

Chapter 2: Particle in a Box

In this chapter, we will develop the theoretical problem of a particle in a box. The purpose here is to explore the capabilities of quantum mechanics and see how some of the mathematical machinery works. The reason for “kicking the tires” of quantum theory with this particular problem is that the math is fairly simple (at least by comparison!) and the results are relatively easy to interpret. After developing a toolbox of methods in this chapter, we can focus more on the results as applied to more complex problems of greater chemical importance.

Background

At the beginning of the 1900s, there was actually a great deal of debate as to whether or not science was a valuable subject for study. At the time, Newtonian physics had proven to be a very reliable model for predicting the behavior of the observable universe. However, as was discussed in Chapter 1, the figurative scientific roof was about to collapse with the advent of a quantum theory.

Quantum theory attempts to do many of the same things that classical (Newtonian) physics does. The goal is to be able to model the behavior of particles and predict how they will behave in the future. In classical physics, this is accomplished by deriving an **equation of motion** for a particle. With such an equation, and a few initial parameters (such as position, velocity and acceleration at time $t=0$) the entire trajectory of a particle can be predicted as time moves forward.

The equivalent construct in the quantum theory is a **wavefunction**. The wavefunction for a system contains all of the information needed to predict what can be measured and observed in terms of the properties of the particle or system. The rules describing a wavefunction are not arbitrary, however. Based on a few simple postulates (given below) the requirements of the wavefunction are outlined, and the entire quantum theory is defined.

The Postulates of Quantum Mechanics

There are only a small number of postulates of quantum mechanics. Upon them is built all of the conclusions of this powerful theory.

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 (\mathbf{r}) and the time (t). This function, called the *wavefunction* has the important property that

$$\Psi^*(\mathbf{r},t) \Psi(\mathbf{r},t) dx dy dz$$

is the probability of finding the particle within the infinitesimally small volume element $dx dy dz$ located at position \mathbf{r} at time t .

Postulate 2

To every physical observable in classical mechanics, there corresponds an operator in quantum mechanics. This operator will be both linear and Hermitian.

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

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

It is important to note that the wavefunction describing the particle need not be an eigenfunction of the operator \hat{A} . However, well defined wavefunctions (those meeting the requirements of all of the postulates of quantum mechanics) will have the possibility of being described as a linear combination of eigenfunctions of any of the needed operators. The **Superposition Principle** is invaluable in working with this concept.

Postulate 4

If a system is in a state described by a normalized wavefunction (Ψ) then the average measured value of the observable corresponding to \hat{A} is given by

$$\langle a \rangle = \int \Psi^* \hat{A} \Psi d\tau \quad \text{or} \quad \langle a \rangle = \frac{\int \Psi^* \hat{A} \Psi d\tau}{\int \Psi^* \Psi d\tau}$$

Postulate 5

The wavefunction of a system evolves in time according to the time dependent Schrödinger equation

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

Each of these postulates has important consequences and ramifications as to what quantum theory can (and cannot) tell us about a particle or system. In the remainder of this section, we will explore each postulate individually in order to lay a foundation of what quantum mechanics can predict for us about the nature of matter.

Postulate 1: a Squared Wavefunction is a Probability Distribution

This postulate describes the commonly accepted interpretation of a wavefunction. First and foremost, a wavefunction is a mathematical function. It must be single valued in that for each point in space, there is only one value that can be calculated from the function. When considering all space which a particle may occupy, the squared wavefunction must create a smooth¹ and continuous probability distribution describing where the particle might be observed to be located. (for our purposes, “smooth” means that the first derivative of the function must be continuous.) Since the square of the wavefunction is a probability distribution for the location of the particle, any location in space where the squared wavefunction is zero, has a corresponding probability of zero that the particle will be observed at that location.

Example. Consider a particle of mass m in box of length a that is prepared such that its wave function is given by

$$\psi(x) = \sqrt{\frac{30}{a^5}} \cdot x(a-x)$$

Calculate the probability that the particle will have a position measurement reveal the particle to be in the middle half of the box (with the measured position satisfying $a/4 \leq x \leq 3a/4$.)

Solution. The squared wavefunction gives the probability distribution for where the particle's position will be measured to be.

$$(\psi(x))^2 = \frac{30}{a^5} (a^2 x^2 - 2ax^3 + x^4)$$

The total probability will be given by the following integral.

$$\begin{aligned} P &= \int_{a/4}^{3a/4} [\psi(x)]^2 dx \\ &= \frac{30}{a^5} \int_{a/4}^{3a/4} (a^2 x^2 - 2ax^3 + x^4) dx \\ &= \frac{30}{a^5} \left[\frac{a^2 x^3}{3} - \frac{2ax^4}{4} + \frac{x^5}{5} \right]_{a/4}^{3a/4} \\ &= \frac{30}{a^5} \left(\frac{27a^5}{192} - \frac{162a^5}{1024} + \frac{243a^5}{5120} - \frac{a^5}{192} + \frac{2a^5}{1024} - \frac{a^5}{5120} \right) \\ &= \frac{30}{a^5} \left(\frac{26a^5}{192} - \frac{164a^5}{1024} + \frac{242a^5}{5120} \right) \\ &= 0.520 \end{aligned}$$

¹ The wavefunction will be smooth provided that the potential energy function is not discontinuous. A discontinuous potential energy function (such as a step function) will lead to a wavefunction that which single-valued, will not have a continuous first derivative, and therefore, not be “smooth” in the strictest sense.

Note that the final probability is unitless!

The wavefunction contains all of the information about a system that is needed to understand how the system behaves and how it will behave in the future, at least within the limits of the quantum theory! Information on such properties as energy, momentum and position are all contained in the wavefunction.

Postulate 2: Quantum Mechanical Operators

The second postulate describes the nature of quantum mechanical operators and their relationship to those properties of a system which we can observe. The operators are the tools that pull physical information from the wavefunction and reveal the properties of the quantum mechanical system. The following table shows some operators and their corresponding physically observable quantities.

	Physical Observable	One Dimension	Three Dimensions
\hat{x}	Position	x	\mathbf{r}
\hat{p}	Momentum	$-i\hbar \frac{d}{dx}$	$-i\hbar \vec{\nabla}$
\hat{H}	Energy	$\hat{T} + \hat{U}$	
\hat{T}	Kinetic	$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$	$-\frac{\hbar^2}{2m} \nabla^2$
\hat{U}	Potential	$U(x)$	$U(\mathbf{r})$

A derivation of the momentum operator in one dimension

Let's assume that we can describe the spatial part of a wave function using a plane wave expression

$$\psi(x) = e^{ikx}$$

Where k is the plane wave vector, which can be expressed as

$$k = \frac{2\pi}{\lambda}$$

If we use the de Broglie expression for the wavelength $\lambda = \frac{h}{p}$,

$$k = \frac{2\pi p}{h} = \frac{p}{\hbar}$$

So

$$\psi(x) = e^{\frac{ipx}{\hbar}}$$

Each of these operators will have two very important properties. 1) Each is **linear** and 2) each is **Hermitian**. In one dimension, an operator (\hat{A}) is defined to be linear if the following condition holds:

$$\hat{A}(af(x) + bg(x)) = a\hat{A}f(x) + b\hat{A}g(x)$$

where a and b are scalar values. An example of a linear operator is multiplication by a constant or a function. Taking a derivative (or integrating) is also a linear operation, as is adding a constant or a function. An example of a non-linear operator is taking a logarithm or raising a function to a power other than one.

The Hermitian nature of quantum mechanical operators has many important consequences. An operator (\hat{A}) is Hermitian if it satisfies the following relationship:

$$\int g^* \hat{A} f \, d\tau = \int f \hat{A}^* g^* \, d\tau$$

for well-behaved² functions f and g , where the asterisk (*) indicated the complex conjugate of the function or operator. Hermitian operators have the important properties that 1) their **eigenfunctions** are **orthogonal** and 2) their **eigenvalues** are real. This will be demonstrated later for the eigenfunctions of the **Hamiltonian**.

Example: Is the operator $\frac{d}{dx}$ a Hermitian operator?

Solution: For an operator \hat{A} to be Hermitian, the following relationship must hold (for well-behaved functions f and g):

$$\int g^* \hat{A} f \, d\tau = \int f \hat{A}^* g^* \, d\tau$$

So if we choose arbitrary functions f and g , we can evaluate the left-hand side of the above relationship by noting the pattern $d(uv) = u \, dv + v \, du$ and integrating by parts. Using this approach

$$\int u \, dv = uv - \int v \, du$$

Making the substitutions that

$$u = g^*$$

² A well-behaved function is one that is normalizable and continuous over the relevant space of the problem.
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$$dv = \frac{d}{dx} f dx$$

it should be clear that

$$du = \frac{d}{dx} g^* dx$$

$$v = f$$

So

$$\int g^* \frac{d}{dx} f dx = g^* f|_{-\infty}^{\infty} - \int f \frac{d}{dx} g^* dx$$

In order for f and g to meet the criteria that they are normalizable, they must vanish as x approaches $\pm\infty$. As such,

$$g^* f|_{-\infty}^{\infty} = 0$$

And we are left with

$$\int g^* \frac{d}{dx} f dx = - \int f \frac{d}{dx} g^* dx$$

Which clearly can not be true. Therefore, the operator $\frac{d}{dx}$ is not Hermitian. You should, however, be able to use the same method to show that the operator $\hat{A} = i \frac{d}{dx}$ is in fact Hermitian!

