

2 The Postulates of Quantum Mechanics

2.1 Introduction

In light of the series of experiments performed in the early 20th century that we have discussed, it became clear that existing theories of classical physics did not adequately describe these newly discovered phenomena, particularly the quantization of the energies of atoms and molecules, the quantization of light itself, and the wave-particle duality of both light and matter.

Think about the process by which science moves forward. One proposes a theory that describes the existing experimental phenomena. One then tests the theory by performing additional experiments. If the theory describes all known phenomena, one begins to accept it as being true. There may be a small number of observations that a theory doesn't predict, and in some cases it may cause one to reexamine the experiment to make sure it was done properly. However, as the number of experimental observations that the theory cannot account for increases, the theory must be replaced. Sometimes this happens by making slight modifications of the existing theory, and sometimes the old theory is completely overturned and replaced by one with a totally different perspective.

This is what occurred in 1925 when Erwin Schrödinger and Werner Heisenberg, working independently, formulated a general quantum theory. The quantum theory provided a completely different way to view physical systems. It was a revolutionary way of thinking and requires abandoning much of the intuition that one develops from the macroscopic world. In certain limits, the quantum theory reduces to the classical theory, so that not only does it describe the newly observed phenomena, but the existing body of scientific results as well.

The theories independently formulated by Schrödinger and Heisenberg are mathematically different. Schrödinger used a differential equation approach whereas Heisenberg used a matrix formalism. While at first the two theories appeared different in substance, a year later Schrödinger demonstrated that the two formulations are mathematically equivalent.

In this course, I will follow the differential equation approach formulated by Schrödinger, although later in the course I may introduce aspects of the Heisenberg approach. I will not present quantum mechanics in an historical manner, however--that is by following the way that Schrödinger first developed it. We will take advantage of hindsight, particularly in the interpretations of certain aspects of the theory. I will present to you a new way of thinking, and ask you to try to abandon much of the intuition you have developed during your first year of physics.

I will introduce the quantum theory by presenting to you a series of **6 postulates**. All my further development of quantum mechanics will be based on those six postulates. It is important to realize what a postulate is (and what it is not). A **postulate** is a statement of thesis, not particularly a statement of fact. It is not a law. It can always come under scrutiny and should do so. The test of whether a postulate is correct is if it describes experimental results -- that is, that it works!!

I will present and briefly discuss each of these 6 postulates and give examples of applications to simple quantum mechanical systems where necessary.

We will treat these postulates like laws in the sense we will base our intuition and predictions about the properties of molecules on these postulates. One must always recognize, however that tomorrow someone might observe some property or phenomena that is not in accord with these postulates.

This may seem a bit disturbing to approach science in this way in that we like to have laws that one can derive mathematically. While it might seem a bit uncomfortable, it is no different from classical physics, for example. At the very depth of our laws and rules in science there are always postulates that are accepted simply because they work, *i.e.*, the theory based upon them predicts the results of experiment. Examples are Coulombs law or the gravitational force.



[Werner Heisenberg](#)



[Erwin Schrödinger](#)

Two primary concepts are involved in the postulates of quantum mechanics:

- The state of a system
- Physical observables

A physical observable is simply some variable that can be measured. Examples are position, momentum, angular momentum, and energy.

2.2 Postulate 1

The state of a quantum mechanical system is completely specified by a function $\Psi(\mathbf{r},t)$ that depends on the coordinates of the particle and on the time. $\Psi(\mathbf{r},t)$ is called the wave function or state function and has the property that $\Psi^*(\mathbf{r},t)\Psi(\mathbf{r},t)dxdydz$ is the probability that the particle lies in the volume element $dxdydz$ at position \mathbf{r} at time t .

- This postulate says that $\Psi(\mathbf{r},t)$ exists and in principle can be determined.
- If $\Psi(\mathbf{r},t)$ is known, it can predict how the system changes with time (*i.e.* how the probability distribution changes).

This situation is in contrast to that of classical mechanics. In a classical mechanical system, given Newton's equations of motion and a set of initial coordinates and momenta, one can determine the trajectories of the particles for all time. This is not possible in Quantum Mechanics due to the Heisenberg Uncertainty Principle. All we can do is see how the probability distribution changes with time.

Because of the interpretation of $\Psi^*(\mathbf{r},t)\Psi(\mathbf{r},t)dxdydz$ as a probability, $\Psi(\mathbf{r},t)$ must meet certain conditions:

- $$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \Psi^*(\mathbf{r},t)\Psi(\mathbf{r},t)dxdydz = 1$$

The probability integrated over all space equals 1.

To save time and paper I will abbreviate integrals like this as $\int_{-\infty}^{\infty} \Psi^*(\mathbf{r},t)\Psi(\mathbf{r},t)d\tau = 1$

- $\Psi(\mathbf{r},t)$ must be finite over the possible range of values of the coordinates
- $\Psi(\mathbf{r},t)$ must be single valued, continuous (*i.e.* a well behaved function)
- $\nabla\Psi(\mathbf{r},t)$ must be single valued, continuous

Remember we discussed Einstein's explanation of the relationship between the wave and particle behavior of light. In the wave picture, the intensity of an electromagnetic wave is proportional to the amplitude of the wave squared.

$$I = \epsilon_0 c \bar{E}^2 \quad \text{where} \quad E = E_0 \cos(\omega t) \quad \text{for the electric field}$$

In the particle picture however,

$$I = N h \nu \quad \text{where } N \text{ is the number of photons per unit area per unit time.}$$

Thus, $N \propto \bar{E}^2$

That is, the probability of detecting a photon at a certain point is proportional to the square of the average wave amplitude.

In analogy to this, the square of a wavefunction $\Psi(\mathbf{r}, t)$

$$\Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t) \quad \text{or} \quad |\Psi(\mathbf{r}, t)|^2$$

can be interpreted as the probability density of finding a particle at a particular point in space. This is known as the Copenhagen interpretation and was proposed by Niels Bohr. One should realize that also other interpretations exist, but none of them is as widely accepted as the Copenhagen interpretation. Although the interpretations might be different, the physics described by the theory remains the same.

2.3 Digression on operators

Before we go on to postulate 2, I need to make a brief digression and discuss operators.

Definition of an Operator:

A rule which transforms one function, $f(x)$ for example, into some other function, $g(x)$.

Basically it is any mathematical operation.

Examples of operators:

$$\int, \frac{d}{dx}, \sqrt{\quad}, x^2, \log, \cdot 3$$

These are (in order), integrating, taking the derivative with respect to x , taking the square root, multiplying by x^2 , taking the log, multiplying by the number 3.

I will sometimes designate an operator with a hat or carrot, \hat{A} , for example, but I will often omit it. In such cases, the fact that it is an operator should be evident from the context.

It is important to note that in Quantum Mechanics, we will deal only with *linear operators*.

Definition of a Linear Operator:

An operator is said to be linear if

$$\hat{A}[c_1 f_1(x) + c_2 f_2(x)] = c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x)$$

where c_1 and c_2 are constants.

Clearly, $\frac{d}{dx}$ (differentiation) or \int (integration) are linear since

$$\frac{d}{dx}[c_1 f_1(x) + c_2 f_2(x)] = c_1 \frac{df_1(x)}{dx} + c_2 \frac{df_2(x)}{dx}$$

$$\int [c_1 f_1(x) + c_2 f_2(x)] dx = c_1 \int f_1(x) dx + c_2 \int f_2(x) dx$$

Whereas the $\sqrt{\quad}$ is *not* a linear operator

$$\sqrt{c_1 f_1(x) + c_2 f_2(x)} \neq c_1 \sqrt{f_1(x)} + c_2 \sqrt{f_2(x)}$$

When an operator operates on a function and returns the function multiplied by a constant, the function is said to be an **eigenfunction** of that operator. The constant is called an **eigenvalue** of that operator.

That is: $\hat{A}f(x) = af(x)$

where f is an eigenfunction of \hat{A} and a is the corresponding eigenvalue.

For example:

Let $\hat{A} = \frac{d^2}{dx^2}$ and $f(x) = e^{\alpha x}$

$$\hat{A}f(x) = \frac{d^2}{dx^2} e^{\alpha x} = \alpha^2 e^{\alpha x}$$

Here we would say that $e^{\alpha x}$ is an **eigenfunction** of $\frac{d^2}{dx^2}$ with an **eigenvalue** of α^2 .

The equation is called an **eigenvalue problem** or **eigenvalue equation**. For a given operator, solving an eigenvalue equation involves finding both the eigenfunctions and the eigenvalues for a given operator. As we will see shortly, solving the eigenvalue equation plays a central role in quantum mechanics.

We also need to define what we mean by the square of an operator. This simply means the operator applied twice.

If we define an operator (we will see soon that this is the operator describing momentum in the x-direction):

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

then the square of the operator would be given by:

$$\hat{p}_x^2 = \hat{p}_x \hat{p}_x = \left(-i\hbar \frac{d}{dx}\right) \left(-i\hbar \frac{d}{dx}\right) = -\hbar^2 \frac{d^2}{dx^2}$$

It is obvious that one cannot simply take the square root to get back the original.

2.4 Postulate 2

To every physical observable in classical mechanics, there corresponds a linear, Hermitian operator in quantum mechanics.

Hermitian operators are linear operators and have the property that their eigenvalues are real. This is necessary if they are to represent physical observables.

For a Hermitian operator \hat{A} the following relation holds for all permissible wavefunctions $\Psi(\mathbf{r}, t)$:

$$\int_{-\infty}^{\infty} \Psi^*(\mathbf{r}, t) (\hat{A} \Psi(\mathbf{r}, t)) d\tau = \int_{-\infty}^{\infty} (\hat{A} \Psi(\mathbf{r}, t))^* \Psi(\mathbf{r}, t) d\tau$$

Prescription for finding an operator for a particular observable:

Write the classical expression for the observable expressed in terms of the Cartesian coordinates and their corresponding momenta.

$$\begin{array}{lll} x \rightarrow \hat{x} = x & \text{or in general} & q \rightarrow \hat{q} = q \\ p_x \rightarrow \hat{p}_x = -i\hbar \frac{d}{dx} & \text{or in general} & p_q \rightarrow \hat{p}_q = -i\hbar \frac{d}{dq} \end{array}$$

where $q = x, y, \text{ or } z$.

This prescription **must** involve the **Cartesian coordinates**. After this substitution, one can convert to other coordinate systems.

You can see from the table on the next page that just knowing the expressions for position and momenta operators will enable you to find the others.

For example, one can write the expression for kinetic energy as:

$$K = \frac{1}{2} m v^2$$

Since we know that the momentum $\mathbf{p} = m\mathbf{v}$, one can write:

$$K = \frac{p^2}{2m}$$

The same relationships that hold between the observables will hold between the operators.

