Survival Facts from Quantum Mechanics

Operators, Eigenvalues and Eigenfunctions

An operator \( \hat{O} \) may be thought as “something” that operates on a function to produce another function. (We denote operators with “hats”, but also use “hats” to indicate unit vectors like \( \hat{x} \), \( \hat{y} \) and \( \hat{z} \). The context should make it clear which is which!):

\[
\hat{O}f(x) = g(x)
\]

In most cases, the operators of quantum mechanics are linear. Operators are linear if they have properties:

\[
\hat{O}[f(x) + g(x)] = \hat{O}f(x) + \hat{O}g(x)
\]

\[
\hat{O}cf(x) = c\hat{O}f(x)
\]

where \( c \) is a constant (\( c \) can be a complex number: \( c = a + ib, i = \sqrt{-1} \))

Examples:

Linear operators:

- \( x \) (multiplication by \( x \)):

\[
x[f(x) + g(x)] = xf(x) + xg(x)
\]

- \( \frac{d}{dx} \) (differentiation with respect to \( x \)):

\[
\frac{d}{dx}[f(x) + g(x)] = \frac{d}{dx}f(x) + \frac{d}{dx}g(x)
\]

A non-linear operator: \( \sqrt{\cdot} \) (square root operator):

\[
\sqrt{f(x) + g(x)} \neq \sqrt{f(x)} + \sqrt{g(x)}
\]

The eigenvalues and eigenfunctions of an operator \( \hat{A} \) are those numbers \( a_j \) and functions \( \varphi_j \) which satisfy

\[
\hat{A}\varphi_j = a_j \varphi_j
\]

where \( j \) is just a label for the various eigenfunctions and corresponding eigenvalues which satisfy this equation. In other words, when \( \hat{A} \) operates on one of its eigenfunctions, say \( \varphi_3 \), the result is \( a_3 \varphi_3 \) - just \( \varphi_3 \) back again, multiplied by the eigenvalue \( a_3 \).

Note that if we multiply an eigenfunction of a linear operator by a constant \( c \) we still have an eigenfunction:

\[
\hat{A}\varphi_j = a_j \varphi_j
\]

\[
\hat{A}(c\varphi_j) = c\hat{A}\varphi_j = c(a_j \varphi_j) = a_j (c\varphi_j)
\]
so that an eigenfunction $\phi_j$ and the function $\chi_j = c \phi_j$ are not considered as independent eigenfunctions. (i.e., Since any eigenfunction is still an eigenfunction when multiplied by a constant, eigenfunctions which differ only by a multiplicative constant are not considered to be “distinct”.)

Examples:

1. The differential operator \( \{d/dx\} \) has an infinite set of eigenfunctions \( \{e^{kx}\} \) with eigenvalues $k$:

\[
\frac{d}{dx} e^{kx} = ke^x
\]

where $k$ may take on any value.

2. The operator \( \{x \frac{d}{dx}\} \) also has an infinite set of eigenfunctions \( \{x^n; n \neq 0\} \):

\[
\left\{x \frac{d}{dx}\right\} x^n = x(nx^{n-1}) = nx^n
\]

This example allows us to demonstrate that a linear combination of eigenfunctions is not an eigenfunction (unless the two eigenfunctions have the same eigenvalue). For example, there is no number $c$ that satisfies the equation:

\[
\left\{x \frac{d}{dx}\right\} \left[x^2 + x^3\right] = c\left[x^2 + x^3\right]
\]

3. The operator \( \{d^2/dx^2\} \) has a set eigenfunctions of the form \( \{\cos kx; k = \text{any real number}\} \) and $-k^2$ is the eigenvalue:

\[
\frac{d^2}{dx^2} \cos kx = \frac{d}{dx}[-k \sin kx] = -k^2 \cos kx
\]

Note that the set of functions \( \{\sin kx; k = \text{any real number}\} \) are also eigenfunctions with the same eigenvalue:

\[
\left\{\frac{d^2}{dx^2}\right\} \sin kx = \frac{d}{dx}[k \cos kx] = -k^2 \sin kx
\]

