

Chapter 1: Foundations and Review

The study of any discipline requires some grounding in fundamentals. Without this common experience, there is little hope of communicating any complex concepts. For example, in order to make use of a textbook, one must be comfortable with reading. In a mathematically intensive discipline such as physical chemistry, one's comfort level must extend to following discussions that incorporate mathematics and mathematical equations and relationships. As an example, consider the proof of conservation of energy as a means to frame a discussion of this concept.

Some Newtonian Physics

Consider the definition of **acceleration** (a) as the first time-derivative of **velocity** (v) and the second time-derivative of **position** (x).

$$a = \frac{dv}{dt} = \frac{d^2x}{dt^2}$$

Newton's second law states that **force** (F) is the product of **mass** (m) and acceleration.

$$F = ma$$

$$= m \frac{dv}{dt}$$

$$= m \frac{d^2x}{dt^2}$$

Since **momentum** (p) is related to velocity and mass through the definition

$$p = mv$$

(and mass is invariant to time) the following must hold.

$$\frac{dp}{dt} = \frac{d(mv)}{dt} = m \frac{dv}{dt} = ma = F$$

Now consider **potential energy** (U) – which is also related to force through the first derivative with respect to position.

$$F = -\frac{dU}{dx}$$

This indicates that the following equation must hold for any particle that can be described by Newtonian motion.

$$-\frac{dU}{dx} = \frac{dp}{dt}$$

The classical **Hamiltonian** (H) is the sum of **kinetic energy** (T) and **potential energy** (U). And as it turns out, the kinetic energy can be expressed in terms of momentum.

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

So the Hamiltonian function, which gives the sum of the kinetic and potential energies is given by

$$H = \frac{p^2}{2m} + U$$

The time-rate-of-change of the total energy can be found from the first derivative of H with respect to t .

$$\begin{aligned}\frac{d}{dt}H &= \frac{d}{dt}\left(\frac{p^2}{2m} + U\right) \\ &= \frac{1}{2m} \cdot 2p \cdot \frac{dp}{dt} + \frac{dU}{dt} \\ &= \frac{2mv}{2m} \cdot \frac{dp}{dt} + \frac{dU}{dx} \frac{dx}{dt} \\ &= \frac{dx}{dt} \left(\frac{dp}{dt} + \frac{dU}{dx} \right)\end{aligned}$$

And since

$$-\frac{dU}{dx} = \frac{dp}{dt}$$

it follows that

$$\frac{d}{dt}H = \frac{dx}{dt} \left(-\frac{dU}{dx} + \frac{dU}{dx} \right)$$

$$\begin{aligned}
 &= \frac{dx}{dt}(0) \\
 &= 0
 \end{aligned}$$

This indicates that the total energy of a system that follows Newtonian physics does not change in time. Another way to state this is that energy is conserved, or that total energy is a “constant of the motion”. This is also a mathematical proof that the sum of potential and kinetic energy must be conserved in all processes, since this sum cannot change in time.

Many discussions in this text will rely on derivations such as above in order to make specific points about the nature of matter. Keep in mind that the important points are the conclusions as well as the pathway to relating the conclusions to the initial parameters of the problem. The more you can focus on these aspects, rather than getting bogged down in the specifics of the math, the more sense quantum mechanics will make to you.

Some Vectors and Dot Products

The concepts of **linear combinations** and **orthogonality** show up repeatedly in quantum chemistry. But these are generally not new concepts to students at this level, as the same concepts are used to describe forces and motions in a standard physics course in classical mechanics.

Consider a pair of vectors (**u** and **v**) in three-dimensional space can be described as a linear combination of basis vectors in the x, y and z directions (**i**, **j** and **k**, respectively.)

$$\begin{aligned}
 \mathbf{u} &= a\mathbf{i} + b\mathbf{j} + c\mathbf{k} \\
 \mathbf{v} &= d\mathbf{i} + e\mathbf{j} + f\mathbf{k}
 \end{aligned}$$

The inner product of two vectors **u** and **v** is given the symbol $\langle \mathbf{u} | \mathbf{v} \rangle$. There are many possible definitions for an inner product, but most students are familiar with the dot product. The dot product of these two vectors can be calculated by

$$\langle \mathbf{u} | \mathbf{v} \rangle = \mathbf{u} \cdot \mathbf{v} = (a \cdot d) + (b \cdot e) + (c \cdot f)$$

If the dot product is zero, the two vectors are said to be **orthogonal**. In three dimensional space, this is oftentimes interpreted as the vectors having a 90° angle between them as the dot product can also be calculated from

$$\mathbf{u} \cdot \mathbf{v} = \|\mathbf{u}\| \|\mathbf{v}\| \cos(\alpha)$$

where $\|\mathbf{u}\|$ indicates the magnitude of the vector **u** and α is the angle formed between the two vectors **u** and **v**. Given this definition, the only way two vectors of non-zero magnitude can be orthogonal is if the $\cos(\alpha)$ term vanishes. In other words, the angle between them must be 90° or $\pi/2$ radians.

The concept of orthogonality can also be extended to include functions. All that is necessary is a definition for an inner product for two functions. The definition that we will encounter most in quantum mechanics is the integral over all relevant space of the product of the two functions.

$$\langle f(x)|g(x)\rangle = \int f(x) \cdot g(x) dx$$

In the event that this integral is zero, the two functions are orthogonal in the same sense that two vectors whose dot product is zero are orthogonal.

In addition to being orthogonal, vectors can also be **normalized**. A vector is said to be normalized if it has a unit magnitude. The magnitude of a vector is determined by taking the square root of the dot product of the vector with itself.

$$\|\mathbf{u}\| = \sqrt{\langle \mathbf{u} | \mathbf{u} \rangle} = \sqrt{a^2 + b^2 + c^2}$$

The vector has unit magnitude and is normalized if its magnitude is unity.

In the case of vectors, **i**, **j** and **k** form an **orthonormal set**. That is to say that each vector in the set is orthogonal to the other two and is normalized as each has a unit magnitude. This property can be defined for any set of vectors **e**₁, **e**₂ ... **e**_N by the following relationship

$$\langle \mathbf{e}_i | \mathbf{e}_j \rangle = \delta_{ij}$$

where δ_{ij} is a function called the **Kronecker Delta** and has the properties

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

Similarly, functions (**f**₁(x), **f**₂(x) ... **f**_N(x)) can form an orthonormal set if

$$\langle f_i(x) | f_j(x) \rangle = \int f_i(x) \cdot f_j(x) d\tau = \delta_{ij}$$

As we will see, this relationship is common in quantum mechanics, and has many useful properties which we will exploit as they make calculations simpler. This will be particularly evident when we discuss the **superposition theorem**.

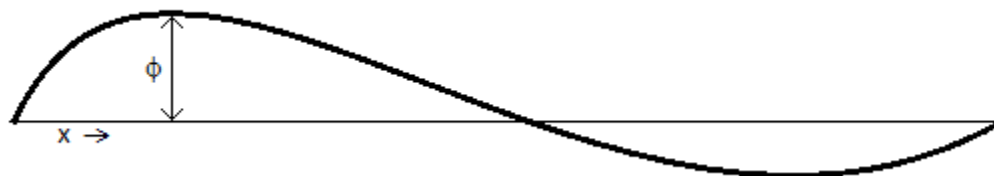
Classical Description of a Wave on a String

The mathematics used in solving quantum mechanical problems follow the same basic process for each of the different problems we will examine. In this section, those mathematics will be developed in order to describe a (hopefully) familiar problem in classical physics.

Consider a wave on a string of length a which is fixed at both ends ($x=0$ and $x=a$.) Classical physics tells us that the wave will obey the following condition

$$\frac{\partial^2}{\partial x^2} \phi(x, t) = \frac{1}{v^2} \frac{\partial^2}{\partial t^2} \phi(x, t)$$

where $\phi(x, t)$ gives the displacement of the string from equilibrium at position x and time t .



