Now that we have constructed a bit of a toolkit for how to work with quantum operators and their eigenfunctions, we can finally start to lay out the Postulates – the governing rules of quantum mechanics. Today we will work towards summarizing five Postulates. Today’s lecture covers material in Chapter 4 of McQuarrie.

1 Postulate 1: Wavefunctions are probability distributions

The state of a quantum mechanical system is completely described by its wavefunction $\Psi(\vec{r}, t)$, which depends on spatial coordinates $\vec{r} = [x, y, z]$, time $t$, and sometimes other parameters (for instance spin, $\vec{s}$).

The wavefunction encodes a probability distribution of where we expect to find the particle in space at a given time. For a 1D wavefunction $\Psi(x, t)$, the probability that the particle lies in the window $[x_1, x_2]$ can be expressed as:

$$P = \int_{x_1}^{x_2} \Psi^*(x, t)\Psi(x, t)dx = \int_{x_1}^{x_2} |\Psi(x, t)|^2 dx$$  \hspace{1cm} (1)

assuming of course that $\Psi(x, t)$ is normalized to unity, with $\int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx = 1$.

In order to be a valid wavefunction, $\Psi(x, t)$ must be single-valued. Otherwise a particle would have multiple contradictory probabilities for being found in the same region of space. $\Psi(x, t)$ and its derivative must also be continuous.

**Example:** let’s consider the ground state of a 1D particle in a box of size $a$, which we know to be:

$$\psi_1(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right)$$  \hspace{1cm} (2)

What’s the probability that we find the particle in the left half of the box, between $x = 0$ and $x = a/2$? By inspection of the symmetry of $|\psi_1(x)|^2$, we can guess that the probability will be $1/2$:
Let’s confirm this suspicion mathematically. The probability that the particle lies in the window \(x = [0, a/2]\) is given by:

\[
P[0, a/2] = \int_0^{a/2} |\psi_1|^2 dx
\]

(3)

\[
P[0, a/2] = \int_0^{a/2} \sqrt{\frac{2}{a}} \sin \left( \frac{\pi x}{a} \right)^2 dx
\]

(4)

\[
P[0, a/2] = \frac{2}{a} \int_0^{a/2} \sin^2 \left( \frac{\pi x}{a} \right) dx
\]

(5)

Let’s make use of the trigonometric integral:

\[
\int \sin^2(\alpha x) = \frac{x}{2} - \frac{\sin(2\alpha x)}{4\alpha}
\]

(6)

where we will take \(\alpha = \frac{\pi}{a}\). Therefore:

\[
P[0, a/2] = \frac{2}{a} \left[ \frac{x}{2} - \frac{\sin(2\cdot \frac{\pi}{a} x)}{4\pi/a} \right]_0^{a/2}
\]

(7)

\[
P[0, a/2] = \frac{2}{a} \left[ \frac{a}{4} - \frac{\sin(2\cdot \frac{\pi}{a} \cdot \frac{a}{2})}{4\pi/a} - \frac{\sin(0)}{4\pi/a} \right]
\]

(8)

\[
P[0, a/2] = \frac{2}{a} \left[ \frac{a}{4} - \frac{\sin(\pi)}{4\pi/a} \right]
\]

(9)

\[
P[0, a/2] = \frac{2}{4} = \frac{1}{2}
\]

(10)

1.1 Postulate 2: Every observable has a corresponding operator

For every measurable property of a system, there must be a corresponding quantum mechanical operator. A lab experiment that measures a value for that observable is represented in quantum mechanics by operating on the system’s wavefunction with the corresponding operator.