Therefore, for any given value of $k$, $\cos kx$, and $\sin kx$ are eigenfunctions of \( \{d^2/dx^2\} \) with the same eigenvalue $-k^2$. This means that any combination of $\cos kx$ and $\sin kx$ is also an eigenfunction.

\[
\left\{\frac{d^2}{dx^2}\right\} [a \cos kx + b \sin kx] = -k^2 [a \cos kx + b \sin kx]
\]

In particular, if $a = 1$ and $b = i = \sqrt{-1}$ we have

\[
\left\{\frac{d^2}{dx^2}\right\} [\cos kx + i \sin kx] = \left\{\frac{d^2}{dx^2}\right\} [e^{ikx}] = -k^2 [e^{ikx}]
\]

so that \( \{e^{ikx}, k = \text{any real number}\} \) is an alternative set of eigenfunctions of \( \{d^2/dx^2\} \).
Commutators

The \textit{commutator} of two operators \( \hat{A} \) and \( \hat{B} \) is defined as

\[
\left[ \hat{A}, \hat{B} \right] = \hat{A}\hat{B} - \hat{B}\hat{A}
\]

if \( [\hat{A}, \hat{B}] = 0 \), then \( \hat{A} \) and \( \hat{B} \) are said to \textit{commute}. In general, quantum mechanical operators cannot be assumed to commute.

Examples:

When evaluating the commutator for two operators, it is sometimes helpful to keep track of things by operating the commutator on an arbitrary function, \( f(x) \).

(1) Evaluate \( [x, \frac{d}{dx}] \):

\[
\left[ x, \frac{d}{dx} \right] f(x) = \left( x \frac{d}{dx} - \frac{d}{dx} x \right) f(x) = x \frac{d}{dx} f(x) - f(x) \frac{d}{dx} x = x \frac{d}{dx} f(x) - f(x) = [x, \frac{d}{dx}] f(x) = - f(x) \quad \Rightarrow \quad [x, \frac{d}{dx}] = -1
\]

We see that the effect of operating on any arbitrary \( f(x) \) with \( [x, d/dx] \) is to produce \(-f(x)\), so that the last equation is generally true.

(2) In quantum mechanics, the operator for linear momentum in the \( x \) direction is \( \hat{p}_x = \frac{\hbar}{i} \frac{d}{dx} \) (where \( \hbar = h/2\pi \)). Let's evaluate \([x, \hat{p}_x] \):

\[
\left[ x, \hat{p}_x \right] = x\hat{p}_x - \hat{p}_x x = \frac{\hbar}{i} \left( x \frac{d}{dx} - \frac{d}{dx} x \right) = \frac{\hbar}{i} \left[ x, \frac{d}{dx} \right] = - \frac{\hbar}{i} = i\hbar
\]

(3) In \textit{classical} mechanics, the angular momentum of a particle around the origin is a vector quantity, \( \mathbf{L} \), which is defined as \( \mathbf{L} = \mathbf{r} \times \mathbf{p} \). The angular momentum of a charged particle (like an electron) is related to its magnetic moment, \( \mathbf{m} \), as shown in the illustration below.

![Diagram of angular momentum](image)

\[
\mathbf{m} = -\frac{e}{2c} \left( \mathbf{r} \times \mathbf{v} \right) = -\frac{e}{2m_e c} \left( \mathbf{r} \times \mathbf{p} \right) = -\frac{e}{2m_e c} \mathbf{L}
\]

so, identifying the components of \( \mathbf{L} \),

\[
L_x = yp_z - zp_y \quad ; \quad L_y = zp_x - xp_z \quad ; \quad L_z = xp_y - yp_x
\]
$L_x$, $L_y$, and $L_z$ are the components of a single particle’s angular momentum. To get the quantum mechanical operators $\hat{\mathbf{L}} = \hat{L}_x \hat{\mathbf{x}} + \hat{L}_y \hat{\mathbf{y}} + \hat{L}_z \hat{\mathbf{z}}$ we insert the quantum mechanical operators for the linear momenta, $\hat{p}_u = (\hbar/i) \partial/\partial u (u = x, y, z)$, to obtain:

$$
\hat{L}_x = \frac{\hbar}{i} \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) ; \quad \hat{L}_y = \frac{\hbar}{i} \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) ; \quad \hat{L}_z = \frac{\hbar}{i} \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)
$$

