

Chapter 1 (Lecture 1-3)

Postulates of Quantum Mechanics

Now we turn to an application of the preceding material, and move into the foundations of quantum mechanics. Quantum mechanics is based on a series of postulates which lead to a very good description of the microphysical realm.

The set of statements we find in the literature as ‘postulates’ or ‘principles’ can be split into three subsets: the main postulates which cannot be derived from more fundamental ones, the secondary postulates which are often presented as ‘postulates’ but can actually be derived from the main ones, and then statements often called ‘principles’ which are well known to be as mere consequences of the postulates.

Main postulates

(1) **Operator representation.** To every dynamical variable of classical mechanics there corresponds in quantum mechanics a linear, Hermitian operator. When the operators act upon the wavefunction associated with a definite value of that observable yields this value times the wavefunction. Mathematically we can write:

$$A\psi = a\psi$$

Where A is operator, a is eigenvalue of the operator A , and ψ is eigenfunction. The equation is named eigenvalue equation. The requirement that the operators are Hermitian ensures that the observables have real values. Almost all operators can be derived from position and momentum operator.

The more common operators occurring in quantum mechanics for a single particle are listed below and are constructed using the position and momentum operators.

Operator	Abbreviation		Math representation	
	1D	3D	1D	3D
Position	x	r	x	r
Momentum	p_x	p	$-i\hbar \frac{d}{dx}$	$-i\hbar \nabla$
Kinetic Energy	K, T, KE	K, T, KE	$\frac{p_x^2}{2m}$	$\frac{p^2}{2m}$
Hamiltonian (time dependent)	E, H	E, H	$i\hbar \frac{\partial}{\partial t}$	$i\hbar \frac{\partial}{\partial t}$
Hamiltonian (time independent)	E, H	E, H	$\frac{p_x^2}{2m} + V(x)$	$\frac{p^2}{2m} + V(r)$
Angular momentum	L_x	L	$yp_z - zp_y$	$\mathbf{r} \times \mathbf{p}$

The wavefunction (eigenfunction) include quantum numbers. For example if n , and l are quantum numbers then the function can be written as: ψ_{nl} . For the sake of simplicity that can be represented in Dirac notation or Bra-Ket notation, such that

$$\psi_{nl} \rightarrow |nl\rangle;$$

$|nl\rangle$ is called eigenstate or state function. When an operator act on a state, it can be written as

$$A|nl\rangle = a(n, l)|nl\rangle$$

where $a(n, l)$ is eigenvalues the operator A and $|nl\rangle$ is eigenstate of the operator A . Conjugate of the wave function in Bra-Ket notation is

$$\psi_{nl}^* = \langle nl|$$

Operator Algebra

Here its is worth to give brief information about operator algebra. We must be careful when replacing the classical x and p with operator x and p since *the order in which they appear is important*. This is because two given operators A and B do not in general commute. Classical variables always commute, that is

$$AB = BA$$

Operators, similar to the matrices and they may not commute:

$$AB \neq BA$$

We can define the commutator (or commutation relation)

$$[A, B] = AB - BA$$

If $[A, B] = 0$ we say that A and B commute this physical means that the eigenvalues of observables A and B can be measured simultaneously, there is no uncertainty relation between them OR they have the same eigenfunction.

Example:

Find the commutators of the momentum and position operator $[p, x]$.

Solution

The commutator can be written as

$$\left[\frac{\hbar}{i} \frac{d}{dx}, x \right] = \frac{\hbar}{i} \frac{d}{dx} x - x \frac{\hbar}{i} \frac{d}{dx}$$

Important!!!!

The first term can be evaluated as follows:

$$\frac{\hbar}{i} \frac{d}{dx} x, \text{ multiply with a function } f, \quad \frac{\hbar}{i} \frac{d}{dx} (xf) = \frac{\hbar}{i} \left(x \frac{df}{dx} + f \right)$$

We have used derivative of product of two function. Then

$$\frac{\hbar}{i} \frac{d}{dx} (xf) = \frac{\hbar}{i} \left(x \frac{df}{dx} + f \right), \text{ remove } f, \frac{\hbar}{i} \frac{d}{dx} x = \frac{\hbar}{i} \left(x \frac{d}{dx} + 1 \right)$$

Therefore the commutator can be written as

$$\left[\frac{\hbar}{i} \frac{d}{dx}, x \right] = \frac{\hbar}{i} \left(x \frac{d}{dx} + 1 \right) - x \frac{\hbar}{i} \frac{d}{dx} = \frac{\hbar}{i}$$

!Remember uncertainty relation (at the last page of this lecture)

(2) **State or Wavefunction.** Each physical system is described by a state function $\Psi_n(r, t)$ which determines all can be known about the system.