One can therefore get the kinetic energy operator in the x -direction by applying the momentum operator twice and dividing by $2m$:

$$\hat{K}_x = \frac{\hat{p}_x \hat{p}_x}{2m} = \frac{1}{2m} \left(-i\hbar \frac{d}{dx} \right) \left(-i\hbar \frac{d}{dx} \right) = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$$

One can do the same with angular momentum. Recall that the angular momentum vector \mathbf{l} is given by:

$$\mathbf{l} = \mathbf{r} \times \mathbf{p}$$

Observable		Operator	
Name	Symbol	Symbol	Operation
Position	x	\hat{x}	multiply by x
	\mathbf{r}	$\hat{\mathbf{r}}$	multiply by \mathbf{r}
Momentum	p_x	\hat{p}_x	$-i\hbar \frac{\partial}{\partial x}$
	\mathbf{p}	$\hat{\mathbf{p}}$	$-i\hbar \left(\mathbf{i} \frac{\partial}{\partial x} + \mathbf{j} \frac{\partial}{\partial y} + \mathbf{k} \frac{\partial}{\partial z} \right)$
Kinetic Energy	K_x	\hat{K}_x	$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$
	K	\hat{K}	$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) = -\frac{\hbar^2}{2m} \nabla^2$
Potential Energy	$U(x)$	$U(\hat{x})$	multiply by $U(x)$
	$U(x,y,z)$	$U(\hat{x}, \hat{y}, \hat{z})$	multiply by $U(x,y,z)$
Total Energy	E	\hat{H}	$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + U(x,y,z) = -\frac{\hbar^2}{2m} \nabla^2 + U(x,y,z)$
Angular Momentum	$L_x = y p_z - z p_y$	\hat{L}_x	$-i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$
	$L_y = z p_x - x p_z$	\hat{L}_y	$-i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right)$
	$L_z = x p_y - y p_x$	\hat{L}_z	$-i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$

The cross product of two vectors, $\mathbf{r} \times \mathbf{p}$ gives you another vector of magnitude $|\mathbf{r}| |\mathbf{p}| \sin\theta$ with the direction determined by the right hand rule. To find the individual components of the resultant vector one calculates:

$$\mathbf{r} \times \mathbf{p} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

$$= (y p_z - z p_y) \hat{i} - (x p_z - z p_x) \hat{j} + (x p_y - y p_x) \hat{k}$$

Therefore:

$$L_x = y p_z - z p_y$$

$$L_y = z p_x - x p_z$$

$$L_z = x p_y - y p_x$$

We can take these expressions and substitute the appropriate operators for the position and momentum coordinates.

As you will soon see, a particularly important operator in quantum chemistry is the total energy operator, otherwise known as the Hamiltonian and given the symbol \hat{H} .

This operator is found by writing down the classical expression for the sum of the kinetic and potential energy of a system.

$$H = E_{kin} + U$$

In three dimensions this reads in terms of position and momentum coordinates:

$$H = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + U(x, y, z)$$

where $U(x, y, z)$ is the potential energy as a function of the coordinates.

Making the substitution as prescribed above one finds for the Hamiltonian operator:

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + U(x, y, z) = -\frac{\hbar^2}{2m}\nabla^2 + U(x, y, z)$$

As we will see shortly, solving the eigenvalue problem for this operator will provide us with the energy of the system.

2.5 Postulate 3

In any measurement of the observable associated with the operator \hat{A} , the only values that will ever be observed are the eigenvalues, a , which satisfy the eigenvalue equation

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

Remember that for any operator we can find a set of **eigenfunctions** and **eigenvalues**.

Recall that an eigenfunction of an operator is defined by the fact that when it is operated on, the result is a constant times the same function. That constant is called the eigenvalue.

This postulate says that a measurement of A can only result in one of its eigenvalues -- **no matter what the wave function is!!**. Thus even if the wavefunction is not an eigenfunction of the operator

Example: Total energy operator \hat{H} (Hamiltonian)

If one makes a measurement of the energy, the only possible values you could obtain are the E_n such that:

$$\hat{H}\Psi_n = E_n\Psi_n$$

where the Ψ_n are the eigenfunctions of \hat{H} .

In other words, if you measure the energy, you can only get as a result one of the eigenvalues of the energy operator, the Hamiltonian. Thus even if the wave function is not one of the eigenfunctions of \hat{H} , upon measurement, you will only get one of the eigenvalues of \hat{H} .

There is an eigenvalue equation for each operator, and any possible measurement of a quantity corresponding to \hat{A} will result in a_n , one of the eigenvalues of \hat{A} .

The eigenvalue equation for the total energy operator (*i.e.*, the Hamiltonian) plays a very important role in quantum chemistry. As we will see shortly, the equation

$$\hat{H}\Psi_n = E_n\Psi_n$$

is called the **Time Independent Schrödinger Equation**

This equation provides us with the possible values of the energy of a system and which are of course extremely important in chemistry.

In order to discuss specific examples, I want to make a digression and look at the eigenvalues of the Hamiltonian for a specific quantum mechanical system called the particle in a one-dimensional well or a particle-in-a-box. Although this example might seem farfetched at first it turns out that it can be used to describe the delocalized π electrons in linear conjugated hydrocarbons.

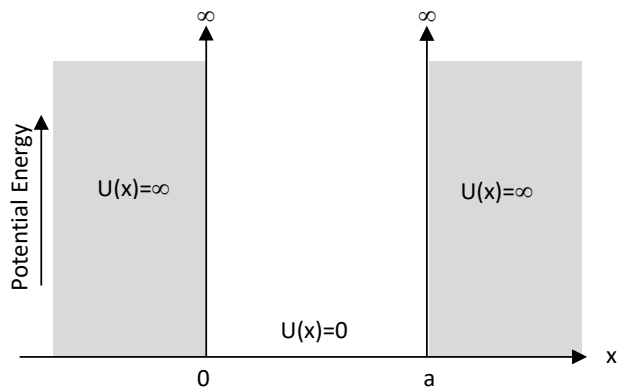
2.5.1 Particle in a 1-dimensional potential well

Consider a particle in a one-dimensional "box" with infinitely high walls (*i.e.*, an infinitely high potential for escaping the box).

Outside the box, the potential is infinite, which means it would take an infinite amount of energy for the particle to exist in that region. Therefore, the wave amplitude or the probability of finding the particle in that region is zero.

So for $x \leq 0$ $\psi(x) = 0$ and for $x \geq a$ $\psi(x) = 0$

These define the boundary conditions for the wave function "inside" the box.



Let us say we want to determine the possible values for the total energy of the system and the eigenfunctions that are associated with those eigenvalues. According to postulate 2, we must write down the operator for the total energy, which we called \hat{H} , the Hamiltonian.

Recall that the procedure is to first write down the classical expressions and then substitute operators according to the prescription of postulate 2. We have already done this in the table that I gave you.

The Hamiltonian operator, \hat{H} , in one dimension is:

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U(x)$$

The first term is the kinetic energy term and the second term the potential energy.

Since the potential inside the "box" equals zero, the eigenvalue equation for the energy is:

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

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

Rearranging this gives:

$$\frac{d^2\psi(x)}{dx^2} + \frac{2mE}{\hbar^2}\psi(x) = 0 \quad 0 \leq x \leq a$$

and the boundary conditions are $\psi(0) = \psi(a) = 0$. This is because we must require the wave function to be continuous.

This is a second order linear differential equation with constant coefficients. We can solve this by simply looking at it and guessing.

Try $\psi(x) = e^{\alpha x}$ then $\frac{d^2\psi(x)}{dx^2} = \alpha^2 e^{\alpha x}$

Substitute $\psi(x)$ and its second derivative back into the differential equation to get the auxiliary equation.

$$\alpha^2 e^{\alpha x} + \frac{2mE}{\hbar^2} e^{\alpha x} = 0$$

This has to hold for all values of x , hence

$$\alpha^2 + \frac{2mE}{\hbar^2} = 0$$

$$\alpha = \pm i \frac{\sqrt{2mE}}{\hbar}$$

The most general solution of the differential equation is a linear combination of the + and - solutions.

$$\psi(x) = c_1 e^{i \frac{\sqrt{2mE}}{\hbar} x} + c_2 e^{-i \frac{\sqrt{2mE}}{\hbar} x}$$

or using Euler's formula: $e^{\pm i\theta} = \cos\theta \pm i\sin\theta$

$$\psi(x) = A \sin\left(\frac{\sqrt{2mE}}{\hbar} x\right) + B \cos\left(\frac{\sqrt{2mE}}{\hbar} x\right)$$

The relation between the coefficients c_1 and c_2 and A and B is simply

$$A = i(c_1 - c_2) \quad B = c_1 + c_2$$

Let's now apply the boundary conditions:

$$\text{At } x = 0 : \quad \psi(0) = A\sin(0) + B\cos(0) = 0$$

$$\Rightarrow B = 0$$

At $x = a$ we then find:

$$\psi(a) = A\sin\left(\frac{\sqrt{2mE}}{\hbar}a\right) = 0$$

If we say $A = 0$, this gives us a trivial solution (*i.e.* the solution will be zero everywhere, $\psi(x) = 0$).

$$\text{Therefore} \quad \sin\left(\frac{\sqrt{2mE}}{\hbar}a\right) = 0 \quad \text{must hold.}$$

This is only possible if:

$$\frac{\sqrt{2mE}}{\hbar}a = n\pi \quad n = 1, 2, 3, \dots$$

We can then solve this equation for the energy, E , and get

$$E = \frac{n^2 \hbar^2}{8ma^2} \quad n = 1, 2, 3, \dots$$

These are the eigenvalues of the energy operator (*i.e.*, the Hamiltonian). They represent the allowed values for the total energy of the system.

The eigenfunctions are then given by:

$$\psi(x) = A\sin\left(\frac{\sqrt{2mE}}{\hbar}x\right) = A\sin\left(\frac{n\pi}{a}x\right)$$

We can determine the constant A by requiring the eigenfunction to be normalized. Since $\psi^* \psi$ represents a probability, it must equal one if integrated over all space. I will omit the details, but this gives

$$A = \sqrt{\frac{2}{a}}$$

where a is the length of the box.

There are a few important points to note:

- The energy is quantized, *i.e.* it can only have certain values which are determined by the integer n . Note that the quantization arose when we imposed the boundary conditions. This is a general principle of quantum mechanics.
- The energy level spacing increases with decreasing dimensions of the box. The more localized a particle is, the greater the quantization. Another way to look at this is as the dimensions of the box approach the wavelength of the particle, you get quantum effects. As the size of the box or the mass of the particle increases, the energy levels get closer and closer. Quantum effects begin to become less apparent.

Let us look in some detail at the eigenfunctions of the particle-in-a-box Hamiltonian. Let us assume for the moment that the wave function for a particle-in-a-box happens to be one of the eigenfunctions of the Hamiltonian. This need not be the case. The only requirements for an acceptable wave function are given by postulate 1. Nothing says that the wavefunctions for this system must be eigenfunctions of the Hamiltonian. However, one of the eigenfunctions of the Hamiltonian certainly could be a wavefunction for a particle-in-a-box.