To solve this second order partial differential equation, we separate the function into the product of a function which deals only in position and one which deals only in time.

$$\text{Let } \phi(x, t) = X(x) T(t)$$

Substituting this form in to the equation above and gathering spatial variables on one side and time variables on the other, we get

$$\frac{\partial^2}{\partial x^2} X(x) T(t) = \frac{1}{v^2} \frac{\partial^2}{\partial t^2} X(x) T(t)$$

$$T(t) \frac{d^2}{dx^2} X(x) = \frac{X(x)}{v^2} \frac{d^2}{dt^2} T(t)$$

Notice how the partial derivatives become total derivatives since the functions on which they operate depend only on the variables in the given derivative operators. Now dividing both sides by $X(x)T(t)$ yields

$$\frac{1}{X(x)} \frac{d^2}{dx^2} X(x) = \frac{1}{v^2 T(t)} \frac{d^2}{dt^2} T(t)$$

The only way this can be true is if each side is equal to a constant. Since I already know the answer, I am going to cheat and let that constant be $-k^2$ since this will avoid imaginary numbers in the solution. So now we generate two separated second order differential equations:

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

$$\frac{d^2}{dt^2} T(t) = -v^2 k^2 T(t)$$

These two equations are of a special type called **eigenvalue-eigenfunction** relationship. In these type of relationships, the operator (in this case a second derivative) operates on a function, yielding the same function multiplied by a constant. These type of relationships exist throughout quantum mechanics.

The Spatial Solutions

Let's consider only the spatial portion for the time being. Being a second order normal differential equation, there will be two linearly independent functions $X(x)$ which satisfy the equation. Two fairly obvious choices to this **eigenvalue-eigenfunction** problem are

$$X(x) = \sin(kx) \text{ and } X(x) = \cos(kx)$$

As mathematics would have it, any linear combination of these two solutions will also be a solution. Thus, it is convenient to write a general solution that is a linear combination of the two linearly independent functions.

$$X(x) = A\sin(kx) + B\cos(kx)$$

We will now employ the boundary conditions to find values for the variables A, B and k. The boundary conditions are that the string is fixed at both ends. Thus we know that

$$X(0) = 0 \text{ and } X(a) = 0$$

Using the first condition, we see that

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

This can only be true if $B = 0$ since the cosine term will give a non-zero contribution for any non-zero value of B implying that the string is displaced from its fixed position, which it can not be since it is fixed at that position. For the remainder of the solution to this problem, the cosine term will be neglected since it must vanish in order to ensure that $X(0) = 0$.

The second condition is that $X(a) = 0$. This requires that

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

One way of making this true is if $A = 0$. This is known as a trivial solution since it implies that $X(x)$ is zero for any value of x (meaning the string is never displaced from equilibrium at any point.) Many problems have trivial solutions, but these are generally ignored as they add no useful insight into the physical behavior of a system.

To get the non-trivial solutions, it is useful to know when $\sin(\alpha) = 0$. This will be true if α is an integral multiple of π . Thus,

$$k \cdot a = n\pi \quad n = 1, 2, 3 \dots$$

Or

$$k = \frac{n\pi}{a} \quad n = 1, 2, 3 \dots$$

Another way to think of this is that the second condition ($X(a) = 0$) can only be met if the length of the string (a) is a half integral multiple of the wavelength of the sine function.

Since there are several (an infinite number, really) possible values of n , the solution implies an infinite number of functions as solutions. Further, there is no reason to expect that A needs to be the same for each value of n .

$$X_n(x) = A_n \sin\left(\frac{n\pi x}{a}\right)$$

$$n = 1, 2, 3 \dots$$

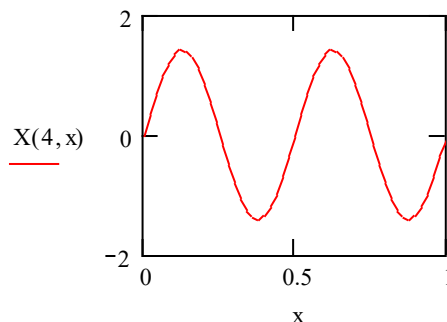
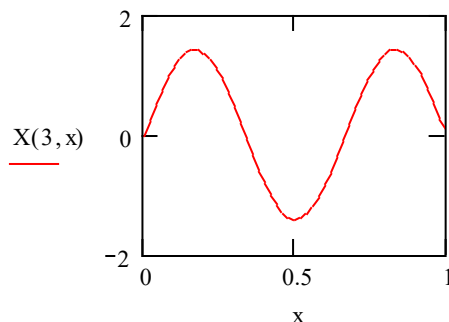
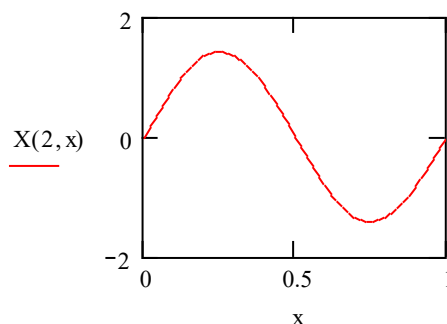
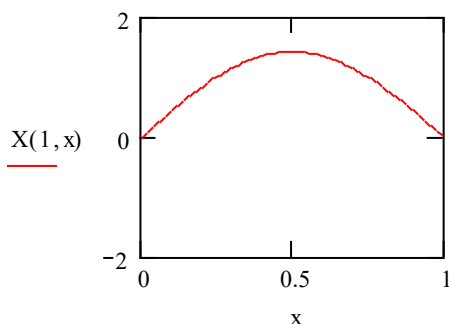
Time independent solutions to the classical description of a wave on a string.

$$a := 1$$

$$x := 0, 0.02.. a$$

$$n := 1, 2.. 4$$

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



Since we have only two boundary conditions, we can only determine two of the unknown quantities. The last one, A_n , will govern the amplitude of the particular function. A large value implies that the string will be displaced a large amount from its equilibrium position. Thus, there may be a different value of A_n for each value of n (which is why the subscript is included.) For the time being though, let's leave A_n as a symbolic variable and evaluate it later.

Before continuing with the time portion of the problem, let's note some interesting properties of the solutions of the spatial portion. The functions $X_n(x)$ are called the "normal modes" of vibration for the string (sometimes they are called the time-independent modes.) That means that a string which is prepared to vibrate with the displacements given by one of the functions $X_n(x)$ will have a standing wave. In other words, the nodes (the places along the string where the string does not move or $X_n(x) = 0$) are stationary.

Further, the functions $X_n(x)$ form an orthogonal set. This implies that

$$\int X_n(x)X_m(x)dx = A_nA_m \int \sin\left(\frac{n\pi x}{a}\right) \sin\left(\frac{m\pi x}{a}\right) dx = A_nA_m\delta_{nm}$$

To prove this, it is useful to consider the following result that can be found in a standard table of integrals.

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

Substitution into the above expression yields

$$\begin{aligned} A_n A_m \int_{x=0}^{x=a} \sin\left(\frac{n\pi x}{a}\right) \sin\left(\frac{m\pi x}{a}\right) dx &= A_n A_m \left[\frac{\sin\left(\frac{(n-m)\pi x}{a}\right)}{2(n-m)\pi/a} - \frac{\sin\left(\frac{(n+m)\pi x}{a}\right)}{2(n+m)\pi/a} \right]_{x=0}^{x=a} \\ &= A_n A_m \left[\frac{\sin((n-m)\pi)}{2(n-m)\pi/a} - \frac{\sin((n+m)\pi)}{2(n+m)\pi/a} - 0 + 0 \right] \end{aligned}$$

Since both n and m are integers, $n+m$ and $n-m$ will be integers as well and both sine terms will vanish. Hence, for any $n \neq m$, the integral will vanish. As such, any pair of functions in this set are mutually orthogonal, or the functions form an orthogonal set.

But what happens when $n = m$? Again, it is useful to pull the following result from a standard table of integrals.