Physical interpretation of wave function

In quantum physics particles have wave properties and they are described by a wave function. Therefore position of the particle is not function of time.

In the classical wave theory intensity of a wave is proportional to the square of its wave function. For the photon the intensity is interpreted as the probability of finding a photon in the given space.

Properties of wave function

A wave function $\Psi(x, t)$ must be

- a) Single valued.

A single-valued function is function that, for each point in the domain, has a unique value in the range. It is therefore one-to-one or many-to-one. At every point in space have only one value associated with it (single valued). If a wave function was not single valued, it would have multiple values for the same position, thereby ruining the probabilistic interpretation of the wave function.

- b) Continuous

The function has finite value at any point in the given space. Otherwise it implies that particle does not exist at some points in the corresponding space.

- c) Differentiable

Derivative of wave function is related to the flow of the particles. Therefore particle flow in the corresponding space should be continuous.

- d) Square integrable

The wave function contains information about where the particle is located, its square being probability density. Therefore

$$\int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx < \infty$$

Where $|\Psi(x, t)|^2 = \Psi(x, t)\Psi(x, t)^*$. $\Psi(x, t)^*$ is conjugate of the wave function.

Example. The wave function of a particle is given by $\psi(x) = A \sin\left(\frac{n\pi}{a}x\right)$ and defined $0 \leq x \leq a$. Is it valid wave function?

Solution:

The function is single valued, continuous, differentiable and square integrable if the constant A is finite. Therefore the function is a valid wave function.

Example. Let two functions $\phi = Ax$ and $\psi = Ae^{-ax}$ be defined for $0 \leq x \leq \infty$. Explain why $\phi = Ax$ cannot be a wavefunction but $\psi = Ae^{-ax}$ could be a valid wavefunction.

Solution

Both functions are continuous and defined on the interval of interest. They are both single valued and differentiable. However, consider the integral of x :

$$\int_0^{\infty} A^2 x^2 dx = \frac{A^2 x^3}{3} \Big|_0^{\infty} \rightarrow \infty.$$

is not square integrable over this range it cannot be a valid wavefunction.

(3) **Equation for the wave function (Schrödinger equation).** The time evolution of the wave function of a non-relativistic physical system is given by the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi$$

where $i^2 = -1$, and the Hamiltonian $H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$ is a linear Hermitian¹ operator, whose expression is constructed from the correspondence principle. For example classically kinetic energy can be expressed as $K = \frac{p^2}{2m}$. When we substitute operator representation of momentum we obtain kinetic energy part of Schrödinger equation. The time independent form of the equation can be written as²:

$$E\psi = H\psi$$

The equation is called eigenvalue equation and E eigenvalue of the operator H. Since H is energy operator then E is associated to energy. The equation also called eigenvalue equation. The wave function ψ is called eigenfunction and it can be obtained by solving eigenvalue equation. We shall have a great deal to say about the Schrödinger equation and its solutions in the rest of the text. When we compare last two equation, obviously energy operator is given by

$$\hat{E} = i\hbar \frac{\partial}{\partial t}.$$

Example: Particle in the infinite well box (figure given in the class)

Show that $\Psi(x, t) = Ae^{-\frac{iE}{\hbar}t} \sin kx$ is the solution of the Schrödinger equation for $V(x) = 0$. ($k^2 = \frac{2mE}{\hbar^2}$).

Solution: For $V(x) = 0$ we can write

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2}$$

Substitute given wave function into the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \left(Ae^{-\frac{iE}{\hbar}t} \sin kx \right) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \left(Ae^{-\frac{iE}{\hbar}t} \sin kx \right)$$

Evaluating derivatives:

¹ An operator is said to be Hermitian if it satisfies: $A^\dagger = A$, where A^\dagger is conjugate transpose of operator A. It is alternatively called 'self adjoint'. In QM we will see that all observable properties must be represented by Hermitian operators that have real eigen values.

² **Time independent Schrödinger equation**

If the potential time independent then time part of the Schrödinger equation can be separated by substituting

$$\Psi(x, t) = \psi(x)f(t)$$

And defining $f(t) = e^{-\frac{iEt}{\hbar}}$, the time dependent Schrödinger equation takes the form:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} + V(x)\psi(x) = E\psi(x).$$

$$i\hbar\left(-\frac{iE}{\hbar}\right)\left(Ae^{-\frac{iE}{\hbar}t}\sin kx\right) = -\frac{\hbar^2}{2m}(-k^2)\left(Ae^{-\frac{iE}{\hbar}t}\sin kx\right)$$

is satisfied.