Recall the information carried by the wave function for a system. The wave function times its complex conjugate gives the probability of finding the system at a particular point in space.

The eigenfunctions of the Hamiltonian for a particle-in-a-box are given by

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) \quad n=1,2,3,\dots$$

The probability distributions are given by:

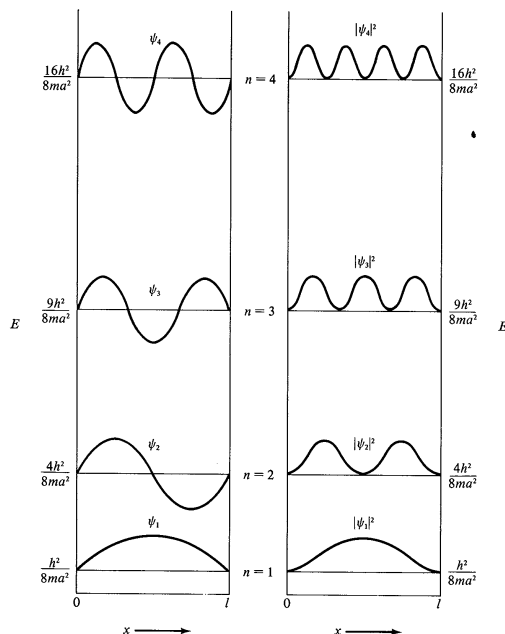
$$|\psi_n(x)|^2 = \psi_n^*(x)\psi_n(x) = \frac{2}{a} \sin^2\left(\frac{n\pi}{a}x\right)$$


Both of these are plotted in the figure on the next page. As we already saw, there is zero probability of finding the particle outside the box or potential well, because the potential is infinite.

Quantum Mechanically, there are places inside the box where the wave function ψ and $|\psi|^2$ are zero (*i.e.*, places where the particle has no probability of being found). These are called **nodes**. The higher the quantum number n (and the energy), the more nodes. This will be true for all bound systems. It is always the case in quantum mechanics that the lowest energy wavefunction will have no nodes, the next, one node, etc.... Qualitatively, wavefunctions look similar for different bound potentials.

How can a particle get from one side of the node to the other without crossing the middle of the box? One can't think of it that way! $|\psi|^2$ simply gives us a probability. One cannot think of trajectories of macroscopic particles in quantum mechanics.

Classically one would expect a particle to bounce back and forth in the box and show equal probability of being found anywhere.



However, note that as n gets large, $\psi \rightarrow$ 

The number of nodes increases, but the probability spreads out evenly. Thus, at large quantum numbers, the quantum mechanical result approaches the classical result. This is an example of the Bohr Correspondence Principle.

Remember that postulate 3 says the only result of measuring A is one of the eigenvalues of \hat{A} **no matter what the wave function is**.

Postulate 1 does not say that the wave function for a system, Ψ , must be an eigenfunction of the Hamiltonian. For example, in the case of a particle in a 1- dimensional potential well, postulate 1 does not say that the wave function must be one of the eigenfunctions of the Hamiltonian that we found above. Nor does it say that Ψ has to be an eigenfunction of any operator. It simply requires that it be well behaved.

No matter what the wave function is, the only result of measuring A is one of the eigenvalues of \hat{A} . If, however, Ψ *happens to be* an eigenfunction of the operator you measure, then, as we will see when discussing postulate 4, you know exactly the result you will get when you make the measurement, the eigenvalue that corresponds to that eigenfunction.

If Ψ *is not* an eigenfunction of the operator you measure, you could get any of the eigenvalues corresponding to operator A .

To help you understand this concept further, I need to introduce several important properties of eigenfunctions.

2.5.2 Some important properties of eigenfunctions

DEFINITION - Complete set of eigenfunctions

A set of eigenfunctions, φ_n , is considered complete if, for any well behaved function, f , we can write:

$$f = \sum_n c_n \varphi_n$$

DEFINITION - Orthonormality of eigenfunctions

A set of eigenfunctions is considered orthonormal if

$$\int_{-\infty}^{\infty} \varphi_i^* \varphi_j d\tau = \delta_{ij}$$

here δ_{ij} is the Kronecker delta with the properties:

$$\begin{aligned} \delta_{ij} &= 0 & \text{if } i \neq j \\ \delta_{ij} &= 1 & \text{if } i = j \end{aligned}$$

That is, if $i \neq j$ they are orthogonal, and the case in which $i = j$ expresses the normalization condition.

Auxiliary postulate:

The eigenfunctions of a Hermitian operator form a complete, orthonormal set.

One can prove the fact that the eigenfunctions of a Hermitian operator are orthonormal. However, the completeness of the set cannot be proved mathematically. It must be taken as an additional postulate.

2.5.3 Return to postulate 3

Although a wave function does not have to be a single eigenfunction of any operator, it can **always** be written as a linear combination of eigenfunctions of **any operator that corresponds to a physical observable** (i.e. a Hermitian operator), because the eigenfunctions of a Hermitian operator form a complete orthonormal set. Let us choose to write a wave function for the system we want to measure as a linear combination of the eigenfunctions that correspond to the operator (i.e., the observable) we want to measure. (Note that we are free to choose any set of functions as long as it is complete.)

$$\Psi(x,t) = \sum_n c_n \varphi_n(x,t)$$

There could be any number of functions in this expansion.

If you then make a measurement on a system described by such a wave function, the result will be an eigenvalue of one of the eigenfunctions in the linear combination. *Which one you do not know (unless there is only one function in the linear expansion).*

Postulate 4 will tell us the average result you will get if you make repeated measurements on identical systems. Before I discuss postulate 4, I need to remind you of a few concepts related to statistics.

2.6 Some statistical concepts

2.6.1 Expectation values

In general the probability P_j of a certain event can be given by:

$$P_j = \lim_{N \rightarrow \infty} \frac{N_j}{N}$$

where N = the total number of tries or measurements

and N_j = the number of times event j was observed.

Note that $0 \leq P_j \leq 1$ since the maximum value N_j can have is N .

Also, because $\sum_{j=1}^n N_j = N$

we have the condition that

$$\sum_{j=1}^n P_j = 1$$

where n is the number of possible outcomes for the measurement.

Now consider the case in which a particular event has a value associated with it, as in the case of an experimental measurement. We define the **average value** or **expectation value** to be:

$$\bar{x} = \langle x \rangle = \sum_{j=1}^n x_j P_j = \sum_{j=1}^n x_j P(x_j)$$

where $P(x_j)$ represents the probability of realizing the number x_j .

Example:

What is the average value observed in rolling a die? *i.e.* What is $\langle x \rangle$ where x is the number on the die?

$$\langle x \rangle = \sum_{j=1}^6 x_j P_j = 1 \cdot P_1 + 2 \cdot P_2 + 3 \cdot P_3 + 4 \cdot P_4 + 5 \cdot P_5 + 6 \cdot P_6$$

If it is an honest die then:

$$P_1 = P_2 = P_3 = P_4 = P_5 = P_6 = \frac{1}{6}$$

Then one would find

$$\langle x \rangle = \frac{1}{6} + \frac{2}{6} + \frac{3}{6} + \frac{4}{6} + \frac{5}{6} + \frac{6}{6} = 3.5$$

Note that the average value does not have to equal a value of the die.

2.6.2 Variance

The **variance** is an indication of the distribution or spread in a series of measurements; *i.e.* the distribution about the mean or average value. The variance gives some indication of the precision of a measured result. If a measurement always gives the same number, the variance is zero.

$$\sigma_x^2 = \langle (x - \langle x \rangle)^2 \rangle$$

It is a measure of the difference of a measurement x from the mean $\langle x \rangle$. Using our definition of average value we can also write this as

$$\sigma_x^2 = \sum_{j=1}^n (x_j - \langle x \rangle)^2 P_j$$

You can see that σ_x^2 is a sum of positive terms and so $\sigma_x^2 \geq 0$

Let's expand the expression for σ_x^2 :

$$\begin{aligned} \sigma_x^2 &= \sum_{j=1}^n (x_j^2 - 2\langle x \rangle x_j + \langle x \rangle^2) P_j \\ &= \sum_{j=1}^n x_j^2 P_j - 2 \sum_{j=1}^n \langle x \rangle x_j P_j + \sum_{j=1}^n \langle x \rangle^2 P_j \\ &= \langle x^2 \rangle - 2\langle x \rangle \langle x \rangle + \langle x \rangle^2 \\ &= \langle x^2 \rangle - \langle x \rangle^2 \end{aligned}$$

So,
$$\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2 \geq 0$$

And thus
$$\sigma_x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$$

The variance is always greater than or equal to zero and tells us how precise a measurement is or how precisely it can be made. If the variance equals zero we will always measure the same result.

2.7 Postulate 4

If a system is in a state described by a normalized wave function Ψ , then the average value or expectation value of the observable corresponding to the operator \hat{A} is given by:

$$\langle a \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{A} \Psi d\tau$$

I need to define more clearly what we mean by an average or expectation value in quantum mechanics.

It **does not** mean making repeated measurements on the same system. This is because in making a measurement in quantum mechanics you disturb the system and influence the subsequent result. We will discuss this in more detail later.

It **does** mean making the same measurement on a series of identical systems.

Let's have a look at some examples.

Example 1:

Calculate the expectation value for the position of a particle in a one-dimensional box of length a that is described by an eigenfunction of the Hamiltonian of the particle-in-a-box problem, furthermore calculate σ_x^2 .

We saw before that the wavefunctions are given by:

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) \quad n = 1, 2, 3, \dots \quad \text{for } 0 < x < a$$

the probability of finding the particle between x and $x + dx$.

$$\psi^*(x)\psi(x)dx$$

The average position is given by:

$$\langle x \rangle = \int_0^a \psi^*(x) x \psi(x) dx$$

In the present example we have:

$$\begin{aligned} \langle x \rangle &= \int_0^a \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) x \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) dx \\ &= \frac{2}{a} \int_0^a x \sin^2\left(\frac{n\pi}{a}x\right) dx \end{aligned}$$

Evaluation of this integral gives us:

$$\langle x \rangle = \frac{2}{a} \frac{a^2}{4} = \frac{a}{2}$$

This result makes sense. The box is perfectly symmetrical, and there is nothing to favor one side of the box over the other, thus the average position is in the center.

