

Principles of Quantum Mechanics

1 More on Energy Eigenfunctions

In classical mechanics, we identify the forces acting on a particle and write down Newton's law of motion. This enables us to identify its acceleration. We integrate it to obtain its velocity and position. From these we can calculate its energy, angular momentum etc. Having done these calculations, we then compare them with the experimentally measured values of the above quantities.

In quantum mechanics, the prescription so far is that we identify the potential under whose influence the particle is moving and write down the corresponding time dependent Schroedinger equation. From this we are naturally led to time independent Schroedinger equation, containing the same potential. Solution of this equation gives us **discrete** energy eigenfunctions and energy eigenvalues. We also emphasized the following properties these eigenfunctions must satisfy.

1. The probability of finding the particle in the region $x \pm dx/2$ has to be **unique**. Which means $\phi(x)$ has to be **single valued**.
2. Since E is finite, time independent Schroedinger equation implies that the second derivative $d^2\phi(x)/dx^2$ is finite for all x . This implies that the first derivative $d\phi(x)/dx$ also must exist. This, in turn, means that $\phi(x)$ must be **continuous** and **differentiable**.
3. The wave function must be finite for all x and must vanish as $x \rightarrow \pm\infty$.
4. The integral

$$\int_{-\infty}^{\infty} |\phi(x)|^2 dx,$$

must be finite. OR the wave function should be **normalizable**.

I will demonstrate explicitly in later classes, but it is straight forward to see that discrete set of eigentfunctions (and their eigenvalues) can be labelled by positive integers. So, we have a set of eigenfunctions, $\phi_n(x)$ with eigenvalues

E_n , all of which satisfy time independent Schroedinger equation with potential $V(x)$. We also saw that the time evolution of energy eigenfunctions is particularly simple.

$$\phi_n(x, t) = e^{-iE_n t/\hbar} \phi_n(x),$$

where we assumed that $\phi_n(x, 0) = \phi_n(x)$. It can be shown (highly non-trivial) that the energy eigenfunctions of any potential $V(x)$ satisfy the **orthogonality condition**

$$\int_{-\infty}^{\infty} \phi_m^*(x) \phi_n(x) dx = 0 \quad \text{for } m \neq n.$$

Suppose a particle, moving under the influence of $V(x)$, has the wave function $\phi_n(x)$ at $t = 0$. The probability of finding this particle in the range $x \pm dx/2$ is given by $|\phi_n(x)|^2 dx$. Consider the same particle at a later time t . Its wave function is $\phi_n(x, t)$ and the probability of finding the particle, at time t , in the region $x \pm dx/2$ is $|\phi_n(x, t)|^2 dx = |\phi_n(x)|^2 dx$! It is exactly the same probability we had $t = 0$ and, is **independent of time!** In words, we say this as **if a particle is in an energy eigenstate at $t = 0$ and is not undisturbed, then it remains in the same energy eigenstate at all times.** This is also the reason, the energy eigenstates are called **stationary states**. Note that I have made a *subtle* change of language. Previously, $\phi_n(x)$ were called energy eigenfunctions. That was a *mathematical* definition, where $\phi_n(x)$ were simply eigenfunctions of a given differential equation. Here, we are switching to a physics based view point and we call $\phi_n(x)$ an **energy eigenstate** because it represents the wave function of a particle with energy E_n .

Consider a general wave function of the form, at time $t = 0$,

$$\psi(x) = \sum_n C_n \phi_n(x),$$

where C_n are numbers (which, in general, can be complex). Using the orthogonality of $\phi_n(x)$, it is straight forward to show that the normalization of $\psi(x)$ leads to the constraint $\sum_n |C_n|^2 = 1$. Now, operate the Hamiltonian $H = [p^2/2m + V(x)]$ on $\psi(x)$. You will get

$$H \sum_n C_n \phi_n(x) = \sum_n C_n H \phi_n(x) = \sum_n C_n E_n \phi_n(x).$$

The RHS of the above equation **can not** be written as $E \sum_n C_n \phi_n(x)$. So a linear combination of energy eigenfunctions **is not** a solution to time independent Schroedinger equation. But, now consider the same wave function

at a later time. Since $\phi_n(x)$ becomes $\phi_n(x, t)$ at a later time, we will have

$$\psi(x, t) = \sum_n C_n \phi_n(x, t) = \sum_n C_n e^{-iE_n t/\hbar} \phi_n(x).$$

It is straight forward to show, by direct substitution, that $\psi(x, t)$ satisfies **time dependent Schroedinger equation**. We can construct general wave functions by taking linear combinations of energy eigenstates. Even though such wave functions **are not solutions** of time independent Schroedinger equation, they **are solutions** of time dependent Schroedinger equation and hence **can represent a state of the particle**. In particular, $|\psi(x, t)|^2 dx$ gives the probability of finding the particle in the region $x \pm dx/2$ at time t .

2 Physical Observables and Operators

Given the problem of a particle of mass m moving under the influence of potential $V(x)$, we learnt that

- we should solve time independent Schroedinger equation to find energy eigenfunctions and energy eigenvalues
- we can construct a general wave function by taking linear combinations of energy eigenfunctions.
- this general wave function represents the **state** of the particle and also gives the probability of finding the particle in the region $x \pm dx/2$, at time t , by $|\psi(x, t)|^2 dx$.

