2. POSTULATES OF QUANTUM MECHANICS

2.1 Introducing the state function

Quantum physicists are interested in all kinds of physical systems (photons, conduction electrons in metals and semiconductors, atoms, etc.). State of these rather diverse systems are represented by the same type of functions \rightarrow STATE FUNCTIONS.

First postulate of Quantum mechanics:

Every physically-realizable state of the system is described in quantum mechanics by a state function ψ that contains all accessible physical information about the system in that state.

- > Physically realizable states \rightarrow states that can be studied in laboratory
- > Accesible information \rightarrow the information we can extract from the wavefunction
- State function → function of position, momentum, energy that is spatially localized.

Principle of superposition:

If ψ_1 and ψ_2 represent two physically-realizable states of the system, then the linear combination

$$\Psi = c_1 \Psi_1 + c_2 \Psi_2,$$

where c_1 and c_2 are arbitrary complex constants, represents a third physically realizable state of the system.

Note:

Wavefunction $\psi(x,t) \rightarrow position$ and time probability amplitude

Quantum mechanics describes the outcome of an ensemble of measurements, where an ensemble of measurements consists of a very large number of identical experiments performed on identical non-interacting systems, all of which have been identically prepared so as to be in the same state.

Second postulate of Quantum mechanics:

If a system is in a quantum state represented by a wavefunction ψ , then

$$PdV = |\psi|^2 dV$$

is the probability that in a position measurement at time t the particle will be detected in the infinitesimal volume dV.

Note:

$|\psi(x,t)|^2 \rightarrow$ position and time probability density

The importance of normalization follows from the Born interpretation of the state function as a position probability amplitude. According to the second postulate of quantum mechanics, the integrated probability density can be interpreted as a probability that in a position measurement at time t, we will find the particle anywhere in space. Therefore, the normalization condition for the wavefunction is:

$$\int PdV = \int \left| \Psi(x, y, z) \right|^2 dV = \int \Psi^*(x, y, z) \Psi(x, y, z) dV = 1$$

Limitations on the wavefunction:

- Only normalizable functions can represent a quantum state and these are called physically admissible functions.
- State function must be continuous and single valued function.
- State function must be a smoothly-varying function (continuous derivative).

2.2 Expectation values and uncertainties

The Born interpretation of quantum mechanics enables us to determine from a wavefunction, the probabilistic information. For example, we can answer the following question: In an ensemble measurement of position at time *t*, what is the probability that a member of the ensemble will exhibit a value in the range from *x* to x+dx?

To characterize the results of an experiment, we use two statistical quantities:

- Ensemble average <x>
- Standard deviation Δx

Ensemble average:

In quantum theory, the ensemble average of an observable for a particular state of the system is called the EXPECTATION VALUE OF THAT OBSERVABLE:

$$\langle x \rangle = \int x P(x,t) dx = \int \psi^*(x,t) x \psi(x,t) dx = (\psi, x\psi)$$

Note:

- > The expectation value can be time dependent, i.e. $\langle x \rangle = \langle x(t) \rangle$
- The expectation value depends upon the state of the system. Different states, represented by different state functions have different ensemble averages.

Example:

Consider a microscopic particle with a simple harmonic oscillator potential in a quantum state represented by the wavefunction

$$\Psi(x,t) = \left(\frac{1}{\pi}\right)^{1/4} e^{-x^2/2} e^{-iEt/\hbar}$$

Calculate the average value we would obtain in a measurement at t=0 of the position of an ensemble of particles in this state.

Solution:

Using the definition for ensemble average, we get:

$$< x >= \left(\frac{1}{\pi}\right)^{1/2} \int_{-\infty}^{+\infty} e^{-x^2/2} x e^{-x^2/2} dx = \left(\frac{1}{\pi}\right)^{1/2} \int_{-\infty}^{+\infty} x e^{-x^2} dx = 0$$

Generalization:

Lets denote a generic observable Q(x) that depends only upon position. The expectation value of this observable is given by:

$$\langle Q(t) \rangle = \int \psi^*(x,t)Q(x)\psi(x,t)dx$$

The other statistical quantity that one uses in quantum physics is the standard deviation of an observable - otherwise known as **uncertainty**. For a position measurement, the uncertainty in *x* answers the following question: In an ensemble measurement at time *t* of the position of a particle in a state $\psi(x,t)$, what is the spread of the individual results around the expectation value $\langle x \rangle$?

To answer this question, one needs to calculate the **dispersion**:

$$\Delta x^{2} = \int \psi^{*}(x,t) [x - \langle x \rangle]^{2} \psi(x,t) dx = \langle x^{2} \rangle - \langle x \rangle^{2}$$

The uncertainty, or the standard deviation is given by:

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

or the uncertainty equals the square-root of the dispersion.