Postulate 3: Measurable Values

Postulate three states that the only measurable values for a system are those values that are eigenvalues of the corresponding quantum mechanical operator. The first measurable value which we will explore is the energy of the system (see below.) Because the wavefunction provides a probability distribution, it also provides a means of predicting the statistics for a theoretical infinite set of measurements on a system. The ramifications of that point are developed in the discussion of the fourth postulate.

Postulate 4: Expectation Values

An expectation value is an average value that would be expected based on an infinite number of measurements. Since wavefunctions give us probability information, it stands to reason that we can calculate a great deal of statistical information about a system based on the wavefunction and the corresponding operators. This will be discussed in detail in section D with Quantum Chemistry with Applications in Molecular Spectroscopy: Particle in a Box © 2023 Patrick E. Fleming – Available under Creative Commons Attribution-Noncommercial-Share Alike license 4.0 ([CC BY-NC-SA 4.0](https://creativecommons.org/licenses/by-nc-sa/4.0/))

regards to expectation values calculated for position, momentum and energy. It is important to note that the expectation value does not indicate the most probable measurement or observation that will be made, nor must it even give a value that can ever be measured; it just gives the average.

This postulate has very important (and controversial) ramifications. It forms the basis for how the Heisenberg Uncertainty Principle can be discussed. The problem is that quantum mechanics cannot tell you what *will* be measured, but rather only the probability that a certain value can be measured for a specific property. While a subtle point, it shakes the very nature of our intuition as to what it means for a system to *have* a certain property. In most cases, the properties we associate with classical particles do not even exist in quantum mechanical particles (at least in any sense to which we are accustomed) until those properties are measured. This has led to numerous debates as to the validity of quantum mechanics as a model, and even led one of the original developers of quantum theory (Erwin Schrödinger) to change his mind completely on the model.

Postulate 5: the evolution of a system in time

The 5th postulate indicates how a system will evolve in time. It also gives the definition of the time dependent Schrödinger equation.

We will explore many of these properties based on the particle in a box problem in order to gain some insight into what quantum mechanics can and can not tell us about a system. The particle in a box problem actually has limited physical application (although it does have some), but does provide a “thought sandbox” in which we can explore the concepts, powers and limitations of the quantum theory. Hopefully then when we apply the theory to problems of greater chemical interest, we can focus more on the conclusions than on the specific mathematics.

The One-Dimensional Particle in a Box

Imagine a particle of mass m constrained to travel back and forth in a one dimensional box of length a . For convenience, we define the endpoints of the box to be located at $x = 0$ and $x = a$. The derivation of wavefunctions and energy levels and the properties of the system using the tools of quantum mechanics will be instructive as we move forward in our studies of quantum mechanics.

The Hamiltonian

Whenever we begin a new quantum mechanical problem, the first challenge is to write the **Hamiltonian** that describes the system. This always has two parts – a **Kinetic Energy** term (which is always the same for each particle) and a **Potential Energy** term (that is different for each new system.)

The kinetic energy term in one dimension for a single particle is always given by

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

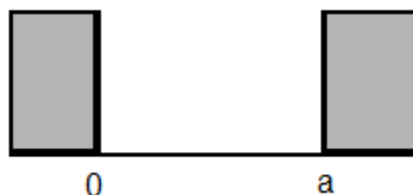
This operator can be derived from the momentum operator based on the relationship between momentum and kinetic energy that comes from classical physics. Namely

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

As such,

$$\begin{aligned}\hat{T} &= \frac{p^2}{2m} \\ &= \frac{1}{2m} \left(-i\hbar \frac{d}{dx} \right) \\ &= \frac{(-i\hbar)^2}{2m} \frac{d^2}{dx^2} \\ &= -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}\end{aligned}$$

The potential energy function is also fairly simple for this problem. The potential energy is infinite outside of the box ($x < 0$ and $x > a$) and zero everywhere else. This forces the particle to be in the box at all times. It also limits the relevant space of the problem to lie between $x = 0$ and $x = a$ since the infinite potential energy precludes the particle from ever existing outside of the limits of $x = 0$ and $x = a$.



$$U(x) = \begin{cases} \infty & \text{if } x < 0 \\ 0 & \text{if } 0 \leq x \leq a \\ \infty & \text{if } x > a \end{cases}$$

So for the problem, limited to the space inside the box, the Hamiltonian can be written

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

And the Schrödinger equation can be written as

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

where $\psi(x)$ is the wavefunction describing the state of the particle. There are a number of approaches that can be used to solve this equation to find the wavefunctions $\psi(x)$ which satisfy the differential equation.

The Solution

We will solve this problem two different ways. First, we will solve it using the de Broglie wavelength (an algebraic solution) and then using the Schrödinger equation (an eigenvalue/eigenfunction approach.)

The de Broglie Approach

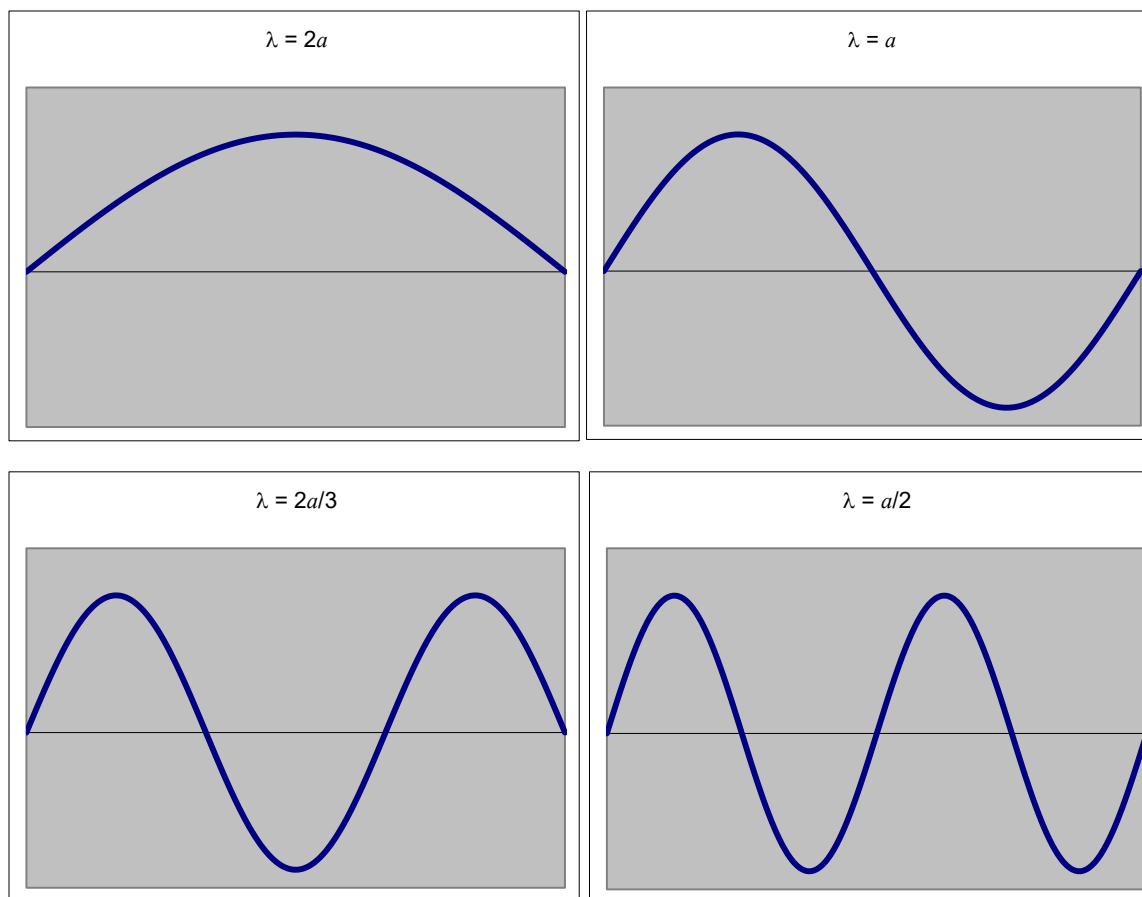
Before trying to solve the problem using Schrödinger's equation, let's use the de Broglie condition to solve the problem algebraically. Recall that de Broglie suggested that a particle can be treated as a wave, the wavelength of which is given by $\lambda = h/p$, where h is Planck's constant, and p is the momentum of the particle.

The necessary conditions on the de Broglie wave are that the wave itself must vanish at the ends of the box (in order to satisfy the first postulate, since the particle can never escape the box.) This will happen for very specific wavelengths which are dependent on the length of the box itself. This is very common in physics for any system with a wave nature. When the wave is constrained to a specific geometry, the system will “ring” with frequencies (and thus wavelengths) characteristic of the medium and the geometry. Quantum mechanical systems are no different in that regard.

What will be required in order to create a standing wave is that the length of the box (a) must be an integral multiple of half de Broglie wavelengths ($\lambda/2$).

$$a = n \frac{\lambda}{2}$$

Given that the de Broglie wavelength is related to momentum, it is simple to derive the following relationship, indicating the possible values for momentum.