(4) **Measurements (eigen value and expectation value) (Von Neumann's postulate).** If a measurement of the observable A yields some value a_i , the wavefunction of the system just after the measurement is the corresponding eigenstate ψ_i . The expectation value will simply be the eigenvalue a_i .

On other words in any measurement of the observable associated with operator \hat{A} , the only values that will ever be observed are the eigenvalues a , which satisfy the eigenvalue equation

$$\hat{A}\Psi(x, t) = a\Psi(x, t)$$

This postulate captures the central point of quantum mechanics--the values of dynamical variables can be quantized (although it is still possible to have a continuum of eigenvalues in the case of unbound states). If the system is in an eigenstate of \hat{O} with eigenvalue a , then any measurement of the quantity \hat{A} will yield a .

Additional postulate: **Born's postulate: probabilistic interpretation of the wavefunction.** The squared norm of the wavefunction $|\psi|^2 d\tau$ is interpreted as the probability of the finding of the particle in volume $d\tau$. More specifically, if $\psi(r, t)$ is the wavefunction of a single particle, $\psi^*(r, t)\psi(r, t)d\tau$ is the probability that the particle lies in the volume element $d\tau$ located at τ at time t . Because of this interpretation and since the probability of finding a single particle somewhere is 1, the wavefunction of this particle must fulfill the **normalization condition**

$$\int_{-\infty}^{\infty} \psi^*(r, t)\psi(r, t)d\tau = 1$$

Orthogonal state: The wave functions $\Psi_n(x, t)$ and $\Psi_m(x, t)$ of a particle corresponding two different state satisfy the orthogonality relation

$$\int_{all} \Psi_n(x, t)^*\Psi_m(x, t)dx = 0, \text{ if } m \neq n.$$

If the wavefunctions are normalized then above relation is said to be orthonormal state.

Example. The wave function for a particle confined to $0 \leq x \leq a$ in the ground state was found to be:

$$\psi(x) = A\sin\left(\frac{\pi x}{a}\right)$$

where A is the normalization constant. Find A .

Solution:

Using normalization condition

$$P = \int_0^a |\Psi(x, t)|^2 dx = 1$$

we can obtain

$$P = \int_0^a A^2 \sin^2\left(\frac{\pi x}{a}\right) dx = 1$$

evaluate the integral, then you can obtain

$$A = \sqrt{\frac{2}{a}}$$

Example. The wave functions for a particle confined to $0 \leq x \leq a$ are found to be:

$$\psi_1(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{\pi x}{a}\right); \psi_2(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{2\pi x}{a}\right)$$

Show that the wave functions are orthogonal.

Solution:

Using orthogonalization condition

$$\int_0^a \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right) \sqrt{\frac{2}{a}} \sin\left(\frac{2\pi x}{a}\right) dx = 0$$

this is condition for orthogonality or orthonormality.

Secondary postulates

One can find in the some books other statements which are often presented as ‘postulates’ but

which are mere consequences of the above five ‘main’ postulates. We examine below some of them and show how we can derive them from these ‘main’ postulates.

(1) **Superposition principle and expansion of wavefunction.** Quantum superposition states that a linear combination of state functions of a given physical system is a state function of this system. This principle follows from the linearity of the H operator in the Schrödinger equation, which is therefore a linear second order differential equation to which this principle applies.

The set of eigenfunctions of an operator A forms a complete set of linearly independent functions. Therefore, an arbitrary state ψ can be expanded in the complete set of eigenfunctions of A ($A\psi_n = a_n\psi_n$), i.e., as

$$\psi = \sum_n c_n \psi_n$$

where the sum may go to infinity. For the case where the eigenvalue spectrum is discrete and non-degenerate and where the system is in the normalized state ψ , the probability of obtaining as a result of a measurement of A the eigenvalue a_n is $|c_n|^2$. This statement can be straightforwardly generalized to the degenerate and continuous spectrum cases. The statements

$$\int_{-\infty}^{\infty} \psi_n^* \psi_m dx = \begin{cases} 1 & \text{if } n = m \\ 0 & \text{if } n \neq m \end{cases}$$

Hermitian operators are known to exhibit the two following properties: (i) two eigenvectors of a Hermitian operator corresponding to two different eigenvalues are orthogonal, (ii) in an Hilbert space with finite dimension N , a Hermitian operator always possesses N eigenvectors that are linearly independent. This implies that, in such a finite dimensional space, it is always possible to construct a base with the eigenvectors of a Hermitian operator and to expand any wavefunction in this base.

