OPERATORS

We begin by writing the one-particle, one-dimensional time-independent Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right]\psi(x)=E\,\psi(x)$$

The entity in bracket is an **operator**. An operator is a rule that transforms a given function into another function

$$\hat{A}f(x)=g(x)$$

Example: let $\hat{G}$ be the operator that differentiates a function with respect to x

$$\hat{G}[x^2+3e^{2x}]=2x+6\,e^{2x}$$

OPERATORS

We define the **sum** and the **difference** of two operators by

$$\left(\hat{A} + \hat{B}\right) f(x) = \hat{A} f(x) + \hat{B} f(x)$$

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

For example, if $\widehat{D} \equiv d/dx$, then

$$\left(\widehat{D} + \hat{3}\right)(x^3 - 5) = \widehat{D}(x^3 - 5) + \hat{3}(x^3 - 5)$$

$$= 3x^3 + 3x^2 - 15$$

OPERATORS

The **product** of two operators is defined by

$$\hat{A}\hat{B}f(x) \equiv \hat{A}\left[\hat{B}f(x)\right]$$

We first operate on $f(x)$ with the operator on the right of the operator product, and then we take the resulting function and operate on it with the operator on the left of the operator product

For example: $\hat{D}\hat{x}f(x) = \frac{d}{dx}[xf(x)] = f(x) + xf'(x) = \left(\hat{1} + \hat{x}\hat{D}\right)f(x)$

In general, we cannot assume that $\hat{A}\hat{C}$ and $\hat{C}\hat{A}$ have the same effect. In fact:

$$\hat{x}\hat{D}f(x) = \hat{x}\left[\frac{d}{dx}f(x)\right] = xf'(x)$$

OPERATORS

Two operators $\hat{A}$ and $\hat{C}$ are said to be **equal** if $\hat{A}f = \hat{C}f$ for all functions

Operators obey the **associative law** of multiplication:

$$\hat{A}\left(\hat{B}\hat{C}\right) = \left(\hat{A}\hat{B}\right)\hat{C}$$

We define the **commutator** of operators as

$$\boxed{\left[\hat{A},\hat{B}\right] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}}$$

OPERATORS

If $\hat{A}\hat{B} = \hat{B}\hat{A}$, then $[\hat{A}, \hat{B}] = 0$, and we say that $\hat{A}$ and $\hat{B}$ ***commute.*** If $\hat{A}\hat{B} \neq \hat{B}\hat{A}$, then $\hat{A}$ and $\hat{B}$ do not commute. Note that $[\hat{A}, \hat{B}]f = \hat{A}\hat{B}f - \hat{B}\hat{A}f$. Since the order in which we apply the operators 3 and d/dx makes no difference, we have

$$\left[\hat{3}, \frac{d}{dx}\right] = \hat{3}\,\frac{d}{dx} - \frac{d}{dx}\,\hat{3} = 0$$

The operators d/dx and $\hat{x}$ do not commute.

$$\left[\frac{d}{dx}, \hat{x}\right] = \hat{D}\hat{x} - \hat{x}\hat{D} = 1$$

The ***square*** of an operator is defined as the product of the operator with itself: $\hat{A}^2 = \hat{A}\hat{A}$. Let us find the square of the differentiation operator:

$$\hat{D}^2 f(x) = \hat{D}(\hat{D}f) = \hat{D}f' = f''$$
$$\hat{D}^2 = d^2/dx^2$$

OPERATORS

It turns out that the operators occurring in quantum mechanics are linear. $\hat{A}$ is a ***linear operator*** if and only if it has the following two properties:

$$\hat{A}[f(x) + g(x)] = \hat{A}f(x) + \hat{A}g(x) \quad \textbf{(3.9)*}$$

$$\hat{A}[cf(x)] = c\hat{A}f(x) \quad \textbf{(3.10)*}$$

where f and g are arbitrary functions and c is an arbitrary constant (not necessarily real). Examples of linear operators include $\hat{x}^2$, d/dx, and d^2/dx^2. Some nonlinear operators are cos and $(\quad)^2$, where $(\quad)^2$ squares the function it acts on.