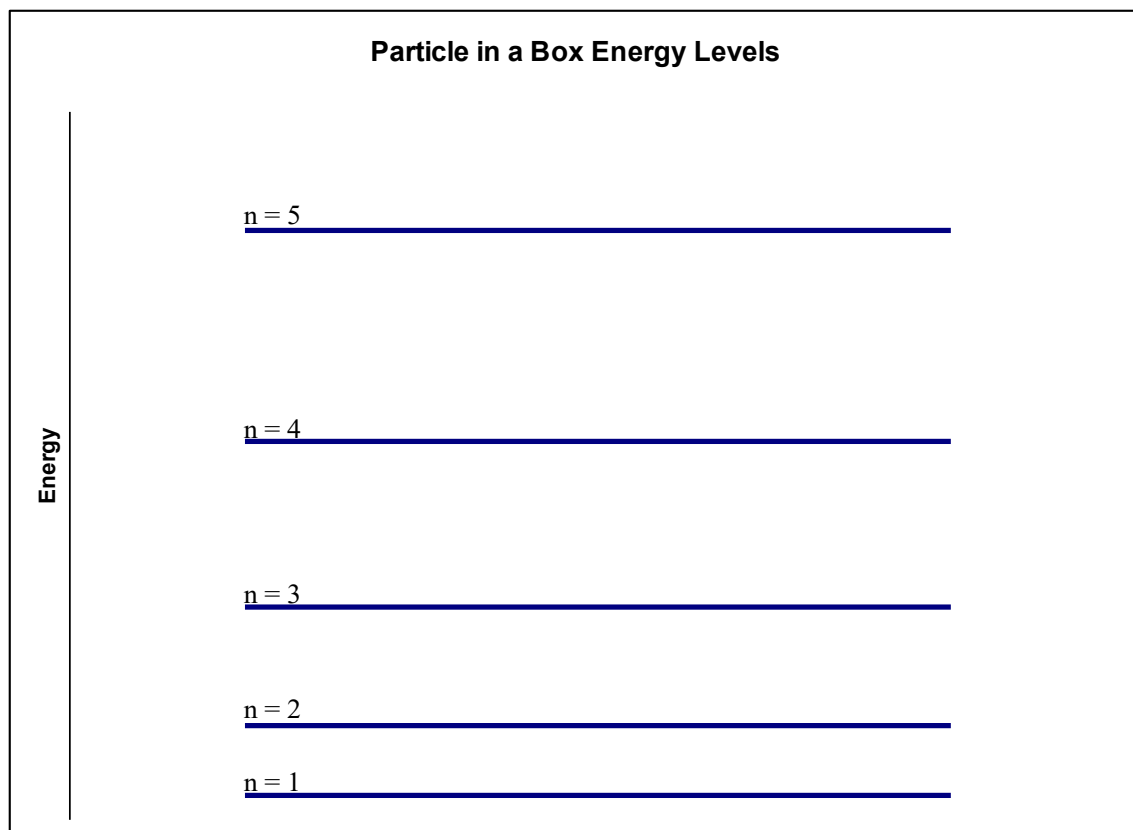


$$\begin{aligned}
 a &= n \frac{\lambda}{2} \\
 &= \frac{nh}{2p} \\
 p &= \frac{nh}{2a}
 \end{aligned}$$

Given the relationship between momentum and kinetic energy, the expected expression for energy levels can be derived.

$$E = \frac{p^2}{2m} = \frac{1}{2m} \left(\frac{nh}{2a} \right)^2 = \frac{n^2 h^2}{8ma^2}$$

And since the energy depends on n^2 , the spacings between successive energy levels increases as the energy increases.



Now let's see if we can derive this expression based on the Schrödinger equation.

The Schrödinger equation: the wavefunctions

The time-independent Schrödinger equation can be written

$$\hat{H}\psi = E\psi$$

Where H is the Hamiltonian operator that was derived in section B.2, ψ is the wavefunction describing the system, and E , the eigenvalue of the Hamiltonian, gives the energy. The wavefunctions are derived so that they are eigenfunctions of the Hamiltonian operator. Substituting the specific statement of the Hamiltonian

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi = E\psi$$

For convenience, we can gather all of the constants in one place by making a substitution

$$-k^2 = -\frac{2mE}{\hbar^2}$$

The particular choice of the form of this substitution is made to simplify the solutions by avoiding (for now) imaginary functions. With the substitution, the Schrödinger equation can be rewritten as

$$\frac{d^2}{dx^2}\psi = -k^2\psi$$

As was the case for the classical wave-on-a-string problem, this is a second order ordinary differential equation, and this has two linearly independent solutions. A general solution is given by a linear combination of two linearly independent solutions, so one way to write a solution is

$$\psi = A \sin(kx) + B \cos(kx)$$

Now we can focus on evaluating A, B and k based on the boundary conditions. The boundary conditions are that the wavefunction must go to 0 at the ends of the box, in accordance with the first postulate.

The first boundary condition, $\psi(0) = 0$, yields the following result:

$$\begin{aligned}\psi(0) &= A \sin(k \cdot 0) + B \cos(k \cdot 0) \\ &= 0 + B = 0\end{aligned}$$

So $B = 0$ and the cosine term must vanish. Focusing only on what has not vanished from the solutions, the second boundary condition, $\psi(a) = 0$, can be applied.

$$\psi(a) = A \sin(k \cdot a) = 0$$

There are two trivial ways to make this true. One is to make $A = 0$ and the other is to make $k = 0$. Both are trivial solutions and unimportant (but fun to mention in class!) The other way to force the function to 0 at $x = a$ is to insure that the sine function is zero by forcing

$$k \cdot a = n\pi$$

where n is an integer ($n = 1, 2, 3 \dots$), since the sine function crosses zero every $n\pi$ radians. This is an important point: the application of a boundary condition leads to the introduction of a quantum number and fixed the results to only functions where that number has a value taken from a very specific list. In fact, the origin of quantum numbers in all problems is the result of the application of boundary conditions.

Solving for k and substituting yields

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

This is as far as the boundary conditions can get us. The value of A is determined based on the first postulate of quantum mechanics, which says that the square of the wavefunction must give a

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probability distribution as to where the particle can be measured to be. Since all measurements must place the particle in the box, the sum of probabilities at all of the possible locations in the box must equal unity. This implies the condition that

$$\int_0^a (\psi(x))^2 dx = 1$$

Solving for A yields

$$\begin{aligned} \int_0^a (\psi(x))^2 dx &= A^2 \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx \\ &= A^2 \left[\frac{x}{2} - \frac{\sin\left(\frac{2n\pi x}{a}\right)}{\left(\frac{4n\pi}{a}\right)} \right]_0^a \\ &= A^2 \left(\frac{a}{2} - 0 - 0 + 0 \right) \\ A &= \sqrt{\frac{2}{a}} \end{aligned}$$

Notice that the value of A did not depend on the quantum number n. Normalization constants usually do have some dependence on the quantum numbers that arise from the application of boundary conditions, but this is one of the rare problems in which the normalization constant does not.

The Schrödinger Equation: the energy levels

Whenever we solve a quantum mechanical problem, there are two important things at which we must look: the energy levels and the wavefunctions. To chemists, the energy levels are the most important part, as the energy levels govern the chemistry the system can do. To a physicist, it is the wavefunctions that are important as they contain all of the information about the physical nature of the system.

The energy levels can be derived using the normalized wavefunctions and the Schrödinger equation.

$$\begin{aligned} \hat{H}\psi &= E\psi \\ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) &= \frac{\hbar^2}{2m} \left(\frac{n\pi}{a}\right)^2 \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \end{aligned}$$

Comparison (or solving for E) yields the following

$$E = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$

which looks similar to, but not exactly like the result reproduced using the de Broglie relationship. In fact, it is the identical result! Making the substitution $\hbar = h/2\pi$, it is easy to show that

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

These energy levels depend on n^2 , and so doubling the quantum number n quadruples the energy. Another way of saying this is that the energy level spacings (the difference in energy between two successive levels) increase with increasing n or energy.

It is also interesting to note that the energy levels are given by a real (non-imaginary) expression. This is to be expected since the energy is the eigenvalue of a Hermitian operator, the Hamiltonian, and thus must be a real value.

Properties of the Wavefunctions

The wavefunctions for the one-dimensional particle in a box problem are given by

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

These wavefunctions have many important properties.

Orthogonality

Similar to the relationship of Hermitian operators having real eigenvalues, the eigenfunctions of Hermitian operators must be orthogonal. Our wavefunctions are actually an infinite set of function, any pair of which must cause the inner product integral to vanish. Mathematically, this looks like

$$\int_0^a \psi_n(x) \cdot \psi_m(x) dx = 0 \quad n \neq m$$

This relationship is easy to verify. To do so, we will make use of the following result taken from a standard table of integrals.

$$\int \sin(\alpha x) \sin(\beta x) dx = \frac{\sin[(\alpha - \beta)x]}{2(\alpha - \beta)} - \frac{\sin[(\alpha + \beta)x]}{2(\alpha + \beta)} \quad \alpha \neq \beta$$

Noting that $\alpha = \frac{n\pi}{a}$ and $\beta = \frac{m\pi}{a}$, substitution into the above relationship yields

$$\begin{aligned}\int_0^a \psi_n(x) \cdot \psi_m(x) dx &= \left[\frac{\sin\left[\frac{\pi}{a}(n-m)x\right]}{2\left(\frac{\pi}{a}(n-m)\right)} - \frac{\sin\left[\frac{\pi}{a}(n+m)x\right]}{2\left(\frac{\pi}{a}(n+m)\right)} \right]_0^a \\ &= \left[\frac{\sin[\pi(n-m)]}{2\left(\frac{\pi}{a}(n-m)\right)} - \frac{\sin[\pi(n+m)]}{2\left(\frac{\pi}{a}(n+m)\right)} - 0 + 0 \right]\end{aligned}$$

And since n and m are integer, n-m and n+m must also be integers. And the sine of an integral multiple of π is always zero, it is easy to show that this function vanishes for any $n \neq m$.

