3.1 Operators in quantum mechanics

An **operator** is a rule that transforms a given function into another function. E.g. d/dx, sin, log

Eigenfunctions and Eigenvalues $\hat{A}f(x) \equiv kf(x)$

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*.

Eigen is a German word meaning *characteristic*.

Operators obey the associative law of multiplication:

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

A linear operator means

$$\hat{A}(\psi_1 + \psi_2) = \hat{A}\psi_1 + \hat{A}\psi_2$$

$$\hat{A}c\psi = c\hat{A}\psi$$

Is $\frac{d}{dx}$ a linear operator?

$$\left(\frac{d}{dx}\right)[f(x)+g(x)] = \frac{df}{dx}+\frac{dg}{dx} = \left(\frac{d}{dx}\right)f(x)+\left(\frac{d}{dx}\right)g(x)$$

$$\left(\frac{d}{dx}\right)[Cf(x)] = C\frac{df}{dx}$$

$\sqrt{\ }$?

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

$$(\hat{A}+\hat{B})f(x) \equiv \hat{A}f(x)+\hat{B}f(x)$$

$$(\hat{A}-\hat{B})f(x) \equiv \hat{A}f(x)-\hat{B}f(x)$$

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

3.2 Hermiticity

Every operator $\hat{Q}$ has a *Hermitian conjugate*, conventionally denoted $\hat{Q}^{\dagger}$, which has the property that for any ψ_1 and ψ_2 satisfying the boundary conditions for the problem,

$$\int \psi_1^{*} \hat{Q} \psi_2 \mathrm{d}\tau = \int \left(\hat{Q}^{+} \psi_1 \right)^{*} \psi_2 \mathrm{d}\tau$$

An operator that is equal to its Hermitian conjugate is said to be *Hermitian*.

Operators corresponding to physical observables must be Hermitian

$$\int \psi_1^{*} x \psi_2 \mathrm{d}x = \int \left(x \psi_1 \right)^{*} \psi_2 \mathrm{d}x$$

so $\hat{x}^{\dagger} = \hat{x}$, and $\hat{x}$ is Hermitian.

$$\int \psi_1^{*} \frac{\mathrm{d}}{\mathrm{d}x} \psi_2 \mathrm{d}x = \left[\psi_1^{*} \psi_2 \right]_{-\infty}^{\infty} - \int \left(\frac{\mathrm{d}}{\mathrm{d}x} \psi_1^{*} \right) \psi_2 \mathrm{d}x = \int \left(-\frac{\mathrm{d}}{\mathrm{d}x} \psi_1 \right)^{*} \psi_2 \mathrm{d}x$$

So $\left(\frac{\mathrm{d}}{\mathrm{d}x} \right)^{+} = -\frac{\mathrm{d}}{\mathrm{d}x}$

and $\mathrm{d}/\mathrm{d}x$ is not a Hermitian operator. However $i\mathrm{d}/\mathrm{d}x$ is Hermitian

Dirac notation

We sometimes use a notation due originally to Dirac. The idea is to reduce notational clutter and give more prominence to the labels identifying the wavefunctions.

In this notation $|n\rangle$ is used for the wavefunction ψ_n . $|n\rangle$ is called a *ket*.

$\langle n|$ is a *bra*. The bra notation implies the complex conjugate $\psi_n{}^*$.

A complete *bracket* expression, like $\langle n|n\rangle$ or $\langle n|\hat{Q}|n\rangle$, implies integration over all space.

Thus the notation $\langle n|n\rangle$ means the integral $\int \psi_n{}^* \psi_n \,\mathrm{d}\tau$, and $\langle m|\hat{Q}|n\rangle$ means $\int \psi_m{}^* \hat{Q}\psi_n \,\mathrm{d}\tau$.

Using this notation, the expectation value integral can be written more compactly as

$$\langle Q\rangle = \frac{\int \psi^* \hat{Q}\psi \,\mathrm{d}\tau}{\int \psi^* \psi \,\mathrm{d}\tau} \quad \Longrightarrow \quad \langle Q\rangle = \frac{\langle n|\hat{Q}|n\rangle}{\langle n|n\rangle}$$

Hermiticity

Properties of Hermitian operators:

- Their eigenvalues are always real.
- Eigenfunctions corresponding to different eigenvalues are orthogonal.

In the proof of these properties we use Dirac's angle-bracket notation. First note that if $\hat{Q}$ is Hermitian, then

$$\begin{aligned}\langle m|\hat{Q}|n\rangle^* &\equiv \left(\int \psi_m{}^* \hat{Q}\psi_n \mathrm{d}\tau\right)^* \\ &= \left(\int \left(\hat{Q}\psi_m\right)^* \psi_n \mathrm{d}\tau\right)^* \\ &= \int \psi_n{}^* \hat{Q}\psi_m \mathrm{d}\tau \\ &= \langle n|\hat{Q}|m\rangle\end{aligned}$$

Note also that $\langle m|n\rangle^* = \left(\int \psi_m{}^* \psi_n \,\mathrm{d}\tau\right)^* = \int \psi_n{}^* \psi_m \,\mathrm{d}\tau = \langle n|m\rangle$.

