

## Expectation values and the momentum operator

The expectation value of position is defined as

$$\langle x \rangle = \int_{-\infty}^{+\infty} x p(x,t) dx = \int_{-\infty}^{+\infty} x |\Psi(x,t)|^2 dx = \int_{-\infty}^{+\infty} \Psi^*(x,t) \cdot x \cdot \Psi(x,t) dx$$

Here we assume that we deal with a single particle moving in 1D. The above expectation (or mean) value gives us the average outcome of an experiment in which we prepare a large ensemble of systems in the same state  $\Psi(x,t)$  and measure the position,  $x$ , in each member of that ensemble. In other words it is the average over an ensemble, not the average over time. Quite contrary, if we pick a single system and repeatedly measure  $x$  we will get the same value  $x_0$  and over again because once the measurement is made the wave function collapses into the state that corresponds to  $x_0$ .

We can also consider other expectation values, for example  $\langle x^2 \rangle$ :

$$\langle x^2 \rangle = \int_{-\infty}^{+\infty} \Psi^*(x,t) x^2 \Psi(x,t) dx$$

Note that in general expectation values are functions of time.

We know that in classical mechanics  $\frac{dx}{dt} \equiv v$ . Since in quantum mechanics  $x$  is an independent variable (i.e. not a function of time  $x(t)$  we want to find) we cannot really compute  $\frac{dx}{dt}$ . However, we can consider another object -  $\frac{d\langle x \rangle}{dt}$ :

$$\frac{d\langle x \rangle}{dt} = \int_{-\infty}^{+\infty} \frac{\partial}{\partial t} [\Psi^*(x,t) \times \Psi(x,t)] dx = \int_{-\infty}^{+\infty} x \frac{\partial |\Psi|^2}{\partial t} dx$$

Using the Schrödinger equation and its complex conjugate (assuming that the potential  $V$  is real) we can calculate  $\frac{\partial |\Psi|^2}{\partial t} = \frac{\partial \Psi}{\partial t} \Psi^* + \Psi \frac{\partial \Psi^*}{\partial t}$ :

$$\frac{\partial |\Psi|^2}{\partial t} = \frac{i\hbar}{2m} \left( \Psi^* \frac{\partial^2 \Psi}{\partial x^2} - \frac{\partial^2 \Psi^*}{\partial x^2} \Psi \right) = \frac{\partial}{\partial x} \left[ \frac{i\hbar}{2m} \left( \Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) \right]$$

with that we have

$$\begin{aligned} \frac{d\langle x \rangle}{dt} &= \frac{i\hbar}{2m} \int_{-\infty}^{+\infty} x \frac{\partial}{\partial x} \left( \Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) dx \quad \text{integration by parts} \\ &= \frac{i\hbar}{2m} x \left( \Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) \Big|_{-\infty}^{+\infty} - \frac{i\hbar}{2m} \int_{-\infty}^{+\infty} \left( \Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) dx \\ &\quad \underbrace{\hspace{10em}}_{0 \text{ at end points}} \end{aligned}$$

$$= -\frac{i\hbar}{2m} \int_{-\infty}^{+\infty} \Psi^* \frac{\partial \Psi}{\partial x} dx + \frac{i\hbar}{2m} \int_{-\infty}^{+\infty} \frac{\partial \Psi^*}{\partial x} \Psi dx$$

If we integrate the last term by parts we will get the same expression as in the first term. Hence,

$$\frac{d\langle x \rangle}{dt} = -\frac{i\hbar}{m} \int_{-\infty}^{+\infty} \Psi^* \frac{\partial \Psi}{\partial x} dx$$

or if we multiply by  $m$

$$m \frac{d\langle x \rangle}{dt} = \int_{-\infty}^{+\infty} \Psi^* \left[ -i\hbar \frac{\partial}{\partial x} \right] \Psi dx$$

Based on the analogy with classical mechanics we can assume or postulate that

$$\frac{d\langle x \rangle}{dt} \equiv \langle v \rangle \quad \text{and} \quad m \frac{d\langle x \rangle}{dt} \equiv \langle p \rangle$$

With that the expectation value of the momentum is

$$\langle p \rangle = \int_{-\infty}^{+\infty} \Psi^* \left[ -i\hbar \frac{\partial}{\partial x} \right] \Psi dx$$

Hence, the expression for the momentum contains

$-i\hbar \frac{\partial}{\partial x}$  We will call that the momentum operator:

operator:

$$p_x \equiv -i\hbar \frac{\partial}{\partial x}$$

Now all classical dynamical variables can be expressed in terms of position and momentum:

$$T = \frac{p_x^2}{2m} \quad \text{— kinetic energy (in 1D)}$$

$$\vec{L} = \vec{r} \times \vec{p} \quad \text{— angular momentum}$$

This suggests us a way of computing expectation values of any quantities. We simply express everything in terms of  $x$  and  $p$ , then replace  $p$  with  $-i\hbar \frac{\partial}{\partial x}$ . For example

$$\langle T \rangle = \int_{-\infty}^{+\infty} \Psi^* \left[ \frac{\hat{p}_x^2}{2m} \right] \Psi dx = -\frac{\hbar^2}{2m} \int \Psi^* \frac{\partial^2 \Psi}{\partial x^2} dx$$

It is important not to mess with the order of operations here:  $\Psi^*$  comes first, then comes the operator that "acts" on  $\Psi$ . Also it is important to remember that  $\Psi$  is a complex function in general.