Recall these examples, some of which we have already discussed:

<table>
<thead>
<tr>
<th>(x)</th>
<th>(\hat{x})</th>
</tr>
</thead>
<tbody>
<tr>
<td>position</td>
<td>position operator</td>
</tr>
</tbody>
</table>

\[
p_x \rightarrow \hat{p}_x = -i\hbar \frac{d}{dx}
\]

momentum | momentum operator

<table>
<thead>
<tr>
<th>(T_x)</th>
<th>(\hat{T}_x = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>kinetic energy</td>
<td>kinetic energy operator</td>
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</table>

\[
E \rightarrow \hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)
\]

energy | Hamiltonian operator
All quantum mechanical operators belong to a class called *Hermitian operators*. One of the important properties of Hermitian operators is that they have real eigenvalues. This is consistent with the fact that physical objects can never have complex or imaginary positions, momenta, energies, etc.

2 Postulate 3: A measurement reads out an eigenvalue

If we measure an observable that corresponds to the operator $\hat{A}$, then the result of that measurement will always be an eigenvalue of $\hat{A}$.

For example, if we measure the energy level of a hydrogen atom in the lab and read out the value $E$, we have just acted with the Hamiltonian energy operator on the atom’s wavefunction and the value $E$ that we have measured must be an eigenvalue of $\hat{H}$. This makes a certain amount of sense! We know that the hydrogen atom has discrete allowed energies, so we expect to only be able to measure those discrete values. However, what might be a little surprising is that the state of the system need not be an eigenfunction of $\hat{H}$ in order for us to measure the eigenvalue $E$.

**Example:** Suppose we have a system with the following normalized wavefunction:

$$\phi(x) = c_1 \psi_1(x) + c_2 \psi_2(x)$$  \hspace{1cm} (11)

where $\psi_1(x)$ and $\psi_2(x)$ are eigenfunctions of the Hamiltonian energy operator $\hat{H}$ with energies $e_1$ and $e_2$. You can imagine that these are the two lowest energy states of the 1D particle in a box, for instance. What values of energy will you observe experimentally when you make a measurement $\hat{H}\phi(x)$ on the system? What is the likelihood of measuring each energy value?

Since our wavefunction consists of a linear combination of energy eigenfunctions $\psi_1(x)$ and $\psi_2(x)$, we expect to only measure one of two possible energies when we make the measurement $\hat{H}\phi(x)$. We will either measure $e_1$ or $e_2$. The probabilities of each of these values being measured is given by the relative weighting of the eigenfunctions $\psi_1(x)$ and $\psi_2(x)$ in $\phi(x)$. In particular, we will measure $e_1$ with probability $|c_1|^2$ and $e_2$ with probability $|c_2|^2$.

For an evenly weighted superposition state:

$$\phi(x) = \frac{1}{\sqrt{2}} \psi_1(x) + \frac{1}{\sqrt{2}} \psi_2(x)$$  \hspace{1cm} (12)

we are equally likely to measure $e_1$ or $e_2$ when we apply the Hamiltonian operator to our wavefunction.

In the most general case, if we have

$$\phi(x) = \sum_{n=1}^{\infty} c_n \psi_n(x)$$  \hspace{1cm} (13)

where the eigenvalue of $\psi_n(x)$ is $e_n$, then the probability that we measure $e_n$ when we take $\hat{H}\phi(x)$ is $|c_n|^2$.

3 Postulate 4: Expectation values

Say we have a system in the state $\phi(x)$, and we measure the observable $A$ by applying the operator $\hat{A}$. If we were to repeat this measurement many times, the average of our many measured values
of $A$, also known as the *expectation value*, is given by

$$\langle A \rangle = \int_{-\infty}^{\infty} \phi^*(x) \hat{A} \phi(x) \, dx \quad (14)$$

where $\phi(x)$ is normalized.

Let’s unpack this a bit. If $\phi(x)$ is an eigenvector of $\hat{A}$, e.g. $\phi(x) = \psi_n(x)$ with $\hat{A}\psi_n(x) = a_n\psi_n(x)$, then we have:

$$\langle A \rangle = \int_{-\infty}^{\infty} \psi_n^*(x) \hat{A} \psi_n(x) \, dx \quad (15)$$

$$= \int \psi_n^* a_n \psi_n \, dx \quad (16)$$

$$= a_n \int \psi_n^* \psi_n \, dx \quad (17)$$

$$= |a_n|^2 \quad (18)$$

This is what we should expect. When $\phi(x)$ is an eigenvector, the expected value of the measurement is simply the relevant eigenvalue.