We also wanted to calculate the variance σ_x^2 . To do this we need to calculate $\langle x^2 \rangle$.

$$\begin{aligned}\langle x^2 \rangle &= \frac{2}{a} \int_0^a x^2 \sin\left(\frac{n\pi}{a}x\right) dx \\ &= \left(\frac{a}{2\pi n}\right)^2 \left(\frac{4\pi^2 n^2}{3} - 2\right)\end{aligned}$$

So,

$$\begin{aligned}\sigma_x^2 &= \langle x^2 \rangle - \langle x \rangle^2 = \left(\frac{a}{2\pi n}\right)^2 \left(\frac{4\pi^2 n^2}{3} - 2\right) - \frac{a^2}{4} \\ &= \left(\frac{a}{2\pi n}\right)^2 \left(\frac{\pi^2 n^2}{3} - 2\right)\end{aligned}$$

Thus there is some distribution of possible values, represented by the fact that $\sigma_x^2 \neq 0$.

Example 2:

Suppose a particle in a 1-dimensional box is in a state described by the following wave function

$$\psi(x) = A(a^2 x^2 - x^4)$$

where $A = \sqrt{\frac{315}{8a^9}}$

is the normalization constant and a represents the length of the box. This is a perfectly well behaved wave function that satisfies the boundary conditions of the particle in the box properly, but clearly is not an eigenfunction of the Hamiltonian. Let us use postulate 4 to calculate the average energy.

For a particle in a 1-dimensional box:

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$$

So,

$$\begin{aligned}\langle E \rangle &= A^2 \int_0^a (a^2 x^2 - x^4) \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2}\right) (a^2 x^2 - x^4) dx \\ &= -\frac{A^2 \hbar^2}{2m} \int_0^a (a^2 x^2 - x^4)(2a^2 - 12x^2) dx \\ &= -\frac{A^2 \hbar^2}{2m} \int_0^a (2a^4 x^2 - 14a^2 x^4 + 12x^6) dx \\ &= -\frac{A^2 \hbar^2}{2m} \left[\frac{2}{3} a^4 x^3 - \frac{14}{5} a^2 x^5 + \frac{12}{7} x^7 \right]_0^a \\ &= -\frac{A^2 \hbar^2}{2m} \left(-\frac{44}{105} a^7 \right) = \frac{22A^2 \hbar^2 a^7}{105m}\end{aligned}$$

Substituting for A:

$$A = \sqrt{\frac{315}{8a^9}}$$

We finally find:

$$\langle E \rangle = \frac{33}{2\pi^2} \frac{h^2}{8ma^2}$$

This is clearly **not** one of the eigenvalues of the Hamiltonian, but remember, this is an average, not a single measurement. Note, this is similar to what we have seen when we calculated the average value for throwing a die.

Recall that
$$E_n = n^2 \frac{h^2}{8ma^2}$$

The **average** or expectation value doesn't need to be an eigenvalue of the Hamiltonian. It is the average of a series of measurements on identical systems.

Postulate 3 says that **upon any one measurement**, the value we obtain can only be one of the eigenvalues of the operator corresponding to the quantity we measure. However, because each time we make a measurement we get a different answer, the average value will not be a single eigenvalue.

Although I won't do it here, if we were to calculate the variance in our measurements

$$\sigma_E^2 = \langle E^2 \rangle - \langle E \rangle^2$$

we would find that it is larger than zero. One gets a spread in the values obtained upon measuring the energy. Clearly the wavefunction is not an eigenfunction of the Hamiltonian.

Example 3:

Now let's consider a case in which the wave function happens to be an eigenfunction of the particle-in-a-box Hamiltonian, \hat{H} .

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

Let us find the average value for repeated measurements of the energy. We could do this one of two ways. The hard way is to evaluate the integral as we did before:

$$\langle E \rangle = \int_0^a \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right) \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) dx$$

The easy way would be to realize that since the wave function ψ is one of the eigenfunctions of the Hamiltonian, we can write:

$$\begin{aligned} \langle E \rangle &= \int_0^a \psi_n^*(x) \hat{H} \psi_n(x) dx = \int_0^a \psi_n^*(x) E_n \psi_n(x) dx = E_n \int_0^a \psi_n^*(x) \psi_n(x) dx \\ &= E_n \end{aligned}$$

Thus

$$\langle E \rangle = E_n = \frac{n^2 h^2}{8ma^2}$$

If we now calculate the variance of the energy measurement:

$$\langle E^2 \rangle = \int_0^a \psi_n^*(x) \hat{H}^2 \psi_n(x) dx = E_n^2$$

$$\sigma_E^2 = \langle E^2 \rangle - \langle E \rangle^2 = E_n^2 - E_n^2 = 0$$

we find that the variance equals zero. There is no uncertainty in the measurement!!

If the wave function is an eigenfunction of the operator you measure, then upon making a measurement, you will always get a single value: the eigenvalue corresponding to that eigenfunction.

Example 4:

Let us try one more example in which the wave function is written as a linear combination of eigenfunctions of the particle-in-a-box Hamiltonian. However, let us assume there are only two terms in the expansion.

Let us assume the form:

$$\psi(x) = c_1 \psi_1(x) + c_2 \psi_2(x)$$

where $\psi_n(x)$ are the eigenfunctions of the particle-in-a-box Hamiltonian and c_1 and c_2 are just the coefficients in the expansion.

As $\psi(x)$ has to be normalized, one can derive a relation between the coefficients c_1 and c_2 :

$$\begin{aligned} \int \psi^*(x) \psi(x) dx &= \int (c_1^* \psi_1^*(x) + c_2^* \psi_2^*(x)) (c_1 \psi_1(x) + c_2 \psi_2(x)) dx = 1 \\ &= \int (c_1^* c_1 \psi_1^*(x) \psi_1(x) + c_2^* c_1 \psi_2^*(x) \psi_1(x) + c_1^* c_2 \psi_1^*(x) \psi_2(x) + c_2^* c_2 \psi_2^*(x) \psi_2(x)) dx \\ &= |c_1|^2 \int \psi_1^*(x) \psi_1(x) dx + c_2^* c_1 \int \psi_2^*(x) \psi_1(x) dx + c_1^* c_2 \int \psi_1^*(x) \psi_2(x) dx + |c_2|^2 \int \psi_2^*(x) \psi_2(x) dx \\ &= |c_1|^2 + |c_2|^2 = 1 \end{aligned}$$

Here we made explicit use of the fact that the eigenfunctions of the Hamiltonian form a complete orthonormal set.

Let's choose $c_1 = \sqrt{\frac{2}{3}}$ and $c_2 = \sqrt{\frac{1}{3}}$, so that we have

$$|c_1|^2 = \frac{2}{3} \quad \text{and} \quad |c_2|^2 = \frac{1}{3} \quad \text{giving} \quad |c_1|^2 + |c_2|^2 = 1$$

The wave function is then

$$\psi(x) = \sqrt{\frac{2}{3}} \sqrt{\frac{2}{a}} \sin\left(\frac{\pi}{a} x\right) + \sqrt{\frac{1}{3}} \sqrt{\frac{2}{a}} \sin\left(\frac{2\pi}{a} x\right)$$

where I have purposely not combined the constants in front of each function.

Let us now calculate the expectation value. Note that to simplify the writing and to make things more suggestive, I will use $\psi_1(x)$ and $\psi_2(x)$ instead of writing the sine functions explicitly.

$$\begin{aligned}
\langle E \rangle &= \int_0^a \psi^*(x) \hat{H} \psi(x) dx \\
&= \int_0^a \left(\sqrt{\frac{2}{3}} \psi_1^*(x) + \sqrt{\frac{1}{3}} \psi_2^*(x) \right) \hat{H} \left(\sqrt{\frac{2}{3}} \psi_1(x) + \sqrt{\frac{1}{3}} \psi_2(x) \right) dx \\
&= \frac{2}{3} \int_0^a \psi_1^*(x) \hat{H} \psi_1(x) dx + \frac{\sqrt{2}}{3} \int_0^a \psi_1^*(x) \hat{H} \psi_2(x) dx + \frac{\sqrt{2}}{3} \int_0^a \psi_2^*(x) \hat{H} \psi_1(x) dx + \frac{1}{3} \int_0^a \psi_2^*(x) \hat{H} \psi_2(x) dx \\
&= \frac{2}{3} E_1 \int_0^a \psi_1^*(x) \psi_1(x) dx + \frac{\sqrt{2}}{3} E_2 \int_0^a \psi_1^*(x) \psi_2(x) dx + \frac{\sqrt{2}}{3} E_1 \int_0^a \psi_2^*(x) \psi_1(x) dx + \frac{1}{3} E_2 \int_0^a \psi_2^*(x) \psi_2(x) dx \\
&= \frac{2}{3} E_1 + \frac{1}{3} E_2
\end{aligned}$$

To calculate the variance, we need $\langle E^2 \rangle$. By repeating the same procedure, you can convince yourself that

$$\langle E^2 \rangle = \frac{2}{3} E_1^2 + \frac{1}{3} E_2^2$$

Thus the variance in the measurement of the energy is:

$$\begin{aligned}
\sigma_E^2 &= \langle E^2 \rangle - \langle E \rangle^2 = \frac{2}{3} E_1^2 + \frac{1}{3} E_2^2 - \left(\frac{2}{3} E_1 + \frac{1}{3} E_2 \right)^2 \\
&= \frac{2}{3} E_1^2 + \frac{1}{3} E_2^2 - \frac{4}{9} E_1^2 - \frac{1}{9} E_2^2 - \frac{4}{9} E_1 E_2 \\
&= \frac{2}{9} E_1^2 + \frac{2}{9} E_2^2 - \frac{4}{9} E_1 E_2 = \frac{2}{9} (E_1 - E_2)^2 \neq 0
\end{aligned}$$

Therefore, the result of your measurement will not be the same every time. You only get a single value for your measurement each time if ψ is an eigenfunction, not a linear combination of eigenfunctions.

There is one other very important point to note, however. Look again at our expression for the average energy $\langle E \rangle$.

$$\langle E \rangle = \frac{2}{3} E_1 + \frac{1}{3} E_2$$

Remember that we had originally chosen the expansion coefficients $c_1 = \sqrt{\frac{2}{3}}$ and $c_2 = \sqrt{\frac{1}{3}}$

The probability of obtaining either result is simply $|c_1|^2 = \frac{2}{3}$ and $|c_2|^2 = \frac{1}{3}$

In general, the probability of obtaining a particular eigenvalue is simply the square of the expansion coefficient for the eigenfunction corresponding to that eigenvalue.

That is: $P_n = |c_n|^2$

Proof:

We start with the expression for an average value, according to postulate 4:

$$\langle a \rangle = \int_{-\infty}^{\infty} \psi^*(x) \hat{A} \psi(x) dx$$

(Note that I have not included the time dependence of the wave function here. I will explain shortly why I can do that).