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

Substitution into this expression yields the following:

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

A convenient result comes from choosing values for A_n such that the result is unity.

$$1 = A_n^2 \left(\frac{a}{2} \right) \quad \text{or} \quad A_n = \sqrt{\frac{2}{a}}$$

A_n is called a **normalization constant**, and has a value chosen to insure that the integral of the square of the function over all relevant space is unity. Another way of saying this is that A_n is chosen so as to **normalize** the function. We will see this concept throughout our development of quantum mechanics. Note that A_n does not depend on n . (This will not be the case for most normalization constants.)

These functions

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

form an orthonormal set of functions. They have the property that

$$\int_{x=0}^{x=a} X_n X_m dx = \delta_{nm}$$

where δ_{nm} is the *Kronecker delta* and has the property

$$\delta_{nm} = \begin{cases} 1 & \text{if } n = m \\ 0 & \text{if } n \neq m \end{cases}$$

The Time Solutions

The solution to the time dependence part of the problem is very similar to that of the spatial part. Recall that the equation

$$\frac{d^2}{dt^2} T(t) = -v^2 k^2 T(t)$$

must be satisfied. The value of k has already been determined from the spatial solutions and is given by $k = n\pi/a$. For convenience, let's make the substitution

$$\omega_n = vk = \frac{vn\pi}{a}$$

such that ω_n gives a frequency to the oscillation of the string that is parameterized by the velocity of the wave. Further, if n is doubled, the frequency of the wave is doubled. This would be manifested in the audible tone of the vibrating string going up by one octave. Those familiar with the acoustic nature of overtones on strings (such as those that can be produced on the strings of a guitar) are familiar with this concept.

The substitution creates the rather familiar looking eigenvalue-eigenfunction problem

$$\frac{d^2}{dt^2} T(t) = -\omega_n^2 T(t)$$

As was the case in the spatial part, the second order ordinary differential equation must have two linearly independent solutions, and any linear combination of those two functions will also be a solution to the equation. Thus, one can write

$$T(t) = C \sin(\omega_n t) + D \cos(\omega_n t)$$

The rest of the development requires a simple trick. Since there are no remaining boundary conditions by which we can evaluate C and D, we can choose a constant δ such that

$$C = -\sin(\delta) \quad \text{and} \quad D = \cos(\delta)$$

so that the time function can be expressed

$$T(t) = \cos(\omega_n t) \cos(\delta) - \sin(\omega_n t) \sin(\delta)$$

and since

$$\cos(\alpha + \beta) = \cos(\alpha) \cos(\beta) - \sin(\alpha) \sin(\beta)$$

the function can be expressed

$$T(t) = \cos(\omega_n t + \delta)$$

In this expression, δ is a phase shift in time. For a given choice of $t = 0$, δ can be forced to be zero. Given this constraint, the time function can be expressed

$$T(t) = \cos(\omega_n t)$$

The final result, then, for the normalized **wavefunctions** that describe the motion of the string are given by

$$\phi_n(x, t) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \cos(\omega_n t)$$

The Superposition Principle

For the following discussion, we will only concern ourselves with the time-independent solutions (the spatial functions) for simplicity. The time functions could be included to give the time evolution of each component of a superposition of waves, but the discussion of the

mathematics involved would be identical to that for the spatial part of the problem. As such, we will focus just on the result for a fixed point in time of $t = 0$.

As it turns out, any well-constructed wave (specifically one that obey the boundary conditions of the original problem) can be expressed as a linear combination of normal mode waves.

$$\Phi(x) = \sum_n c_n \cdot X_n(x)$$

where $\Phi(x)$ gives the function that describes the shape of the arbitrary wave, $X_n(x)$ are the time-independent functions that were derived in the previous section, given by

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

And the factor c_n gives the amplitude of the n^{th} component of the superposition.

The coefficients c_n (known as **Fourier coefficients**) are easily calculated from the following expression

$$c_n = \int \Phi(x) \cdot X_n(x) dx$$

This is easily shown by making the substitution $\Phi(x) = \sum_m c_m X_m(x)$ into the above equation.

$$\begin{aligned} c_n &= \int \Phi(x) \cdot X_n(x) dx \\ &= \int \left(\sum_m c_m X_m(x) \right) X_n(x) dx \end{aligned}$$

Since integration is a linear operation, and multiplication is distributive, the result can be simplified

$$\begin{aligned} \int \left(\sum_m c_m X_m(x) \right) X_n(x) dx &= \sum_m c_m \int X_m(x) X_n(x) dx \\ &= \sum_m c_m \delta_{mn} \end{aligned}$$

using the orthonormality property of the functions $X_n(x)$ as developed above. The sum is also easy to simplify based on the properties of the Kronecker delta.

$$\begin{aligned}
 \sum_m c_m \delta_{mn} &= c_1 \delta_{1n} + c_2 \delta_{2n} + c_3 \delta_{3n} + \dots + c_n \delta_{nn} + \dots \\
 &= c_1 \cdot 0 + c_2 \cdot 0 + c_3 \cdot 0 + \dots + c_n \cdot 1 + \dots \\
 &= c_n
 \end{aligned}$$

The description of the function $\Phi(x) = \sum_n c_n X_n(x)$ is known as a Fourier expansion, and is the same sort of mathematics used by a Fourier Transform spectrometer. The spectrometer, through interferometry, measures the values of the amplitudes (c_n) and then mathematically reconstructs the spectrum by superimposing the constituent functions $X_n(x)$ and adding them all up.

To illustrate the concept, consider a function that is defined as

$$\Phi(x) = \begin{cases} \sqrt{\frac{\pi}{2a}} \sin\left(\frac{2\pi x}{a}\right) & \text{if } 0 \leq x \leq a/2 \\ 0 & \text{if } a/2 \leq x \leq a \end{cases}$$

This function can be expanded in the **basis set** of normal mode (time independent) functions. The following MathCad worksheet calculates the values of the coefficients and demonstrates the superposition of waves.

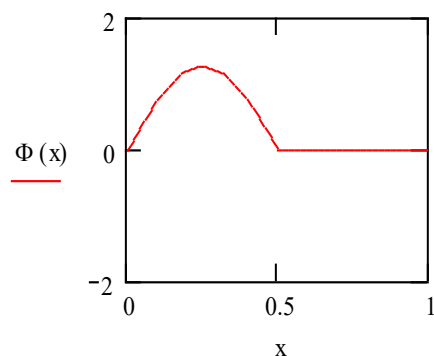
First, define the parameters of the problem.

$$a := 1 \quad x := 0, 0.02.. a \quad n := 1, 2.. 10$$

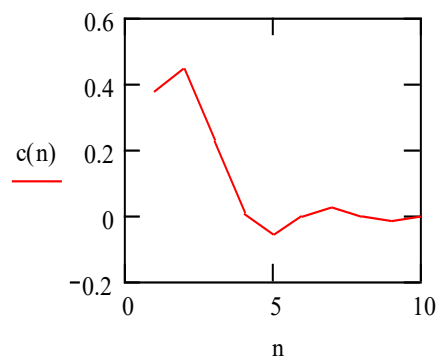
Now the basis functions and the arbitrary function.

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

Here is a graph of the arbitrary function:



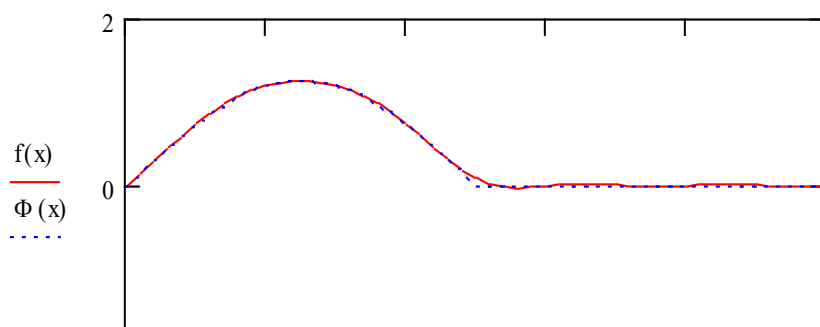
$$c(n) := \int_0^a \Phi(x) \cdot X(n, x) dx$$



And to calculate the superposition:

$$m := 10$$

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



This sort of expansion in a set of basis functions occurs throughout chemistry including the construction of an sp^3 hybridized orbital set used in the description of bonding in a methane

molecule or the addition of p-orbitals to for π -bonding and antibonding orbitals. Expect to see this concept again!