Hermiticity and orthogonality

Now consider two eigenfunctions $|m\rangle$ and $|n\rangle$. We have

$$\hat{Q}|m\rangle = q_m|m\rangle \qquad \hat{Q}|n\rangle = q_n|n\rangle$$

$$\langle n|\hat{Q}|m\rangle = q_m\langle n|m\rangle \quad \text{and} \quad \langle m|\hat{Q}|n\rangle = q_n\langle m|n\rangle$$

$$\langle m|\hat{Q}|n\rangle = q_m{}^*\langle m|n\rangle$$

where the last line on the left comes from taking the complex conjugate.

Subtracting, we find

$$0 = \left(q_n - q_m{}^*\right)\langle m|n\rangle$$

and from this we can deduce

(a) If $m = n$, then $\langle m|n\rangle = \langle m|m\rangle \neq 0$, so $q_m = q_m{}^*$ and q_m is real.

(b) If $q_m \neq q_n$, then since both are real, $q_n - qm{}^* \neq 0$ and $\langle m|n\rangle = 0$.

Hermitian operator ensures that the eigenvalue of the operator is a real number

The eigenvalue of a Hermitian operator is a real number

Proof:

$$\hat{A}\psi = a\psi$$

$$\int \psi^* \hat{A}\psi \, d\tau = \int \psi (\hat{A}\psi)^* \, d\tau$$

$$a\int |\psi|^2 d\tau = a^* \int |\psi|^2 \, d\tau$$

$$|\psi|^2 \geq 0$$

but : $\psi \neq 0$

$$\therefore \quad a_i = a_i^*$$

Quantum mechanical operators have to have real eigenvalues

The eigenfunctions of Hermitian operators are orthogonal

Proof:

$$\int \psi_i {}^* \psi_j dx = \delta_{ij}$$

Consider these two eigen equations

$$\hat{A}\psi_n = a_n \psi_n$$
$$\hat{A}\psi_m = a_m \psi_m$$

Multiply the left of eq 1 by $\boldsymbol{\psi_m}$* and integrate, then take the complex conjugate of eq 2, multiply by $\boldsymbol{\psi_n}$ and integrate

$$\int \psi_m^* \hat{A} \psi_n dx = \mathrm{a_n} \int \psi_m^* \psi_n dx$$

$$\int \psi_n \hat{A}^* \psi_m^* dx = \mathrm{a_m^*} \int \psi_n \psi_m^* dx$$

Subtracting these two equations gives -

$$\int \psi_m^* \hat{A} \psi_n dx - \int \psi_n \hat{A} {}^* \psi_m^* dx = (\mathrm{a_n} - \mathrm{a}_m^*) \int \psi_m^* \psi_n dx = 0$$

If n = m, the integral = 1, by normalization, so $a_n = a_n^*$

If $n \neq m$, and the system is **nondegenerate** (i.e. different eigenfunctions do not have the same eigenvalues, $a_n \neq a_m$), then

$$(a_n - a_m)\int \psi_m{}^* \psi_n dx = 0 \quad \Rightarrow \quad \int \psi_m{}^* \psi_n dx = 0$$

Eignefunctions of *B* that belong to a degenerate eigenvalue can always be chosen to be orthogonal.

$$\hat{B}F = sF\,, \quad \hat{B}G = sG$$

$$g_1 = F\,, \quad g_2 = G + cF$$

$$we\ want \int g_1^* g_2 d\tau = 0$$

$$\int F^* \left(G + cF\right) d\tau = \int F^* G d\tau + c\int F^* F d\tau = 0$$

$$c = \frac{-\int F^* G d\tau}{\int F^* F d\tau}$$

Schmidt Orthogonalization

The eigenfunctions of Hermitian operators are orthogonal $\int \psi_i{}^* \psi_j dx = \delta_{ij}$