Let us substitute for ψ a linear combination of eigenfunctions φ_n of the operator \hat{A} , i.e.:

$$\hat{A} \varphi_n(x) = a_n \varphi_n(x)$$

We then find

$$\begin{aligned} \langle a \rangle &= \int_{-\infty}^{\infty} \psi^*(x) \hat{A} \psi(x) dx \\ &= \int_{-\infty}^{\infty} \left(\sum_n c_n^* \varphi_n^*(x) \right) \hat{A} \left(\sum_m c_m \varphi_m(x) \right) dx \\ &= \sum_n \sum_m c_n^* c_m \int_{-\infty}^{\infty} \varphi_n^*(x) \hat{A} \varphi_m(x) dx \\ &= \sum_n \sum_m c_n^* c_m a_m \int_{-\infty}^{\infty} \varphi_n^*(x) \varphi_m(x) dx \\ &= \sum_n \sum_m c_n^* c_m a_m \delta_{nm} \\ &= \sum_n c_n^* c_n a_n = \sum_n |c_n|^2 a_n \end{aligned}$$

Remember how we define the average value:

$$\langle x \rangle = \sum_j x_j P_j$$

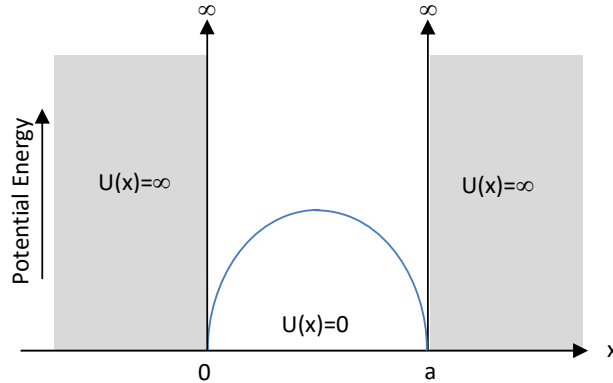
where x_j are the possible values and P_j the probability of obtaining that value.

By analogy, one can see that in our case we see that $P_n = |c_n|^2$

Note that when $c_n = 0$ the probability for obtaining result a_n is zero. One will therefore never measure result a_n . In my previous example, one will only measure E_1 or E_2 and no other value.

In general, the expansion of a wave function may have many terms, and these terms will not be equally weighted; hence, there are many possible results to a measurement. However, those which are weighted more will have a higher probability and will influence the average more heavily.

For the moment, I will demonstrate this physically. Later we will do it in a more mathematical way. Assume that for the particle-in-a-box problem we had a wave function that looked like this.



You can see that this is not an eigenfunction of the particle-in-a-box Hamiltonian (*i.e.*, it is not a sine function) but it has a similar shape. This means that in an expansion of this function in terms of the eigenfunctions of the particle-in-a-box Hamiltonian, the term with the largest expansion coefficient would be ψ_1 (*i.e.*, the term c_1 would be the largest). If you start to think about it you can tell a few other qualitative things as well. Since this wave function is symmetrical, only those functions in the expansion that have the same symmetry will have a non-zero expansion coefficient.

2.7.1 Calculation of coefficients in an eigenfunction expansion

If we are given a functional form for a wavefunction $f(x)$, we can find the coefficients in the following way:

Assume we have a complete orthonormal set of eigenfunctions ψ_n of some Hermitian operator so that we can write

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x)$$

If we multiply both sides of this expression by ψ_m^* and integrate, we get

$$\begin{aligned} \int_{-\infty}^{\infty} \psi_m^*(x) f(x) dx &= \sum_{n=1}^{\infty} c_n \int_{-\infty}^{\infty} \psi_m^*(x) \psi_n(x) dx \\ &= \sum_{n=1}^{\infty} c_n \delta_{nm} = c_m \end{aligned}$$

So,

$$c_m = \int_{-\infty}^{\infty} \psi_m^*(x) f(x) dx$$

That is, to find an expansion coefficient corresponding to a particular eigenfunction, just multiply the function $f(x)$ by the complex conjugate of the eigenfunction of interest and integrate over all space.

The probability of obtaining the m^{th} eigenvalue upon measuring the quantity whose eigenfunctions form the basis for the expansion is then

$$P_m = \left| \int_{-\infty}^{\infty} \psi_m^*(x) f(x) dx \right|^2$$

Example 1:

This example is trivial, but serves to illustrate a point.

Take the wave function for a particle-in-a-box that is a combination of two eigenfunctions

$$\psi(x) = \frac{1}{\sqrt{2}}\psi_1(x) + \frac{1}{\sqrt{2}}\psi_2(x)$$

where ψ_1 and ψ_2 are the first two eigenfunctions of the particle-in-a-box Hamiltonian. We can look at this and see what the expansion coefficients are, but let's go through the procedure we just introduced.

To find c_1 :

$$\begin{aligned} c_1 &= \int_{-\infty}^{\infty} \psi_1^*(x)\psi(x)dx \\ &= \int_{-\infty}^{\infty} \psi_1^*(x) \left(\frac{1}{\sqrt{2}}\psi_1(x) + \frac{1}{\sqrt{2}}\psi_2(x) \right) dx \\ &= \frac{1}{\sqrt{2}} \int_{-\infty}^{\infty} \psi_1^*(x)\psi_1(x)dx + \frac{1}{\sqrt{2}} \int_{-\infty}^{\infty} \psi_1^*(x)\psi_2(x)dx \\ &= \frac{1}{\sqrt{2}} \end{aligned}$$

The probability of measuring E_1 is then

$$P_1 = \left| \frac{1}{\sqrt{2}} \right|^2 = \frac{1}{2}$$

Example 2:

Let
$$\psi(x) = \sqrt{\frac{30}{a^5}}x(a-x) \quad 0 \leq x \leq a$$

We want to expand this as a linear combination of particle-in-a-box wave functions

$$\psi(x) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right)$$

and determine the values of the coefficients c_n . Let us calculate the value of the general term c_n .

From the formula that I gave

$$\begin{aligned} c_n &= \int_{-\infty}^{\infty} \psi_n^*(x)\psi(x)dx \\ &= \sqrt{\frac{2}{a}} \sqrt{\frac{30}{a^5}} \int_0^a \sin\left(\frac{n\pi}{a}x\right)x(a-x)dx \\ &= \sqrt{\frac{60}{a^6}} \left[2\left(\frac{a}{n\pi}\right)^3 (1 - \cos n\pi) \right] \end{aligned}$$

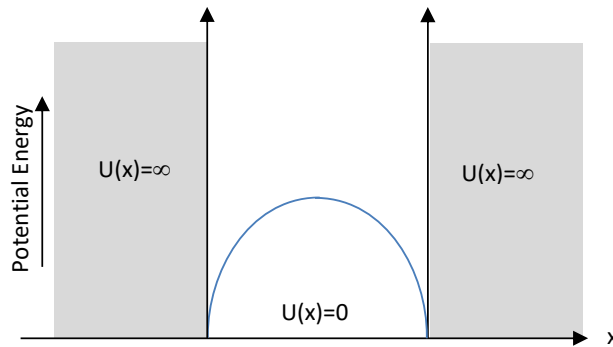
$$= \frac{\sqrt{240}}{\pi^3 n^3} [1 - (-1)^n]$$

Let us look at this result more closely.

Notice that the coefficients corresponding to even values of n are 0. That is

$$c_n = \begin{cases} \frac{2\sqrt{240}}{\pi^3 n^3} & n = \text{odd} \\ 0 & n = \text{even} \end{cases}$$

Why do the coefficients vanish for even n ? To understand this we need to look at the function. It looks something like this:



There are two things to notice:

- The symmetry of the function requires the even terms to be zero.
- $n = 1$ should have the largest contribution. You can see that this will be true because $c_n \propto \frac{1}{n^3}$

2.8 Postulate 5

The wave function of a system evolves in time according to the time-dependent Schrödinger equation

$$\hat{H} \Psi(x, t) = i\hbar \frac{\partial \Psi(x, t)}{\partial t}$$

For most systems \hat{H} does not contain time explicitly. In that case, we can seek solutions of the form

$$\Psi(x, t) = \psi(x) f(t)$$

That does not mean that all solutions must have this form, however we will see that those that do have a special property: they are the steady-state solutions of the Schrödinger equation, *i.e.*, their probability density does not evolve in time.

If we substitute this into the time-dependent Schrödinger equation:

$$\hat{H} \psi(x) f(t) = i\hbar \frac{\partial}{\partial t} \psi(x) f(t)$$

and realize that since \hat{H} does not depend on time, it will have no effect on $f(t)$ and the derivative with respect to time will have no effect on $\psi(x)$:

$$f(t)\hat{H}\psi(x) = i\hbar\psi(x)\frac{\partial f(t)}{\partial t}$$

If we now divide both sides by $\psi(x)f(t)$ we get

$$\frac{1}{\psi(x)}\hat{H}\psi(x) = \frac{i\hbar}{f(t)}\frac{\partial f(t)}{\partial t}$$

Note that the left side of this equation is only a function of x and the right side is only a function of t .

For the two sides to be equal as the variables x and t are varied, they must each be equal to a constant, which I will call E .

$$\frac{1}{\psi(x)}\hat{H}\psi(x) = E = \frac{i\hbar}{f(t)}\frac{\partial f(t)}{\partial t}$$

First, the left hand side:

$$\frac{1}{\psi(x)}\hat{H}\psi(x) = E \quad \Rightarrow \quad \hat{H}\psi(x) = E\psi(x)$$

You can see that this is simply the eigenvalue equation for the Hamiltonian (total energy).

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

is called the **Time Independent Schrödinger Equation**.

We will see in a moment that the solution of this equation not only provides the allowed values of the total energy of the system, but the wave functions $\psi(x)$ have special properties.

Now the right hand side:

$$\frac{i\hbar}{f(t)}\frac{\partial f(t)}{\partial t} = E$$

Rearranging this gives:

$$\frac{\partial f(t)}{\partial t} = -\frac{iE}{\hbar}f(t)$$

The solution of this differential equation is given by:

$$f(t) = Ae^{-\frac{iE}{\hbar}t}$$

Putting the time independent and time dependent parts together, we have

$$\Psi(x,t) = \psi(x)e^{-\frac{iE}{\hbar}t}$$

where $\psi(x)$ is the solution to the Time Independent Schrödinger Equation (note that we have incorporated the constant A into $\psi(x)$).

Since there is a whole set of solutions to the Time Independent Schrödinger Equation, denoted by the index n (just as we did with the particle-in-a-box wave functions), we write the above equation

$$\Psi_n(x,t) = \psi_n(x)e^{-\frac{iE_n t}{\hbar}}$$

Recall that from postulate 1, $|\Psi(x,t)|^2$ represents a probability distribution for finding the particle in an interval dx at a particular value of x .

Using the wave function above one gets

$$\begin{aligned} |\Psi_n(x,t)|^2 &= \left(\psi_n^*(x)e^{+\frac{iE_n t}{\hbar}} \right) \left(\psi_n(x)e^{-\frac{iE_n t}{\hbar}} \right) \\ &= \psi_n^*(x)\psi_n(x)e^{+\frac{iE_n t}{\hbar}} e^{-\frac{iE_n t}{\hbar}} \\ &= \psi_n^*(x)\psi_n(x) \end{aligned}$$

That is for wave functions that satisfy the form

$$\Psi_n(x,t) = \psi_n(x)e^{-\frac{iE_n t}{\hbar}}$$

where $\psi_n(x)$ are solutions to the Time Independent Schrödinger Equation, the probability density has no time dependence. These are called **stationary states** or **eigenstates**. (Note that the wave function has time dependence, but not the probability density.)