Example. The wavefunction is given by:

$$\psi = \frac{i}{2} \sqrt{\frac{2}{a}} \sin\left(\frac{\pi}{a}x\right) + c_2 \sqrt{\frac{2}{a}} \sin\left(\frac{2\pi}{a}x\right) + \sqrt{\frac{1}{a}} \sin\left(\frac{3\pi}{a}x\right)$$

Calculate c_1 . If the energy is measured, what are the possible results and what is the probability of obtaining each result?

Solution

Then we can write the superposition of the wave functions:

$$\psi = \frac{i}{2} \psi_1 + c_2 \psi_2 + \sqrt{\frac{1}{2}} \psi_3$$

Using normalization

$$\langle \psi | \psi \rangle = c_1 c_1^* + c_2 c_2^* + c_3 c_3^* = 1 \Rightarrow$$

$$\frac{1}{4} + c_2 c_2^* + \frac{1}{2} = 1 \Rightarrow c_2 = \mp \frac{1}{2}$$

Therefore the wave function takes the form

$$\psi = \frac{i}{2} \psi_1 + \frac{1}{2} \psi_2 + \sqrt{\frac{1}{2}} \psi_3$$

(2) **Eigenvalues and eigenfunctions.** Any measurement of an observable A will give as a result one of the eigenvalues a of the associated operator A , which satisfy the equation $A\psi = a\psi$. This is the consequences of corresponding principle.

(3) **Expectation value.** For a system described by a normalized wavefunction ψ , the expectation value of an observable A is given by

$$\langle A \rangle = \int_{-\infty}^{\infty} \psi^* A \psi dx$$

This statement follows from the probabilistic interpretation attached to ψ , i.e., from Born's Postulate.

Note that if the wave function ψ is eigenfunction of the operator A then eigenvalues and expectation values of the A of the same state is equal to each others.

Important! Let us discuss expectation value of the momentum p ? We will show the new quantum theory we are studying must not contradict the old classical theory in the situations where the latter can be successfully applied. In other words quantum theory must include Newton theory as a special case holding within the appropriate limits. The following theorem shows this limit.

Derived principles.

(1) **Heisenberg's uncertainty principle.** If p and x are two conjugate observables such that, they are not commute, it is easy to show that they satisfy the relation

$$\Delta x \Delta p \geq \frac{\hbar}{2}$$

In general

$$\Delta A \Delta B \geq \frac{1}{2} |\langle [A, B] \rangle|$$

where the root mean square deviation of A is defined as

$$\Delta A = \sqrt{\langle A^2 \rangle - \langle A \rangle^2}$$

Finally, it is appropriate at this point to make a few remarks about the so-called energy–time uncertainty relation. Although the energy operator is well defined (it is the Hamiltonian for the system), there is no operator for time in quantum mechanics. Time is a parameter, not an observable. Therefore, strictly speaking, there is no uncertainty relation between energy and time. The true significance of the energy–time ‘uncertainty principle’ is that it is a relation between the uncertainty in the energy of a system that has a finite lifetime τ (tau), and is of the form $\delta E = \hbar/2\tau$.

Example. Calculate uncertainty between the operators x and p .

Solution:

Momentum operator $p = -i\hbar \frac{d}{dx}$ and position operator x , then

$$[p, x] = px - xp = -i\hbar \frac{d}{dx} x + xi\hbar \frac{d}{dx} = -i\hbar$$

Therefore

$$\Delta x \Delta p \geq \frac{1}{2} |\langle [p, x] \rangle| = \frac{\hbar}{2}$$

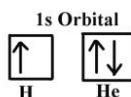
(2) **The spin-statistics theorem.** The spin-statistics theorem states that integer spin particles are bosons, while half-integer spin particles are fermions. The theorem states that:

The wave function of a system of identical integer-spin particles has the same value when the positions of any two particles are swapped. Particles with wavefunctions symmetric under exchange are called bosons;

The wave function of a system of identical half-integer spin particles changes sign when two particles are swapped. Particles with wavefunctions anti-symmetric under exchange are called fermions.

(3) **The Pauli exclusion principle.** Two identical fermions cannot be in the same quantum state. This is a mere consequence of the spin-statistic theorem. We state that in an atom, no two electrons can have the **same** four [electronic quantum numbers](#).