Failures of Classical Physics

Imagine being a scientist in the year 1900. At the time, there was significant debate in society as to whether or not science was a valuable discipline for study. The argument was that Isaac Newton and others had already solved all of the important problems of physics and as such, there was nothing more to be learned. There were still a few problems remaining that didn't work perfectly according to Newtonian physics, but the prevailing thought was that it was a simple matter of finding the one small piece that people were missing and the entire package would be complete. As it turned out, they couldn't have been more incorrect!

Every new detail that was discovered on these pesky problems seemed to indicate something that was not commensurate with Newtonian physics at all. And the deeper investigators looked, the more perplexing the problems became – and the further from classical physics the solutions took them.

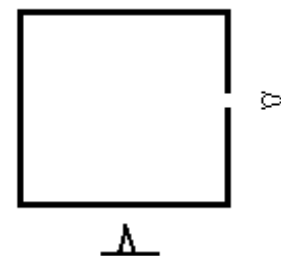
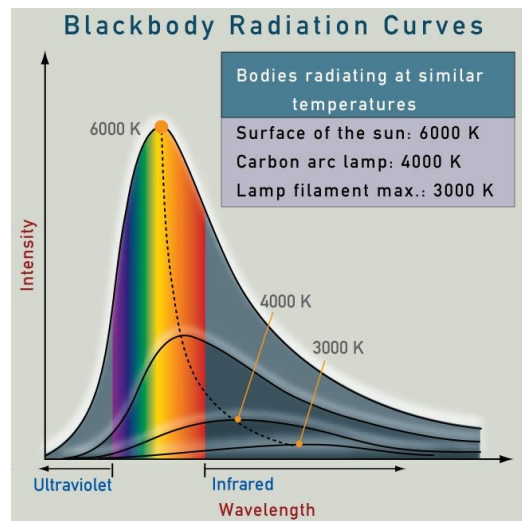
But the modeling of these problems formed the foundations of a new quantum theory. That theory, while completely counter-intuitive to scientists of the time, is now engrained in every aspect of how we think of the atomic and molecular nature of matter. As such, no study of chemistry is complete without exploring this bizarre world of quantum mechanics. So sit back, relax, and enjoy the story of the origins of the quantum theory.

Max Planck and Blackbody Radiation

One of the problems that perplexed scientists at the turn of the 20th century was that of the description of black-body radiation. The term “Black Body” was introduced by Gustav Kirchhoff in 1860. It refers to an object that absorbs all light that falls on it (i.e. it reflects no light.) The thermal radiation emitted by a black body is called **black body radiation**.

Black-body radiation is the light that is given off from a body that glows from being hot. Examples of blackbody radiators include incandescent light bulbs and the sun. In the laboratory, a black body radiator can be constructed by painting the inside of a metal box black (so that light is not reflected inside) and heating the box. The light given off by the box will be black body radiation.

The emission spectrum of a black-body radiator was well established and reproducible. The intensity increases at all wavelengths and the maximum intensity shifts to shorter wavelengths at higher temperatures. But while the experimental result was well established and



A black body radiator experimental set up.

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agreed upon, there was no theoretical model that predicted the result. Existing classical models could predict either the long-wavelength side of the spectrum or the short wavelength side, but not both.

Max Planck (1858-1947) produced the first theory that could predict both sides of the spectrum. He did this by making a ridiculous assumption about the nature of light. Despite the prevailing classical theories of the wave-nature of light and numerous experimental observations confirming these theories, Planck decided to model a light beam as a shower of energy packets (which he called Quanta) where the energy was proportional to the frequency of the light wave.

$$E = h \nu$$

In this model, E is the energy of a quantum, h is a constant of proportionality and ν is the frequency of the light wave.

This dual nature of light (having properties of both particles and waves) was revolutionary, and was thus met with great skepticism. Planck's model, published in 1901 [1], can be expressed by

$$I(\nu, T) = \frac{2h\nu^3}{c^2} \left(\frac{1}{e^{\frac{h\nu}{k_B T}} - 1} \right)$$

in which I is the intensity, T the temperature and c the speed of light, successfully described both sides of the black body radiation curve. It also provided a value of h, the constant of proportionality of

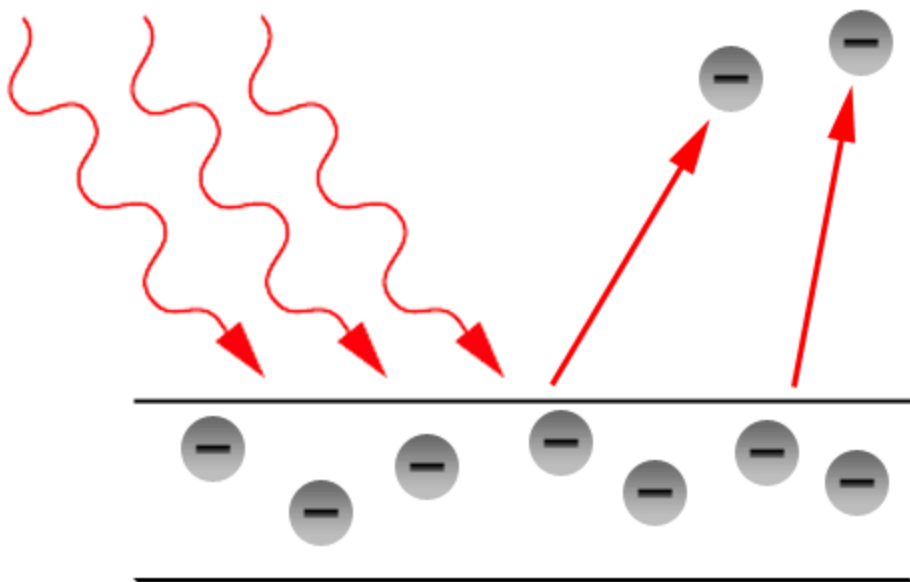
$$h = 6.36 \times 10^{-34} \text{ J}\cdot\text{s}$$

Planck was awarded the Nobel Prize in Physics in 1918 for this theory. But while interesting, Planck's theory only provided one possible explanation of the black body radiation problem. But without corroboration from other experiments involving other phenomena, Planck's theory of light quanta would not have gained any meaningful attention. That corroboration came in a paper published by Albert Einstein describing a quantum theory of the photoelectric effect.

Albert Einstein and the Photoelectric Effect

When Planck published his paper in 1901, Albert Einstein was working as a scientific expert in the Swiss patent office while working to secure a professorship in physics. He read Planck's paper. Through studying Planck's work, Einstein was able to apply a quantum theory of light to make sense out of another well-established, but as of then not understood experiment, the photoelectric effect.

The photoelectric effect involves shining light on the polished surface of metal under a vacuum. If the light has a wavelength shorter than a threshold value (characteristic of the individual metal), electrons are emitted from the surface.