One can find the stationary states of the system by solving the Time Independent Schrödinger Equation and adding the time dependent part.

There is nothing to say that a wave function has to be a stationary state, however if not, the probability will evolve in time.

If we solve the Time independent Schrödinger equation, $\psi^*(x)\psi(x)$ and hence $\Psi^*(x,t)\Psi(x,t)$ are independent of time. In this case, any calculations of probability or of average values need only use $\psi(x)$. These so-called *stationary state wave functions* and their corresponding energies are of central importance in chemistry and in spectroscopy!

Because the stationary states of the system are eigenfunctions of a Hermitian operator (*i.e.*, the Hamiltonian), they form a complete basis set. This means that we can write any wave function as a linear combination of stationary state wave functions.

I showed previously, however, that if we take a linear combination of solutions to the Schrödinger equation with different eigenvalues, they no longer have fixed energy. Such a linear combination is a perfectly valid wave function but does not solve the Schrödinger equation and hence will not be a stationary state.

So the general wave function which we can write as a linear combination of eigenfunctions of the Hamiltonian (or stationary state solutions)

$$\Psi(x,t) = \sum_n c_n \Psi_n(x,t) = \sum_n c_n \psi_n(x) e^{\frac{iE_n t}{\hbar}}$$

is not itself a stationary state solution.

Example:

Let us again consider a particle-in-a-box where the wave function happens to be a linear combination of the first two eigenfunctions of the Hamiltonian, but now let us include the time dependent part explicitly:

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

or more simply

$$\Psi(x,t) = \frac{1}{\sqrt{2}} \psi_1(x) e^{\frac{iE_1 t}{\hbar}} + \frac{1}{\sqrt{2}} \psi_2(x) e^{\frac{iE_2 t}{\hbar}}$$

Let us look at the probability density of this wave function:

$$\begin{aligned} \Psi^*(x,t)\Psi(x,t) &= \frac{1}{\sqrt{2}} \left(\psi_1^*(x) e^{\frac{iE_1 t}{\hbar}} + \psi_2^*(x) e^{\frac{iE_2 t}{\hbar}} \right) \times \frac{1}{\sqrt{2}} \left(\psi_1(x) e^{\frac{iE_1 t}{\hbar}} + \psi_2(x) e^{\frac{iE_2 t}{\hbar}} \right) \\ &= \frac{1}{2} \psi_1^*(x)\psi_1(x) + \frac{1}{2} \psi_2^*(x)\psi_2(x) + \frac{1}{2} \psi_1^*(x)\psi_2(x) e^{\frac{i(E_1-E_2)t}{\hbar}} + \frac{1}{2} \psi_2^*(x)\psi_1(x) e^{\frac{i(E_1-E_2)t}{\hbar}} \end{aligned}$$

You can see that the time dependence **does not drop out** of the probability distribution.

Since the functions $\psi_1(x)$ and $\psi_2(x)$ for the particle in a box are real we can write

$$\psi_1^*(x)\psi_2(x) = \psi_2^*(x)\psi_1(x) = \psi_1(x)\psi_2(x)$$

and then rewrite the probability as

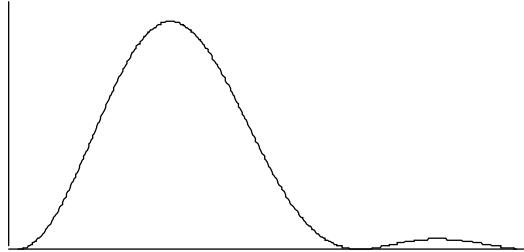
$$\begin{aligned} \Psi^*(x,t)\Psi(x,t) &= \frac{1}{2} |\psi_1(x)|^2 + |\psi_2(x)|^2 + \frac{1}{2} \psi_1(x)\psi_2(x) \left[e^{\frac{i(E_1-E_2)t}{\hbar}} + e^{\frac{i(E_1-E_2)t}{\hbar}} \right] \\ &= \frac{1}{2} |\psi_1(x)|^2 + \frac{1}{2} |\psi_2(x)|^2 + \psi_1(x)\psi_2(x) \cos\left(\frac{E_1-E_2}{\hbar}t\right) \end{aligned}$$

In this case, the probability distribution looks like the average of the distributions from each of the two functions plus an oscillatory cosine term. The frequency of the oscillation depends on the energy separation of the two states; *i.e.* the cosine oscillates with frequency $(E_1 - E_2)/\hbar$.

To get a physical feel for what is happening, let's look at the time dependence of such a probability distribution.

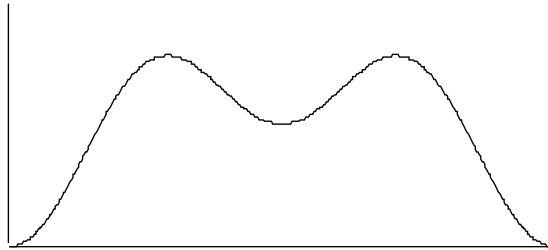
When the cosine term = 1

$$|\psi(x)|^2 = \frac{1}{2}|\psi_1(x)|^2 + \frac{1}{2}|\psi_2(x)|^2 + \psi_1(x)\psi_2(x) = \frac{1}{2}(\psi_1(x) + \psi_2(x))^2$$



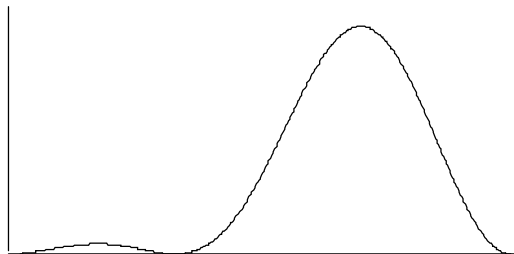
When the cosine term = 0

$$|\psi(x)|^2 = \frac{1}{2}|\psi_1(x)|^2 + \frac{1}{2}|\psi_2(x)|^2$$



Finally, when the cosine term = -1

$$|\psi(x)|^2 = \frac{1}{2}|\psi_1(x)|^2 + \frac{1}{2}|\psi_2(x)|^2 - \psi_1(x)\psi_2(x) = \frac{1}{2}(\psi_1(x) - \psi_2(x))^2$$



So the probability distribution beats back and forth with a frequency $(E_1 - E_2)/\hbar$.

Before I discuss postulate 6, I want to take care of a few loose ends regarding some properties of operators that are important for further understanding measurements in quantum mechanical systems.

2.9 Some properties of operators

When more than one operator operates on a function, you apply the operator closest to the function first (the operator on the right), and then apply the second operator to the function that results from the first operation.

For example:

$$\hat{A}\hat{B}f(x) = \hat{A}(\hat{B}f(x)) = \hat{A}h(x) \quad \text{here} \quad h(x) = \hat{B}f(x)$$

Operators do not necessarily obey the commutative law of multiplication.

That is $\hat{A}\hat{B}f(x) \neq \hat{B}\hat{A}f(x)$ in general.

If one can write an = sign here, we say that the operators **commute**. Otherwise, we say they **do not commute**.

Let us look at an example.

Let $\hat{A} = \frac{d}{dx}$ and $\hat{B} = x$

$$\hat{A}\hat{B}f(x) = \frac{d}{dx}x f(x) = f(x) + x \frac{d}{dx}f(x) = (\hat{I} + \hat{B}\hat{A})f(x)$$

where \hat{I} is the identity operator which multiplies a function by one.

So $\hat{A}\hat{B}f(x) \neq \hat{B}\hat{A}f(x)$

One way to characterize this property is to define what is called a **commutator**.

The commutator of \hat{A} and \hat{B} is given by

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$$

and is denoted by two operators in square brackets.

If the operators **commute** then $[\hat{A}, \hat{B}] = 0$. If the operators **do not commute**, $[\hat{A}, \hat{B}] \neq 0$.

The commutator defines a new operator and to evaluate this operator one must operate on a function.

That is $[\hat{A}, \hat{B}]f(x)$

Let me give you a simple example:

Let $\hat{A} = \frac{d}{dx}$ and $\hat{B} = x^2$

$$\begin{aligned}
[\hat{A}, \hat{B}]f(x) &= \hat{A}\hat{B}f(x) - \hat{B}\hat{A}f(x) \\
&= \frac{d}{dx}(x^2 f(x)) - x^2 \frac{df(x)}{dx} \\
&= x^2 \frac{df(x)}{dx} + 2x f(x) - x^2 \frac{df(x)}{dx} \\
&= 2x f(x)
\end{aligned}$$

So $[\hat{A}, \hat{B}]f(x) = 2x f(x)$

Thus $[\hat{A}, \hat{B}] = 2x$

So we say that the operators $\hat{A} = \frac{d}{dx}$ and $\hat{B} = x^2$ do not commute.

It turns out that the commutator plays an important role in making measurements in quantum mechanical systems, and has a direct relationship to the Heisenberg Uncertainty Principle. To fully understand the connection between commutators and the measurement process, we need to introduce a theorem.

THEOREM: *If (Hermitian) operators \hat{A} and \hat{B} commute, they possess a common, complete set of eigenfunctions.*

Proof: Consider \hat{A} and \hat{B} such that $[\hat{A}, \hat{B}] = 0$,

Start with $\hat{B}\varphi_i = b_i \varphi_i$

If we operate on both sides with \hat{A} we get:

$$\hat{A}\hat{B}\varphi_i = \hat{A}b_i \varphi_i$$

Since \hat{A} and \hat{B} commute we also have:

$$\hat{A}\hat{B}\varphi_i = \hat{B}\hat{A}\varphi_i$$

Consequently, we can write:

$$\hat{B}(\hat{A}\varphi_i) = \hat{A}\hat{B}\varphi_i = \hat{A}b_i \varphi_i = b_i (\hat{A}\varphi_i)$$

This says that if φ_i is an eigenfunction of \hat{B} with eigenvalues b_i then the function $\hat{A}\varphi_i$ is also an eigenfunction of \hat{B} with eigenvalue b_i .

If we assume that the eigenvalues of \hat{B} are non-degenerate (no two the same), then b_i determines in a unique way the eigenfunction φ_i . (Remember we showed that eigenfunctions of a Hermitian operator form an orthonormal set. This means that eigenfunctions corresponding to different eigenvalues are orthogonal.) So then if the function $\hat{A}\varphi_i$ also has an eigenvalue b_i , it must be linearly dependent on φ_i , that is

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

This will be true for every eigenfunction, and hence it forms a complete set. The inverse is also true.