Normalized $g_1, g_2, g_3 \ldots$

$$g_1' = g_1$$

$$g_2' = g_2 - \langle g_1' | g_2 \rangle g_1'$$

$$g_3' = g_3 - \langle g_1' | g_3 \rangle g_1' - \langle g_2' | g_3 \rangle g_2'$$

$$\bullet\bullet\bullet$$

$$S_{ij} = \langle g_i | g_j \rangle$$

$$\begin{pmatrix} \langle g_1 | \\ \langle g_2 | \\ \ldots \end{pmatrix} \begin{pmatrix} | g_1 \rangle & | g_2 \rangle & \ldots \end{pmatrix} = S \qquad \boxed{S = LL^T}$$

$$I$$

$$L^{-1} \begin{pmatrix} \langle g_1 | \\ \langle g_2 | \\ \ldots \end{pmatrix} \begin{pmatrix} | g_1 \rangle & | g_2 \rangle & \ldots \end{pmatrix} (L^T)^{-1} = I$$

$$L^{-1} \begin{pmatrix} \langle g_1 | \\ \langle g_2 | \\ \ldots \end{pmatrix} \left(L^{-1} \begin{pmatrix} \langle g_1 | \\ \langle g_2 | \\ \ldots \end{pmatrix} \right)^T = I \qquad L:\ S^{1/2}$$

L is triangular matrix: Schmidt Orthogonalization

$L = L^T$: Löwdin Orthogonalization

3.3 Expansion in terms of eigenfunctions

Expansion of a funcition Using Particle-in-a-Box W.F.

$$\psi_n = \left(\frac{2}{a}\right)^{1/2} \sin\left(\frac{n\pi x}{a}\right), \quad n = 1, 2, \cdots$$

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n = \left(\frac{2}{a}\right)^{1/2} \sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi x}{a}\right), \quad 0 \le x \le a$$

- ✓ Same boundary conditions
- ✓ Finite, single-valued, continuous

$g_1, g_2, \ldots\ldots, g_i, \ldots\ldots$ is said to be a complete set if any well-behaved function f that obeys the same boundary conditions as g_i can be expanded as linear combination of the g_i .

We now postulate that the set of eigenfunctions of any Hermitonian Operator that represent a physical quantity forms a complete set.

$$\int g_j^* f d\tau = \sum_i c_i \int g_j^* g_i d\tau = c_j$$

$$c_j = \int g_j^* f d\tau$$

$$f = \sum_i c_i g_i = \sum_i \left[\int g_i^* f d\tau \right] g_i = \sum_i \langle g_i \mid f \rangle g_i$$

Postulate: If ψ_1, ψ_2,… ψ_n are the possible states of a microscopic system, then the linear combination of these states is also a possible state of the system.

$$\Psi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 \cdots + c_n\psi_n = \sum_i c_i\psi_i$$

3.4 Commutation

When two or more operators are applied to a wavefunction, the order matters. $\hat{P}\hat{Q}\psi$ is defined to mean $\hat{P}(\hat{Q}\psi)$, and it may be different from $\hat{Q}\hat{P}\psi \equiv \hat{Q}(\hat{P}\psi)$.

Example: For any $\psi(x)$,

$$\hat{x}\hat{p}_x\psi = -i\hbar x\frac{\mathrm{d}\psi}{\mathrm{d}x}$$

but

$$\hat{p}_x\hat{x}\psi = -i\hbar\frac{\mathrm{d}}{\mathrm{d}x}(x\psi) = -i\hbar\left(\psi + x\frac{\mathrm{d}\psi}{\mathrm{d}x}\right)$$

Subtracting the second of these from the first:

$$\left(\hat{x}\hat{p}_x - \hat{p}_x\hat{x}\right)\psi = i\hbar\psi \quad \Longrightarrow \quad \hat{x}\hat{p}_x - \hat{p}_x\hat{x} = i\hbar$$

This is true for any wavefunction ψ, so we can extract the *operator identity*

We say that $\hat{x}$ *and* $\hat{p}_x$ *do not commute*.

The expression $\hat{x}\hat{p}_x - \hat{p}_x\hat{x}$ is called the *commutator* of $\hat{x}$ and $\hat{p}_x$, and there is a special notation for it: $[\hat{x}, \hat{p}_x]$.

Commutation and eigenfunctions

The uncertainties in two observables P and Q satisfy

$$\Delta P \Delta Q \geq \frac{1}{2}\left|\left\langle\left[\hat{P},\hat{Q}\right]\right\rangle\right|$$

This is *Heisenberg's uncertainty principle* in a more general form than before.

Since $[\hat{x},\hat{p}_x] = i\hbar$, we see that $\Delta x \Delta px \geq \frac{1}{2}\hbar$,

If $\hat{P}\hat{Q} = \hat{Q}\hat{P}$, $\hat{P}$ and $\hat{Q}$ are said to *commute*. A constant commutes with any operator: $\left[k,\hat{P}\right] = 0$.

If $\hat{P}$ and $\hat{Q}$ commute, i.e., $\left[\hat{P},\hat{Q}\right] = 0$, it is possible for both ΔP and ΔQ to be zero — that is, we can **find wavefunctions that are eigenfunctions of both.**

In fact, in this case, a non-degenerate eigenfunction of $\hat{P}$ must also be an eigenfunction of $\hat{Q}$

Commutation can tell us when will it be possible for Ψ to be simultaneously an eigenfunction of two different operators.