The challenge to understanding the result came from changing the intensity of the light. Classical physics tells us that the energy of a wave is determined by its amplitude, or in the case of light, the intensity. An increase in the intensity of incident light, therefore, should lead to an increase in the kinetic energy possessed by the emitted electrons. However, the kinetic energy of the electrons seemed to be a function not of the intensity of the light, but rather it's frequency. Einstein was able to explain [2] this using Planck's theory that light consisted of a shower of quant, each of which was a packet of energy the magnitude of which was proportional to the frequency of the light. ($E_{\text{photon}} = h\nu$)

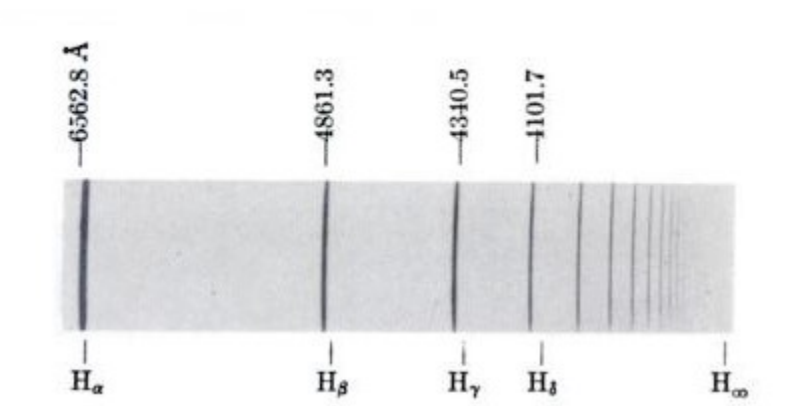
In Einstein's model, the kinetic energy of the photoelectrons was determined as the difference between the photon energy and the "work function" or the energy necessary to rip an electron from the surface of the metal.

$$E_{\text{kin}} = h\nu - \varepsilon$$

In this case, each quantum of light, or photon, can produce one photoelectron. If the energy of the photons are too small (less than ε), no photoelectrons are produced. But at frequencies that exceeded the threshold value, the kinetic energy was a linear function of the light frequency, with the slope of that line giving a value for Planck's constant of proportionality. Einstein's model provided a separate measurement for Planck's constant but yielded an identical result. At this point, the scientific community could no longer ignore this new quantum theory of light. Einstein was awarded the Nobel Prize in Physics in 1921 for explaining the photoelectric effect.

Johannes Balmer and the Emission Spectrum of Hydrogen

In 1885, J.J. Balmer [3] (a high school teacher and amateur scientist) wrote about the series of lines in the visible emission spectrum of atomic hydrogen. The lines formed a pattern



where the spacing decreased in decreasing wavelength and seemed to converge on a series limit. The wavelengths (λ) of lines in this spectrum fit the pattern:

$$\lambda = G \left(\frac{n^2}{n^2 - 4} \right)$$

where $G = 3647.053 \text{ Å}$, or the series limit, and $n = 3, 4, 5, \dots$

In modern terms, this expression is given as

$$\frac{1}{\lambda} = \tilde{\nu} = R_H \left(\frac{1}{n_l^2} - \frac{1}{n_u^2} \right)$$

where R_H is known as the “Rydberg constant” for hydrogen, and has the value given by $R_H = 109677.581 \text{ cm}^{-1}$. Also, $n_l < n_u$ and either value must obey $n = 1, 2, 3, \dots$

In Balmer’s paper, the expression is purely empirical (meaning it is based only on observation and not tied to any theoretical value.) While he was unable to provide any theory for the pattern he had derived from data, he did state that such a simple pattern could not be a coincidence.

The job of theoretical physics was to derive a theory of the H-atom that would yield energy levels, transitions between which would produce the observed spectrum and the simple pattern determined by Balmer. The first quantum theory of the hydrogen atom was proposed by Niel’s Bohr (who was born in 1885 – the year that Balmer’s paper was published!) Bohr’s model is consistent with the wave nature of matter predicted by Louis de Broglie.

Louis de Broglie and wave nature of matter

Louis de Broglie (1892-1987) was intrigued by the notion that light, which every sensible physicist knew propagated as waves, could be described as though it was a stream of particles. Not to be outdone, he decided to examine the ramifications of doing something equally preposterous – treat something everyone knew was a particle, as a wave. de Broglie proposed that all particles would behave with a wave nature, and would have a wavelength determined by their momentum and Planck's constant.

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

Based on this theory, de Broglie predicted in his 1923 Ph.D. dissertation that interference patterns could be observed in electron beams diffracted by regular patterns, much in the same way that such results could be seen with light waves or water waves. This phenomenon was observed in electron beams diffracted off of nickel surfaces in 1927 [4]. de Broglie was awarded the Nobel Prize in physics in 1929 for the work in his dissertation – the first time the prize was awarded for a PhD thesis!

Niels Bohr and the Hydrogen Atom

Niels Bohr (1885-1962) was the first person to offer a quantum theory of the hydrogen atom that satisfactorily predicted the patterns seen in the emission spectra of atomic hydrogen. Basically, Bohr suggested that the electron in a hydrogen atom orbited the nucleus (a proton) in a circle, the circumference of which had to be an integral multiple of de Broglie wavelengths. (Bohr's model was actually published in 1913 [5] – 10 years before de Broglie's Nobel Prize winning thesis, but it is easily explained based on the de Broglie principle.)

Bohr suggested that the angular momentum of an orbiting electron had to be an integral multiple of Planck's constant divided by 2π .

$$mvr = \frac{nh}{2\pi} = n\hbar$$

This expression is easily rearranged to yield the de Broglie relationship:

$$\begin{aligned} mvr &= \frac{nh}{2\pi} \\ 2\pi r &= \frac{nh}{mv} = n\lambda \end{aligned}$$

Based on this relationship, and balancing the electrostatic attractive forces with the centripetal force acting on the orbiting electron, Bohr was able to derive the value of the Rydberg constant for hydrogen and predict the pattern seen in the emission spectrum of hydrogen.

While the theory does a remarkable job of describing the empirical model of Balmer, it has many shortcomings as well. For example, a charged electron orbiting a charged proton should eventually see its orbit decay and the electron will crash into the proton. Clearly this does not happen, contrary to the predictions of classical physics. Also, the Bohr theory is not applicable to atoms that have more than one electron, meaning it has not real application on most of the atoms in which chemists have interest. None the less, Bohr's foothold into the quantum world was important. And some important aspects of a quantum theory can be easily demonstrated using the model as well.

Heisenberg, Schrödinger and Dirac

While quantum mechanics is most often taught (and will be discussed in this text) in terms of the formalisms of Erwin Schrödinger (1887-1961), the first formal theory was derived by Werner Heisenberg (1901-1976) in 1925 (he was awarded the Nobel Prize in physics in 1932 for this theory) using a matrix formalism. Schrödinger's methodology uses integrals and eigenvalue-eigenfunction relationships and was first published in 1926. Schrödinger was awarded the Nobel Prize in Physics in 1933. Two years later, he proposed the famous "Schrödinger's Cat" thought experiment (after consulting with Albert Einstein, who never fully excepted quantum mechanics) aimed at disproving the very theory that had won Schrödinger the Nobel Prize. Schrödinger clearly lamented his contributions to the scientific foofaraw that quantum theory would become. In particular, he was dissatisfied by the notion of "quantum jumps" that were needed to describe electronic transitions in the hydrogen atom. In one heated debate with Niels Bohr, Schrödinger exasperated

If we are going to have to put up with these damn quantum jumps, I'm sorry that I ever had anything to do with quantum theory. [6]

Paul Dirac's (1902-1984) seminal textbook on quantum theory published in 1930 showed that the formalisms of Heisenberg and Schrödinger were mathematically identical. Dirac shared the 1933 Nobel Prize with Schrödinger. Among the many significant contributions that Dirac made, was a January 1928 paper in the *Proceedings of the Royal Society* that helped to explain the nature of electron spin. The consequences of his relativistic interpretation of the nature of an electron also predicted the existence of antimatter.

There is a lot more to the story of the development of quantum theory and a great many colorful characters involved. While this text will focus on the applications of quantum theory to understand molecular behavior rather than the history of its development, the history of the science is definitely something about which reading is extremely worthwhile.