Normalization

When $n = m$ the integral becomes

$$\int_0^a [\psi_n(x)]^2 dx = \frac{2}{a} \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx$$

which can be evaluated using the result from a table of integrals

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

So making the substitution $\alpha = \frac{n\pi}{a}$

$$\begin{aligned}\frac{2}{a} \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx &= \frac{2}{a} \left[\frac{x}{2} - \frac{\sin\left(\frac{2n\pi x}{a}\right)}{4\left(\frac{n\pi}{a}\right)} \right]_0^a \\ &= \frac{2}{a} \left[\frac{a}{2} - 0 - 0 + 0 \right] \\ &= 1\end{aligned}$$

This result shouldn't be surprising since the value $A = \sqrt{\frac{2}{a}}$ was chosen to ensure the result! Specifically, it was chosen so as to normalize the wave functions.

Example: Show that the wavefunction

$$\Psi(x) = \sqrt{\frac{30}{a^5}} \cdot x(a-x)$$

is normalized for a particle in a box of length a .

Solution: The wavefunction is normalized if

$$\int_0^a \Psi(x)\Psi(x) dx = 1$$

This can be demonstrated by plugging the wavefunction into the relationship and testing to see if it is true:

$$\begin{aligned} \int_0^a \sqrt{\frac{30}{a^5}} \cdot x(a-x) \sqrt{\frac{30}{a^5}} \cdot x(a-x) dx &= \frac{30}{a^5} \int_0^a x^2(a^2 - 2ax + x^2) dx \\ &= \frac{30}{a^5} \int_0^a (a^2x^2 - 2ax^3 + x^4) dx \\ &= \frac{30}{a^5} \left[\frac{a^2x^3}{3} - \frac{2ax^4}{4} + \frac{x^5}{5} \right]_0^a \\ &= \frac{30}{a^5} \left(\frac{a^5}{3} - \frac{a^5}{2} + \frac{a^5}{5} - 0 + 0 - 0 \right) \\ &= \frac{30}{a^5} \left(\frac{10a^5}{30} - \frac{15a^5}{30} + \frac{6a^5}{30} \right) \\ &= \frac{30}{a^5} \left(\frac{a^5}{30} \right) \\ &= 1 \end{aligned}$$

Therefore the wavefunction is normalized!

The Tools of Quantum Mechanics

Quantum mechanics is a model that can predict many properties of systems. The prediction of these properties can be made by examining the results of operations on the Quantum Chemistry with Applications in Molecular Spectroscopy: Particle in a Box © 2023 Patrick E. Fleming – Available under Creative Commons Attribution-Noncommercial-Share Alike license 4.0 ([CC BY-NC-SA 4.0](https://creativecommons.org/licenses/by-nc-sa/4.0/))

wavefunctions describing systems. In order to develop a quantum mechanical “toolbox”, we utilize the results of the Particle in a Box model.

Expectation Values

The fourth postulate of quantum mechanics gives a recipe for calculating the expectation value of a particular measurement. The expectation value is a prediction of the average value measured based on an infinite number of measurements of the property.

The Expectation value of Energy $\langle E \rangle$

One of the most useful properties to know for a system is its energy. As chemists, the energy is what is most useful to understand for atoms and molecules as all of the thermodynamics of the system are determined by the energies of the atoms and molecules in the system.

For illustrative convenience, consider a system that is prepared such that its wavefunction is given by one of the eigenfunctions of the Hamiltonian.

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

These functions satisfy the important relationship

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

This greatly simplifies the calculation of the expectation value! To get the expectation value of E , we need simply the following expression:

$$\langle E \rangle = \int \psi_n^* \hat{H} \psi_n d\tau$$

Making the substitution from above yields:

$$\begin{aligned} \langle E \rangle &= \int \psi_n^* \hat{H} \psi_n d\tau \\ &= \int \psi_n^* E_n \psi_n d\tau \\ &= E_n \int \psi_n^* \psi_n d\tau \\ &= E_n \end{aligned}$$

In fact it is easy to prove that for a system whose wavefunction is an eigenfunction of any operator, the expectation value for the property corresponding to that operator is the eigenvalue for the given operator operating on the wavefunction. The proof for this is almost trivial!

Proof: For a system prepared in a state such that its wavefunction is given by ψ , and ψ satisfies

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the relationship

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

The expectation value for the property associated with operator \hat{A} will be the eigenvalue a .

$$\begin{aligned}\langle a \rangle &= \int \psi^* \hat{A} \psi d\tau \\ &= \int \psi^* a \psi d\tau \\ &= a \int \psi^* \psi d\tau \\ &= a\end{aligned}$$

since the wavefunction ψ is normalized.

The Expectation value of position $\langle x \rangle$

To illustrate the concept, let's calculate $\langle x \rangle$ or the expectation value of position for a particle in a box that is in the n^{th} eigenstate

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

Again, it helps to find the result for the integral in a table of integrals.

$$\int x \sin^2(\alpha x) dx = \frac{x^2}{4} - \frac{x \sin(2\alpha x)}{4\alpha} - \frac{\cos(2\alpha x)}{8\alpha^2}$$

Substitution yields

$$\begin{aligned}\frac{2}{a} \int_0^a x \sin^2\left(\frac{n\pi x}{a}\right) dx &= \frac{2}{a} \left[\frac{x^2}{4} - \frac{x \sin\left(2 \frac{n\pi}{a} x\right)}{4 \frac{n\pi}{a}} - \frac{\cos\left(2 \frac{n\pi}{a} x\right)}{8 \left(\frac{n\pi}{a}\right)^2} \right]_0^a \\ &= \frac{2}{a} \left[\frac{a^2}{4} - 0 - \frac{1}{8 \left(\frac{n\pi}{a}\right)^2} - 0 + 0 + \frac{1}{8 \left(\frac{n\pi}{a}\right)^2} \right] \\ &= \frac{a}{2}\end{aligned}$$

This result is interesting for two reasons. First off, $a/2$ is the middle of the box. So the result implies that we might find the particle on the left side of the box half the time and the right side of the box the other half. Averaging all of the results yields a mean value of the middle of the box. Secondly, the result is independent of the quantum number n – which means that we get the same result irrespective of the quantum state in which the system is. This is a remarkable result, really, (well, not really, but it is fun to claim it is) since it means that for the $n = 2$ eigenstate, which has a node at the center of the box, meaning we will never measure the particle to be there, still has an expectation value of position centered in the box. This should really drive home the idea that an expectation value is an average. We need never measure the particle to be at the position indicated by the expectation value. The average of the measured positions must, instead, be at the position indicated by the expectation value.

The Expectation Value of Momentum $\langle p \rangle$

It is also easy to calculate the expectation value for momentum, $\langle p \rangle$. In fact, it is almost trivially easy! Based on the fourth postulate, $\langle p \rangle$ is found from the expression

$$\begin{aligned}\langle p \rangle &= \int_0^a \psi \hat{p} \psi dx \\ &= -i\hbar \int_0^a \psi \frac{d}{dx} \psi dx\end{aligned}$$

At this point it is convenient to make a substitution. If we let $u = \psi$ then $du = \frac{d\psi}{dx} dx$. Now the problem can be restated in terms of u . But since we have changed from x to u , we must change the limits of integration to the values of u at the endpoints. As it turns out, $\psi(0)$ and $\psi(a)$ are both 0!

$$\begin{aligned}\langle p \rangle &= -i\hbar \int_0^0 u du \\ &= -i\hbar \left[\frac{u^2}{2} \right]_0^0 \\ &= 0\end{aligned}$$

Wow! The expectation value of momentum is zero! What makes this so remarkable is that the particle is always moving since it has a non-zero kinetic energy. (How can this be?) Keeping in mind that the expectation value is the average of a theoretical infinite number of measurements, and that momentum is a vector quantity it is easy to see why the average is zero. Half of the time, the momentum is measured in the positive x direction and the other half in the negative x direction. These cancel one another and the average result is zero.

Variance

Quantum mechanics provides enough information to also calculate the variance of a theoretical infinite set of measurements. Based on normal statistics, the variance of any value be calculated from

$$\sigma_a^2 = \langle a^2 \rangle - \langle a \rangle^2$$

That result does not come from quantum mechanics, by the way. Quantum mechanics just tells us how to calculate the expectation values. The above expression for variance can be applied to any set of measurements of any property on any system.

So, to calculate σ_x^2 and σ_p^2 it is simply necessary to know $\langle x \rangle$, $\langle x^2 \rangle$, $\langle p \rangle$ and $\langle p^2 \rangle$. Two of those quantities we already know from the previous sections.

The variance in x (σ_x^2)

To calculate $\langle x^2 \rangle$, we set up the usual expression.

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

From a table of integrals, it can be found that

$$\int x^2 \sin^2(\alpha x) dx = \frac{x^3}{6} - \left(\frac{x^2}{4\alpha} - \frac{1}{8\alpha^3} \right) \sin(2\alpha x) - \frac{x \cos(2\alpha x)}{4\alpha^2}$$

Letting $\alpha = \frac{n\pi}{a}$ and noting that $\cos(2n\pi x) = 1$ and $\sin(2n\pi x) = 0$ for any value of n , we see that

$$\begin{aligned}\langle x^2 \rangle &= \frac{2}{a} \left[\frac{x^3}{6} - \left(\frac{ax^2}{4n\pi} - \frac{a^3}{8n^3\pi^3} \right) \sin\left(\frac{2n\pi x}{a}\right) - \frac{a^2 x \cos\left(\frac{2n\pi x}{a}\right)}{4n^2\pi^2} \right]_0^a \\ &= \frac{2}{a} \left(\frac{a^3}{6} - 0 - \frac{a^3}{4n^2\pi^2} - 0 + 0 + 0 \right) \\ &= \frac{a^2}{3} - \frac{a^2}{2n^2\pi^2}\end{aligned}$$

Notice that this result has units of length squared (due to the a^2 dependence) which is to be expected for $\langle x^2 \rangle$.