Let us now explore the implications of this. Recall Postulates 3 and 4. Postulate 3 said that upon making a measurement of the quantity represented by \hat{A} , the only possible results are the eigenvalues of \hat{A} . Postulate 4 gave us a prescription for calculating average values:

$$\langle a \rangle = \int_{-\infty}^{\infty} \psi^*(x) \hat{A} \psi(x) dx$$

Recall what happens when the wave function $\psi(x)$ happens to be one of the eigenfunctions of the operator corresponding to the quantity that you measure.

Let us assume we are measuring the energy of a particle-in-a-box and the wave function is in an eigenfunction of the particle-in-a-box Hamiltonian.

$$\psi(x) = \psi_2(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{2\pi}{a} x\right)$$

What happens when we measure the energy? We could calculate the average value

$$\langle E \rangle = \int_{-\infty}^{\infty} \psi_2^*(x) \hat{H} \psi_2(x) dx = E_2 \int_{-\infty}^{\infty} \psi_2^*(x) \psi_2(x) dx = E_2$$

(We could have done this explicitly by substituting in the proper Hamiltonian and operating on the function)

If we calculate the variance in our measurement, we would find that the variance equals zero.

→→ we would get E_2 every time we measured.

If the wave function is an eigenfunction of the operator you are measuring, then you **know** what the result will be

→→ the eigenvalue of that operator corresponding to the eigenfunction.

In this case, you do not need to take an average value. Just use the eigenvalue equation:

$$\hat{H} \psi_2(x) = E_2 \psi_2(x)$$

where

$$E_2 = \frac{2^2 h^2}{8ma^2}$$

Now let us consider the implications of the theorem we just introduced. Suppose a system is in a wave function that is an eigenfunction of an operator \hat{A} . But now, instead of measuring the quantity corresponding to \hat{A} you measure a quantity which is represented by the operator \hat{B} which commutes with \hat{A} .

The theorem I just introduced says that if \hat{A} and \hat{B} commute, they have a common set of eigenfunctions. Thus, when you measure \hat{B} , you know exactly what you will get: the eigenvalue of \hat{B} that corresponds to that particular eigenfunction. There is no need to calculate an average value here.

Let me give you a specific example of how the commutator of two operators affects the measurement process in quantum mechanical systems.

Let us consider a particle which is fixed to move in a circular orbit of radius a . This problem is sometimes called a particle-on-a-ring and represents the rotation of a molecule in two dimensions. I will give you this problem to work out the details in your exercises.

The Hamiltonian operator for a particle constrained to move on a circle of radius a is given by:

$$\hat{H} = -\frac{\hbar^2}{2I} \frac{d^2}{d\theta^2}$$

where $I = ma^2$

The eigenfunctions of \hat{H} for this system are:

$$\psi(\theta) = \frac{1}{\sqrt{2\pi}} e^{in\theta}$$

and the energies are:

$$E_n = \frac{n^2 \hbar^2}{2I} = \frac{n^2 \hbar^2}{2ma^2} \quad \text{where } n=0, \pm 1, \pm 2, \dots$$

(We could verify this simply by operating on the eigenfunction with the Hamiltonian.)

Let us say the system is in an eigenfunction of the particle on a ring Hamiltonian corresponding to $n=+3$. The wave function is then:

$$\psi(\theta) = \frac{1}{\sqrt{2\pi}} e^{i3\theta}$$

If we made a measurement of the energy we know exactly what we will get, E_3 .

Let us just show this.

$$\hat{H} = -\frac{\hbar^2}{2I} \frac{d^2}{d\theta^2}$$

$$\hat{H}\psi(\theta) = -\frac{\hbar^2}{2I} \frac{d^2}{d\theta^2} \frac{1}{\sqrt{2\pi}} e^{i3\theta} = \frac{9\hbar^2}{2I} \frac{1}{\sqrt{2\pi}} e^{i3\theta} = E_3 \psi(\theta)$$

But instead of measuring energy, let us measure angular momentum.

By applying the prescription of postulate 2, we could easily determine that the angular momentum operator is

$$\hat{L} = -i\hbar \frac{d}{d\theta}$$

We can also easily show that this operator commutes with the Hamiltonian for the particle on a ring, that is

$$[\hat{H}, \hat{L}] = 0$$

$$\begin{aligned} [\hat{H}, \hat{L}]f(\theta) &= (\hat{H}\hat{L} - \hat{L}\hat{H})f(\theta) \\ &= \frac{i\hbar^3}{2I} \left(\frac{d^2}{d\theta^2} \frac{df(\theta)}{d\theta} - \frac{d}{d\theta} \frac{d^2 f(\theta)}{d\theta^2} \right) \\ &= \frac{i\hbar^3}{2I} \left(\frac{d^3 f(\theta)}{d\theta^3} - \frac{d^3 f(\theta)}{d\theta^3} \right) \\ &= 0f(\theta) \end{aligned}$$

So
$$[\hat{H}, \hat{L}] = 0$$

Just as an aside, it is a general rule that the commutator of an operator with that operator raised to a power will be zero.

That is
$$[\hat{A}, \hat{A}^n] = 0$$

So we could have simply looked at the commutator and known it equals zero.

Since $[\hat{H}, \hat{L}] = 0$, from the theorem we introduced, if the system is in a state that is an eigenfunction of the angular momentum operator, \hat{L} , it is also in an eigenfunction of the Hamiltonian, \hat{H} . If we make a measurement of the angular momentum, we know what we will get, the eigenvalue of \hat{L} . However, if we make a measurement of the energy, we also know exactly what we will get, the eigenvalue of \hat{H} that corresponds to that eigenfunction. There will be no uncertainty in repeated measurements, *i.e.* the variance is zero, because the system is in an eigenfunction of that operator.

That is
$$\Delta E \Delta L = 0$$

There is no uncertainty in the relative precision with which these two operators can be measured.

One can prove that there exists a direct relationship between the value of the commutator of two operators and the relative precision with which the corresponding observable quantities can be measured. The prove goes as follows.

Let us consider two observables A and B with average values,

$$\langle A \rangle = \int \psi^* \hat{A} \psi d\tau \quad \text{and} \quad \langle B \rangle = \int \psi^* \hat{B} \psi d\tau$$

where ψ is any acceptable wavefunction.

Let us define
$$\Delta A = \sqrt{\sigma_A^2} = \sqrt{\langle (A - \langle A \rangle)^2 \rangle} = \sqrt{\langle A^2 \rangle - \langle A \rangle^2}$$

and
$$\Delta B = \sqrt{\sigma_B^2} = \sqrt{\langle (B - \langle B \rangle)^2 \rangle} = \sqrt{\langle B^2 \rangle - \langle B \rangle^2}$$

We now introduce new Hermitian operators defined as:

$$\hat{\bar{A}} = \hat{A} - \langle A \rangle \quad \text{and} \quad \hat{\bar{B}} = \hat{B} - \langle B \rangle$$

From this follows that

$$(\Delta A)^2 = \langle \bar{A}^2 \rangle \quad \text{and} \quad (\Delta B)^2 = \langle \bar{B}^2 \rangle$$

Define a linear (not Hermitian) operator,

$$\hat{C} = \hat{\bar{A}} + i\lambda \hat{\bar{B}}$$

with λ being a real number, and its complex conjugate,

$$\hat{C}^* = \hat{\bar{A}} - i\lambda \hat{\bar{B}}$$

We find that

$$\langle CC^* \rangle = \langle (\bar{A} + i\lambda\bar{B})(\bar{A} - i\lambda\bar{B}) \rangle = \langle \bar{A}^2 + \lambda^2\bar{B}^2 - i\lambda(\bar{A}\bar{B} - \bar{B}\bar{A}) \rangle = \langle \bar{A}^2 + \lambda^2\bar{B}^2 - i\lambda[\bar{A}, \bar{B}] \rangle$$

Since $\langle CC^* \rangle = \int \psi^* \hat{C} \hat{C}^* \psi d\tau = \int (\hat{C}^* \psi)^* \hat{C}^* \psi d\tau \geq 0$ and real

we have that

$$f(\lambda) = \langle \bar{A}^2 + \lambda^2\bar{B}^2 - i\lambda[\bar{A}, \bar{B}] \rangle = \langle \bar{A}^2 \rangle + \lambda^2 \langle \bar{B}^2 \rangle - i\lambda \langle [\bar{A}, \bar{B}] \rangle = (\Delta A)^2 + \lambda^2 (\Delta B)^2 - i\lambda \langle [A, B] \rangle \geq 0$$

is real and non-negative and consequently $\langle [A, B] \rangle$ is purely imaginary.

The function $f(\lambda)$ will have a minimum. We can find this minimum by setting

$$\frac{df(\lambda)}{d\lambda} = 2\lambda(\Delta B)^2 - i\langle [A, B] \rangle = 0$$

giving
$$\lambda_{\min} = \frac{i\langle [A, B] \rangle}{2(\Delta B)^2}$$

with which we find that

$$f(\lambda_{\min}) = (\Delta A)^2 + \left(\frac{i\langle [A, B] \rangle}{2(\Delta B)^2} \right)^2 (\Delta B)^2 - i \frac{i\langle [A, B] \rangle}{2(\Delta B)^2} \langle [A, B] \rangle = (\Delta A)^2 + \frac{1}{4} \frac{\langle [A, B] \rangle^2}{(\Delta B)^2} \geq 0$$

Consequently,

$$(\Delta A)^2 (\Delta B)^2 \geq -\frac{1}{4} \langle [A, B] \rangle^2 = -\frac{1}{4} \left(\int \psi^* [A, B] \psi d\tau \right)^2$$

Using the expression before

As an example, consider the commutator $[\hat{p}_x, \hat{x}]$.

Let us calculate the value of this commutator. Remember the golden rule in evaluating commutators: You must always operate on a function. You can do it other ways, but is very easy to make a mistake.

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

To evaluate:

$$\begin{aligned} \left[-i\hbar \frac{d}{dx}, x \right] f(x) &= -i\hbar \left(\frac{d}{dx} x f(x) - x \frac{df(x)}{dx} \right) \\ &= -i\hbar \left(x \frac{df(x)}{dx} + f(x) - x \frac{df(x)}{dx} \right) \\ &= -i\hbar f(x) \end{aligned}$$

So,
$$[\hat{p}_x, \hat{x}] = -i\hbar$$

If we now substitute this into our equation for the relative variance we get

$$\begin{aligned} (\Delta P_x)^2 (\Delta x)^2 &\geq -\frac{1}{4} \left(\int \psi^*(x) (-i\hbar) \psi(x) dx \right)^2 \\ &\geq -\frac{1}{4} (-i\hbar)^2 = \frac{\hbar^2}{4} \end{aligned}$$

By taking the square root of both sides we get

$$\Delta P_x \Delta x \geq \frac{\hbar}{2}$$

which is known as the **Heisenberg Uncertainty Principle**.

So the Heisenberg uncertainty principle relationship does not only hold for position and momentum, but it is a more general rule that pertains to many other pairs of observables. It depends upon the value of their commutator.