## Heisenberg uncertainty principle

One of the consequences of the particle-wave duality in quantum mechanics is the inability to

determine the momentum ( $p_x = \frac{h}{\lambda}$ ) and position (x) simultaneously:

$$\Delta x \cdot \Delta p_x \geq \frac{\hbar}{2}$$

Later in the course we will derive a more general expression for the uncertainty principle and we will do it more or less rigorously. For now let us see how the uncertainty principle works for the electron in the hydrogen atom

$$E = T + V = \frac{p^2}{2m} - \frac{1}{4\pi\epsilon_0} \frac{e^2}{r}$$

Let us assume that the uncertainties in  $p$  and  $r$  are of the same order of magnitude as the values themselves:

$$\Delta p \sim p \quad \Delta r \sim r$$

then

$$E \sim \frac{\Delta p^2}{2m} - \frac{1}{4\pi\epsilon_0} \frac{e^2}{\Delta r}$$

Using  $\Delta r \sim \frac{\hbar}{\Delta p}$  we get  $E = \frac{\Delta p^2}{2m} - \frac{e^2 \Delta p}{4\pi\epsilon_0 \hbar}$

Let us minimize the latter expression (in a search for the lowest energy state)

$$\min E \rightarrow \frac{\partial E}{\partial \Delta p} = 0 \Rightarrow \frac{\Delta p}{m} - \frac{e^2}{4\pi\epsilon_0 \hbar} = 0$$

$$\Delta p = \frac{me^2}{4\pi\epsilon_0 \hbar} \quad \Delta r = \frac{\hbar}{\Delta p} = \frac{4\pi\epsilon_0 \hbar^2}{me^2} \leftarrow \text{Bohr radius!}$$

$$E = \frac{1}{2m} \left( \frac{me^2}{4\pi\epsilon_0 \hbar} \right)^2 - \frac{e^2 me^2}{(4\pi\epsilon_0)^2 \hbar^4} = -\frac{1}{2} \frac{1}{(4\pi\epsilon_0)^2} \frac{me^4}{\hbar^2} \leftarrow \text{precisely the energy of the first Bohr orbit}$$

Now we can see why no energy lower than

$$E_1 = -\frac{1}{2} \frac{me^4}{\hbar^2} \quad (\text{approximately})$$

is possible.

The energy can be lowered by decreasing  $p$  or decreasing  $r$  in

$$E = \frac{p^2}{2m} - \frac{e^2}{r}$$

However, the uncertainty principle prevents such a possibility.

### Stationary states and time-independent Schrödinger equation

The solution of the Schrödinger equation is greatly simplified when the potential does not depend on time explicitly, i.e.  $V = V(x)$  (not  $V(x,t)$ ). In this case we can employ the method of separation of variables, in which we look for solutions in the form of a product

$$\Psi(x,t) = \psi(x)\varphi(t)$$

By plugging this expression into the Schrödinger equation

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

we obtain

$$i\hbar \psi(x) \frac{d\varphi(t)}{dt} = -\frac{\hbar^2}{2m} \varphi(t) \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x)\varphi(t)$$

Now let us divide everything by  $\psi(x)\varphi(t)$ .

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

Each side must be a constant (as  $t$  and  $x$  are independent variables). Let us call this constant  $E$ .

$$i\hbar \frac{1}{\psi} \frac{d\psi}{dt} = E \quad \text{or} \quad \frac{d\psi}{dt} = -\frac{iE}{\hbar} \psi$$

$$-\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{d^2\psi}{dx^2} + V = E \quad \text{or} \quad -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi = E\psi$$

$$\psi(t) = A e^{-\frac{iEt}{\hbar}}$$

$$\Psi(x,t) = \psi(x) e^{-\frac{iEt}{\hbar}}$$

Note that with such a form of  $\Psi(x,t)$  any operator's expectation value remains constant in time (as long as the operator is not explicitly dependent on time)

$$\langle Q \rangle = \int \psi^* Q(\hat{x}, \hat{p}) \psi dx \neq f(t)$$

and

$$|\Psi(x,t)|^2 = |\psi(x)|^2$$

$\Psi(x,t) = \psi(x) e^{-\frac{iEt}{\hbar}}$  are called stationary solutions to the Schrödinger equation. They are states of definite energy because they are eigenfunctions of the Hamiltonian.

$$H(p,x) = \frac{p^2}{2m} + V(x) \quad (\text{recall that } p = -i\hbar \frac{\partial}{\partial x})$$

Hence,

$$H\psi = E\psi \quad \leftarrow \text{stationary Schrödinger equation}$$

$$\text{and} \quad \langle H \rangle = \int \psi^* H\psi dx = E \int |\psi|^2 dx = E \int |\Psi(x,t)|^2 dx = E$$

$$\text{Similarly,} \quad \langle H^2 \rangle = E^2 \quad \text{and} \quad \Delta H = \sqrt{\langle H^2 \rangle - \langle H \rangle^2} = 0$$

The general solution in the method of separation

of variables  $i$  sought as a linear combination of  $\psi_{E_i}(x)\psi_{E_i}(t)$  where  $E_i$  are the allowed values of  $E$  (which must be determined by solving the equation  $H\psi_{E_i} = E_i\psi_{E_i}$ )

$$\Psi(x,t) = \sum_k c_k \psi_k(x) e^{-\frac{iE_k t}{\hbar}}$$

Note that  $c_k$ 's are constants (i.e. independent of time)