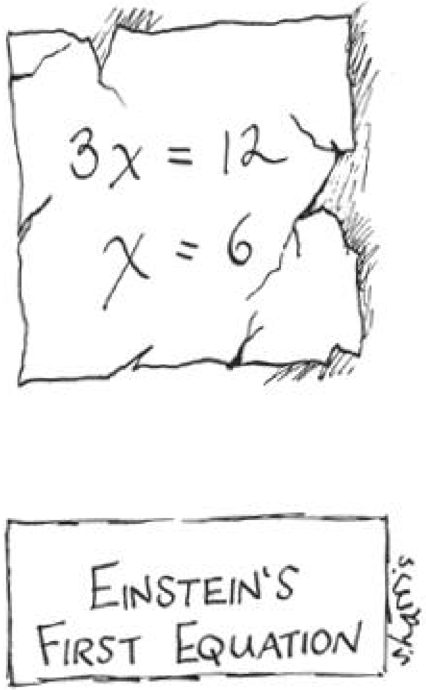
The representation of observables

...some simple formulae for operators



The recipe for cooking up operators

1. take classical variable
2. replace as follows:

$$x \rightarrow \boldsymbol{x}\psi = x\psi$$

$$p_x \rightarrow \boldsymbol{p_x}\psi = -i\frac{h}{2\pi}\frac{\partial\psi}{\partial x}$$

3. do the same for y and z
4. same applies to relations between variables

The position operator(s)

A vector* operator

$$\boldsymbol{R} = \boldsymbol{x}\vec{u}_x + \boldsymbol{y}\vec{u}_y + \boldsymbol{z}\vec{u}_z$$

operators act
only
on wavefunctions

where

$$\boldsymbol{x}\psi = x\psi, \quad \boldsymbol{y}\psi = y\psi \text{ and } \boldsymbol{z}\psi = z\psi$$

are the component operators

* Operators of this form are *not* ordinary 3d vectors!

The linear momentum operator(s)

A vector operator

$$\boldsymbol{p} = \boldsymbol{p_x}\vec{u}_x + \boldsymbol{p_y}\vec{u}_y + \boldsymbol{p_z}\vec{u}_z$$

where

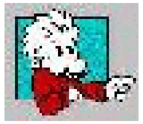
$$\boldsymbol{p_x}\Psi = -i\frac{h}{2\pi}\frac{\partial\Psi}{\partial x},\ \boldsymbol{p_y}\Psi = -i\frac{h}{2\pi}\frac{\partial\Psi}{\partial y} \text{ and } \boldsymbol{p_z}\Psi = -i\frac{h}{2\pi}\frac{\partial\Psi}{\partial z}$$

are the component operators

- *What is the operator for* p^2 *?*

Multiplication of operators

What does it mean to 'multiply' operators?



It means that we apply the operator to a wavefunction more than once:

e.g. $\boldsymbol{p}_{\boldsymbol{x}}^2\psi = \boldsymbol{p}_{\boldsymbol{x}}(\boldsymbol{p}_{\boldsymbol{x}}\psi)$ where $\boldsymbol{p}_{\boldsymbol{x}}\psi = -i\frac{h}{2\pi}\frac{\partial\psi}{\partial x}$

gives us

$$\boldsymbol{p}_{\boldsymbol{x}}^2\psi = \left(-i\frac{h}{2\pi}\right)\boldsymbol{p}_{\boldsymbol{x}}\left(\frac{\partial\psi}{\partial x}\right) = \left(-i\frac{h}{2\pi}\right)^2\frac{\partial}{\partial x}\left(\frac{\partial\psi}{\partial x}\right) = -\left(\frac{h}{2\pi}\right)^2\frac{\partial^2\psi}{\partial x^2}$$

The operator for orbital angular momentum

The classical representation (variable) is $\vec{L} = \vec{r} \times \vec{p}$, so the quantum mechanical representation (operator) will be $\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}$, which gives

$$\boldsymbol{L_x} = (\boldsymbol{yp_z} - \boldsymbol{zp_y}),\ \boldsymbol{L_y} = (\boldsymbol{zp_x} - \boldsymbol{xp_z}),\ \boldsymbol{L_z} = (\boldsymbol{xp_y} - \boldsymbol{yp_x})$$

For example,

$$\boldsymbol{L_x}\psi = (\boldsymbol{yp_z} - \boldsymbol{zp_y})\psi = \boldsymbol{yp_z}\psi - \boldsymbol{zp_y}\psi = \boldsymbol{y}(\boldsymbol{p_z}\psi) - \boldsymbol{z}(\boldsymbol{p_y}\psi)$$

$$\boldsymbol{L_x}\psi = -i\frac{h}{2\pi}\left(y\frac{\partial\psi}{\partial z} - z\frac{\partial\psi}{\partial y}\right)$$

The kinetic energy operator

We use the formula of classical mechanics:

$$\boldsymbol{K} = \frac{1}{2m}\boldsymbol{p}^2 = \frac{1}{2m}(\boldsymbol{p}_{\boldsymbol{x}}^2 + \boldsymbol{p}_{\boldsymbol{y}}^2 + \boldsymbol{p}_{\boldsymbol{z}}^2) = -\frac{1}{2m}\left(\frac{h}{2\pi}\right)^2 \tilde{N}^2$$

where

$$\tilde{N}^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

The total energy operator (when $E=K+V$)

