1, Ψ_2, Ψ_3 ... Ψ_n are the mathematical description for S_n states

Hence, if a function is not single-valued, continuous and finite; it will not be able to represent any wave-like behavior at all. That is why every function that correlates a quantum mechanical state must be single-valued, continuous and finite; and this function describes the corresponding state completely.

- ***The Second Postulate***

For every physical property like linear momentum or the kinetic energy, a particular operator exists in quantum mechanics, the nature of which depends upon the classical expression of the same property.

Explanation: In classical mechanics, there are simply straight forward formulas for all physical properties; like linear momentum can simply be calculated by multiplying the mass with velocity. However, in case of quantum mechanical systems, the value of a certain physical property for a particular state cannot be calculated simply by using its classical formula but from an operator. It does sound silly but the classical formulas which are so well-tested on the scale of time fail in quantum world. For instance, you can use the $mv^2/2$ to calculate the kinetic energy of a moving particle in classical world by just putting its mass and velocity; but if the mass of the moving particle is extremely less, you will not get any rational results.

It is also worthy to note it again that though the classical formulas fail to give the value of physical property, they are still important as they form the basis of the derivations for corresponding quantum mechanical operators. For instance, the operator for kinetic energy (T) along x-axis can be derived as:

$$K.E.(T) = \frac{1}{2}mv^2 = \frac{(mv)^2}{2m} = \frac{p^2}{2m} \tag{1}$$

Where m and v are mass and the velocity, respectively; and p represents the angular momentum whose squared operator is:

$$\hat{p}_x^2 = \frac{-h^2}{4\pi^2}\frac{\partial^2}{\partial x^2} \tag{2}$$

Now putting the value of momentum squared from equation (2) into equation (1), we get:

$$\hat{T}_x = \frac{-h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2} \tag{3}$$

The expressions of various quantum mechanical operators are given below.

Table 1. Various important physical properties and their corresponding quantum mechanical operators.

Physical property		Operator	
Name	*Symbol*	*Symbol*	*Operation*
Position	x	$\hat{x}$	Multiplication by x
Position squared	x^2	$\hat{x}^2$	Multiplication by x^2
Momentum	p_x	$\hat{p}_x$	$\frac{h}{2\pi i}\frac{\partial}{\partial x}$
Momentum squared	p_x^2	$\hat{p}_x^2$	$\frac{-h^2}{4\pi^2}\frac{\partial^2}{\partial x^2}$
Kinetic energy	$T = \frac{P^2}{2m}$	$\hat{T}_x$	$\frac{-h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2}$
Potential energy	$V(x)$	$\hat{V}(x)$	Multiplication by $V(x)$
Total energy	$E = T + V(x)$	$\hat{H}$	$\frac{-h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2} + V(x)$

For three dimensional systems, the total operator can be obtained by summing the individual operators along three different axes. For instance, some important three-dimensional operators are:

$$\hat{T} = \frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) \tag{4}$$

$$\hat{p} = \frac{h}{2\pi i}\left(\frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z}\right) \tag{5}$$

$$\hat{H} = \frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(x, y, z) \tag{6}$$

➢ ***The Third Postulate***

If ψ is a well-behaved function for the given state of system and $\hat{A}$ is a suitable operator for a particular physical property, then the operation on ψ by the operator $\hat{A}$ gives the function ψ multiplied by the value of the physical property which can be constant or variable but always real (R). Mathematically, it can be shown as:

$$\hat{A}\psi = R\psi \tag{7}$$

Explanation: The third postulate of quantum mechanics actually connects the first and second postulate of quantum mechanics. The first postulate talks about the possibility of describing a quantum mechanical state mathematically, while the second postulate says that the values of all physical properties in the quantum world are obtained by the operator rather than the simple classical formula. Now the third postulate says that if we operate the operator (from second postulate) over the wave function (from first postulate), we will get the value of the corresponding physical property.

However, at this point, a new problem arises as we do not know the exact mathematical description i.e. the wave function of any quantum mechanical state; and the operators need the absolute mathematical description of the quantum mechanical state to yield any actual result. Now though we know the expressions of different operators proposed by the second postulate; the first postulate speaks only about the presence of a single-valued, continuous and finite mathematical function but does not give actual function itself; and without the knowledge of actual "wave functions", the operators are pretty much useless. Therefore, one would think that there must be some route by which the wave functions are obtained first, which would be used as operand afterward. However, the procedure to find the exact mathematical descriptions of various quantum mechanical states is somewhat more synergistic. The "magic mystery" is that all the operators need absolute expression of the wave function that defines the quantum mechanical state except one, the most famous "Hamiltonian operator". The special thing about the Hamiltonian operator is that it does not necessarily need the absolute form but the symbolic form only to yield the value of its physical property i.e. energy. Nevertheless, in the process of applying the Hamiltonian operator over the symbolic form of the wave function, the absolute expression is also obtained. Mathematically,

$$\hat{H}\psi = E\psi \tag{8}$$

After putting the expression of the Hamiltonian operator in equation (8) and then rearranging, we get:

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m(E-V)\psi}{h^2} = 0 \tag{9}$$

The second-order differential equation i.e. equation (9) is the famous Schrodinger wave equation, the solution of which gives not only the energy but the wave function as well. Now, once the exact expression of the wave function representing a particular state is known, other operators can be operated over it to find their values.

➢ *The Fourth Postulate*

If the value of the physical property obtained after multiplying the wave function by the corresponding operator is constant (postulate 3), the value is called as the eigen-value and is directly reportable; and the wave function will be labeled as the eigen-function of the operator used.