Example:

Calculate the uncertainty Δx in the previous example.

Solution:

$$< x^{2} >= \left(\frac{1}{\pi}\right)^{1/2} \int_{-\infty}^{+\infty} e^{-x^{2}/2} x^{2} e^{-x^{2}/2} dx = \left(\frac{1}{\pi}\right)^{1/2} \int_{-\infty}^{+\infty} x^{2} e^{-x^{2}} dx = \frac{1}{2}$$

Therefore:

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \sqrt{1/2}$$

Generalization:

The uncertainty in the measurement of the observable Q(x) is given by:

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

2.3 Momentum

 $\psi(x,t)$ is the state function of a system in **position representation**. It must be normalizable since it describes a localized particle. Therefore, one can define a Fourier transform of this function:

$$\Psi(x,0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk e^{ikx} \phi(k),$$

where $\phi(k)$ is the Fourier coefficient, or in this particular case it represents the **momentum wavefunction** also known as the **amplitude function**. The description of the particle in momentum state is achieved using these momentum wavefunctions. The expectation value of the momentum can then be calculated in two different ways:

Approach 1:

One can use the expressions for the expectation value and standard deviation (uncertainty) given in the previous section, i.e:

- \blacktriangleright Expectation value: $\langle p \rangle = \int \phi^*(k) \hbar k \phi(k) dk$
- ➤ Dispersion: $\langle p^2 \rangle = \int \phi^*(k) (\hbar k)^2 \phi(k) dk$
- $\blacktriangleright \quad \text{Uncertainty: } \Delta p = \sqrt{\langle p^2 \rangle \langle p \rangle^2}$

Example:

Consider a wavefunction in position representation given by:

$$\Psi(x,0) = \left(\frac{1}{2\pi}\right)^{1/4} \frac{1}{\sqrt{\sigma}} \exp\left(-\frac{x^2}{4\sigma^2}\right)$$

Solution:

To calculate the expectation value and the uncertainty of the particle's position, we need to use the position wavefunction $\psi(x,t)$ to get:

$$< x \ge \int_{-\infty}^{\infty} \psi^*(x,0) x \psi(x,0) dx = \frac{1}{\sqrt{2\pi\sigma}} \int_{-\infty}^{\infty} x \exp(-x^2/2\sigma^2) dx = 0$$
$$< x^2 \ge \int_{-\infty}^{\infty} \psi^*(x,0) x^2 \psi(x,0) dx = \frac{1}{\sqrt{2\pi\sigma}} \int_{-\infty}^{\infty} x^2 \exp(-x^2/2\sigma^2) dx = \sigma^2$$
$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \sigma$$

To calculate the expectation value and the uncertainty in the measurement of the particle's momentum, we first need to evaluate the momentum wavefunction:

$$\phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(x,0) e^{-ikx} dx = \left(\frac{2}{\pi}\right)^{1/4} \sqrt{\sigma} \exp(-k^2 \sigma^2)$$

Once we know $\phi(k)$, we can evaluate $\langle p \rangle$ and Δp , using the corresponding definitions:

$$=< \hbar k >= \hbar \int \phi^*(k) k \phi(k) dk = \hbar \sigma \sqrt{\frac{2}{\pi}} \int_{-\infty}^{\infty} k \exp(-2k^2 \sigma^2) dk = 0$$
$$< p^2 >= \hbar^2 < k^2 >= \hbar^2 \sigma \sqrt{\frac{2}{\pi}} \int_{-\infty}^{\infty} k^2 \exp(-2k^2 \sigma^2) dk = \left(\frac{\hbar}{2\sigma}\right)^2$$
$$\Delta p = \frac{\hbar}{2\sigma}$$

Using the results for the position and the momentum uncertainty, it follows that:

$$\Delta x \cdot \Delta p = \mathbf{\sigma} \cdot \frac{\hbar}{2\mathbf{\sigma}} = \frac{\hbar}{2}$$

which essentially represents the **minimum uncertainty description**. The equality in the Heisenberg uncertainty principle is only valid for Gaussian functions. For any other function $\Delta x \cdot \Delta p > \hbar/2$. In qualitative terms, the uncertainty principle states that the greater the spread of the amplitude function, the narrower the extent of the wavefunction and the position probability density of the state.

Normalization of the amplitude function:

From the normalization condition for the wavefunction, one has that:

$$\int \psi^*(x,0)\psi(x,0)dx = 1 = \int \phi^*(k)\phi(k)dk$$

which is also known as the Bessel-Parseval theorem.