The reader should use these expressions to operate on an arbitrary function $f(x, y, z)$ to evaluate the commutators

$$
[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z ; \quad [\hat{L}_y, \hat{L}_z] = i\hbar \hat{L}_x ; \quad [\hat{L}_z, \hat{L}_x] = i\hbar \hat{L}_y
$$

Quantum Mechanical Operators and Wavefunctions

If $\varphi$ is to be considered a "well behaved" function, then we demand that it have the following properties:

(a) $\varphi$ must be continuous (no "breaks")
(b) $\varphi$ must have continuous derivatives (no "kinks")
(c) $\varphi$ must be normalizable. To be normalizable, $\varphi$ must obey the condition (the symbol $d\tau$ symbolizes integration over all space):

$$
\int \varphi^* \varphi \, d\tau = C, \text{ where } C \text{ is a finite constant.}
$$

Then we can normalize $\varphi$ if we multiply by $1/\sqrt{C}$:

$$
\int \left( \frac{\varphi^*}{\sqrt{C}} \right) \left( \frac{\varphi}{\sqrt{C}} \right) \, d\tau = 1.
$$

Of central importance is the time-independent Schrödinger equation

$$
\mathcal{H} \Psi = E \Psi.
$$

where $\mathcal{H}$ is the Hamiltonian (or energy) operator for the system. $\Psi$ is called the wavefunction or state function for the system and must be "well behaved" in the sense indicated above. In quantum mechanics, physically observable quantities are associated with Hermitian operators (eg., the energy of the system, the momentum of the system or of particles within the system, the position of particles in the system, etc.) If an operator $\hat{A}$ is Hermitian it has the property

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

for all well-behaved functions $\varphi$ and $\chi$.

If a system is in a state described by $\Psi$, then the expectation value we would observe for the property associated with the Hermitian operator $\hat{A}$ is given by

$$
\langle \hat{A} \rangle \equiv \int \Psi^* \hat{A} \Psi \, d\tau,
$$

if it is a physically observable quantity, it must real:
\[
\langle \hat{A} \rangle^* = \langle \hat{A} \rangle \text{ so } \int \Psi^* \hat{A} \Psi \, d\tau = \int \Psi (\hat{A} \Psi)^* \, d\tau .
\]

Thus, the Hermitian property of operators associated with observables guarantees that calculated quantities for these observables will be real.

Example: Is \( \hat{p}_x \) Hermitian?

\[
\int_{-\infty}^{\infty} \Psi^* \hat{p}_x \Psi \, dx = \int_{-\infty}^{\infty} \Psi^* \left( \frac{\hbar}{i} \frac{d}{dx} \right) \Psi \, dx = \frac{\hbar}{i} \int_{-\infty}^{\infty} \Psi^* \left( \frac{d}{dx} \Psi \right) \, dx = \int \Psi (\hat{p}_x \Psi)^* \, dx
\]

(Integrate by parts, \( \int u \, dv = uv \big|_{-\infty}^{\infty} - \int v \, du \))

\[
= \frac{\hbar}{i} \Psi \Psi^* \bigg|_{-\infty}^{\infty} - \frac{\hbar}{i} \int_{-\infty}^{\infty} \Psi \left( \frac{d}{dx} \Psi^* \right) \, dx = \int \Psi \left( \frac{\hbar}{i} \frac{d}{dx} \Psi \right)^* \, dx = \int \Psi (\hat{p}_x \Psi)^* \, dx
\]

Note that if \( \hat{p}_x \) didn't have the factor of \( i \) in front, it wouldn't be Hermitian.