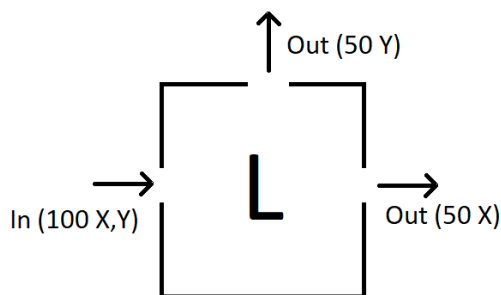
Also, given the efforts towards a unified field theory in physics, there is no time that studying quantum mechanics could be more valuable. In the development of these theories, quantum mechanics and relativity often struggle against one another, but it is quantum mechanics that always seems to win these struggles. As such, quantum theory is bound to play an enormous role as modern physics continues to evolve. It is my sincerest hope that this introduction will not only provide a background required to make sense out of modern

chemistry, but also whet the appetite for more knowledge and understanding on this fascinating subject.

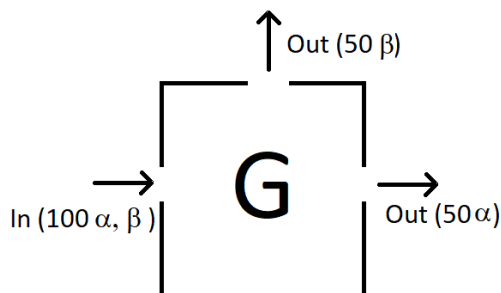
On Superposition and the Weirdness of Quantum Mechanics¹

In order to better appreciate the fascinating (and sometimes shocking!) results of the quantum world, let's consider some measurable properties of electrons. Consider in particular two specific properties they exhibit. It doesn't really matter what these properties actually are, but it does matter that there are only two possible outcomes when measuring these properties. For the purposes of this discussion, we can call these properties Latin and Greek, and the two measurable values of these properties are X or Y (for Latin) and α or β (for Greek.)

For the purposes of this discussion, let us assume that we can build a perfect sorting box for each property. For example, we can build a "Latin" box that will direct electrons through an aperture based on whether the electron is detected to have the value X, and a different aperture if the electron is found to have the value Y. Such a box would work as follows:



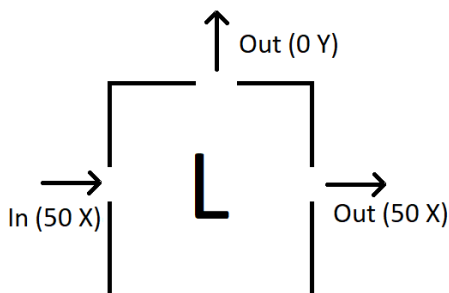
Similarly, we can build a "Greek" box that will sort in the same manner, except according to the measured value of the Greek property:



¹ This discussion is mostly taken from the first lecture from course 8.04 at the Massachusetts Institute of Technology (MIT), Alan Adams, 8.04 Quantum Physics I, Spring 2014. (Massachusetts Institute of Technology: MIT OpenCourseWare), <http://ocw.mit.edu> (Accessed May 21, 2022). License: Creative Commons BY-NC-SA Quantum Chemistry with Applications in Molecular Spectroscopy: Foundations and Review © 2022 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/))

Are the Properties Repeatable?

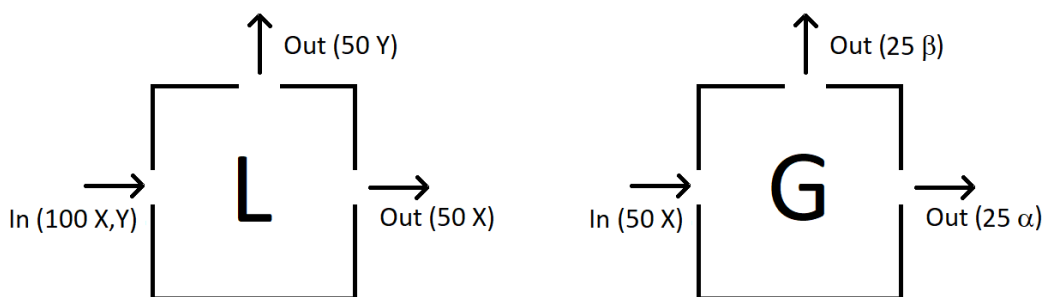
We can use these boxes to test whether or not the measured values of the Greek and Latin properties are repeatable. In order to do this, consider directing the X aperture output of a Latin box into a second Latin box. If the measured value of the property is repeatable, we would expect all of the electrons to exit the second Latin box through the X aperture. Pictorially, the second box would look as follows



demonstrating that the property is indeed repeatable. The same behavior is observed using the Greek box, in that previously measured α electrons will always exit the α aperture of the Greek box.

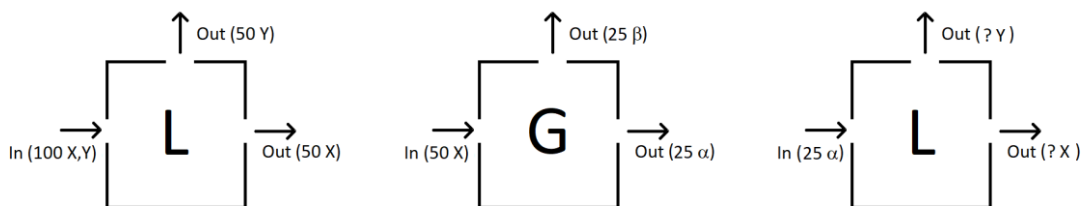
Are the Properties Correlated?

A reasonable question to ask is whether or not the properties are **correlated**. An example of this correlation would be observed if previously measured X electrons were more likely to be measured as α electrons afterward. The apparatus for testing for this kind of correlation might look as follows:



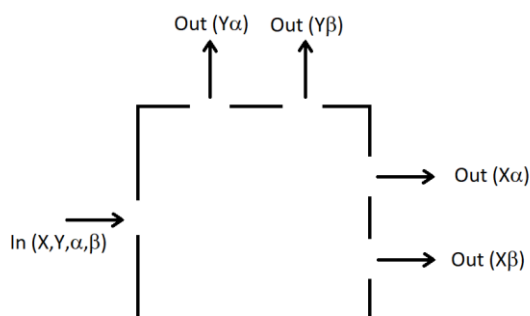
As is suggested in the diagram, the outcome of the Greek measurement does not show any preference for α or β for previously measured X electrons. The outcome for measuring α electrons with a Latin box is similar, in that half of the electrons exit the X aperture and half exit the Y aperture. The conclusion, therefore, would be that the Latin and Greek properties are not correlated.

Now, suppose we try a third variation and create a three-box experiment. In this experiment, we will use a Latin box to select the X electrons out of an initial random stream of electrons. These will then run through a Greek box. We will then take the α aperture output of the Greek box and run that through a Latin box. The box arrangement for this experiment would look as follows:



What do you expect for the percentages of electrons leaving the Latin box apertures? As it turns out, half of the α electrons leaving the Greek box will exit the X aperture and half will exit the Y aperture. As crazy as it seems, it appears that measuring the Greek property made the electrons “forget” that they were previously measured to be X electrons!

This has an important implication about the nature of these sorting boxes. It implies that it would be impossible to build a compound box (a larger box constructed for Latin and Greek boxes) that would simultaneously sort electrons by both Latin and Greek properties. In other words, the following device would not work:



The reason this box will not work is that the electrons do not behave as though they carry definite values of Latin or Greek properties. Rather, these properties have to be determined at the time of measurement. The result is contrary to the behavior of any particle that is well-described by Newtonian physics!

To help illustrate this, consider randomizing the state of a quarter (\$0.25) by flipping it. We know that it will land as either heads or tails. But we can also imagine it landing with the head (or tail) upright or upside down. The coin can, in effect, land in one of four states. For convenience, let's label them as HU, TU, HD, and TD (H/T for heads or tails, and U/D for up or down).



For a classical object, like a coin, we expect all of the physical properties to persist. For example, if we flip the coin, and then measure in order, heads or tails, up or down, and then heads or tails, we expect the results of the first and third measurements to yield the same result.