What about when $\phi(x)$ is *not* an eigenvector of $\hat{A}$? Let’s say that $\phi(x)$ is a linear combination of $\psi_1(x)$ and $\psi_2(x)$, which are eigenvectors of $\hat{A}$ with eigenvalues of $a_1$ and $a_2$:

$$\phi(x) = c_1\psi_1(x) + c_2\psi_2(x) \quad (19)$$

Then, we can calculate $\langle a \rangle$ as:

$$\langle A \rangle = \int \phi^*(x) \hat{A} \phi(x) \, dx \quad (20)$$

$$= \int \left[ c_1^* \psi_1^*(x) + c_2^* \psi_2^*(x) \right] \hat{A} \left[ c_1\psi_1(x) + c_2\psi_2(x) \right] \, dx \quad (21)$$

$$= \int \left[ c_1^* \psi_1^*(x) + c_2^* \psi_2^*(x) \right] \left[ a_1 c_1\psi_1(x) + a_2 c_2\psi_2(x) \right] \, dx \quad (22)$$

$$= \int \left[ c_1^* \psi_1^*(x) + c_2^* \psi_2^*(x) \right] \left[ a_1 c_1\psi_1(x) + a_2 c_2\psi_2(x) \right] \, dx \quad (23)$$

Because $\psi_1(x)$ and $\psi_2(x)$ are eigenfunctions of the same operator, we have learned they must be orthogonal. Therefore their cross-terms in the expression above will vanish, and we are left with:

$$\langle A \rangle = a_1 |b_1|^2 + a_2 |b_2|^2 \quad (24)$$

The expected value $\langle A \rangle$ is therefore an average of the two eigenvalues $a_1$ and $a_2$ weighted by the relative contributions of their two eigenvectors to $\psi(x)$.

We can generalize this finding to say that if $\phi(x)$ is written as a full expansion of eigenvectors:

$$\phi(x) = \sum_n b_n \psi_n(x) \quad (26)$$
then we must have

$$
\langle A \rangle = \sum_n a_n |b_n|^2
$$

(27)

**Example:** For the superposition state given by

$$
\phi(x) = \frac{\sqrt{3}}{2} \psi_1(x) + \frac{i}{2} \psi_2(x)
$$

(28)

What is the expected value of the energy you would get from averaging together many repeated measurements?

**Another example:** We can use this same way of calculating expectation values to extract other interesting information about quantum particles. For instance: what is the average value of momentum $p$ for a 1D particle in a box in its ground state? We know the momentum operator is:

$$
\hat{p} = -i\hbar \frac{d}{dx}
$$

(29)

and ground state 1D PIB wavefunction is

$$
\psi_1(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right)
$$

(30)

therefore:

$$
\langle p \rangle = \int_0^a \psi_1^*(x) \cdot \hat{p} \cdot \psi_1(x) dx
$$

(31)

$$
= \int_0^a \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right) \cdot \left(-i\hbar \frac{d}{dx}\right) \cdot \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right) dx
$$

(32)

$$
= -i\hbar \cdot \frac{2}{a} \int_0^a \sin\left(\frac{\pi x}{a}\right) \frac{d}{dx} \left[ \sin\left(\frac{\pi x}{a}\right) \right] dx
$$

(33)

$$
= -i\hbar \cdot \frac{2}{a} \int_0^a \sin\left(\frac{\pi x}{a}\right) \cdot \frac{\pi}{a} \cdot \cos\left(\frac{\pi x}{a}\right) dx
$$

(34)

$$
= -i\hbar \cdot \frac{2\pi}{a^2} \int_0^a \sin\left(\frac{\pi x}{a}\right) \cos\left(\frac{\pi x}{a}\right) dx
$$

(35)