However, in an experiment, the quantities that are measured are the position/momentum/energy of the particle. Given the wave function, how do we calculate these quantities? Also, what do we mean by the statement **the wave function represents the state of the particle**?

To make the connection between physical observables and the probabilistic interpretation of the wave function, we introduce **Operators**. Let us take the example of the observable **position**. Given that $|\psi(x, t)|^2 dx$ is the probability of finding the particle in the region $x \pm dx/2$, the **expected value of the position** (or the average value of the position) is

$$\begin{aligned} \langle x(t) \rangle &= \int_{-\infty}^{\infty} x |\psi(x, t)|^2 dx \\ &= \int_{-\infty}^{\infty} \psi^*(x, t) x \psi(x, t) dx, \end{aligned}$$

where $\psi^*(x, t)$ is the complex conjugate of $\psi(x, t)$. Now we define **position Operator** X (quite often denoted by \hat{X} , where "hat" symbol is added to emphasize that it is an operator). When this operator **acts** on a wave function, the net result is

$$X\psi(x, t) = x\psi(x, t).$$

You can say that $\psi(x, t)$ is an eigenfunction of the operator X , with eigenvalue x . With this definition of X and its action on $\psi(x, t)$, we see that the expectation value of the position is

$$\langle x(t) \rangle = \int_{-\infty}^{\infty} \psi^*(x, t) X \psi(x, t) dx.$$

Now we address the more general problem. Given the wave function $\psi(x, t)$ of a particle, how do we find the corresponding physical observables. We do two things:

1. We identify a suitable operator \mathcal{O} which corresponds to the physical observable.
2. We calculate the **expectation value** of the physical observable by calculating

$$\langle \mathcal{O}(t) \rangle = \int_{-\infty}^{\infty} \psi^*(x, t) \mathcal{O} \psi(x, t) dx.$$

We have already identified the operator for position. For momentum, the operator is already defined by Schroedinger $p = -i\hbar d/dx$. In three dimensions, it is $\vec{p} = -i\hbar \nabla$, where

$$\nabla = \hat{i} \frac{\partial}{\partial x} + \hat{j} \frac{\partial}{\partial y} + \hat{k} \frac{\partial}{\partial z}.$$

The expectation value of the momentum is given by

$$\langle p(t) \rangle = \int_{-\infty}^{\infty} \psi^*(x, t) \left[-i\hbar \frac{d\psi(x, t)}{dx} \right] dx.$$

The operator for energy, as mentioned in last week, is the Hamiltonian $H = p^2/2m + V(x)$. More explicitly,

$$\begin{aligned} H &= -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \quad \text{in one - dimension} \\ &= -\frac{\hbar^2}{2m} \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] + V(x, y, z) \quad \text{in three - dimensions} \end{aligned}$$

The expectation value of energy is

$$E(t) = \langle H(t) \rangle = \int_{-\infty}^{\infty} \psi^*(x, t) H \psi(x, t) dx.$$

We can substitute $\psi(x, t)$ to be a linear combination of the energy eigenfunctions, as mentioned above. We get

$$\begin{aligned} E(t) &= \int_{-\infty}^{\infty} \sum_m C_m^* e^{iE_m t/\hbar} \phi_m^*(x) H \sum_n C_n e^{-iE_n t/\hbar} \phi_n(x) dx \\ &= \int_{-\infty}^{\infty} \sum_m C_m^* e^{iE_m t/\hbar} \phi_m^*(x) \sum_n C_n E_n e^{-iE_n t/\hbar} \phi_n(x) dx \\ &= \sum_n |C_n|^2 E_n \end{aligned}$$

The last step is non-trivial but not very complicated. It follows if you use the orthogonality of the energy eigenfunctions. The **expectation value of the energy does not depend on time**, which is a consequence of the energy conservation.

In addition to calculating the expectation values, we can also calculate the uncertainties in various physical quantities using definitions, very similar to those above. For a given operator \mathcal{O} , we can define

$$\langle \mathcal{O}^2(t) \rangle = \int_{-\infty}^{\infty} \psi^*(x, t) \mathcal{O}^2 \psi(x, t) dx.$$

For example, the expectation value of $p^2(t)$ is

$$\langle p^2(t) \rangle = \int_{-\infty}^{\infty} \psi^*(x, t) \left[-\hbar^2 \frac{d^2 \psi(x, t)}{dx^2} \right] dx.$$

Given the two quantities, $\langle \mathcal{O}^2(t) \rangle$ and $\langle \mathcal{O}(t) \rangle$, the uncertainty is defined as

$$\Delta \mathcal{O}(t) = \left[\langle \mathcal{O}^2(t) \rangle - \langle \mathcal{O}(t) \rangle^2 \right]^{1/2}$$

Note that the definition of the uncertainty given above is essentially the same one used to define **standard deviation** in statistics. Thus, a knowledge of the wave function of a particle, enables us to calculate the expectation values and the uncertainties any physical observable. That is the meaning of the statement **the wave function defines the state of the particle**.