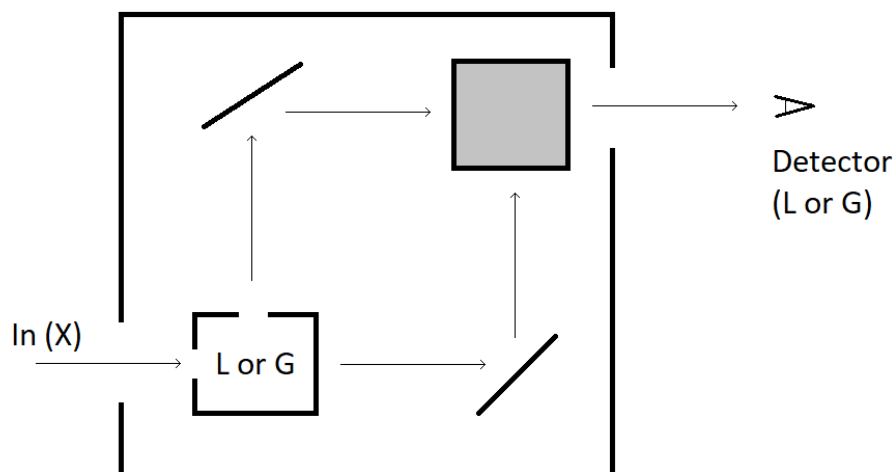
But in the case of the electron, measuring the Greek property seemed to cause the electron to completely forget what was measured about the Latin property. This leads us to the conclusion that there is not an internal property that determines the outcome of the measurement of that Latin property – at least not one that can survive the measurement of the Greek property.

Do the Properties Interfere with One Another?

While it is true that electrons can not be definitively sorted simultaneously by Latin and Greek properties due to the lack of persistence of the measured outcomes when mixing boxes, one might ask if measuring one outcome interferes with the measurement of a second. Consider a new type of compound box, into which we will introduce two new devices: mirrors, and what we can consider a “combining” box. The role of the mirrors is simply to redirect a beam, but they will not alter the beam in any other way that its direction of travel. Similarly, the “combining” box will only collect the beams and cause them to travel in the same direction.

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The box will be designed to accept the input of a beam of electrons previously selected as X electrons. It will then sort by Latin or Greek properties, redirect and combine the beams and then measure for either Latin or Greek properties at the exit aperture. Such a compound device might look as follows:



Such a device could be configured for four different interesting experiments. These experiments are described below:

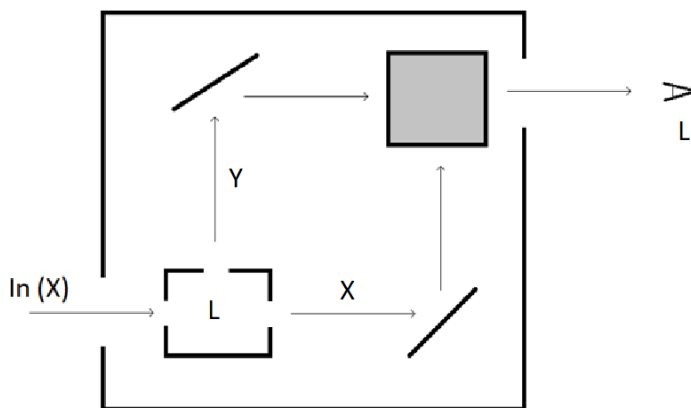
- I. Sort the X electrons using a Latin box, and measure the Latin property at the exit
- II. Sort the X electrons using a Latin box, and measure the Greek property at the exit
- III. Sort the X electrons using a Greek box, and measure the Greek property at the exit
- IV. Sort the X electrons using a Greek box, and measure the Latin property at the exit

The results of these experiments are summarized in the table below:

Experiment	Input	Sorter	Detector	Result?
I	100% X	Latin	Latin	100% X
II	100% X	Latin	Greek	50% α , 50% β
III	100% X	Greek	Greek	50% α , 50% β
IV	100% X	Greek	Latin	???

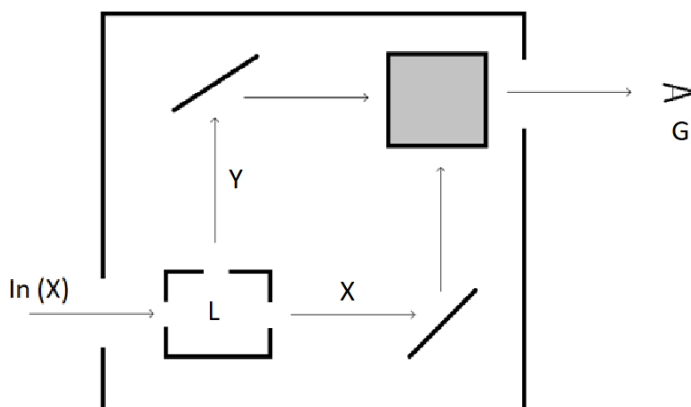
Let's consider the results individually.

Experiment I



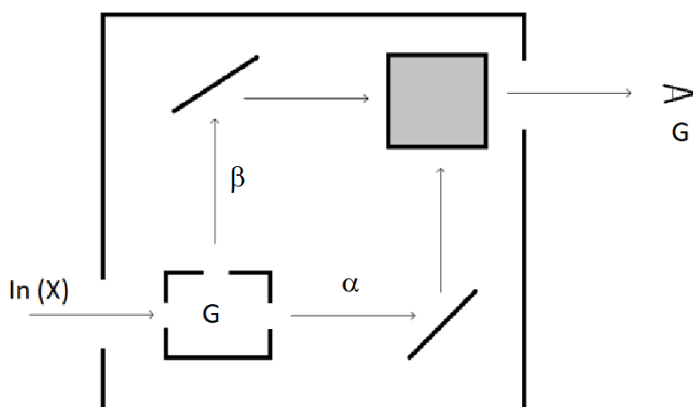
The results of this experiment are not surprising based on the results of the previous sections. Consider the path that the electrons will take as they pass through the apparatus. All of the X electrons incident on the box will be sorted to exit the X aperture of the Latin box and travel to the detector where they will again be measured as X electrons. This is the expected result because the property is measured to be repeatable by successive boxes of the same type.

Experiment II



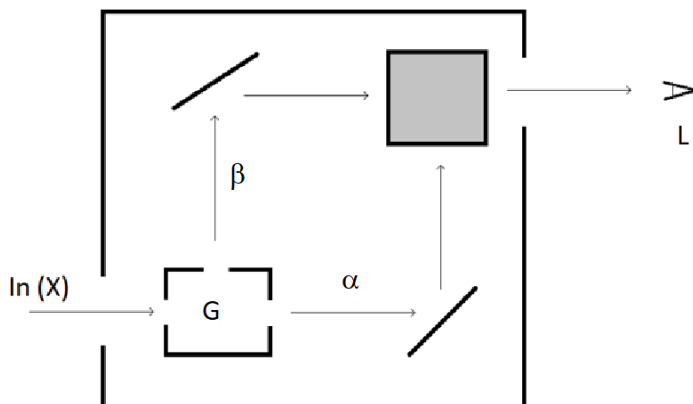
Again, the result is not too surprising. We expect all of the electrons to exit the “sorting” box along the X pathway. And since the Greek property is not correlated to the Latin property, when measured at the Greek detector, we expect 50% α and 50% β electrons to be detected.

Experiment III



In this experiment, things are getting to be more interesting, as we have to consider electrons exiting the “sorting” box along both the α and β paths, each accounting for half of the initial X electrons. Of the electrons that travel along the α path (which is expected to be 50% of the incident X electrons), we expect them all to be measured as α electrons. Similarly for those electrons which follow the β path, we expect them to be detected as β electrons at the detector.