EXAMPLE Is d/dx a linear operator? Is $\sqrt{\quad}$ a linear operator?

We have

$$(d/dx)[f(x) + g(x)] = df/dx + dg/dx = (d/dx)f(x) + (d/dx)g(x)$$

$$(d/dx)[cf(x)] = c\, df(x)/dx$$

so d/dx obeys (3.9) and (3.10) and is a linear operator. However,

$$\sqrt{f(x) + g(x)} \neq \sqrt{f(x)} + \sqrt{g(x)}$$

so $\sqrt{\quad}$ does not obey (3.9) and is nonlinear.

EIGENFUNCTIONS and EIGENVALUES

Suppose that the effect of operating on some function $f(x)$ with the operator $\hat{A}$ is simply to multiply $f(x)$ by a certain constant k. We then say that $f(x)$ is an **eigenfunction** of $\hat{A}$ with **eigenvalue** k. As part of the definition, we shall require that the eigenfunction $\boldsymbol{f(x)}$ **is not identically zero**. By this we mean that, although $f(x)$ may vanish at various points, it is not zero everywhere. We have

$$\boxed{\hat{A}f(x) = k\,f(x)}$$

Examples:

$(d/dx)e^{2x} = 2e^{2x}$ e^{2x} is eigenfunction of d/dx

$(d/dx)x^2 = 2x$ x^2 is not eigenfunction of d/dx

EIGENFUNCTIONS and EIGENVALUES

Theorem:

If $f(x)$ is an eigenfunction of the linear operator $\hat{\mathrm{A}}$ and c is any constant, then $cf(x)$ is an eigenfunction of $\hat{\mathrm{A}}$ with the same eigenvalue as $f(x)$

If $$\hat{A}f(x) = k\, f(x)$$

then $$\hat{A}[cf(x)] = k\,[cf(x)]$$

(Lev.4/Lev.5 p. 39-40)

OPERATORS and QUANTUM MECHANICS

Time-independent Schrödinger equation $\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right]\psi(x)=E\,\psi(x)$

Eigenvalue problem $\hat{H}\psi(x)=E\,\psi(x)$

$\psi(x)$ eigenfunction

E eigenvalue

$\hat{H}$ is the Hamiltonian of the system and represents its energy

In classical mechanics: $E=\frac{p^2}{2m}+V(x)$

OPERATORS and QUANTUM MECHANICS

This correspondence between physical quantities in classical mechanics and operators in QM is general. It is a fundamental **postulate** of QM that **to every physical property** (for example, the energy, the *x* coordinate, the momentum) **there corresponds a QM operator**. We will see that **QM operators are linear** (this is not a postulate)

OPERATORS and QUANTUM MECHANICS

We further **postulate** that the operator corresponding to the property B is obtained by writing the classical-mechanical expression for B as a function of Cartesian coordinates and corresponding momenta and then making the following replacements

Each Cartesian coordinate q is replaced by the operator multiplication by that coordinate:

$$\hat{q} = q$$

Each Cartesian component of linear momentum p_q is replaced by the operator

$$\hat{p}_q = -i\hbar \frac{\partial}{\partial q}$$

OPERATORS and QUANTUM MECHANICS

Specifically $\hat{x} = x \qquad \hat{y} = y \qquad \hat{z} = z$

$$\hat{p}_x = -i\hbar\frac{\partial}{\partial x} \qquad \hat{p}_y = -i\hbar\frac{\partial}{\partial y} \qquad \hat{p}_z = -i\hbar\frac{\partial}{\partial z}$$

Example: $$\hat{p}_x^2 = \left(-i\hbar\,\frac{\partial}{\partial x}\right)^2 = -\hbar^2\frac{\partial^2}{\partial x^2}$$

