PH 107: Quantum Physics and applications

Operators, Separation of variables and superposition of states

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Operators continued ……

For every physical quantity (observables) there is an operator.

Consider an operators such that $\hat{O}$ such that ; $\hat{O}\ \Psi(x,t) = \alpha\Psi(x,t)$

$\hat{O}\ \ is\ an\ \boldsymbol{operator}, operation\ on$ $\Psi(x,t)$ gives back $\Psi(x,t)$.

- $\Psi(x,t)$ is an **eigen function** for operator $\hat{O}$.
- $\boldsymbol{\alpha}$ is an **eigen value** . In general, eigen values are related to an Observables.

Expectation value is the average value of an operator (O) that one would get after a very large number of measurements are made on identical systems.

The expectation value of x

$$\langle\hat{X}\rangle = \frac{\int_{-\infty}^{\infty} \Psi^{*} \hat{X}\ \Psi dx}{\int_{-\infty}^{\infty} \Psi^{*} \Psi dx}$$

where Ψ^* is the **complex conjugate** of Ψ

Recap

Momentum operator $\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$

$$\boxed{\hat{p}_x \Psi(x,t) = p_x \Psi(x,t)}$$

$$\langle p_x \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t)\left(-i\hbar \frac{\partial}{\partial x}\right)\Psi(x,t)dx = -i\hbar \int_{-\infty}^{\infty} \Psi^*(x,t)\frac{\partial}{\partial x}\Psi(x,t)dx$$

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

$$\boxed{\hat{E}\Psi(x,t) = E\Psi(x,t)}$$

$$\langle E \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t)\left(i\hbar \frac{\partial}{\partial t}\right)\Psi(x,t)dx = i\hbar \int_{-\infty}^{\infty} \Psi^*(x,t)\frac{\partial}{\partial t}\Psi(x,t)dx$$

Kinetic energy operator $\hat{K} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$

$$\boxed{\hat{K}\Psi(x,t) = K\Psi(x,t)}$$

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

Commuting and Non-commuting Operators

Consider two operators $\widehat{\mathrm{A}}$ and $\widehat{\mathrm{B}}$, and perform the operation

$$\hat{A}\left(\hat{B}\,f(x)\right)\;-\hat{B}\,\left(\hat{A}\,f(x)\right)=\;\left(\hat{A}\hat{B}-\hat{B}A\right)f(x)$$

$Notation,\left[\hat{A},\hat{B}\right]$ = $\hat{A}\hat{B}-\hat{B}A$ is called commutator

Two operators $\widehat{\mathrm{A}}$ and $\widehat{\mathrm{B}}$ are said to be **commuting** if $\left[\hat{A},\hat{B}\right]=0$

Order in which the operators operate is not important ($\hat{A}\hat{B}=\hat{B}A$).

Two operators $\widehat{\mathrm{A}}$ and $\widehat{\mathrm{B}}$ are said to be **commuting** if $\left[\hat{A},\hat{B}\right]\neq 0$

Order in which the operators operate is important.

Heisenberg Uncertainty relation and Commuting Operators

- Heisenberg Uncertainty relation involves Non-commuting operators.

- Observables belonging to Non-commuting operators cannot be measured with unlimited precision.

- Observables belonging to commuting operators can be measured simultaneously with unlimited precision.

Position - Momentum and Energy-time are set of Non-Commuting operators

Lets Check for $\widehat{p_x}$ and $\hat{X}$.

Commutator of $\left[\hat{X}, \widehat{p_x}\right]$

$$(\hat{x}\,\widehat{p_x} - \widehat{p_x}\hat{x})\,\psi(x) = \hat{x}\left(-i\hbar\frac{\partial\psi(x)}{\partial x}\right) - \left(-i\hbar\frac{\partial}{\partial x}\right)\hat{x}\,\psi(x)$$

$$= -i\hbar\hat{x}\left(\frac{\partial\psi(x)}{\partial x}\right) + \left(i\hbar\frac{\partial\,(x\psi(x))}{\partial x}\right)$$

$$= -i\hbar\hat{x}\left(\frac{\partial\psi(x)}{\partial x}\right) + i\hbar\,\psi(x) + \left(i\hbar\,x\frac{\partial\,\psi(x)}{\partial x}\right)$$

Therefore,

$$(\hat{x}\,\widehat{p_x} - \widehat{p_x}\hat{x})\,\psi(x) = i\hbar\,\psi(x)$$

$$\Rightarrow \quad \left[\hat{X}, \widehat{p_x}\right] = i\hbar$$

Position and Momentum operators do not commute !