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Proof : Suppose that

$$\hat{P}\psi = p\psi$$

and that there is no other wavefunction with this eigenvalue for $\hat{P}$ (except for numerical multiples of ψ, which are essentially the same).

Now consider $\hat{Q}\psi$. $\hat{P}$ and $\hat{Q}$ commute, so

$$\hat{P}\left(\hat{Q}\psi\right) = \hat{Q}\hat{P}\psi = \hat{Q}p\psi = p\left(\hat{Q}\psi\right)$$

So $(\hat{Q}\psi)$ is an eigenfunction of $\hat{P}$ with eigenvalue p.

But ψ, or a multiple of it, is the only such function. Therefore $\hat{Q}\psi = q\psi$, for some number q; i.e., ψ is an eigenfunction of $\hat{Q}$.

A necessary condition for the existence of a complete set of simultaneous eigenfunctions of two operators is that the operators commute with each other.

Conversely, if $\hat{P}$ and $\hat{Q}$ are two commuting operators, there exists a complete set of functions that are eigenfuntions of both $\hat{P}$ and $\hat{Q}$.

$$[A, B+C] = [A, B] + [A, C]$$
$$[A, BC] = B[A, B] + [A, B]C$$
$$[AB, C] = A[B, C] + [A, C]B$$

$$[A, [B, C]] + [B, [C, A]] + [C, [A, B]] = 0$$

Example:

$$[\hat{x}, \hat{p}_x^2] = [\hat{x}, \hat{p}_x]\hat{p}_x + \hat{p}_x[\hat{x}, \hat{p}_x] = i\hbar\frac{\hbar}{i}\frac{\partial}{\partial x} + \frac{\hbar}{i}\frac{\partial}{\partial x}i\hbar = 2\hbar^2\frac{\partial}{\partial x}$$

$$[\hat{x}, \hat{H}] = [\hat{x}, \hat{T} + \hat{V}] = [\hat{x}, \hat{T}] + [\hat{x}, V(x, y, z)] = [\hat{x}, \hat{T}]$$

$$= [\hat{x}, \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right)]$$

$$= \frac{\hbar^2}{m}\frac{\partial}{\partial x}$$

$$= \frac{i\hbar}{m}\hat{p}_x$$

We could not predict the position of particle for a stationary state.

Time evolution of expectation

$$\boxed{\bar{F} = \langle \Psi | \hat{F} | \Psi \rangle}$$

$$\frac{d\bar{F}}{dt} = \left\langle \frac{\partial \Psi}{\partial t} \right| \hat{F} \left| \Psi \right\rangle + \left\langle \Psi \right| \hat{F} \left| \frac{\partial \Psi}{\partial t} \right\rangle + \left\langle \Psi \left| \frac{\partial \hat{F}}{\partial t} \right| \Psi \right\rangle$$

$$\boxed{-i\hbar \frac{d\psi^*}{dt} = H\psi^* \quad i\hbar \frac{d\psi}{dt} = H\psi}$$

$$= -\frac{1}{i\hbar} \langle \hat{H}\Psi | \hat{F} | \Psi \rangle + \frac{1}{i\hbar} \langle \Psi | \hat{F}\hat{H} | \Psi \rangle + \overline{\frac{\partial \hat{F}}{\partial t}}$$

$$= -\frac{1}{i\hbar} \langle \Psi | \hat{H}\hat{F} | \Psi \rangle + \frac{1}{i\hbar} \langle \Psi | \hat{F}\hat{H} | \Psi \rangle + \overline{\frac{\partial \hat{F}}{\partial t}}$$

$$= \frac{1}{i\hbar} \overline{[\hat{F}, \hat{H}]} + \overline{\frac{\partial \hat{F}}{\partial t}}$$

$$\boxed{\frac{d\bar{F}}{dt} = \overline{\frac{\partial \hat{F}}{\partial t}} + \frac{1}{i\hbar} \overline{[\hat{F}, \hat{H}]}}$$

If $\partial\hat{F}/\partial t = 0$ $\quad \dfrac{d\bar{F}}{dt} = \dfrac{1}{i\hbar}\overline{[\hat{F},\hat{H}]}$

If F commutes with H, $[\hat{F},\hat{H}] = 0$ $\quad d\bar{F}/dt = 0$

F and **H** have a common complete set of eigen wavefunction. Therefore, when a time-independent operator commutes with H, it is a constant of motion.

$$\frac{d\bar{H}}{dt} = \overline{\frac{\partial\hat{H}}{\partial t}} + \frac{1}{i\hbar}\overline{[\hat{H},\hat{H}]} = 0$$