Based on these results, it is easy to calculate the variance, and thus the standard deviation of the theoretical infinite set of measurements of position.

$$\begin{aligned}\sigma_x^2 &= \langle x^2 \rangle - \langle x \rangle^2 \\ &= \left(\frac{a^2}{3} - \frac{a^2}{2n^2\pi^2} \right) - \left(\frac{a}{2} \right)^2 \\ &= \frac{(8n^2\pi^2 - 12 - 6n^2\pi^2)a}{24n^2\pi^2} \\ &= \frac{(n^2\pi^2 - 6)a^2}{12n^2\pi^2}\end{aligned}$$

The variance in p (σ_p^2)

The relationship between energy and momentum simplifies the calculation of $\langle p^2 \rangle$ greatly. Recall that

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

And since all of the energy in this system is kinetic energy, it follows that

$$\langle p^2 \rangle = 2m\langle H \rangle$$

Further, $\langle H \rangle$ (or $\langle E \rangle$) is simply the energy expression since the wavefunctions are eigenfunctions of the Hamiltonian! ($\hat{H}\psi_n = E_n\psi_n$.)

$$\begin{aligned}\langle H \rangle &= \int_0^a \psi_n \hat{H} \psi_n dx \\ &= \int_0^a \psi_n E_n \psi_n dx \\ &= E_n \int_0^a \psi_n \psi_n dx \\ &= E_n\end{aligned}$$

Basically, this means that the expectation value for energy for a system in an eigenstate is always given by the eigenvalue of the Hamiltonian. In a later section we'll discuss the expectation value of energy when the system is not in an eigenstate.

Another important aspect of the above relationship is how the integral simply went away. It didn't, really. It's just that the wavefunctions are normalized, so the integral is unity. Recall that for orthonormalized wavefunctions

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

which is a property of which we will make great use throughout our development of quantum theory.

So from the result for the expectation value for energy, it follows that

$$\begin{aligned}\langle p^2 \rangle &= 2mE \\ &= 2m \left(\frac{n^2 h^2}{8ma^2} \right) \\ &= \frac{n^2 h^2}{4a^2}\end{aligned}$$

Note that the variance of the position measurement decreases with increasing n .

For momentum, the variance is given by

$$\begin{aligned}\sigma_p^2 &= \langle p^2 \rangle - \langle p \rangle^2 \\ &= \left(\frac{n^2 h^2}{4a^2} \right) - (0)^2 \\ &= \frac{n^2 h^2}{4a^2}\end{aligned}$$

The variance of momentum measurements *increases* with increasing n !

We shall place these results on hold for now, and revisit them when we look at the Heisenberg Uncertainty Principle. But in order to make sense of that rather important consequence of quantum theory, we must first examine commutators and the relationship between pairs of operators as this will have a profound impact on what can be known (or measured) by their associated physical observables.

The Heisenberg Uncertainty Principle

One of the more interesting (and controversial!) consequences of the quantum theory can be seen in the **Heisenberg Uncertainty Principle**. Before examining the Heisenberg Uncertainty principle, it is necessary to examine the relationship that can exist between a pair of quantum mechanical operators. In order to do this, we define an operator for operators, called the commutator.

The Commutator

For a pair of operators \hat{A} and \hat{B} , the **commutator** $[\hat{A}, \hat{B}]$ is defined as follows

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

If the end result of the commutator operating on $f(x)$ is zero, then the two operations are said to **commute**. This means that for the particular pair of operations, it does not matter which order they on the function – the same result is obtained either way.

Relationships for Commutators

There are a number of important mathematical relationships for commutators. First, every operator commutes with itself, and with any power of itself.

$$\begin{aligned} [\hat{A}, \hat{A}] &= 0 \\ [\hat{A}, \hat{A}^n] &= 0 \end{aligned}$$

Second, given the definition of the commutator relationship, it should be fairly obvious that

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

Also, there is a linearity relationship for commutators (of linear operators).

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

Proof: Show that two operators have a common set of eigenfunctions, the operators must commute.

Solution: Consider operators \hat{A} and \hat{B} that have the same set of eigenfunctions ϕ_n such that

$$\hat{A}\phi_n = a_n\phi_n \quad \text{and} \quad \hat{B}\phi_n = b_n\phi_n$$

For any arbitrary function Φ that can be expressed as a linear combination of ϕ_n

$$\Phi = \sum_n c_n \phi_n$$

the commutator of \hat{A} and \hat{B} operating on Φ will give the following result.

$$\begin{aligned} [\hat{A}, \hat{B}]\Phi &= [\hat{A}, \hat{B}]\sum_n c_n \phi_n \\ &= \hat{A}\left(\hat{B}\sum_n c_n \phi_n\right) - \hat{B}\left(\hat{A}\sum_n c_n \phi_n\right) \end{aligned}$$

And since \hat{A} and \hat{B} are linear (as all quantum mechanical operators must be)

$$\begin{aligned}
\hat{A}\left(\hat{B}\sum_n c_n \phi_n\right) - \hat{B}\left(\hat{A}\sum_n c_n \phi_n\right) &= \hat{A}\left(\sum_n c_n \hat{B}\phi_n\right) - \hat{B}\left(\sum_n c_n \hat{A}\phi_n\right) \\
&= \hat{A}\left(\sum_n c_n b_n \phi_n\right) - \hat{B}\left(\sum_n c_n a_n \phi_n\right) \\
&= \sum_n c_n b_n \hat{A}\phi_n - \sum_n c_n a_n \hat{B}\phi_n \\
&= \sum_n c_n b_n a_n \phi_n - \sum_n c_n a_n b_n \phi_n \\
&= 0
\end{aligned}$$

And so it is clear that the operators \hat{A} and \hat{B} must commute.

When Operators do not Commute

An example of operators that do not commute are \hat{x} and \hat{p} . The commutator of these two operators is evaluated below, using a well-behaved function f .

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

The second term requires the product rule to evaluate. Recall that

$$d(uv) = vdu + u dv$$

And so the above expression can be simplified by noting that

$$\frac{d}{dx}(x \cdot f) = f \frac{d}{dx}x + x \frac{d}{dx}f$$

And so

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

So the final result of the operation is to multiply the function by $i\hbar$. Another way to state this is to note

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

The Heisenberg Uncertainty Principle

Among the many contributions that Werner Heisenberg made to the development of quantum theory, one of the most important was the discovery of the uncertainty principle. Heisenberg's observation was based on the prediction of interference of electron beams that was predicted by de Broglie. The uncertainty principle states that for the observables corresponding to a pair of operators \hat{A} and \hat{B} , the following result must hold

$$\sigma_a^2 \sigma_b^2 \geq -\frac{1}{4} \left(\int \psi^* [\hat{A}, \hat{B}] \psi d\tau \right)^2$$

The most popularly taught statement of the uncertainty principle is based on the uncertainty product for position and momentum.

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

This result is easy to derive from the above expression.

$$\begin{aligned} \sigma_x^2 \sigma_p^2 &\geq -\frac{1}{4} \left(\int \psi^* [\hat{x}, \hat{p}] \psi d\tau \right)^2 \\ &\geq -\frac{1}{4} \left(\int \psi^* (i\hbar \psi) d\tau \right)^2 \\ &\geq -\frac{1}{4} (i\hbar)^2 \left(\int \psi^* \psi d\tau \right)^2 \\ &\geq -\frac{1}{4} (i\hbar)^2 \\ &\geq \frac{\hbar^2}{4} \\ \sigma_x \sigma_p &\geq \frac{\hbar}{2} \end{aligned}$$

As we saw in a previous section, we have a means of evaluating σ_x and σ_p to verify this relationship for a given state of a particle in a box. (This evaluation is left as an exercise.)

