PH-107

Quantum Physics and Applications

Wave Functions and Operators

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Expectation values

If we make measurements of a dynamical variable (energy, momentum, position) on a large number of identical particles with the same wave function, we can talk of an expected (average) value of the variable.

Calculation of the expected or expectation values are done, just as we know from statistical calculations.

Expectation values

The expectation value of ***x*** $$< x >= \int_{-\infty}^{\infty} \Psi^* \; x \; \Psi \; dx$$

Here, Ψ^* is the **complex conjugate** of Ψ

This is true, provided Ψ is normalized.

Otherwise,

$$< x >= \frac{\int_{-\infty}^{\infty} \Psi^* \; x \; \Psi \; dx}{\int_{-\infty}^{\infty} \Psi^* \; \Psi \; dx}$$

Expectation values

Likewise,

$$< x^2 >= \int_{-\infty}^{\infty} \Psi^* \ x^2 \ \Psi \ dx$$

provided Ψ is normalized.

Otherwise,

$$< x^2 >= \frac{\int_{-\infty}^{\infty} \Psi^* \ x^2 \ \Psi \ dx}{\int_{-\infty}^{\infty} \Psi^* \ \Psi \ dx}$$

We can also calculate the expectation values of energy, momentum etc., but now we need to make use of the corresponding operators.

Expectation values

The expectation value of energy operator $\hat{E}$

$$< \hat{E} >= \int_{-\infty}^{\infty} \Psi^* \ \hat{E} \ \Psi \ dx = \int_{-\infty}^{\infty} \Psi^* \ \left(i\hbar \frac{\partial}{\partial t} \right) \ \Psi \ dx$$

Similarly, the expectation value of momentum operator $\hat{p}$

$$< \hat{p} >= \int_{-\infty}^{\infty} \Psi^* \ \hat{p} \ \Psi \ dx = \int_{-\infty}^{\infty} \Psi^* \ \left(-i\hbar \frac{\partial}{\partial x} \right) \ \Psi \ dx$$

We could also write

$$< \hat{X} >= \int_{-\infty}^{\infty} \Psi^* \ \hat{X} \ \Psi \ dx = \int_{-\infty}^{\infty} \Psi^* \ (x) \ \Psi \ dx$$

Expectation values

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Similarly, the expectation value of momentum operator $\hat{p}$

$$< \hat{p} >= \int_{-\infty}^{\infty} \Psi^* \ \hat{p} \ \Psi \ dx = \int_{-\infty}^{\infty} \Psi^* \ \left(-i\hbar \frac{\partial}{\partial x} \right) \ \Psi \ dx$$

The operator is sandwiched between Ψ^* and Ψ and integrated over the whole space.

TDSE

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

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

in 1D

or

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

in 3D

TDSE

Let us assume that *V* is not a function of *t*, then we can try the solution of

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

is 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**

So, after substituting the function, TDSE can be

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

TDSE

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

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

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*

LHS

$$i\hbar\frac{1}{\chi}\frac{d\chi}{dt} = E \quad \Longrightarrow \chi(t) = e^{-i\frac{E}{\hbar}t}$$

RHS

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

TDSE

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

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

Time-independent Schrödinger Equation (TISE)

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 $V = V(x)$.

What's special about the separable solutions ?

3 answers: 2 physical, 1 mathematical

TDSE and TISE

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 $t = t_1$?

$$\rho(x,t_1) = |\Psi(x,t_1)|^2 = \phi^*(x)e^{i\frac{E}{\hbar}t_1}\phi(x)e^{-i\frac{E}{\hbar}t_1} = |\phi(x)|^2$$

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

$$\rho(x,t_2) = |\Psi(x,t_2)|^2 = \phi^*(x)e^{i\frac{E}{\hbar}t_2}\phi(x)e^{-i\frac{E}{\hbar}t_2} = |\phi(x)|^2$$

The probability density does not depend on time

TDSE and TISE

Likewise, what is the expectation value of an operator $\hat{O}$

in the state $\Psi(x,t)$?

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

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

$< \hat{O} >$ is independent of *t*.

This implies that $< \hat{X} >, < \hat{E} >, < \hat{p} >$ do not change with time in these states.

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

TDSE and 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 equivalently

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

TDSE and TISE

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

$\left(\frac{\hat{p}^2}{2m} + \hat{V}\right)$ 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 Hamiltonian is the operator which acts on ϕ to multiply it with the constant *E*.

TDSE and TISE

Let's find $< \hat{H} >$

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

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

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).

TDSE and TISE

Now, $< \hat{H}^2 >$

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

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

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

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

TDSE and TISE

So,

$$\Delta H = < \hat{H}^2 > - < \hat{H} >^2 = E^2 - (E)^2 = 0$$

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

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

TDSE and TISE

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 $[\phi_1(x), \phi_2(x), ...]$ with energies $[E_1, E_2, ...]$

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, ……).

Definition of stationary states

Let us recall that...

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

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

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

We have not yet verified the constancy

Constancy of Momentum (and Energy)

The state of the particle at time *t*

$$\phi_n(x,t) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L} x\right) e^{-i\frac{E_n}{\hbar}t}$$

Therefore,

$$\begin{aligned}
\langle \hat{p} \rangle &= \int_0^L \phi_n^*(x,t)\ \hat{p}\ \phi_n(x,t)\ dx \\
&= \int_0^L \phi_n^*(x)\ \hat{p}\ \phi_n(x)\ dx = 0
\end{aligned}$$

As we saw before, it is true for any operator $\hat{O}$ that $\langle \hat{O} \rangle(t) = \langle \hat{O} \rangle(0)$ in the stationary states.

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.

Recommended Readings

Schroedinger equation, sections 6.1, 6.2 and 6.3.