Hermitian Operators

An operator $\hat{O}$ is called Hermitian, if

$$\int_{-\infty}^{\infty} \psi^*(x)\hat{O}\psi(x)dx = \int_{-\infty}^{\infty} (\hat{O}\psi(x))^*\psi(x)dx$$

1. Expectation values of Hermitian operator are real.

$$\langle\hat{O}\rangle = \int_{-\infty}^{\infty} \Psi^*\hat{O}\,\Psi dx$$

$$\langle\hat{O}\rangle^* = \left[\int_{-\infty}^{\infty} \Psi^*\hat{O}\,\Psi dx\right]^* = \int_{-\infty}^{\infty} \Psi\hat{O}^*\Psi^* dx$$

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

$\Rightarrow$ $\langle\hat{O}\rangle^* = \langle\hat{O}\rangle$

$\langle\hat{O}\rangle$ is real and is Hermitian operator.

Hermitian Operators

An operator $\hat{O}$ is called Hermitian, if

$$\int_{-\infty}^{\infty} \psi^*(x)\hat{O}\psi(x)dx = \int_{-\infty}^{\infty} (\hat{O}\psi(x))^*\psi(x)dx$$

2. Eigen values of Hermitian operator are real.

$\hat{O}\ \Psi(x) = \alpha\Psi(x)$, α is the eigen value.

$$\int_{-\infty}^{\infty} (\hat{O}\psi(x))^*\psi(x)dx = \int_{-\infty}^{\infty} (\alpha\,\psi(x))^*\psi(x)dx = (\alpha)^*$$

Given $\hat{O}$ is an Hermitian Operator,

$$\int_{-\infty}^{\infty} (\hat{O}\psi(x))^*\psi(x)dx = \int_{-\infty}^{\infty} \psi^*(x)\hat{O}\psi(x)dx = \alpha \int_{-\infty}^{\infty} \psi^*(x)\psi(x)dx$$

$\Rightarrow$ $(\alpha)^* = \alpha$

Eigen value α, is real.

Position operator is Hermitian.

$$\int_{-\infty}^{\infty} (\hat{O}\psi(x))^* \psi(x) dx = \int_{-\infty}^{\infty} \psi^*(x) \hat{O} \psi(x) dx$$

LHS

$$\int_{-\infty}^{\infty} (\hat{x}\psi)^* \psi(x) dx = \int_{-\infty}^{\infty} (x\psi)^* \psi(x) dx$$

$$= \int_{-\infty}^{\infty} \psi^*(x)\, x\, \psi(x) dx$$

$$= \int_{-\infty}^{\infty} \psi^*(x) \hat{x} \psi(x) dx$$

Thus,

$$\boxed{\int_{-\infty}^{\infty} (\hat{x}\psi(x))^* \psi(x) dx = \int_{-\infty}^{\infty} \psi^*(x) \hat{x} \psi(x) dx}$$

$\hat{x}$ is an Hermitian Operator.

Momentum Operator is Hermitian.

$$\hat{P} = -i\hbar \frac{\partial}{\partial x}$$

$$\int_{-\infty}^{\infty} (\hat{P}\psi(x))^* \psi(x) dx = \int_{-\infty}^{\infty} \left(-i\hbar \frac{\partial}{\partial x} \psi(x)\right)^* \psi(x) dx$$

$$= i\hbar \int_{-\infty}^{\infty} \frac{\partial \psi(x)^*}{\partial x} \psi(x)\, dx = i\hbar \int_{-\infty}^{\infty} \frac{\partial \psi(x)^*}{\partial x} \psi(x)\, dx$$

Integrate by parts to show that $\hat{P}$ is Hermitian

$$\boxed{\int_{-\infty}^{\infty} (\hat{P}\psi(x))^* \psi(x) dx = \int_{-\infty}^{\infty} \psi^*(x) \hat{P} \psi(x) dx}$$

Position operator : $\hat{x}$

Momentum operator: $\hat{p}_x = -i\hbar \dfrac{\partial}{\partial x}$

Kinetic energy operator : $\widehat{K} = \dfrac{-\hbar^2}{2m}\dfrac{\partial^2}{\partial x^2}$

Hamiltonian : $\widehat{H} = KE + PE = -\dfrac{\hbar^2}{2m}\dfrac{\partial^2}{\partial x^2} + V(x)$

They are Hermitian operators

Their expectation values are real

They have real eigenvalues (observables)

Separation of variables

Separation of variables (Time Dependent SE (TDSE))

We are now convinced that we need to solve the TDSE to learn about the state of the particle, i.e. solve