If the commutator of two operators is zero (*i.e.*, if they commute), you can measure the observables that correspond to those operators with infinite relative precision.

2.10 Postulate 6

I would like to finish our treatment of the formal postulates of Quantum Mechanics by continuing a little further with our discussion of measurements in quantum mechanical systems. We often talk about quantum mechanical systems like the particle-in-a-box or a particle-on-a-ring being in one particular state or another, but how does the system get into that state initially (or, how does one know what state it is in to start)??

The answer is that the state of the system is determined by the measurement process itself. That is the state of a system is determined by the last measurement on that system.

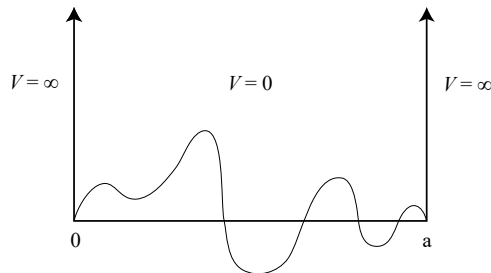
There is one more postulate of quantum mechanics that deals with this.

Postulate 6

Immediately after measuring the quantity corresponding to observable A and getting the result a_n , the wave function representing the state of the system becomes φ_n where $\hat{A}\varphi_n = a_n\varphi_n$. That is, it becomes an eigenfunction of the operator \hat{A} .

The system forgets where it was and finds itself in φ_n .

For example, consider the particle in a box. Let us say the original state $\Psi(r,t)$ looks something like this:



Although this is not one of the solutions to the time-independent Schrodinger equation for the particle-in-a-box, it is a perfectly acceptable wave function. There is nothing to say that the wave function Ψ has to be an eigenfunction of the particle-in-a-box Hamiltonian. In general it can be represented by a linear combination of eigenfunctions. We can choose these eigenfunctions however we want, as long as it is a complete, orthonormal set.

Let us choose to expand them in eigenfunctions of the particle-in-a-box Hamiltonian.

$$\Psi(x,t) = \sum_n c_n \Psi_n(x,t) = \sum_n c_n \psi_n(x) e^{\frac{iE_n t}{\hbar}} = \sum_n c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{\frac{iE_n t}{\hbar}}$$

The exponential comes from the fact that we know the time dependence of the $\Psi_n(x,t)$.

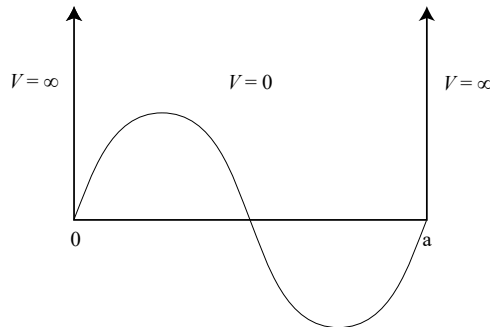
Now, let us say we make a measurement of the energy of the system. The energy we measure will be one of the eigenvalues of the particle-in-a-box Hamiltonian (Postulate 3).

The probability of obtaining a particular result, say E_2 for example, is given by

$$P_2 = c_2 e^{\frac{-iE_2 t}{\hbar}} \cdot c_2^* e^{\frac{+iE_2 t}{\hbar}} = |c_2|^2$$

Let's say we make a measurement of the energy and get the result E_2 .

Postulate 6 says that the wave function Ψ becomes the particle-in-a-box ψ_2 . Our wave function now looks like this:



The wavefunction of the system is then given by:

$$\Psi(x,t) = \psi_2(x) e^{\frac{iE_2 t}{\hbar}}$$

Will the system remain in this state in subsequent measurements of the energy?

Inspection of the wavefunction learns us that:

$$P_2 = c_2 e^{\frac{-iE_2 t}{\hbar}} \cdot c_2^* e^{\frac{+iE_2 t}{\hbar}} = |c_2|^2 = 1$$

and $P_{n \neq 2} = 0$

Thus, if we make a subsequent measurement of the energy on the same system, we know exactly what result we will get – E_2 , since the system is in an eigenfunction of the Hamiltonian ψ_2 . According to postulate 6, immediately after this measurement the system will be in an eigenfunction of the operator we measured

corresponding to the eigenvalue we obtained. That is: it remains in the same state that it was in before the second measurement.

What if we subsequently measure a quantity whose operator commutes with the Hamiltonian?

If the operator commutes with the Hamiltonian, they have a common complete set of eigenfunctions. We know exactly what result the measurement will give -- the eigenvalue of the operator we measure corresponding to the eigenfunction that the state is in. After the measurement it stays in the same state, since it is put in an eigenfunction of the operator we measure, and that function is also an eigenfunction of the operator we originally measured.

What happens if we first measure the energy and then measure something whose operator does not commute with the Hamiltonian?

For example, we could measure the energy of a particle in a box and then measure its position.

Since $[\hat{H}, \hat{x}] \neq 0$, then \hat{x} and \hat{H} do not have a common set of eigenfunctions.

When we make a measurement of x , postulate 6 says that the system forgets where it was and finds itself in an eigenfunction of the position operator. We haven't talked about what this function looks like, but it is not an eigenfunction of \hat{H} . Since this is **not** an eigenfunction of \hat{H} , when we go back and measure the energy we are not exactly sure what we will get. There will be some probability for getting any one of the energy eigenvalues.

Mathematically this can be simply demonstrated. Although the eigenfunctions of \hat{x} are not eigenfunctions of \hat{H} , they can be written as a linear combination of \hat{H} eigenfunctions:

$$X(x,t) = \sum_n c_n \Psi_n(x,t) = \sum_n c_n \psi_n(x) e^{\frac{iE_n t}{\hbar}} = \sum_n c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{\frac{iE_n t}{\hbar}}$$

One can then see that the probability of getting a particular result upon remeasuring the energy is:

$$P_n = |c_n|^2$$

So we need not get the same result that we got last time we measured the energy. How could the system have changed energy?? **Through the interaction of the measurement!**

This is a fairly hard concept to get a handle on, and it takes a little practice to get it right.

At the risk of making it a little more confusing, let me take this one step further in looking at the role of Postulate 6 on the measurement process.

Let us say we start with a particle in a box and have no idea of what state we are in. We then make a measurement of the energy and find it in E_2 , the particle-in-a-box energy corresponding to $n=2$.

Now let us say that we measure the energy again. What will we get? E_2 again since the system is still in ψ_2 as we saw before.

Now let us measure the position. Since the wave function before the measurement is ψ_2 , we know what the probability distribution is for finding the particle at a particular place. Let's say we find it at $a/4$.

Ten seconds later let's measure the position again. Where will we find it? Will it still be at $a/4$? Will it be somewhere else with certainty? Or can it have a distribution of values?

The answer $\rightarrow\rightarrow$ it will have a distribution of values!! The reason is that the wavefunction evolves in time according to:

$$X(x,t) = \sum_n c_n \Psi_n(x,t) = \sum_n c_n \psi_n(x) e^{-\frac{iE_n t}{\hbar}} = \sum_n c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} x\right) e^{-\frac{iE_n t}{\hbar}}$$

Now notice what happened. When we measured the energy twice in a row we got the same result. However when we measured the position twice in a row we did not necessarily get the same result.

Why is this? Is there something special about measuring the energy?

The answer is **yes!!**

Recall that according to Postulate 5 the wave function $\Psi(x,t)$ evolves in time according to the time dependent Schrödinger equation. Using the method of separation of variables to separate the spatial and time dependent parts we found that the part that just depends on position is given by:

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

Note that this is the time independent Schrödinger equation we use to determine the energy of the system.

The time dependent part of the wave function is given by:

$$f(t) = e^{-\frac{iE t}{\hbar}}$$

The total wave function is then

$$\Psi(x,t) = \psi(x) e^{-\frac{iE t}{\hbar}}$$

Remember we called solutions of this form STATIONARY STATE WAVE FUNCTIONS.

This is because the probability density is independent of time, and any average value will be independent of time since any integral involving the product of the complex exponential and its complex conjugate will be independent of time. We can therefore simply use the time independent solution to the Schrödinger equation for calculating average quantities. But these solutions are simply the eigenfunctions of the Hamiltonian.

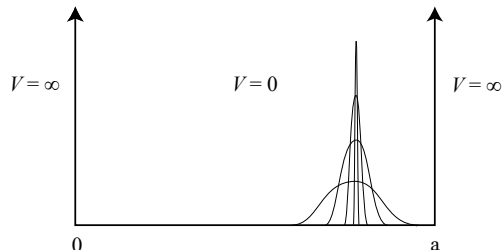
So any time the state of the system becomes one of the eigenfunctions of the Hamiltonian, the wave function has the simple exponential time dependence. Since this state is already a steady state solution to the time dependent Schrödinger equation, we know how it evolves in time--trivially (just a phase factor).

If we measure something which commutes with the Hamiltonian, we have the same situation.

But, if we measure something that does not commute with the Hamiltonian, then the state is changed to a function that is not an eigenfunction of the Hamiltonian and hence will not be a stationary state solution.

Let us say you measure the position. Postulate 6 says that the state of the system becomes an eigenfunction of the position operator. That will not also be an eigenfunction of the Hamiltonian, but can be written as a linear combination of Hamiltonian eigenfunctions. The probability distribution will have a non-trivial time dependence. (REMEMBER that we did an example in class in which we formed a wave function as a superposition of two wave functions and showed that the time dependence didn't drop out).

The time evolution of the eigenfunctions of the position operator is displayed graphically below:



The exact form of the time evolution of the wave function is given by Postulate 5: The time dependent Schrödinger Equation.

But if you subsequently measure the energy or any quantity whose operator commutes with the Hamiltonian, the wave function goes back to the simple complex exponential time dependence (and hence probability distribution stops evolving in time).

Example: Consider the particle on a ring .

1. First we measure the energy and get E_1 . Next, we measure the angular momentum. What will we get? A distribution of values or just a single result? Why? What was the wave function before we measured? What was it afterward?
2. Now measure the energy again. What will we get?
3. Now measure the angular momentum again. What will we get this time? (What is the wavefunction after each measurement?)
4. Now we measure the angular position and get some angle θ_0 . If we measure it again will we get the same result, why?
5. Now we measure the energy again. What will we get? One result or a distribution?

Now that I have finished my introduction of the postulates of quantum mechanics and you have some idea of the basic principles, we will begin to look at the time independent Schrödinger equation for systems that are relevant to chemistry. We will start with 1-dimensional problems and then go to increasingly more complex systems. Along the way I will introduce a number of new concepts that will allow us to go to the next level of complexity.

Our focus will be on determining the eigenvalues and eigenfunctions for chemically relevant systems.

The principles that we have discussed thus far regarding measurements and time dependence in quantum mechanics are independent of the specific systems that we discuss—they hold for all quantum mechanical systems.