

Lecture 2: Operators, Eigenfunctions and the Schrödinger Equation

1 Operators, eigenfunctions, eigenvalues

Corresponding to every physical observable in Classical Mechanics, there is an operator in quantum mechanics which operates on the wavefunction(state) to produce another wavefunction. Thus we have

$$\hat{O}\psi = \psi'$$

All operators in quantum mechanics can be constructed from the basic operators for position and momentum.

$$\begin{aligned}\hat{x}\psi &= x \times \psi \\ \hat{p}_x\psi &= -i\hbar \frac{\partial}{\partial x}\psi\end{aligned}$$

There are some generic properties of operators corresponding to observables. Firstly, they are linear operators so

$$\hat{O}(a\psi_1 + b\psi_2) = a\hat{O}\psi_1 + b\hat{O}\psi_2$$

Thus the form of operators includes multiplication by functions of position and derivatives of different orders of x , but no squares or other powers of the wavefunction or its derivatives. For a particle in 1-dimension, we have the kinetic energy operator derived as follows:

$$\hat{T} = \frac{\hat{p}_x^2}{2m} = \frac{\hat{p}_x\hat{p}_x}{2m} = \frac{-\hbar^2}{2m} \frac{d^2}{dx^2}$$

Similarly, the potential energy is a function of x and is denoted by $V(x)$. The operator for the potential energy is given by

$$\hat{V} = V(x) \times$$

In higher dimensions, we can construct operators for vector quantities and distances as follows:

$$\begin{aligned}\hat{\vec{r}} &= \vec{r} \times \\ \hat{r} &= |\hat{\vec{r}}| = r \times\end{aligned}$$

Two operators \hat{O}_1 and \hat{O}_2 are said to commute if

$$\hat{O}_1\hat{O}_2\psi = \hat{O}_2\hat{O}_1\psi$$

for all ψ . If two operators commute, they can be simultaneously determined precisely. You should check that \hat{x} and \hat{p}_x do not commute. In fact, the form of these operators is chosen to satisfy the uncertainty principle.

Given an operator \hat{O} , it is possible to find a wavefunction $\psi(x)$ such that

$$\hat{O}\psi(x) = \lambda\psi(x)$$

where λ is a constant independent of x . The function ψ is called an eigenfunction of \hat{O} and λ is the corresponding eigenvalue of \hat{O} . Note that, if $\psi(x)$ is an eigenfunction with eigenvalue λ , then $a\psi(x)$ is also an eigenfunction with the same eigenvalue λ . Thus multiplying an eigenfunction by a constant does not change the eigenvalue.

Eigenvalues are related to observed values in experimental measurements as follows. In a single experiment, the measured value is an eigenvalue. In a large number of measurements (or measurement over a long period of time), the measured values is the expectation value or the average value defined as

$$\langle O \rangle = \int_{\mathcal{S}} \psi^*(x)\hat{O}\psi(x)dx$$

where it is assumed that $\psi(x)$ is normalized, so $\int_{\mathcal{S}} \psi^*(x)\psi(x)dx = 1$.

Notice that the expectation value of an eigenfunction state is simply the eigenvalue. If there are two different eigenfunctions with the same eigenvalue, then the eigenfunctions are said to be degenerate eigenfunctions.

Consider two eigenfunctions ψ_1 and ψ_2 of an operator \hat{O} with corresponding eigenvalues λ_1 and λ_2 respectively. The operator \hat{O} is called a Hermitian operator if all its eigenvalues are real and its eigenfunctions corresponding to different eigenvalues are orthogonal so that

$$\int_{\mathcal{S}} \psi_1^*(x)\psi_2(x)dx = 0$$

if $\lambda_1 \neq \lambda_2$. It turns out that even if we have two degenerate eigenfunctions, we can construct orthogonal eigenfunctions.