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V\Psi \qquad (\textit{in 1 dimension})$$

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi \qquad (\textit{in 3 dimensions})$$

Assuming that V is not a function of t, we can try, as a solution (in 1D), a function of the type

$$\Psi(x,t) = \phi(x)\chi(t)$$

This is a physicist's first line of attack for a partial differential equation: **separation of variables.**

TDSE to Time Independent SE (TISE)

Lets substitute $\Psi(x,t) = \phi(x)\chi(t)$, in the equation,

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

$$i\hbar\phi\frac{d\chi}{dt} = -\frac{\hbar^2}{2m}\chi\frac{d^2\phi}{dx^2} + V\phi\chi$$

$$\Longrightarrow \quad i\hbar\frac{1}{\chi}\frac{d\chi}{dt} = -\frac{\hbar^2}{2m}\frac{1}{\phi}\frac{d^2\phi}{dx^2} + V$$

The LHS is a function of *t* only and the RHS is a function of *x* only. This can possibly be true if both sides were constants.

For, reasons which will be apparent soon, we call this constant E.

TDSE to Time Independent SE (TISE)

$$i\hbar \frac{1}{\chi}\frac{d\chi}{dt} = -\frac{\hbar^2}{2m}\frac{1}{\phi}\frac{d^2\phi}{dx^2} + V\phi$$

We get for the LHS, $i\hbar \frac{1}{\chi}\frac{d\chi}{dt} = E \longrightarrow \chi(t) = e^{-i\frac{E}{\hbar}t}$

For the RHS, $-\frac{\hbar^2}{2m}\frac{1}{\phi}\frac{d^2\phi}{dx^2} + V = E$ or

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2\phi}{dx^2} + V\phi = E\phi}$$

This is time independent Schrödinger Equation (TISE).

- For clarity, I will refer ϕ, as solution of TIDSE and χ is solute of TDSE.
- We cannot go any further with solving the TISE, unless we are given the form of $V = V(x)$. We will spend a lot of time in solving TISE for different types of $V(x)$.

What's special about the separable solutions ?

3 answers: 2 physical, 1 mathematical

1) Consider the separable solutions of the TDSE

$$\Psi(x,t) = \phi(x)\chi(t) = \phi(x)e^{-i\frac{E}{\hbar}t}$$

What is the probability density at $t = t_1$?

$\rho(x, t_1)$

What is the probability density at $t = t_2$?

$\rho(x, t_2)$

At any given time t, the probability density does not depend on time.

What's special about the separable solutions ?

Likewise, what is the expectation value of an operator $\hat{O}$, in the state $\Psi(x,t)$?

$$\langle \hat{O} \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{O} \Psi dx = \int_{-\infty}^{\infty} \phi^*(x) e^{+i\frac{E}{\hbar}t} \hat{O} \phi(x) e^{-i\frac{E}{\hbar}t} dx$$

$$= \int_{-\infty}^{\infty} \phi^*(x) \hat{O} \phi(x) dx$$

$\langle \hat{O} \rangle$ is independent of t. This implies that $\langle \hat{X} \rangle, \langle \hat{E} \rangle, \langle \hat{P} \rangle$, do not change with time in these states.

$\boldsymbol{\Psi(x,t) = \phi(x)\chi(t)}$ (or just $\boldsymbol{\phi(x)}$) are therefore called the stationary states.

Stationary states

A stationary state is a state with **constant** position, momentum (= 0) and other physical parameters, and **definite** (and therefore also constant) energy.

Definite value of a physical parameter means that the state is an **eigenstate** of the corresponding operator, with a fixed **eigenvalue**.

Constancy implies that the **average value** of the corresponding operator does not change with time.

In the stationary state , it is true for any operator $\hat{O}$ that

$$\langle \hat{O} \rangle (t) = \langle \hat{O} \rangle (0)$$

Time Independent SE (TISE)

2. Let's look at the TISE again

$$-\frac{\hbar^2}{2m}\frac{d^2\phi}{dx^2} + V\phi = E\phi$$

or equivalently

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V\right)\phi = E\phi$$

or

$$\left(\frac{\hat{P}^2}{2m} + \hat{V}\right)\phi = E\phi$$

Hamiltonian

$$\left(\frac{\hat{P}^2}{2m} + \hat{V}\right)\phi = E\phi$$

$\left(\frac{\hat{P}^2}{2m} + \hat{V}\right)$ is known as the **Hamiltonian** operator $\hat{H}$ which is the sum of the KE and the PE operators.