The correspondence involving the Cartesian coordinates implies that

$$\boxed{\hat{V}(x) = V(x)}$$

OPERATORS and QUANTUM MECHANICS

Example: find the Hamiltonian operator of 2 charged particles

$$E = \frac{1}{2} m_1 v_{x_1}^2 + \frac{1}{2} m_1 v_{x_1}^2 + \frac{1}{2} m_1 v_{x_1}^2 + \frac{1}{2} m_2 v_{x_2}^2 + \frac{1}{2} m_2 v_{y_2}^2 + \frac{1}{2} m_2 v_{z_2}^2 + \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{\sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2}}$$

Sapendo che

$$p_{x_1} = m_1 v_{x_1}$$

$$\frac{1}{2} m_1 v_{x_1}^2 = \frac{p_{x_1}^2}{2m_1} = -\frac{\hbar^2}{2m_1} \frac{\partial^2}{\partial x_1^2}$$

$$\hat{H} = -\frac{\hbar^2}{2m_1} \frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m_1} \frac{\partial^2}{\partial y_1^2} - \frac{\hbar^2}{2m_1} \frac{\partial^2}{\partial z_1^2} - \frac{\hbar^2}{2m_2} \frac{\partial^2}{\partial x_2^2} - \frac{\hbar^2}{2m_2} \frac{\partial^2}{\partial y_2^2} - \frac{\hbar^2}{2m_2} \frac{\partial^2}{\partial z_2^2} + \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{\sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2}}$$

OPERATORS and QUANTUM MECHANICS

POSTULATE

To every physically observable property there corresponds a linear Hermitian (see later) operator. To find this operator, write down the classical-mechanical expression for the observable in terms of Cartesian coordinates and corresponding linear-momentum components, and then replace each coordinate x by the operator "multiplication by x" and each momentum component p_x by the operator $-i\hbar\,\partial/\partial x$. (Replace the time t with the operator t)

3-DIMENSIONAL MANY-PARTICLE SCHRÖDINGER EQUATION

$$\left[-\sum_{i=1}^{n}\frac{\hbar^2}{2m_i}\nabla_i^2+V(x_1,\ldots,z_n)\right]\psi=E\,\psi$$

Laplacian operator

$$\nabla_i^2=\frac{\partial^2}{\partial x_i^2}+\frac{\partial^2}{\partial y_i^2}+\frac{\partial^2}{\partial z_i^2}$$

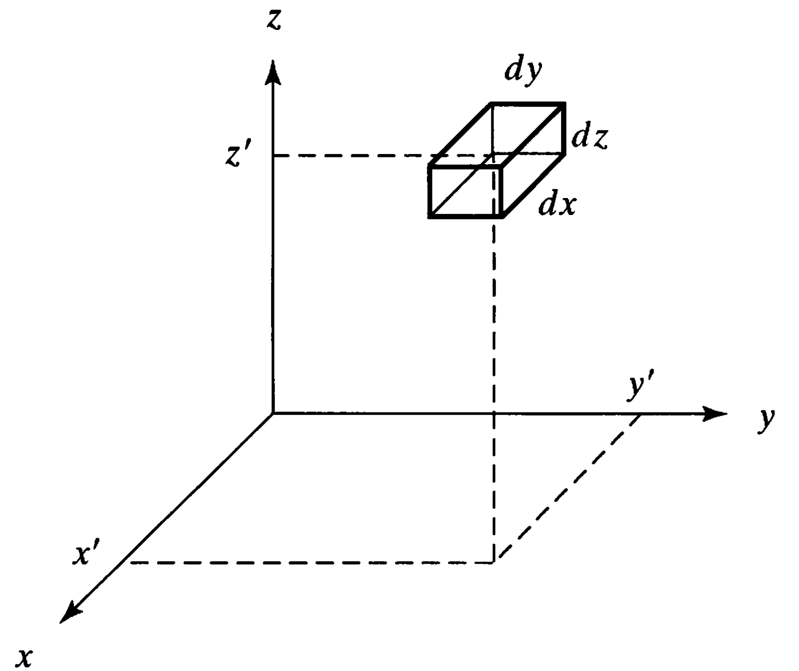
(Lev.4/Lev.5 p. 46-47)