A wavefunction that is not an eigenfunction can be expanded as a linear combination of eigenfunctions

$$\psi(x) = c_1\psi_1(x) + c_2\psi_2(x)$$

Verify that if $\psi_1(x)$ and $\psi_2(x)$ are normalized, then the normalized wavefunction is

$$\psi(x) = \frac{1}{\sqrt{c_1^2 + c_2^2}}c_1\psi_1(x) + c_2\psi_2(x)$$

A generalization of the above statement is the superposition principle

2 Superposition principle

Any wavefunction can be written as a linear combination of eigenfunctions of any operator.

$$\psi(x) = c_1\psi_1(x) + c_2\psi_2(x) + c_3\psi_3(x) + \dots$$

We can show that the expectation value of the observable O is given by

$$\langle \hat{O} \rangle = \frac{1}{\sqrt{c_1^2 + c_2^2}} (c_1^2\lambda_1 + c_2^2\lambda_2 + \dots)$$

The superposition principle is really the heart of the difference between QM and CM. The fact that particles are described by waves whose amplitudes can be added and combined allows mixing of states, something that has no parallel in CM.

Before we go to the next section, we make a little point about the eigenvalue equation.

$$\hat{O}\psi = \lambda\psi$$

This single equation will yield both the allowed values of λ and the corresponding ψ . If the operator has a differential in it, then this equation becomes a differential equation. A crucial question that will be addressed in the following sections is whether the eigenvalues are countable (discrete) or continuous. It turns out that the boundary conditions for the eigenvalue equations will necessarily restrict the set of allowed eigenfunctions and eigenvalues for the system.

3 The equation of motion of the wavefunction

We now move on to an operator called the Hamiltonian operator which plays a central role in quantum mechanics. The Hamiltonian operator corresponds to the total energy of the system. For a single particle moving in 1-dimensions in a potential $V(x)$, the Hamiltonian operator is given by

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$$

In 3-D, we can write

$$\hat{H} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(\vec{r}) = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r})$$

For a many particle system, we have to write the expression for the total energy which consists of the kinetic energy of the particles and the total potential energy of the system. For two particles in 3-dimensions, we can write

$$\hat{H} = -\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 + V(\vec{r}_1, \vec{r}_2)$$

where

$$\nabla_1^2 = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2}$$

and so on. If the particles are interacting via a central potential and there is no external field, then

$$V(\vec{r}_1, \vec{r}_2) = V(|\vec{r}_1 - \vec{r}_2|) = V(r)$$

For example, if the particles are charged particles with charges q_1 and q_2 , then

$$V(r) = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r}$$

In general, you should be able to write the Hamiltonian operator for most simple systems.

The Hamiltonian operator plays a central role in the time dependent evolution of the wavefunction. A time-dependent wavefunction will have its equation of motion given by the **Time dependent Schrödinger equation(TDSE)**

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi$$

Thus the Hamiltonian operator is central to the time-evolution of the system. The above equation is independent of the number of particles. It is a fundamental equation that describes the motion of a quantum mechanical system.

4 Eigenvalues of the Hamiltonian operator, quantization

If there is an eigenfunction ψ of the Hamiltonian operator with energy eigenvalue E , i.e. $\hat{H}\psi = E\psi$, then the time-evolution of the wavefunction starting from ψ at $t=0$ is given by the solution of the TDSE

$$\psi(t) = \psi e^{iEt/\hbar}$$

Note that the wavefunction does not change amplitude but only changes phase. Thus, all eigenvalues are the same. In particular, the energy does not change with time. Therefore, an energy eigenstate is called a Stationary state.

Stationary states are of fundamental importance in description of quantum systems. Therefore, the eigenvalue equation

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

is referred to as the **Time-Independent Schrödinger equation(TISE)**.

For a particle in 1D, we can see that the TISE is a 2nd order Differential equation, that can be solved for any value of E . However, as we shall see, the boundary conditions

of the system and the various properties of the wavefunction will impose restrictions on the allowed values that E can take for there to exist a solution of the TDSE. This will lead to quantization of energy.

For the remaining part of this course, our focus will be on solving the TISE and obtaining the allowed values of energy and their corresponding eigenfunctions for simple systems.

The methodology we adopt in all the systems is the same:

1. Decide on the variables of the system and the boundary conditions.
2. Write the Hamiltonian operator including the kinetic energy and the potential energy.
3. If necessary, simplify the TISE (Separation of variables, change of coordinates, etc.).
4. Solve the various pieces of the TISE and combine them to the final solutions
5. Analyze the solutions

We will put this methodology into action in the next few lectures.