Superposition and Completeness

As stated previously, a system need not be in a state that is described by a single eigenfunction of the Hamiltonian. A system can be prepared such that any well-behaved, single-valued, smooth function that vanishes at endpoints. When the wavefunction is not an eigenfunction of the Hamiltonian, the **Superposition Principle** can be used to greatly simplify how we work with the wave function. This is true because the so-called **normal solutions** ($\psi_n(x)$) to the Schrödinger Equation

$$\hat{H}\psi_n(x) = E_n\psi_n(x)$$

using the language of linear algebra, *span the space* of well-behaved functions that can describe the physics of the particle. That means that any arbitrary function that is 1) continuous, and 2) obeys the boundary conditions, can be expressed as a linear combination of these normal solutions:

$$\Phi(x) = \sum_n c_n \psi_n(x)$$

where the coefficients c_n are calculated using the **Fourier Transform** shown below.

$$c_n = \int_{-\infty}^{\infty} \Phi(x) \psi_n(x) dx$$

Superposition

This description also has a number of other important ramifications. Consider a particle in a box system prepared so that the wavefunction is given by

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

where

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

The first question one might ask is, “Is the wavefunction $\Psi(x)$ normalized?” Well, let’s see!

$$\begin{aligned}
\int_0^a (\Psi(x))^2 dx &= \int_0^a \left[\left(\frac{1}{\sqrt{2}} \right) \psi_1 + \left(\frac{1}{\sqrt{2}} \right) \psi_2 \right]^2 dx \\
&= \int_0^a \left(\frac{1}{2} \psi_1 \psi_1 + \psi_1 \psi_2 + \frac{1}{2} \psi_2 \psi_2 \right) dx \\
&= \frac{1}{2} \int_0^a \psi_1 \psi_1 dx + \int_0^a \psi_1 \psi_2 dx + \frac{1}{2} \int_0^a \psi_2 \psi_2 dx \\
&= \frac{1}{2} (1) + (0) + \frac{1}{2} (1) \\
&= 1
\end{aligned}$$

(Notice how the property $\int \psi_i \psi_j d\tau = \delta_{ij}$ has been used to simplify the problem, by making the integral of the cross product in the middle vanish, and the integrals of the first and third terms go to unity.) So the wavefunction is normalized. Now, let's evaluate the expectation value of energy $\langle E \rangle$.

$$\begin{aligned}
\langle E \rangle &= \int_0^a \Psi \hat{H} \Psi dx \\
&= \int_0^a \left(\frac{1}{\sqrt{2}} \psi_1 + \frac{1}{\sqrt{2}} \psi_2 \right) \hat{H} \left(\frac{1}{\sqrt{2}} \psi_1 + \frac{1}{\sqrt{2}} \psi_2 \right) dx \\
&= \int_0^a \left(\frac{1}{\sqrt{2}} \psi_1 + \frac{1}{\sqrt{2}} \psi_2 \right) \left(\frac{E_1}{\sqrt{2}} \psi_1 + \frac{E_2}{\sqrt{2}} \psi_2 \right) dx \\
&= \int_0^a \left(\frac{E_1}{2} \psi_1 \psi_1 + \frac{E_1}{2} \psi_2 \psi_1 + \frac{E_2}{2} \psi_1 \psi_2 + \frac{E_2}{2} \psi_2 \psi_2 \right) dx \\
&= \frac{E_1}{2} \int_0^a \psi_1 \psi_1 dx + \frac{E_1}{2} \int_0^a \psi_2 \psi_1 dx + \frac{E_2}{2} \int_0^a \psi_1 \psi_2 dx + \frac{E_2}{2} \int_0^a \psi_2 \psi_2 dx \\
&= \frac{E_1}{2} + 0 + 0 + \frac{E_2}{2}
\end{aligned}$$

So the expectation value is given by the average of E_1 and E_2 . This result is only possible if half of the time the energy is measured, the observed value is E_1 and the other half E_2 . In other words, the probability of measuring E_1 is $\frac{1}{2}$ and that of E_2 is $\frac{1}{2}$. It is also important to note that these probabilities are given by the Fourier coefficients of

$$c_1 = \frac{1}{\sqrt{2}}, c_2 = \frac{1}{\sqrt{2}} \text{ and } c_n = 0 \text{ for all other } n$$

It can be concluded that the probability of measuring E_n is given by $|c_n|^2$.

$$P(E_n) = |c_n|^2$$

Completeness

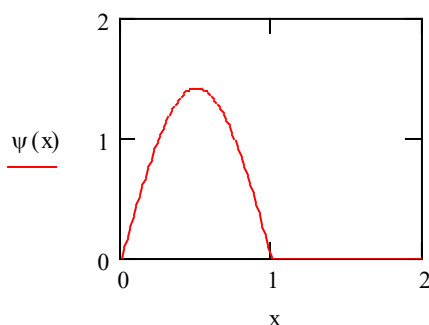
Imagine the following scenario. A quantum mechanical particle of mass m in a one-dimensional box of length a is prepared such that its wavefunction is given by $\psi_1(x)$. Instantaneously, the length of the box increases to $2a$. The particle is no longer in an eigenstate of the new system. Rather, its wavefunction will look like the function depicted below in the MatchCad worksheet.

The function can be described as a superposition of wavefunctions that are eigenfunctions of the Hamiltonian that reflects the new length of the box. A MathCad worksheet that reflects this expansion is given on the next page. The larger the value of m selected, the better the representation of the wavefunction.

$$a := 1$$

$$x := 0, 0.02 \dots 2 \cdot a$$

$$\psi(x) := \text{if} \left(x < a, \sqrt{\frac{2}{a}} \sin \left(\frac{\pi \cdot x}{a} \right), 0 \right)$$



$$n := 1, 2 \dots 15$$

$$\phi(n, x) := \sqrt{\frac{1}{a}} \sin \left(\frac{n \cdot \pi \cdot x}{2 \cdot a} \right)$$

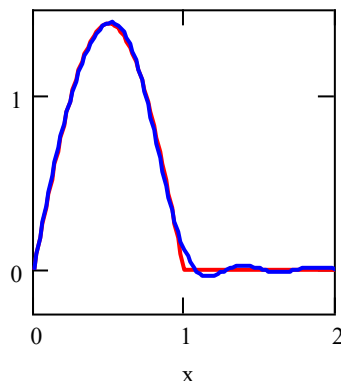
$$c(n) := \int_0^{2 \cdot a} \psi(x) \cdot \phi(n, x) \, dx$$

$$c(n) =$$

0.6
0.707
0.36
0
-0.086
0
0.04
0
-0.023
0
0.015
0
-0.011
0
$8.148 \cdot 10^{-3}$

$$m := 7$$

$$\sum_{n=1}^m (c(n) \cdot \phi(n, x))$$



The above problem is analogous to what happens when an atom undergoes radioactive decay by something such as β -particle emission from the nucleus. In that case, the nuclear charge suddenly changes (changing the potential energy function and thus the Hamiltonian.) The change happens effectively instantaneously compared to the time required for the atom to react. The atom suddenly finds itself in a non-eigenstate, the nature of which will govern how the atom changes in time to respond to the nuclear decay. The superposition of eigenfunctions of the new Hamiltonian will give a description of the atom immediately following the decay, and the overall

wavefunction will evolve in time based on how it is predicted to do so according to the fifth postulate.

The superposition theorem allows for a complete description of a wavefunction according to the needs to the quantum theory – even if the wavefunction being described by a superposition of states is not an eigenfunction of the Hamiltonian! (Now how much would you pay?)

Problems in Multiple Dimensions

As luck would have it, not all quantum mechanical problems are expressible in terms of a single dimension. In fact, most problems will require multiple “dimensions” as they will involve not only electronic state descriptions, but also vibrational descriptions and rotational descriptions as well. In this section, we will discuss how variables are separated in the multidimensional problems, using a particle in a three-dimensional box as an example.

The Particle in a Rectangular Box

Consider a particle of mass m constrained to a three dimensional rectangular box with sides of lengths a , b and c in the x , y and z directions respectively. For this problem, the Hamiltonian will look as follows

$$\begin{aligned}\hat{H} &= -\frac{\hbar^2}{2m}\nabla^2 \\ &= -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\end{aligned}$$

One important thing to notice is that this Hamiltonian can be written as a sum of three separate operators, each affecting only a single variable.

$$\begin{aligned}\hat{H} &= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2} \\ &= \hat{H}_x + \hat{H}_y + \hat{H}_z\end{aligned}$$

When the Hamiltonian takes a form like this, it will also be possible to express the eigenfunctions as a product of functions. Let's give it a try.

The time independent Schrödinger equation looks as follows

$$\begin{aligned}\hat{H}\Psi(x, y, z) &= E\Psi(x, y, z) \\ -\frac{\hbar^2}{2m}\nabla^2\Psi(x, y, z) &= E\Psi(x, y, z) \\ -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\Psi(x, y, z) &= E\Psi(x, y, z)\end{aligned}$$

To simplify things, let's gather variables and make the substitution

$$-\frac{2mE}{\hbar^2} = -k^2$$

To proceed, we make an assumption that the wavefunction can be expressed as a product of functions.

$$\Psi(x, y, z) = X(x)Y(y)Z(z)$$

The wave equation then becomes

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) X(x)Y(y)Z(z) = -k^2 X(x)Y(y)Z(z)$$

$$Y(y)Z(z) \frac{d^2}{dx^2} X(x) + X(x)Z(z) \frac{d^2}{dy^2} Y(y) + X(x)Y(y) \frac{d^2}{dz^2} Z(z) = -k^2 X(x)Y(y)Z(z)$$

Dividing both sides by $X(x)Y(y)Z(z)$ yields

$$\frac{1}{X(x)} \frac{d^2}{dx^2} X(x) + \frac{1}{Y(y)} \frac{d^2}{dy^2} Y(y) + \frac{1}{Z(z)} \frac{d^2}{dz^2} Z(z) = -k^2$$

Since each of these terms is in a different variable, the only way the equation can be true is if each term on the left is equal to a constant. These constants are chosen in a convenient way so as to make the solution of the problem simple. So again, to proceed, we make a substitution.

$$\frac{1}{X(x)} \frac{d^2}{dx^2} X(x) = -k_x^2$$

$$\frac{1}{Y(y)} \frac{d^2}{dy^2} Y(y) = -k_y^2$$

$$\frac{1}{Z(z)} \frac{d^2}{dz^2} Z(z) = -k_z^2$$

where

$$-k_x^2 - k_y^2 - k_z^2 = -k^2$$

These substitutions allow us to separate the problem into three problems in single variables. Further, we know what the solutions to these equations are!