3-DIMENSIONAL MANY-PARTICLE SCHRÖDINGER EQUATION

For a 3-dimensional, 1-particle system, the quantity

$$|\Psi(x', y', z', t)|^2 dx\, dy\, dz$$

is the probability at time t of finding the particle in the infinitesimal region of space with the x coordinate lying between x' and x' $+ dx$, the y coordinate lying between y' and y' $+ dy$, and the z coordinate between z' and z' $+ dz$



3-DIMENSIONAL MANY-PARTICLE SCHRÖDINGER EQUATION

For a 3-dimensional, many-particle system, the quantity

$$|\Psi(x_1', y_1', z_1', \ldots, x_n', y_n', z_n')|^2 dx_1\, dy_1\, dz_1 \ldots dx_n\, dy_n\, dz_n$$

is the probability at time t of simultaneously finding particle 1 in the infinitesimal rectangular box-shaped region at (x_1', y_1', z_1') with edges dx_1, dy_1, dz_1, particle 2 in the infinitesimal box-shaped region at (x_2', y_2', z_2') with edges dx_2, dy_2, dz_2, till the particle n in the infinitesimal box-shaped region at (x_n', y_n', z_n') with edges dx_n, dy_n, dz_n

3-DIMENSIONAL MANY-PARTICLE SCHRÖDINGER EQUATION

The total probability of finding all the particles in the whole space is 1, and the **normalization condition** is

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}|\Psi|^2 dx_1\, dy_1\, dz_1 \ldots dx_n\, dy_n\, dz_n = 1$$

A shorthand of the normalization condition is

$$\int |\Psi|^2 d\tau = 1$$

DEGENERACY

Theorem:

Let us prove an important theorem about the wave functions of an n-fold degenerate energy level. We have n independent wave functions $\psi_1, \psi_2, \ldots, \psi_n$, each having the same energy. Let w be the energy of the degenerate level:

$$\hat{H}\psi_1 = w\psi_1, \quad \hat{H}\psi_2 = w\psi_2, \quad \ldots, \quad \hat{H}\psi_n = w\psi_n \tag{3.76}$$

We wish to prove that any linear combination

$$\phi \equiv c_1\psi_1 + c_2\psi_2 + \cdots + c_n\psi_n \tag{3.77}$$

of the n wave functions of the degenerate level is an eigenfunction of the Hamiltonian with eigenvalue w. [A ***linear combination*** of the functions $\psi_1, \psi_2, \ldots, \psi_n$ is defined as a function of the form (3.77) where the c's are constants.] We must show $\hat{H}\phi = w\phi$

(Lev.4/Lev.5 p. 52-53)

AVERAGE VALUES

How are the QM operators related to the corresponding properties of a system?

POSTULATE

If $\Psi(x, t)$ is the normalized state function of a system at time t, then the average value of a physical observable B at time t is

$$\langle B \rangle = \int \Psi^* \hat{B} \Psi \, \mathrm{d}\tau$$

where $\hat{B}$ is the QM operator corresponding to the observable B

For a stationary state $\langle B \rangle$ is time independent

$$\langle B \rangle = \int \psi^* \hat{B} \psi \, \mathrm{d}\tau$$

(Lev.4 p. 55; Lev.5 p.56)

AVERAGE VALUES

Theorem:

If the wave function $\Psi(x, t)$ of the system is an eigenfunction of $\hat{A}$ with eigenvalue a, then a measurement of the property A is certain to yield the value a

$$\langle A \rangle = a$$

(Lev.4 p. 55; Lev.5 p. 56)