Operators

- The average value of the position of

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

- In quantum mechanics the average value of a physical quantity is also called an expectation value

- Its physical meaning: the average of repeated measurements on an ensemble of identically prepared systems

- How does the expectation value of x change with time?

$$\frac{d\langle x \rangle}{dt}$$

Operators

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

- **Thus:**

$$\langle v\rangle = \int_{-\infty}^{+\infty}\Psi^*\frac{\hbar}{im}\frac{\partial}{\partial x}\Psi dx$$

- **We can write:**

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

- **Synopsizing:**

$$\langle x\rangle = \int_{-\infty}^{+\infty}\Psi^*(x,t)\,x\,\Psi(x,t)dx \qquad \langle p\rangle = \int_{-\infty}^{+\infty}\Psi^*(x,t)\frac{\hbar}{i}\frac{\partial}{\partial x}\Psi(x,t)dx$$

Operators

- Defining operators of position and linear momentum:

$$\hat{x}\Psi(x,t) \equiv x\Psi(x,t) \qquad \hat{p}\Psi(x,t) \equiv \frac{\hbar}{i}\frac{\partial\Psi(x,t)}{\partial x}$$

- We can generalize the definition of an average on an operator:

$$\left\langle \hat{Q} \right\rangle = \int_{-\infty}^{+\infty} \Psi^* \hat{Q} \Psi dx$$

- Synopsizing:

$$\langle x \rangle = \int_{-\infty}^{+\infty} \Psi^*(x,t) x \Psi(x,t) dx \qquad \langle p \rangle = \int_{-\infty}^{+\infty} \Psi^*(x,t) \frac{\hbar}{i}\frac{\partial}{\partial x} \Psi(x,t) dx$$

Operators

- Defining **operators** of position and linear momentum:

$$\hat{x}\Psi(x,t) \equiv x\Psi(x,t) \qquad \hat{p}\Psi(x,t) \equiv \frac{\hbar}{i}\frac{\partial \Psi(x,t)}{\partial x}$$

- We can generalize the definition of an average on an operator:

$$\langle \hat{Q} \rangle = \int_{-\infty}^{+\infty} \Psi^{*} \hat{Q} \Psi dx$$

- For example:

$$\hat{T}\Psi = \frac{\hat{p}^{2}}{2m}\Psi = \frac{\hat{p}\hat{p}}{2m}\Psi = \frac{1}{2m}\frac{\hbar}{i}\frac{\partial}{\partial x}\left(\frac{\hbar}{i}\frac{\partial \Psi}{\partial x}\right) = -\frac{\hbar^{2}}{2m}\frac{\partial^{2}\Psi}{\partial x^{2}}$$

$$\hat{V}(x)\Psi = V(x)\Psi \qquad \hat{E}\Psi = (\hat{T}+\hat{V})\Psi = -\frac{\hbar^{2}}{2m}\frac{\partial^{2}\Psi}{\partial x^{2}} + V\Psi$$

Operators

- **The total energy operator is called the Hamiltonian:**

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

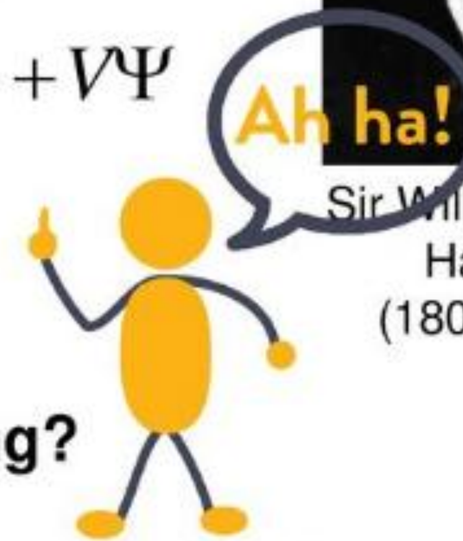
Sir William Rowan Hamilton (1805 – 1865)

- **Let's recall the Schrödinger equation:**

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

- **Thereby:**

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



- **Does this remind us of anything?**

$$\hat{E}\Psi = (\hat{T} + \hat{V})\Psi = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} + V\Psi$$

6.4 EXPECTATION VALUES OF DYNAMICAL VARIABLES

We have seen that in quantum mechanics a particle is represented by a wave function which can be obtained by solving the Schrödinger equation and contains all the available information about the particle. We shall now see how information concerning the dynamical variables of the particle can be extracted from the wave function Ψ. Since Ψ has a probabilistic interpretation, it turns out that exact information about the variables cannot be obtained. Instead, we obtain only the *expectation value* of a quantity, which is the average value of the measurements of the quantity performed on a very large number of independent identical systems represented by the wave function Ψ. Or, equivalently, it is the average of a large number of measurements on the same system.