As an example suppose that we have the first three quantum numbers $n=1, l=0, m_l=0$. Only two electrons can correspond to these, which would be either $m_s=-1/2$ or $m_s=+1/2$. As we already know from our studies of quantum numbers and electron orbitals, we can conclude that these four quantum numbers refer to $1s$ subshell. If only one of the m_s values is given then we would have $1s^1$ (denoting Hydrogen) if both are given we would have $1s^2$ (denoting Helium). Visually this would be represented as:



As you can see, the $1s$ subshell can hold only two electrons and when filled the electrons have opposite spins.

Ehrenfest Theorem: (OMIT)

Newton's fundamental equations of classical dynamics

$$\frac{d\vec{r}}{dt} = \frac{\vec{p}}{m}; \quad \vec{F} = \frac{d\vec{p}}{dt} = -\vec{\nabla}V$$

are exactly satisfied by the expectation values of the corresponding operators in quantum mechanics. i.e. in x-direction,

$$\frac{d}{dt}\langle x \rangle = \frac{\langle p \rangle}{m}; \quad \frac{d}{dt}\langle p_x \rangle = -\left\langle \frac{\partial V}{\partial x} \right\rangle$$

Similar expressions can be written about y, z components of r and p. They represent

the *time rates of change* of the expectation values.

In Newton theory position and momentum are related by

$$p = m \frac{dx}{dt}$$

We thus expect the new quantum theory to be such that

$$\langle p \rangle = m \frac{d}{dt} \langle x \rangle$$

The fact that Newton equation holds, at least in an average sense, constrains the mathematical form of the momentum in the new quantum formalism. To obtain expectation value of momentum let us calculate:

$$m \frac{d}{dt} \langle x \rangle = m \frac{d}{dt} \int_{-\infty}^{\infty} \psi^* x \psi dx$$

$$\langle p \rangle = m \frac{d}{dt} \langle x \rangle = m \int_{-\infty}^{\infty} x \left(\frac{\partial \psi^*}{\partial t} \psi + \psi^* \frac{\partial \psi}{\partial t} \right) dx$$

We have shown before (see probability current density)

$$-\frac{\hbar}{2im} \frac{d}{dx} \left(\frac{\partial \Psi}{\partial x} \Psi^* - \Psi \frac{\partial \Psi^*}{\partial x} \right) = \left(\frac{\partial \psi^*}{\partial t} \psi + \psi^* \frac{\partial \psi}{\partial t} \right)$$

After some tedious calculations we can show that

$$\langle p \rangle = -\frac{\hbar}{2im} m \int_{-\infty}^{\infty} x \frac{d}{dx} \left(\frac{\partial \Psi}{\partial x} \Psi^* - \Psi \frac{\partial \Psi^*}{\partial x} \right) dx$$

$$\langle p \rangle = \frac{\hbar}{i} \int_{-\infty}^{\infty} \psi^* \frac{d\Psi}{dx} dx = \int_{-\infty}^{\infty} \psi^* \left(\frac{\hbar}{i} \frac{d}{dx} \right) \psi dx$$

Then momentum operator can be expressed as

$$p = \frac{\hbar}{i} \frac{d}{dx}$$

Therefore we can obtain an operator for a physicsl observables of the quantum physics. As an example the kinetic energy operator can be obtained as follows:

$$K = \frac{p^2}{2m} = \frac{1}{2m} \frac{\hbar}{i} \frac{d}{dx} \frac{\hbar}{i} \frac{d}{dx} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$$

As expected.

(4) **Probability conservation.** The probability conservation is a consequence of the Hermitian property of \hat{H} . This property first implies that the norm of the state function is time independent and it also implies a local probability conservation which can be written

$$\frac{\partial \rho}{\partial t} + \frac{\partial j}{\partial x} = 0$$

Where $\rho = |\psi|^2$ and $j(x, t) = \frac{\hbar}{2im} \left(\frac{\partial \Psi}{\partial x} \Psi^* - \Psi \frac{\partial \Psi^*}{\partial x} \right)$. Here j is called probability current.

Example: Current of a plane wave

For a plane wave the wave function is $\psi(x) = a e^{ikx}$, where a is a constant and k is wave vector ($k = 2\pi/\lambda$)

The corresponding probability current density is

$$j(x, t) = \frac{\hbar}{2im} \left(\frac{\partial \Psi}{\partial x} \Psi^* - \Psi \frac{\partial \Psi^*}{\partial x} \right) = |a|^2 \left(\frac{\hbar k}{m} \right)$$

using de Broglie relation $p_x = \frac{h}{\lambda} = \hbar k = mv$, and $\rho = |\psi|^2 = |a|^2$ we obtain

$$j(x, t) = \rho v$$