We can make use of a trigonometric identity here: $\sin(\alpha x) \cos(\alpha x) = \frac{1}{2} \sin(2\alpha x)$. So our integral becomes:

$$
\int_0^a \frac{1}{2} \sin\left(\frac{2\pi x}{a}\right) dx
$$

(36)

$$
= \frac{1}{2} \left[ -\frac{a}{2\pi} \cos\left(\frac{2\pi x}{a}\right) \right]_0^a
$$

(37)

$$
= -\frac{a}{4\pi} \left[ \cos\left(\frac{2\pi a}{a}\right) - \cos(0) \right]
$$

(38)

$$
= -\frac{a}{4\pi} \left[ \cos(2\pi) - \cos(0) \right] = 0
$$

(39)

So $\langle p \rangle = 0$ for our particle in a box ground state wavefunction! This turns out to be true for any PIB wavefunction with any value of $n$. A way to rationalize this intuitively is that the particle’s momentum averages out to zero because it’s equally likely to be moving towards the left or right at any given moment, due to the symmetry of the system.
The evolution in time of a quantum wavefunction is determined by the time-dependent Schrodinger equation. I will write it down once more here for posterity. The 1D time-dependent Schrodinger equation takes the form:

\[
\hat{H}\Psi(x, t) = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} + V(x, t)\Psi(x, t) = i\hbar \frac{\partial \Psi(x, t)}{\partial t}
\]  

(40)

Recall that if \( \psi(x) \) is a solution to the time-independent Schrodinger equation (e.g. a stationary state), then its complete time-dependent form can be obtained from solving the time-dependent Schrodinger equation, which gives the following result:

\[
\Psi(x, t) = C \cdot \psi(x) \cdot e^{-i\omega t} \equiv C \cdot \psi(x) \cdot e^{-i(E/h)t}
\]  

(41)

where \( \omega = E/h \), since \( E = h\nu = \hbar \omega \). What makes \( \Psi(x, t) \) a standing wave? In quantum mechanics, a standing wave has a probability distribution that is not time dependent:

\[
|\Psi(x, t)|^2 = |\Psi^*(x, t) \cdot \Psi(x, t)|^2 = |C\psi(x)|^2 \equiv C^*\psi^*(x) \cdot \psi(x) \cdot e^{-i\omega t} \cdot e^{-i\omega t}
\]  

(42)

Which is indeed not a function of time, since the complex conjugates of the temporal component cancel each other out.

Another example: What if we are not in a stationary state? Is there a more interesting time-dependence of our probability distribution in this case? Consider a superposition state

\[
\Phi(x, t) = c_1\psi_1(x)e^{-i\omega_1 t} + c_2\psi_2(x)e^{-i\omega_2 t}
\]  

(46)

where \( \psi_1(x) \) and \( \psi_2(x) \) are stationary states, e.g. solutions of \( \hat{H} \).

The probability density is given by:

\[
|\Phi(x, t)|^2 = |c_1\psi_1(x)e^{-i\omega_1 t} + c_2\psi_2(x)e^{-i\omega_2 t}|^2
\]  

(47)

\[
= |c_1\psi_1^*(x)e^{+i\omega_1 t} + c_2\psi_2^*(x)e^{+i\omega_2 t}| \cdot [c_1\psi_1(x)e^{-i\omega_1 t} + c_2\psi_2(x)e^{-i\omega_2 t}]
\]  

(48)

\[
= |c_1|^2|\psi_1(x)|^2 + |c_2|^2|\psi_2(x)|^2 + c_1^*c_2\psi_1^*(x)\psi_2^*(x)e^{+i(\omega_1 - \omega_2)t}
\]  

(49)

\[
+ c_1c_2^*\psi_1^*(x)\psi_2^*(x)e^{-i(\omega_1 - \omega_2)t}
\]  

(50)

Here our time-dependence does not cancel out neatly! The likelihood that we find the particle in a given region of space changes over time. It’s a general phenomenon that superpositions of stationary states have more complicated temporal dynamics than pure stationary states.