First, let us consider the measurement of the position of the particle. Since $P(\mathbf{r}, t) = \Psi^*(\mathbf{r}, t)\,\Psi(\mathbf{r}, t)$ is interpreted as the position probability density at the point $\mathbf{r}$ at the time t, the *expectation value* of the position vector $\mathbf{r}$ is given by

$$\langle \mathbf{r} \rangle = \int \mathbf{r}\, P(\mathbf{r}, t)\, d\mathbf{r}$$

$$= \int \Psi^*(\mathbf{r}, t)\, \mathbf{r}\, \Psi(\mathbf{r}, t)\, d\mathbf{r} \tag{6.34}$$

where $\Psi(\mathbf{r}, t)$ is normalized. This equation is equivalent to the three equations

$$\langle x \rangle = \int \Psi^*\, x\, \Psi\, d\mathbf{r} \tag{6.35a}$$

$$\langle y \rangle = \int \Psi^*\, y\, \Psi\, d\mathbf{r} \tag{6.35b}$$

$$\langle z \rangle = \int \Psi^*\, z\, \Psi\, d\mathbf{r} \tag{6.35c}$$

The expectation value is a function only of the time because the space coordinates have been integrated out. Further, the expectation value of a physical quantity is always real. Note the order of the factors in the integrand—the vector $\mathbf{r}$ (or each of x, y, z) has been sandwiched between Ψ^* on the left and Ψ on the right. This is immaterial at this stage but is chosen for reason which will be clear shortly.

The *expectation value* of any quantity which is a function of $\mathbf{r}$ and t would be

$$\boxed{\langle f(\mathbf{r}, t) \rangle = \int \Psi^*(\mathbf{r}, t)\, f(\mathbf{r}, t)\, \Psi(\mathbf{r}, t)\, d\mathbf{r}} \tag{6.36}$$

As an example, the expectation value of the potential energy is

$$\langle V(\mathbf{r},t)\rangle = \int \Psi^*(\mathbf{r},t)\, V(\mathbf{r},t)\, \Psi(\mathbf{r},t) d\mathbf{r} \tag{6.37}$$

Let us now see how to obtain the expectation values for quantities which are functions of momentum or of both position and momentum. The most important example of the latter category is the energy. We assume that for this purpose it is possible to use the operator representations:

$$\hat{\mathbf{p}} = -i\hbar\, \boldsymbol{\nabla}$$

$$p^2 = -\hbar^2\, \nabla^2$$

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

The question that arises is: How these differential operators are to be combined with the position probability density $\Psi^*\Psi$ to obtain the desired expressions? This question is answered by using the classical expression for the energy

$$E = \frac{p^2}{2m} + V$$

and requiring, in accordance with the correspondence principle, that the expectation values satisfy

$$\langle E\rangle = \left\langle \frac{p^2}{2m}\right\rangle + \langle V\rangle$$

Replacing E and p^2 by the corresponding operators, we get

$$\left\langle i\hbar\frac{\partial}{\partial t}\right\rangle = \left\langle -\frac{\hbar^2}{2m}\nabla^2\right\rangle + \langle V\rangle \tag{6.38}$$

This equation must be consistent with the Schrödinger equation

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

Multiplying by Ψ^* on the left and integrating, we get

$$\int \Psi^*\left(i\hbar\frac{\partial}{\partial t}\right)\Psi d\mathbf{r} = \int \Psi^*\left(-\frac{\hbar^2\nabla^2}{2m}\right)\Psi d\mathbf{r} + \int \Psi^* V\Psi\, d\mathbf{r} \tag{6.39}$$

The last term on the right-hand side is simply $\langle V\rangle$. Therefore, (6.38) and (6.39) would be consistent provided the *expectation value is defined in the general case with the operator acting on* Ψ, *and multiplied by* Ψ^* *on the left*. We then have

$$\langle E\rangle = \int \Psi^*\, i\hbar\, \frac{\partial\Psi}{\partial t} d\mathbf{r} \tag{6.40}$$

$$\langle \mathbf{p}\rangle = \int \Psi^*\,(-i\hbar)\, \boldsymbol{\nabla}\Psi\, d\mathbf{r} \tag{6.41}$$

The last equation is equivalent to

$$\langle p_x \rangle = -i\hbar \int \Psi^* \frac{\partial \Psi}{\partial x}\, d\mathbf{r} \tag{6.42a}$$

$$\langle p_y \rangle = -i\hbar \int \Psi^* \frac{\partial \Psi}{\partial y}\, d\mathbf{r} \tag{6.42b}$$

$$\langle p_z \rangle = -i\hbar \int \Psi^* \frac{\partial \Psi}{\partial z}\, d\mathbf{r} \tag{6.42c}$$

Generalizing the above results, we are led to the following *postulate*:

Suppose, the dynamical state of a particle is described by the normalized wave function $\Psi(\mathbf{r}, t)$. Let $A(\mathbf{r}, \mathbf{p}, t)$ be a dynamical variable representing a physical quantity associated with the particle. We obtain the operator $\hat{A}(\mathbf{r}, -i\hbar\nabla, t)$ by performing the substitution $\mathbf{p} \to -i\hbar\nabla$, and then calculate the expectation value of A from the expression

$$\boxed{\langle A \rangle = \int \Psi^*(\mathbf{r}, t)\, \hat{A}(\mathbf{r}, -i\hbar\nabla, t)\, \Psi(\mathbf{r}, t)\, d\mathbf{r}} \tag{6.43}$$

Since the expectation value of a physical quantity is always *real*, i.e., $\langle A \rangle^* = \langle A \rangle$, it follows that the operator $\hat{A}$ must satisfy

$$\boxed{\int \Psi^* \hat{A} \Psi\, d\mathbf{r} = \int (\hat{A}\Psi)^* \Psi\, d\mathbf{r}} \tag{6.44}$$

Thus, the operator associated with a dynamical quantity must be *Hermitian*.