Observables in quantum physics:

- > The position probability amplitude $\psi(x,t)$ and the momentum state function $\phi(k)$ are state descriptors for a microscopic system.
- > The second class of basic elements are the observables, which represent the physical attributes of a system that can be measured in a laboratory. Examples of observables are position x(t), momentum p(t) and energy E(x(t),p(t)]. The problem of applying a classical definition of observables for quantum states is that it is impossible to measure the properties of a microscopic system without altering its state.

Approach 2:

If position probability amplitude $\psi(x,t)$ is the quantity that is available to us, it is easier to calculate the momentum expectation value and its uncertainty by using the **position** representation for the momentum operator. The later is obtained in the following manner:

➤ Start with the definition of :

$$= \int \phi^*(k)\hbar k\phi(k)dk$$

Use the fact that:

$$k\phi(k) = \frac{1}{i\sqrt{2\pi}} \int \frac{\partial\psi(x,t)}{\partial x} e^{ikx} dx$$

Substituting this into the expression for gives:

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

We discovered here an operator, i.e. a mathematical instruction that extracts the value of the momentum from the wavefunction in position representation, i.e.

$$\hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial x}$$
 \Rightarrow position representation of the momentum operator

<u>Third postulate of Quantum Mechanics</u>:

Every observable in quantum mechanics is represented by an operator which is used to obtain physical information about the observable from the state function. For an observable that is represented in classical physics by a function Q(x,p), the corresponding operator is $Q(\hat{x}, \hat{p})$.

Observable	Operator
Position	\widehat{x}
Momentum	$\widehat{p} = \frac{\hbar}{i} \frac{\partial}{\partial x}$
Energy	$E = \frac{\hat{p}^2}{2m} + V(\hat{x}) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$

2.4 Operators - Brief introduction

- An operator is an instruction, a symbol which tells us to perform one or more mathematical acts on a function, say f(x). The essential point is that they act on a function.
- > Operators act on everything to the right, unless the action is constrained by brackets.
- Addition and subtraction rule for operators:

$$\left(\widehat{Q}_1 \pm \widehat{Q}_2\right) f(x) = \widehat{Q}_1 f(x) \pm \widehat{Q}_2 f(x)$$

> The product of two operators implies succesive operation:

$$\widehat{Q}_1 \widehat{Q}_2 f(x) = \widehat{Q}_1 \left[\widehat{Q}_2 f(x) \right]$$

> The product of two operators is a third operator:

 $\hat{Q}_3 = \hat{Q}_1 \hat{Q}_2$

> Two operators commute if they obey the simple operator expression:

$$\left[\hat{Q}_1, \hat{Q}_2\right] = \hat{Q}_1 \hat{Q}_2 - \hat{Q}_2 \hat{Q}_1 = 0 \quad \Rightarrow \quad \hat{Q}_1 \hat{Q}_2 = \hat{Q}_2 \hat{Q}_1$$

Note:

The requirement for two operators to be commuting operators is a very important one in quantum mechanics and it means that we can simultaneously measure the observables represented with these two operators. The non-commutivity of the position and the momentum operators (the inability to simultaneously determine particles position and its momentum) is represented with the Heisenberg uncertainty principle, which in mathematical form is expressed as:

$$\Delta x \cdot \Delta p \ge \frac{\hbar}{2} = \frac{1}{2} \left| \left\langle \left[\hat{x}, \, \hat{p} \right] \right\rangle \right|,$$

and can be generalized for any pair of observables.

2.5 The Schrödinger wave equation

1926 Erwin Schrödinger proposed an equation that describes the evolution of a quantummechanical system \rightarrow SWE which represents quantum equations of motion, and is of the form:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x)\psi(x,t) = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi(x,t) = i\hbar\frac{\partial\psi}{\partial t}$$

This work of Schrödinger was stimulated by a 1925 paper by Einstein on the quantum theory of ideal gas, and the de Broglie theory of matter waves.

Note:

Examining the time-dependent SWE, one can also define the following operator for the total energy:

$$\widehat{E} = i\hbar \frac{\partial}{\partial t}$$

Fourth (Fundamental) postulate of Quantum mechanics:

The time development of the state functions of an isolated quantum system is governed by the time-dependent SWE $\hat{H}\psi = i\hbar\partial\psi/\partial t$, where $\hat{H} = \hat{T} + \hat{V}$ is the Hamiltonian of the system.

Note on isolated system:

The TDSWE describes the evolution of a state provided that no observations are made. An observation alters the state of the observed system, and as it is, the TDSWE can not describe such changes.