We assume an object in motion (K) in a region of a potential V:

$$\boldsymbol{H} = \boldsymbol{K} + \boldsymbol{V}(x, y, z) = -\frac{1}{2m}\left(\frac{h}{2\pi}\right)^2 \nabla^2 + V(x, y, z)$$

Observe that the potential operator is given by the classical variable because it depends on x, y, z

The operator H is called the Hamiltonian operator (‘the Hamiltonian of the system’)

<u>The operator *E*</u>

$$\boldsymbol{E} = i\frac{h}{2\pi}\frac{\partial}{\partial t}$$

It gives the time-dependence of energy eigenstates

By combining with the expression *E*=*K*+*V*, we obtain:

$$i\frac{h}{2\pi}\frac{\partial\Psi}{\partial t} = -\frac{1}{2m}\left(\frac{h}{2\pi}\right)^2\nabla^2\Psi + V\Psi$$

<u>the time-dependent Schrödinger equation</u>

The commutator operator

Can we ‘multiply’ two operators $\boldsymbol{A}$ and $\boldsymbol{B}$ in any order?

We can, if their commutator $[\boldsymbol{A}, \boldsymbol{B}]$ is zero.

Definition of the commutator operator:

$$[\boldsymbol{A},\boldsymbol{B}] = \boldsymbol{A}\boldsymbol{B} - \boldsymbol{B}\boldsymbol{A}$$

Physical meaning of $[\boldsymbol{A},\boldsymbol{B}] = 0$:

the operators $\boldsymbol{A}$ and $\boldsymbol{B}$ have

common (simultaneous) eigenstates

Examples of commutators

1. position and momentum in the same direction:

$$[\boldsymbol{x},\boldsymbol{p_x}] = i\frac{h}{2\pi}$$ (same relation for y and z)

2. angular momentum in different directions:

$$[\boldsymbol{L_x},\boldsymbol{L_y}] = i\frac{h}{2\pi}\boldsymbol{L_z}$$ (and cyclic permutations) but

$$[\boldsymbol{L}^2,\boldsymbol{L_x}] = [\boldsymbol{L}^2,\boldsymbol{L_y}] = [\boldsymbol{L}^2,\boldsymbol{L_z}] = 0$$

Common eigenstate problem in atoms

Assume that we have an object (atom) in a potential *V(r)* and we are interested in states of constant total energy, *E*. The following relations hold:

$$[\boldsymbol{x}, \boldsymbol{H}] \neq 0, [\boldsymbol{y}, \boldsymbol{H}] \neq 0, [\boldsymbol{z}, \boldsymbol{H}] \neq 0$$

$$[\boldsymbol{H},\boldsymbol{p}_{\boldsymbol{x}}] \neq 0, [\boldsymbol{H},\boldsymbol{p}_{\boldsymbol{y}}] \neq 0, [\boldsymbol{H},\boldsymbol{p}_{\boldsymbol{z}}] \neq 0$$

$$[\boldsymbol{L}^2,\boldsymbol{H}] = [\boldsymbol{H},\boldsymbol{L}_{\boldsymbol{z}}] = [\boldsymbol{L}^2,\boldsymbol{L}_{\boldsymbol{z}}] = 0$$

So we can measure simultaneously: E, L^2, L_z.

Mean value and Expectation value

We measure the observable A n times: $a_1, a_2, \ldots, a_n$
and we calculate the mean value as

$$\bar{a} = \frac{1}{n}\sum_{i=1}^{n} a_i$$

Postulate of Quantum Mechanics:

$$\bar{a} = \langle \boldsymbol{O} \rangle = \langle \boldsymbol{O} \rangle = \int \psi^* \boldsymbol{O} \psi dV$$

where

$\langle \boldsymbol{O} \rangle$ is the expectation value of the operator $\boldsymbol{O}$ in the state ψ.

The standard deviation

Gives the spread of the measured values around the mean value

$$\Delta O = \sqrt{\sum_k w_k (a_k - \bar{a})^2}$$

where w_k = relative frequence of value a_k

Quantum mechanically, we calculate

$$\Delta O = \sqrt{\int \psi^* (\boldsymbol{O} - \langle \boldsymbol{O} \rangle)^2 \psi dV}$$

The Heisenberg principle

Assume that we measure P and Q in the state ψ (which is not an eigenstate of their operators). The following holds for their standard deviations:

$$(\Delta P)^2 \cdot (\Delta Q)^2 \geq \left(-\frac{1}{4} [\int \psi^* (\boldsymbol{PQ} - \boldsymbol{QP}) \psi dV]^2 \right)$$

If the operators do *not* commute, the right-hand side is not zero. Examples:

$$\Delta \boldsymbol{p_x} \cdot \Delta \boldsymbol{x} = h/(4\pi), \; \Delta E \cdot \Delta t = h/(4\pi)$$

Conserved Observables

An observable is conserved (i.e. its expectation value does not change with time) when its operator commutes with the Hamiltonian (of the system we study)

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \boldsymbol{O} \rangle = \frac{2\pi i}{h}\langle [\boldsymbol{H}, \boldsymbol{O}] \rangle$$

Application: the angular orbital momentum of atoms is a constant of the motion