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

$$Y(y) = \sqrt{\frac{2}{b}} \sin\left(\frac{n_y \pi y}{b}\right) \quad n_y = 1, 2, 3, \dots$$

$$Z(z) = \sqrt{\frac{2}{c}} \sin\left(\frac{n_z \pi z}{c}\right) \quad n_z = 1, 2, 3, \dots$$

The total wavefunction, therefore is

$$\Psi(x, y, z) = \sqrt{\frac{8}{abc}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right)$$

And the energy levels can be expressed as

$$E = E_x + E_y + E_z$$

$$= \left(\frac{n_x^2 h^2}{8ma^2}\right) + \left(\frac{n_y^2 h^2}{8mb^2}\right) + \left(\frac{n_z^2 h^2}{8mc^2}\right)$$

The key element to notice here is that the wavefunctions are expressed as a product and the eigenfunction as a sum. This is a common pattern as it always happens when the operator can be expressed as a sum as was the case for this operator.

This pattern arises often in chemistry, where, for example, the total wavefunction of a molecule might be described as the product of wavefunctions describing the electronic state, the vibrational state and the rotational state.

$$\Psi_{tot} = \psi_{elec} \psi_{vib} \psi_{rot}$$

In the limit that this is a good description, the energy of the molecule can be expressed as a sum of energies.

$$E_{tot} = E_{elec} + E_{vib} + E_{rot}$$

Degeneracy

Let's now consider the case where the particle is confined to a cubic space – a rectangular solid where all edges have the same length. If that length is a , the wavefunction becomes

$$\Psi(x, y, z) = \sqrt{\frac{8}{a^3}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{a}\right) \sin\left(\frac{n_z \pi z}{a}\right)$$

The energy levels are given by

$$E = (n_x^2 + n_y^2 + n_z^2) \frac{h^2}{8ma^2}$$

This result leads to an important possibility. Specifically, several eigenstates of the system can have the same energy. Consider the set of quantum numbers and energies shown in the following table.

Notice that several energies can be generated by a number of combinations of quantum numbers. The degeneracy is indicated by the number of quantum states that yield the same energy. There are many examples in quantum mechanics where several eigenstates yield the same energy. This can have important consequences on the nature of the system being described. This is perhaps the simplest system in which this phenomenon is observed. (Well, a particle in a 2-D box is simpler.)

<i>Level</i>	<i>n_x</i>	<i>n_y</i>	<i>n_z</i>	<i>E/(h²/8ma²)</i>	<i>Degeneracy</i>
1	1	1	1	3	1
2	1	1	2	6	3
3	1	2	1	6	
4	2	1	1	6	
5	1	2	2	9	3
6	2	1	2	9	
7	2	2	1	9	
8	1	1	3	11	3
9	1	3	1	11	
10	3	1	1	11	
11	2	2	2	12	1
12	1	2	3	14	6
13	2	3	1	14	
14	3	2	1	14	
15	1	3	2	14	
16	3	2	1	14	
17	2	1	3	14	

Linear Combinations of Degenerate Wavefunctions

Oftentimes, it is convenient to describe systems using linear combinations of wavefunctions. An example of this is the creation of molecular orbitals as linear combinations of atomic orbitals. Another is the construction of hybrid orbitals such as the sp³ hybrid set that is often used to describe the bonding in methane or other hydrocarbons.

These linear combinations have important properties. In the case that the basis wavefunctions are degenerate eigenfunctions of the same operator (say, the Hamiltonian operator for instance) the linear combinations will also be eigenfunctions of that operator. However, this

will not generally be the case for linear combinations of non-degenerate eigenfunctions. The proof of this is fairly straight forward.

Proof: Show that any linear combination of two functions that are eigenfunctions of the same operator, and have the same eigenvalues is also an eigenfunction of the operator.

Solution: Consider two functions f and g that are eigenfunctions of the operator \hat{A} .

$$\hat{A}f = af \quad \text{and} \quad \hat{A}g = ag$$

Any linear combination of the functions f and g will also be an eigenfunction of the operator \hat{A} .

$$\begin{aligned}\hat{A}(c_1f + c_2g) &= c_1\hat{A}f + c_2\hat{A}g \\ &= ac_1f + ac_2g \\ &= a(c_1f + c_2g)\end{aligned}$$

The Particle on a Ring Problem

Consider a quantum mechanical particle of mass m constrained to a circular path of radius a . In Cartesian coordinates, we can write the potential energy function for this system as

$$V(x,y) = \begin{cases} \infty & \text{for } x^2 + y^2 \neq a^2 \\ 0 & \text{for } x^2 + y^2 = a^2 \end{cases}$$

However, it is much more convenient to work in coordinates that reflect the symmetry of the problem. In plane polar coordinates, the potential energy function is defined as

$$V(r,\theta) = \begin{cases} \infty & \text{for } r \neq a \\ 0 & \text{for } r = a \end{cases}$$

And since the Laplacian operator is given by

$$\nabla^2 = \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2}$$

we can write the time-independent Schrödinger equation as

$$-\frac{\hbar^2}{2m} \cdot \frac{1}{r^2} \cdot \frac{\partial^2}{\partial \theta^2} \psi(r,\theta) = E\psi(r,\theta)$$

As usual, we proceed by separating variables. Let's let $\psi(r,\theta) = R(r)\Theta(\theta)$. We now get

$$-\frac{\hbar^2}{2m} \cdot \frac{R(r)}{r^2} \cdot \frac{d^2}{d\theta^2} \Theta(\theta) = ER(r)\Theta(\theta)$$

Now we can divide both sides by the function $R(r)$ and simply get rid of it. In this problem the only thing we need to know about the r is that it is a constant ($r = a$.)

So after a trivial rearrangement, we see

$$\frac{d^2}{d\theta^2} \Theta(\theta) = -\frac{2mr^2 E}{\hbar^2} \Theta(\theta)$$

This is starting to look more like something we can manage to solve by inspection! Let's make a substitution. Let

$$m_l = \pm \frac{(2mr^2 E)^{1/2}}{\hbar}$$

We'll evaluate m_l later. But now it is easy to show that

$$\Theta(\theta) = Ae^{im_l\theta}$$

is a solution to the eigenvalue, eigenfunction problem. Let's try!

$$\begin{aligned} \frac{d}{d\theta} Ae^{im_l\theta} &= iAm_l e^{im_l\theta} \\ \text{and} \\ \frac{d}{d\theta} iAm_l e^{im_l\theta} &= -Am_l^2 e^{im_l\theta} \end{aligned}$$

So the eigenfunctions are given by $\Theta(\theta) = Ae^{im_l\theta}$ and the eigenvalues are given by $-m_l^2$.

To proceed, we will employ a *cyclical boundary condition*. Since all wavefunctions must be single valued, we see that

$$\Theta(\theta) = \Theta(\theta + 2\pi)$$

So . . .

$$\begin{aligned} Ae^{im_l\theta} &= Ae^{im_l(\theta+2\pi)} \\ &= Ae^{im_l\theta} e^{i2\pi m_l} \end{aligned}$$

Or dividing both sides by $Ae^{im_l\theta}$, we see

$$1 = e^{i2\pi m_l}$$

This is going to quantize the possible values which m_l can take. And since the Euler relation tells us that

$$e^{i\pi} = -1$$

we see that

$$1 = (-1)^{2m_l}$$

which can only be true if m_l is an integer. As it turns out, it doesn't matter if m_l is positive or negative. It just has to be an integer.

$$m_l = 0, \pm 1, \pm 2, \dots$$

As promised, this quantizes the energies possible for the system.

$$\frac{m_l^2 \hbar^2}{2I} = E$$

where the moment of inertia I is given by the mass times the radius squared.

$$I = mr^2$$

Finally, we can obtain the value of the normalization constant A to normalize the wavefunctions.

$$1 = A^2 \int_0^{2\pi} e^{im_l\theta} e^{im_l\theta} d\theta$$

And we see that

$$A = \left(\frac{1}{2\pi} \right)^{1/2}$$

So, in summary, the wavefunctions are given by

$$\psi(r, \theta) = \left(\frac{1}{2\pi} \right)^{1/2} e^{im_l\theta} \quad m_l = 0, \pm 1, \pm 2, \dots$$

And the energies are given by

$$E_{m_l} = \frac{m_l^2 \hbar^2}{2I} \quad \text{where } I = mr^2$$

The Free Electron Model

Consider a long molecule that is a conjugated polyene. Kuhn (Kuhn, 1949) has suggested a model for the electrons involved in this π -bond system in which an electron is said to have a finite potential energy when it is “on” the molecule and an infinite potential energy when it is “off” the molecule. The model (known as the *free electron model*) is very much analogous to the particle in a box problem as we have presented it in class.

Let’s consider a conjugated polyene molecule in which there are twelve atoms in the conjugated polyene chain. Each atom contributes one π electron and each bond contributes 0.139 nm (the C=C bond length in benzene.) We can consider each energy level in the system as one orbital. As in all other cases involving electrons, each orbital can contain two electrons. Using the model, we can predict the wavelength of light the molecule will absorb to excite one electron from the HOMO to the LUMO (highest occupied molecular orbital to the lowest unoccupied molecular orbital.)

First, there are 11 bonds in the chain. Since each bond contributes 0.139 nm, the “box” is 1.529 nm long. The energy levels of the molecular orbitals are then given by:

$$E_n = \frac{n^2 \hbar^2}{8ma^2}$$

where $n = 1, 2, 3 \dots$, \hbar is Plank’s constant ($\hbar = 6.63 \times 10^{-34}$ Js), m is the mass of an electron ($m_e = 9.11 \times 10^{-31}$ kg) and a is the length of the box ($a = 1.529 \times 10^{-9}$ m.)