Experiment IV

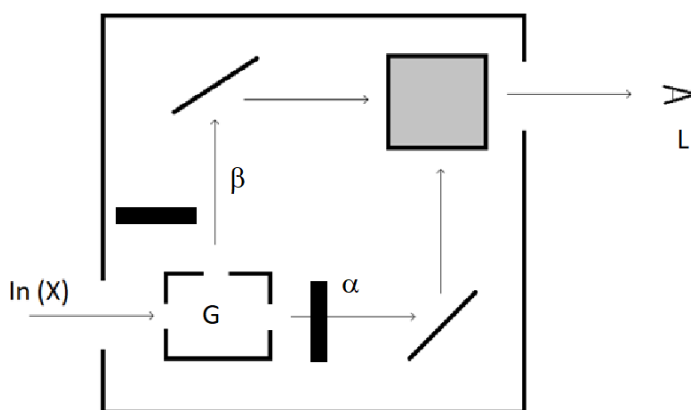


In this configuration, one might expect half of the incident X electrons to exit the sorter along the α path, and when detected, half will be X , and half will be Y . Similarly for those electrons that travel along the β path, half will be detected as X and half will be detected as Y . This would result in a total of 50% X and 50% Y . And this result seems perfectly reasonable based on our initial results.

But the quantum world has a huge surprise for us. In this experiment 100% of the electrons are detected as X electrons! How is this possible? It seems to completely contradict the notion that measuring the Greek property causes the electron to lose its Latin identity. On its face, this result seems completely absurd and impossible, but the behavior is observed on electrons, photons, and even large molecules such as buckyballs (C_{60} molecules)!

Further Developments

Let's consider a new apparatus in which beam stoppers can be introduced to block the individual α and β paths inside the box. This setup might look something like what is depicted in the diagram below.



This suggests four new experiments, the designs and results of which are listed in the table below:

Experiment	α -path	β -path	Latin property detected (% of incident beam)	
A	open	open	100% X	0% Y
B	open	blocked	25% X	25% Y
C	blocked	open	25% X	25% Y
D	blocked	blocked	0% X	0% Y

These results allow us to draw some important (but classically troubling) conclusions about the pathway the electrons are taking through the box.

Do they take the α -path or the β -path?

If the α -path is open (experiments A and B) we detect electrons at the exit, but the intensity is reduced by 50% if the β -path is blocked (Experiment B). This result is consistent with the interpretation that half of the electrons take the α -path and half take the β -path, and also is consistent with what we expect based on previous experiments. However, because we now see a split of both X and Y electrons detected at the exit rather than 100% X, we have to conclude that they electrons are not simply taking the β -path. And further, we can conclude that they are not simply taking the α -path given the results of experiment C!

Are they somehow taking both paths?

It may seem like a silly question, but if they were taking both paths, blocking one of the paths would result in a half electron being detected at the exit if the incident beam was slowed sufficiently – and that never happens! Electrons are always detected whole and intact. So we can conclude that the electrons are also not magically splitting into half with each half taking one of the paths.

Is it possible they take neither path?

The results of experiment D for us to reject this possibility as well, since blocking both paths eliminates any detected signals at the exit. They must be somehow using the pathways but without picking one or the other, and also not using both!

The Superposition Solution

This is where we have to resort to a new kind of description of the state of these electrons. We call this state a **superposition** state. We will explore what this means in great detail, and how we can use the stationary states of waves to form bases in which these superpositions can be expressed, much as we described an arbitrary wave on a string as a superposition of standing waves, each with a unique amplitude.

In the case of our last set of experiments, it would be reasonable to conclude that the superposition state has some sort of an oscillatory amplitude of X and Y states, such that when the beams are combined, the amplitudes of the Y states are removed through destructive interference. And, while this description may eventually be shown to be incorrect or incomplete through further experimentation (a possibility that always exists in science) it is at least consistent with the experiments summarized here.

How to use this information going forward

In this chapter, we have seen how to model waves using classical models, and how superposition allows us to extend our understanding beyond simple standing waves. We have also seen how classical physics was challenged as new observations and technologies forces scientists to develop new models and tools in order to predict behavior in the Universe. It is important to view this as an active and dynamic process.

Remember to always think like a scientist. Our best models are useful only because they are consistent with the current state-of-the-art observations of the behavior of nature. And like in

any area of scientific endeavor, there will be continual tweaks and sometimes even Earth-shattering changes brought for as new experiments allow us to see Nature through more detailed lenses.

But it is this point that makes the study of Quantum Mechanics so exiting right now, as we are on the cusp (perhaps) of these new discoveries and observations as scientists are able to use new instrumentation to make new observations every day. The hope of this book is that it will help you to develop enough insight into the Chemical application of Quantum Theory to enjoy and appreciate the intricacies of this scientific journey as these new discoveries and observations challenge our current best models of Nature.

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Vocabulary and Concepts

acceleration	1	momentum	1
basis set	13	normalization constant	10
black body radiation.....	15	normalize.....	10
correlated.....	22	normalized.....	4
eigenfunction.....	6	orthogonality	3
eigenvalue	6	orthonormal.....	4
force	1	position.....	1
Fourier coefficients	12	potential energy.....	1, 2
Hamiltonian.....	2	superposition	28
kinetic energy	2	superposition theorem	4
Kronecker Delta	4	velocity.....	1
linear combinations	3	wavefunctions	11
mass.....	1		

Problems

1. Consider a sphere with a mass of 1.00 kg rolling on a frictionless parabolic surface where the relationship between the height (h) and the position (x, in meters) is given by

$$h = \left(\frac{x}{m}\right)^2 m$$

- At what point on the surface (what value of x) will the sphere have the maximum kinetic energy?
 - What will the potential energy be at the point you specified in a?
 - If the sphere begins at rest at position $x = -1.00$ m, what is its potential energy?
 - Given that the sum of potential and kinetic energy is a constant, derive an expression for kinetic energy as a function of position for the system.
2. Consider the vectors **u** and **v** given by

$$\begin{aligned}\mathbf{u} &= 3\mathbf{i} + 2\mathbf{j} \\ \mathbf{v} &= 2\mathbf{i} - \mathbf{j}\end{aligned}$$

where **i** and **j** are unit vectors in the x and y directions respectively.

- Calculate the magnitudes of vectors **u** and **v**.
- Find expressions for vectors **e**₁ and **e**₂ which are unit vectors parallel to **u** and **v** respectively.
- Are the vectors **u** and **v** orthogonal? Demonstrate this mathematically.
- Consider a vector **w** = 3**i** – 6**j**. find values for c₁ and c₂ in order to express **w** as a linear combination of **e**₁ and **e**₂.

$$\mathbf{w} = c_1\mathbf{e}_1 + c_2\mathbf{e}_2$$

3. Consider a string that is distorted from equilibrium at time t=0 such that its wavefunction is given by

$$\Psi(x) = \frac{1}{\sqrt{5}}\phi_1(x) + \frac{2}{\sqrt{5}}\phi_2(x)$$

$$\text{where } \phi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right).$$

- Show that the functions $\phi_n(x)$ form an orthogonal set of functions. To do this, show that

$$\int_0^a \phi_n(x) \cdot \phi_m(x) dx = 0 \text{ for } n \neq m$$

b. Show that

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

c. Show that

$$\int_0^a \Psi(x) \cdot \phi_1(x) dx = \frac{1}{\sqrt{5}} \quad \text{and} \quad \int_0^a \Psi(x) \cdot \phi_2(x) dx = \frac{2}{\sqrt{5}}$$

4. Calculate the kinetic energy and de Broglie wavelength for the following particles traveling at a velocity of 500 m/s.
 - a. an electron
 - b. a nitrogen molecule
 - c. a ball bearing with mass = 0.500 g

5. The wavelength of light from one line of an argon ion laser is 488 nm.

- a. Calculate the energy of a photon of this energy in
 - i. J
 - ii. kJ/mol
 - iii. eV

Metal	Work Function (eV)
Al	4.08
Fe	4.5
Co	5.0
Cu	4.7
Ag	4.73
Au	5.1
Na	2.28
K	2.3
Cs	2.1

- b. Of the elements in the table to the left, which (if any) would produce photoelectrons if light of $\lambda = 488 \text{ nm}$ is focused on the surface?
- c. What would be the kinetic energy of a photoelectron ejected from the surface of cesium produced by light of $\lambda = 488 \text{ nm}$?
- d. What is the longest wavelength of light that will produce photoelectrons from the surface of silver?