So we can write,

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

You need to remember that $\hat{H}$ is the (Hamiltonian) operator which acts on ϕ to multiply it with the constant E.

Energy can also be found from expectation value of $\hat{H}$.

Hamiltonian

Let’s find $\langle \hat{H} \rangle$

$$\langle \hat{H} \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{H} \Psi dx = \int_{-\infty}^{\infty} \phi^*(x) \hat{H} \phi(x) dx$$

$$= \int_{-\infty}^{\infty} \phi^*(x) E \phi(x) dx = E$$

So, we learn that the separation constant (E) we chose is the **total energy of the system** (of many particles, all in the state Ψ.)

Hamiltonian

Now $\langle \hat{H}^2 \rangle$

$$\langle \hat{H}^2 \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{H}^2 \Psi dx = \int_{-\infty}^{\infty} \phi^*(x) \hat{H}^2 \phi(x) dx$$

$$= \int_{-\infty}^{\infty} \phi^*(x) \hat{H} \left(\hat{H} \phi(x) \right) dx = \int_{-\infty}^{\infty} \phi^*(x) \hat{H} \left(E \phi(x) \right) dx$$

$$= E \int_{-\infty}^{\infty} \phi^*(x) \hat{H} \phi(x) dx = E^2$$

So, $\Delta H = \langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2 = E^2 - (E)^2 = 0$

This implies, every measurement of the energy yields exactly the same value E.

What's special about the separable solutions ?

Thus the separable solutions of the TDSE, Ψ, (or equivalently ϕ, the solutions of the TISE) are **states of definite or fixed energy**.

3. Finally, to the question: what about the other solutions or a general solution of the TDSE?

Answer: As we will see soon, the TISE yields an infinite collection of solutions $(\phi_1(x), \phi_2(x), \ldots)$ with energies $(E_1, E_2, \ldots)$.

General solution of the TDSE

Any solution of the TDSE can be written as

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n\, \phi_n(x) e^{-i\frac{E_n}{\hbar}t}$$

by using the right constants $(c_1, c_2, \ldots c_n)$.

How do we calculate the coefficients c_n?

Let us perform

$$\int \phi_n(x)^* \Psi(x,0) dx = \sum_{m=1}^{\infty} \int \phi_n(x)^* c_m \phi_m(x) dx$$

The integration limits will be decided by the problem we are trying to solve.

General solution of the TDSE

$$= \sum_{m=1}^{\infty} c_m \int_0^L \phi_n(x)^* \phi_m(x) dx = c_n$$

Since $\int \phi_m(x)^* \phi_n(x) dx = \delta_{m,n}$ **(orthonormality conditions)**

Thus, given a $\Psi(x, 0)$, we can find the coefficients c_n as

$$c_n = \int \phi_n(x)^* \Psi(x, 0) dx$$

This will be worked out for you for specific problems few class later.

Few Questions

$$\langle\hat{H}\rangle(t) = \bar{E}(t) = \int_0^L \Psi^*(x,t)\ \hat{H}\ \Psi(x,t)\ dx$$

$$= \sum_{n,m=1}^{\infty} c_m^* c_n \int_0^L \phi_m^*(x)\ e^{i\frac{E_m}{\hbar}t}\ E_n\ \phi_n(x)\ e^{-i\frac{E_n}{\hbar}t} dx$$

$$= \sum_{n,m=1}^{\infty} c_m^* c_n e^{-i\frac{(E_n - E_m)}{\hbar}t}\ E_n \int_0^L \phi_m^*(x)\ \phi_n(x)\ dx$$

$$= \sum_{n,m=1}^{\infty} c_m^* c_n e^{-i\frac{(E_n - E_m)}{\hbar}t}\ E_n\ \delta_{m,n}$$

$$= \sum_{n=1}^{\infty} |c_n|^2\ E_n \quad = \langle\hat{H}\rangle(0)$$

Few Questions

(a) If $\langle \hat{H} \rangle$ remains constant over time, is $\Psi(x,t)$ a stationary state?

No, stationary states are eigenstates of $\hat{H}$. So they have definite values of energy. Here, we see that $\langle \hat{H} \rangle$ remains constant, but $\Psi(x,t)$ is not an eigenstate of $\hat{H}$

(b) If the answer to (a) is no, then why does $\langle \hat{H} \rangle$ remain constant over time ?

That's just stating the statement of conservation of energy in the language of QM.

Examples: TISE for Stationary States

The TISE ;

$$-\frac{\hbar^2}{2m}\frac{d^2\phi}{dx^2}+V\phi=E\phi$$

We shall look at some simple examples of $V(x)$.