Explanation: The third postulate said that when the wave function of a particular quantum mechanical state is multiplied by the operator of an observable quantity, we get a real value multiplied by the wave function itself; however, the value obtained so can be constant or variable. Mathematically,

$$\hat{O}\,\Psi = \text{Value}\ \Psi$$

Eigen Function, Eigen Value ⟵ Constant | Variable ⟶ Non-eigen Function, Non-eigen Value

The constant value of the observable quantity can be reported directly, and the function is called the eigenfunction of the operator under consideration.

➢ *The Fifth Postulate*

If the value of the physical property obtained after multiplying the wave function by the corresponding operator is variable i.e. non-eigen, the value can be reported only after averaging it over the whole configurational space.

$$< a > or\ \bar{a} = \frac{\oint \psi^* \hat{O} \psi \, d\tau}{\oint \psi^* \psi \, d\tau} \qquad (10)$$

Explanation: As we have seen in the fourth postulate that the value obtained by multiplying the Hermitian operator with any quantum mechanical state can also be variable in nature. For instance, if we multiply a wave function simply by position operator, we will get

$$\hat{x}\psi = x\psi \qquad (11)$$

or

$$\hat{x} = \frac{x\psi}{\psi} \qquad (12)$$

Now because "*x*" is a variable number, it must have reported as an average value before any further rational argument is made.

Therefore, we can say that the fifth postulate is simply an extension of the fourth postulate; i.e. the fourth postulate is used to obtain the value of a particular physical property if it is an eigenvalue, however, the fifth postulate is employed to calculate all non-eigenvalues.

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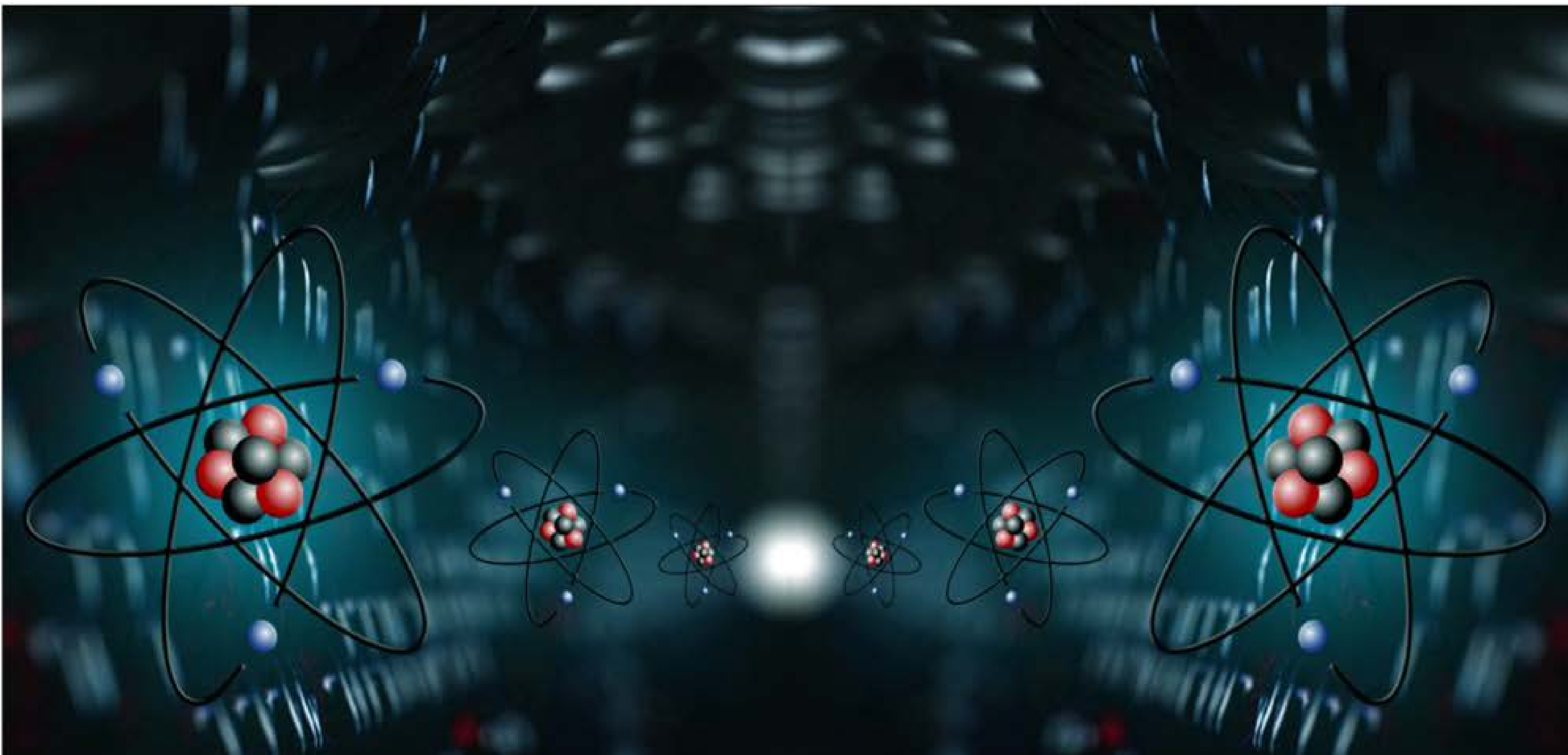

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