

CHM 305 - Lecture 6 - The Rules of Quantum Mechanics (Part 2)

Prof. Marissa Weichman

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:

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

In order to be a valid wavefunction that we can use as a nice, well-behaved probability distribution, we require:

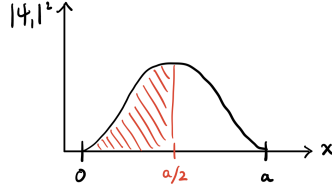
- $\Psi(x, t)$ is **normalized** with $\int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx = 1$. This ensures that the probability of finding the particle *somewhere* is 100%.
- $\Psi(x, t)$ is **single-valued**. Otherwise a particle would have multiple contradictory probabilities for being found in the same region of space.
- $\Psi(x, t)$ is **continuous**.
- $\Psi(x, t)$ is **smooth**, meaning that $\frac{\partial}{\partial x} \Psi(x, t)$ is continuous.

1.1 Example: PIB probabilities

Let's consider the ground state of a 1D particle in a box of size a , which we know to be:

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

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 $x = [0, \frac{a}{2}]$ is given by:

$$P[0, \frac{a}{2}] = \int_0^{\frac{a}{2}} |\psi_1|^2 dx = \int_0^{\frac{a}{2}} \left[\sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right) \right]^2 dx = \frac{2}{a} \int_0^{\frac{a}{2}} \sin^2\left(\frac{\pi x}{a}\right) dx \quad (3)$$

Let's make use of the trigonometric integral:

$$\int \sin^2(\alpha x) = \frac{x}{2} - \frac{\sin(2\alpha x)}{4\alpha} \quad (4)$$

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

$$P[0, \frac{a}{2}] = \frac{2}{a} \left[\frac{x}{2} - \frac{\sin(2 \cdot \frac{\pi}{a} x)}{4\pi/a} \right]_0^{a/2} = \frac{2}{a} \left[\frac{a}{4} - \frac{\sin(\frac{2\pi}{a} \cdot \frac{a}{2})}{4\pi/a} - \frac{0}{2} + \frac{\sin(0)}{4\pi/a} \right] \quad (5)$$

$$= \frac{2}{a} \left[\frac{a}{4} - \frac{\sin(\pi)}{4\pi/a} \right] = \frac{2}{4} = \boxed{\frac{1}{2}} \quad \checkmark \quad (6)$$

Note that solving for, e.g. the probability that the particle lies in the window $x = [0, \frac{a}{4}]$ would be difficult to evaluate visually, and we'd have to use the integral method.

2 Postulate 2: Every observable has a corresponding operator

For every measurable property of a system, there is 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:

making a lab measurement	\longleftrightarrow	applying a quantum operator	
x	\longleftrightarrow	\hat{x}	$\hat{x} \psi(x) \equiv x\psi(x)$
position		position operator	
p_x	\longleftrightarrow	$\hat{p}_x = -i\hbar \frac{d}{dx}$	$\hat{p}_x \psi(x) \equiv -i\hbar \frac{\partial}{\partial x} \psi(x)$
momentum		momentum operator	
T_x	\longleftrightarrow	$\hat{T}_x = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$	
kinetic energy		kinetic energy operator	
E	\longleftrightarrow	$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$	
energy		Hamiltonian operator	

All quantum mechanical operators belong to a class called *Hermitian operators*. Importantly, **Hermitian operators have real eigenvalues**. This captures the fact that physical objects can never have complex or imaginary physical observables (positions, momenta, energies, etc.).

3 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 one of the set of eigenvalues of \hat{A} , which we label $\{a_n\}$.

For example, if we measure the energy level of a hydrogen atom with an instrument in the lab and read out some value e_n , we have just acted with the Hamiltonian energy operator on the atom's wavefunction and the value e_n 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. 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_n !