The energy levels will be filled with the 12 π electrons packing two electrons per orbital. Thus, the HOMO will be the state with $n = 6$. The LUMO will be the state with $n = 7$ - the next state up in energy. The difference in energy is what we want in order to predict the wavelength of light the molecule will absorb.

$$E_6 = \frac{6^2 (6.63 \times 10^{-34} \text{ Js})^2}{8(9.11 \times 10^{-31} \text{ kg})(1.529 \times 10^{-9} \text{ m})^2} = 9.288 \times 10^{-19} \text{ J}$$

$$E_7 = \frac{7^2 (6.63 \times 10^{-34} \text{ Js})^2}{8(9.11 \times 10^{-31} \text{ kg})(1.529 \times 10^{-9} \text{ m})^2} = 1.2642 \times 10^{-18} \text{ J}$$

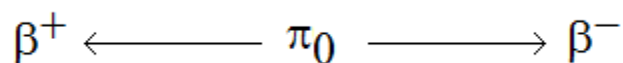
So the energy of excitation will be 3.354×10^{-19} J. This corresponds to an absorption wavelength of 593 nm (which is in the visible region of the spectrum.) How would the absorption wavelength change for more or fewer atoms in the conjugated polyene chain? The solution is left as an exercise.

Entanglement and Schrodinger's Cat

There are many elements of the quantum theory that produce bizarre results (at least compared to our intuition as residents in a classical physics world. As it turns out, some of the early pioneers of a quantum theory (such as Albert Einstein and Erwin Schrödinger) found these elements of strangeness too much to handle. Both expended a great deal of energy to eliminate quantum mechanics as an accepted theory that would shape modern science. As it turns out, all of the bizarreness predicted by quantum mechanics has withstood the tests of experimentation, despite the concerns and well-thought objections of these two scientific giants.

Entanglement and Spooky Action at a Distance

One of Einstein's objections came in the form of what he named “**spooky action at a distance**.” To understand this phenomenon, consider the decomposition of a π -meson into an electron and a positron. Since the original particle has zero spin, in order to conserve angular momentum, must be “spinning” in opposite directions. In other words, one has $m_s = +\frac{1}{2}$ and the other has $m_s = -\frac{1}{2}$.



The wavefunction that describes this system prior to the measurement of the spin of either particle is given by

$$\psi_{spin} = \frac{1}{\sqrt{2}}(\alpha_+\beta_- - \beta_+\alpha_-)$$

which allows for the possibility that either particle is spin up or spin down to be equally likely. But the spins of the two particles are intimately coupled to one another. If the electron (β^-) is spin up (α) then the positron (β^+) must be spin down (β) (and vice versa.) This property is an example of **entanglement** where the properties of one particle are entangled with those of the other through the wavefunction that describes the entire system.

Now suppose that the spin of the electron is measured and determined, the spin of the other is determined at the same time. As such, the measurement of the property of one particle causes the wavefunction of the other particle to change instantaneously. This is what Einstein referred to as “spooky action at a distance.” This action would require information to be transferred across space at a speed faster than the speed of light, violating Einstein's theory of relativity.

This paradox has been studied extensively and remains a topic of research interest. It should be noted that whenever these sort of issues crop up, it is quantum mechanics that seems to prevail over relativity. (Sorry Einstein!)

Schrödinger's Cat

Erwin Schrödinger's involvement in trying to dissuade the scientific community from embracing quantum theory is particularly peculiar, as it was the development of the wave equation that is still used today that won him the Nobel Prize in 1933. None the less, Schrödinger found himself quite troubled by the conclusions of the quantum theory. Toward that end, in 1935, he published a paper in which he described a thought experiment that had to give the scientific world pause where quantum theory was concerned.

The problem was stated thusly. Imagine a box inside of which no observation could be made unless the box was opened. Inside, was placed a cat, a bottle of poison (prussic acid) and a radioactive atom. If the atom decays, a hammer will drop on the poison, killing the cat. The experiment was to wait one half-life of the atom. At that point, the wavefunction for the atom was given by

$$\Psi_{atom} = \frac{1}{\sqrt{2}}\psi_{decayed} + \frac{1}{\sqrt{2}}\psi_{undecayed}$$

This implies that it is equally likely that the atom has decayed as not decayed. And since the life of the cat was tied to the state of the atom, it is equally likely that the cat is dead or alive. Therefore, the “wavefunction” for the cat would be given by

$$\Psi_{cat} = \frac{1}{\sqrt{2}}\psi_{dead} + \frac{1}{\sqrt{2}}\psi_{alive}$$

This implies that the cat is neither dead nor alive, but both with equal probability! And even for the most lethargic of cats, it is very clear that animal is either alive or not. The notion that it is both is simply preposterous! This is the conclusion of which Schrödinger hoped to convince the scientific world. Alas, experimentation has failed to uphold Schrödinger's notion that quantum mechanics provides an incorrect description of the atom.

There have been numerous treatises on these topics and beyond. (The strangeness of quantum mechanics has been a very thought provoking topic indeed!) After completing a course in quantum mechanics (such as this one) a student should be well prepared to explore some of these very intriguing and perplexing predictions.

References

Kuhn, H. J. (1949). *Journal of Chemical Physics*, 17, 1198.

Vocabulary and Concepts

commutator	20	eigenvalues.....	4
commute.....	20	entanglement	35
eigenfunctions	4	equation of motion	1

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Hamiltonian.....	4, 5	orthogonal	4
Heisenberg Uncertainty Principle	20	Potential Energy.....	5
Hermitian	4	spooky action at a distance	35
Kinetic Energy	5	Superposition Principle.....	23
linear	4	wavefunction.....	1

Problems

- Consider the functions $f(x) = A(1-x^2)$ and $g(x) = 3x^3-x$.
 - Find a value for A such that $f(x)$ is normalized on the interval $-1 \leq x \leq 1$.
 - Are the functions $f(x)$ and $g(x)$ orthogonal over the interval $-1 \leq x \leq 1$?
- Consider each of the following functions and the associated intervals. Indicate whether or not the given function is suitable as a wavefunction over the given interval.
 - e^x $0 \leq x \leq \infty$
 - e^{-x} $0 \leq x \leq \infty$
 - $1/x$ $-\infty \leq x \leq \infty$
 - $e^{i\theta}$ $0 \leq x \leq 2\pi$
 - $x(1-x)$ $0 \leq x \leq 1$
- Consider the following operators. Determine whether or not they are Hermitian.
 - d/dx
 - $i d/dx$
 - d^2/dx^2
 - $i d^2/dx^2$

- Consider an operator \hat{A} and associated set of eigenfunctions ϕ_n that satisfies

$$\hat{A}\phi_n = a_n\phi_n$$

Show that if the operator is Hermitian that the eigenvalues a_n must be real-valued.

- Consider the data in the table.

- Calculate $\langle x \rangle$ and $\langle x^2 \rangle$.
- Calculate σ_x^2 for the data set.
- Does $\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2$? If not, what is the difference?

i	x
1	2.3
2	6.4
3	4.2
4	3.5
5	4.9

- Consider a particle of mass m in a rectangular solid box with edge lengths given by $a = a$, $b = 2a$, $c = 2a$. Find the degeneracies of the first 10 energy levels for the system.

7. Consider a particle of mass m that is in a one-dimensional box of length a . The system is prepared so that the wavefunction is given by $\psi(x) = Ax(a-x)$.
- Find a value of A that normalizes the wavefunction.
 - Find the expectation values for x and x^2 ($\langle x \rangle$ and $\langle x^2 \rangle$.)
 - Find the expectation values for p and p^2 ($\langle p \rangle$ and $\langle p^2 \rangle$.)
 - Given that the variance for a measurement is given by $\sigma_a^2 = \langle a^2 \rangle - \langle a \rangle^2$ calculate the variances σ_x^2 and σ_p^2 .
 - Find the value of $\sigma_x \sigma_p$. Does it exceed $\hbar/2$?
8. Consider a particle of mass m in a box of length a . The system is prepared such that the wavefunction is given by $\psi(x) = Ax^2(a-x)$.
- Find a value of A that normalizes the wavefunction.
 - What are the units on the wavefunction?
 - Find $\langle x \rangle$.
 - Is $\langle x \rangle = a/2$? Why or why not?
9. Consider the following pairs of operators and determine whether or not the operators commute.
- d/dx , d^2/dx^2
 - x , d^2/dx^2
 - x , $\int dx$
10. Consider a particle of mass m in a box of length a for which the wavefunction is given by

$$\Psi(x) = (2)^{1/2}/3 \phi_1(x) - (7)^{1/2}/3 \phi_3(x)$$

where $\phi_n(x) = (2/a)^{1/2} \sin(n\pi x/a)$.

- Show that the wavefunction $\Psi(x)$ is normalized.
 - Graph the wavefunction $\Psi(x)$.
 - What is the expectation value for energy $\langle E \rangle$ for the system?
 - What is the most likely energy to be measured for the system?
11. Consider benzene (C_6H_6) as modeled using the free-electron model.
- Using a C-C bond length of $r_{cc} = 0.139$ nm, calculate the circumference of the ring and its radius.
 - Based on the model, what are the degeneracies of the four lowest energy levels?
 - Placing two electrons per particle-on-a-ring "orbital", calculate the energy gap (and corresponding wavelength of light driving a transition) between the HOMO and the LUMO based on this model.
 - How does the value you found in part c compare to the observed band-origin of the $A_{1g} \rightarrow B_{1u}$ transition of benzene ($\lambda = 215$ nm)?