**Orthogonality (Definition):**

Two functions \( \varphi \) and \( \chi \) are said to be orthogonal if

\[ \int \varphi^* \chi \, d\tau = 0 \]

**Important property of Hermitian Operators:** Eigenfunctions of a Hermitian operator are orthogonal. (In the case where two or more eigenfunctions have the same eigenvalue, then the eigenfunctions can be made to be orthogonal).

Proof: suppose \( \varphi_i \) and \( \varphi_j \) are eigenfunctions of \( \hat{A} \) with respective eigenvalues \( a_i \) and \( a_j \) such that \( a_i \neq a_j \):

\[ \hat{A} \varphi_i = a_i \varphi_i \quad ; \quad \hat{A} \varphi_j = a_j \varphi_j \]

By use of the Hermitian property we get:

\[ \int \varphi_i^* \hat{A} \varphi_j \, d\tau = \int \varphi_j (\hat{A} \varphi_i)^* \, d\tau, \]

now operate with \( \hat{A} \) on both sides of the equation:

\[ a_i \int \varphi_i^* \varphi_j \, d\tau = a_i^* \int \varphi_i \varphi_i^* \, d\tau. \]

\( a_i \) is real because \( \hat{A} \) is Hermitian. Then we have

\[ (a_i - a_j) \int \varphi_j \varphi_i^* \, d\tau = 0 \quad \Rightarrow \quad \int \varphi_j \varphi_i^* \, d\tau = 0. \]

Now, if \( a_i = a_j \), then we are free to combine \( \varphi_i \) and \( \varphi_j \) and we will still have an eigenfunction (see the example concerning \( \frac{d}{dx}^2 \) above). For example, suppose \( \varphi_1 \) and \( \varphi_2 \) both have eigenvalue \( a \) with respect to operator \( \hat{A} \). Then we can take

\[ \chi_1 = \varphi_1 \text{ and } \chi_2 = \varphi_2 + c \varphi_1 \]

and we can choose \( c = -\frac{\int \varphi_1^* \varphi_2 \, d\tau}{\int \varphi_1^* \varphi_1 \, d\tau} \).

You can show that \( \chi_1 \) and \( \chi_2 \) are orthogonal and both still have eigenvalue \( a \). \( \text{QED.} \)
**Very Important Fact:** Commuting operators have common eigenfunctions.

Suppose $\hat{A}$ and $\hat{B}$ commute: $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} = 0$.

Let $\{\phi_i\}$ be the set of eigenfunctions of $\hat{A}$:

$$\hat{A}\phi_i = a_i \phi_i$$

then, $\hat{B}(\hat{A}\phi_i) = \hat{B}(a_i \phi_i) = a_i (\hat{B}\phi_i)$

but $\hat{A}\hat{B} = \hat{B}\hat{A}$ so $\hat{A}(\hat{B}\phi_i) = a_i (\hat{B}\phi_i)$

∴ the function $\hat{B}\phi_i$ is an eigenfunction of $\hat{A}$ with eigenvalue $a_i$. If $\phi_i$ is the only eigenfunction of $\hat{A}$ with eigenvalue $a_i$, then $\hat{B}\phi_i \propto \phi_i$ (in other words, $\hat{B}\phi_i$ can only be an eigenfunction of $\hat{A}$ with eigenvalue $a_i$ if it differs from $\phi_i$ by a constant multiplicative factor – p. 2 of this handout). Thus,

$$\hat{B}\phi_i = b_i \phi_i$$

for some constant $b_i$.

If $a_i$ is a degenerate eigenvalue, i.e. there are more than one eigenfunctions of $\hat{A}$ with eigenvalue $a_i$, then we can take linear combinations of these eigenfunctions to satisfy this condition.