Let's make this more concrete. Suppose we have a system with the following normalized wavefunction:

$$\phi(x) = c_1\psi_1(x) + c_2\psi_2(x) \quad (7)$$

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

Let's break this down:

- Let's first note that if $\psi_1(x)$ and $\psi_2(x)$ are normalized, then for $\phi(x)$ to be normalized, we must have $|c_1|^2 + |c_2|^2 = 1$. Therefore, $|c_1|^2$ and $|c_2|^2$ represent the relative **weighting** of the eigenfunctions $\psi_1(x)$ and $\psi_2(x)$ in $\phi(x)$.
- Since our wavefunction consists of a linear combination of only the energy eigenfunctions $\psi_1(x)$ and $\psi_2(x)$, we expect to only measure their two corresponding energy eigenvalues when we make the measurement $\hat{H}\phi(x)$. We will therefore either measure e_1 or e_2 .
- The probability that we measure e_1 or e_2 being measured is given by the relative weighting of the eigenfunctions $\psi_1(x)$ and $\psi_2(x)$ in $\phi(x)$. Therefore, we will measure e_1 with probability $|c_1|^2$ and e_2 with probability $|c_2|^2$.
- The probability that we measure any other eigenvalue with index $n \neq 1, 2$ (e.g. $e_3 \dots e_n$) is exactly zero, because the corresponding eigenfunctions do not contribute to our wavefunction.

For an evenly weighted superposition state

$$\phi(x) = \frac{1}{\sqrt{2}}\psi_1(x) + \frac{1}{\sqrt{2}}\psi_2(x) \quad (8)$$

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

$$\phi(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) \quad (9)$$

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 $|c_n|^2$.

Note again that $\phi(x)$ must be normalized, implying that $\sum |c_n|^2 = 1$. This is convenient, as our probability of measuring one of the values of e_n whose eigenfunction is represented in $\phi(x)$ is 100%.

Practice Problem 1: Consider the superposition state

$$\phi(x) = \frac{\sqrt{3}}{2}\psi_1(x) + \frac{i}{2}\psi_2(x) \quad (10)$$

where $\psi_n(x)$ is the eigenfunction of the \hat{A} operator with eigenvalue a_n .

- What are the possible values we would measure when applying \hat{A} to $\phi(x)$?
- What are the probabilities of making each of those measurements?

4 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

$$\langle A \rangle = \int_{-\infty}^{\infty} \phi^*(x) \hat{A} \phi(x) dx \quad (11)$$

where $\phi(x)$ is normalized.

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

$$\langle A \rangle = \int_{-\infty}^{\infty} \psi_n^*(x) \hat{A} \psi_n(x) dx \quad (12)$$

$$= \int \psi_n^* a_n \psi_n dx \quad (13)$$

$$= a_n \int \psi_n^* \psi_n dx \quad (14)$$

$$= \boxed{a_n} \checkmark \quad (15)$$

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

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

$$\phi(x) = c_1\psi_1(x) + c_2\psi_2(x) \quad (16)$$

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

$$\langle A \rangle = \int \phi^*(x) \hat{A} \phi(x) dx \quad (17)$$

$$= \int \left[c_1^* \psi_1^*(x) + c_2^* \psi_2^*(x) \right] \hat{A} \left[c_1 \psi_1(x) + c_2 \psi_2(x) \right] dx \quad (18)$$

$$= \int \left[c_1^* \psi_1^*(x) + c_2^* \psi_2^*(x) \right] \left[a_1 c_1 \psi_1(x) + a_2 c_2 \psi_2(x) \right] dx \quad (19)$$

Note that we always evaluate expressions like the ones above by applying the operator \hat{A} to the wavefunction that follows it.

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:

$$\langle A \rangle = a_1 c_1 c_1^* \int \psi_1^* \psi_1 dx + a_2 c_2 c_2^* \int \psi_2^* \psi_2 dx \quad (20)$$

$$= a_1 |c_1|^2 + a_2 |c_2|^2 \quad (21)$$

Where we have also assumed that the ψ_n are normalized. 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 corresponding eigenfunctions to $\psi(x)$.

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

$$\phi(x) = \sum_n c_n \psi_n(x) \quad (22)$$

then we must have

$$\langle A \rangle = \sum_n a_n |c_n|^2 \quad (23)$$

assuming, again, that the set of $\{\psi_n(x)\}$ are eigenfunctions of \hat{A} with eigenvalues $\{a_n\}$. In order to evaluate the expectation value of a given operator, you must always start with expressing your system in the basis of eigenstates of that operator!

Practice Problem 2: For the same superposition state from Practice Problem 1, given by

$$\phi(x) = \frac{\sqrt{3}}{2} \psi_1(x) + \frac{i}{2} \psi_2(x) \quad (24)$$

What is the expected value of the energy you would get from averaging together many repeated measurements with the \hat{A} operator?

4.1 Calculating the expectation value of momentum

We can use this method of calculating expectation values to extract all kinds of 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:

$$\hat{p} = -i\hbar \frac{d}{dx} \quad (25)$$

and ground state 1D PIB wavefunction is

$$\psi_1(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right) \quad (26)$$

therefore:

$$\langle p \rangle = \int_0^a \psi_1^*(x) \cdot \hat{p} \cdot \psi_1(x) dx \quad (27)$$

$$= \int_0^a \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right) \cdot \left(-i\hbar \frac{d}{dx}\right) \cdot \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right) dx \quad (28)$$

$$= -i\hbar \cdot \frac{2}{a} \int_0^a \sin\left(\frac{\pi x}{a}\right) \frac{d}{dx} \left[\sin\left(\frac{\pi x}{a}\right)\right] dx \quad (29)$$

$$= -i\hbar \cdot \frac{2}{a} \int_0^a \sin\left(\frac{\pi x}{a}\right) \cdot \frac{\pi}{a} \cdot \cos\left(\frac{\pi x}{a}\right) dx \quad (30)$$

$$= -i\hbar \cdot \frac{2\pi}{a^2} \int_0^a \sin\left(\frac{\pi x}{a}\right) \cos\left(\frac{\pi x}{a}\right) dx \quad (31)$$

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:

$$\int_0^a \frac{1}{2} \sin\left(\frac{2\pi x}{a}\right) dx \quad (32)$$

$$= \frac{1}{2} \left[-\frac{a}{2\pi} \cos\left(\frac{2\pi x}{a}\right) \right]_0^a \quad (33)$$

$$= -\frac{a}{4\pi} \left[\cos\left(\frac{2\pi a}{a}\right) - \cos(0) \right] \quad (34)$$

$$= -\frac{a}{4\pi} [\cos(2\pi) - \cos(0)] = \boxed{0} \quad (35)$$

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.

5 Postulate 5: The Time-Dependent Schrodinger Equation

The evolution in time of a quantum wavefunction is determined by the time-dependent Schrödinger equation. I will write it down once more here for posterity. The 1D time-dependent Schrödinger equation takes the form:

$$\hat{H}\Psi(x, t) = \left[\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x, t) \right] \Psi(x, t) = i\hbar \frac{\partial \Psi(x, t)}{\partial t} \quad (36)$$

5.1 Stationary states

If $\psi_n(x)$ is a solution to the time-*independent* Schrödinger equation (e.g. a stationary state with index n), then we can use separation of variables to solve Eqn. 36 and obtain a very simple time-dependence (see the Lecture 3 notes if this doesn't ring a bell):

$$\Psi_n(x, t) = C \cdot \psi_n(x) \cdot e^{-i(E_n/\hbar)t} \equiv C \cdot \psi_n(x) \cdot e^{-i\omega_n t} \quad (37)$$

where $\omega_n \equiv E_n/\hbar$.

What makes $\Psi(x, t)$ a standing wave? In quantum mechanics, a standing wave has a probability distribution that is not time dependent:

$$|\Psi_n(x, t)|^2 = \Psi_n^*(x, t) \cdot \Psi_n(x, t) \quad (38)$$

$$= \left[C\psi_n(x)e^{-i\omega_n t} \right]^* \cdot \left[C\psi_n(x)e^{-i\omega_n t} \right] \quad (39)$$

$$= \left[C^*\psi_n^*(x)e^{+i\omega_n t} \right] \cdot \left[C\psi_n(x)e^{-i\omega_n t} \right] \quad (40)$$

$$= |C\psi_n(x)|^2 \quad \checkmark \quad (41)$$

Which is indeed not a function of time, since the complex conjugate of the temporal component cancels itself out.

5.2 Superposition states

What if we are not in a stationary state? There is a more interesting time-dependence of our probability distribution in this case. Consider a superposition state

$$\Phi(x, t) = c_1\psi_1(x)e^{-i\omega_1 t} + c_2\psi_2(x)e^{-i\omega_2 t} \quad (42)$$

where $\psi_1(x)$ and $\psi_2(x)$ are energy eigenfunctions (or stationary states).

The probability density is given by:

$$|\Phi(x, t)|^2 = |c_1\psi_1(x)e^{-i\omega_1 t} + c_2\psi_2(x)e^{-i\omega_2 t}|^2 \quad (43)$$

$$= [c_1^*\psi_1^*(x)e^{+i\omega_1 t} + c_2^*\psi_2^*(x)e^{+i\omega_2 t}] [c_1\psi_1(x)e^{-i\omega_1 t} + c_2\psi_2(x)e^{-i\omega_2 t}] \quad (44)$$

$$= |c_1|^2|\psi_1(x)|^2 + |c_2|^2|\psi_2(x)|^2 \quad (45)$$

$$+ c_1^*c_2\psi_1^*(x)\psi_2(x)e^{+i(\omega_1-\omega_2)t} \quad (46)$$

$$+ c_1c_2^*\psi_1(x)\psi_2^*(x)e^{-i(\omega_1-\omega_2)t} \quad (47)$$

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. In fact, the probability distribution oscillates with a frequency of $\omega_1 - \omega_2 = (E_1 - E_2)/\hbar$.

It's a general phenomenon that superposition states have temporal dynamics that oscillate at frequencies related to the energy differences between each pair of energy eigenstates present in the superposition.

6 Some final rules of thumb

Here are a few handy take-aways from what we've learned in this lecture:

1. In general, the probability distribution $|\Psi(x, t)|$ is *time-independent* if $\Psi(x, t)$ is a stationary state / energy eigenfunction.
2. In general, the probability distribution $|\Psi(x, t)|$ will oscillate in time if $\Psi(x, t)$ is a superposition of energy eigenfunctions.
3. In general, the expectation value of some observable $\langle A \rangle$ is *time-independent* if the state of the system $\Psi(x, t)$ is prepared in an eigenfunction of the \hat{A} operator.
4. In general, the expectation value of some observable $\langle A \rangle$ will oscillate in time if the state of the system $\Psi(x, t)$ is prepared in a superposition of eigenfunctions of the \hat{A} operator.
5. The expectation value of *energy* turns out to be special however. The expectation value of the energy $\langle E \rangle$ is *always time-independent*, whether the system is prepared in an energy eigenfunction or in a superposition of energy eigenfunctions.

The exercise is left to the reader to see why this is. Try evaluating $\langle E \rangle$ for the arbitrary superposition state $\Phi(x, t) = \sum_n \psi_n(x) e^{-i\omega_n t}$, where $\psi_n(x)$ are energy eigenfunctions and see what happens.

Practice Problem 3: What is the expected value of the energy of the particle-in-a-box superposition state below?

$$\Phi(x, t) = \frac{1}{\sqrt{2}} \Psi_1(x, t) + \frac{1}{\sqrt{2}} \Psi_2(x, t) \quad (48)$$

$$= \frac{1}{\sqrt{2}} \left(\frac{2}{a}\right)^{1/2} \sin\left(\frac{\pi x}{a}\right) e^{-iE_1 t/\hbar} + \frac{1}{\sqrt{2}} \left(\frac{2}{a}\right)^{1/2} \sin\left(\frac{2\pi x}{a}\right) e^{-iE_2 t/\hbar} \quad (49)$$