QUANTUM CHEMISTRY WITH APPLICATIONS IN SPECTROSCOPY

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Chemical Thermodynamics and Chemical Kinetics (Fleming)

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Preface

This text has grown out of several years of teaching this material at several different colleges. The feedback I have received from my students has been incredibly. I have tried to choose example that seemed to work particularly well in aiding students to gain an understanding of the material while grounding complex concepts in more familiar experiences and intuitions.

In writing this text, I have tried to maintain a connection to measurable phenomena when discussing the otherwise abstract quantum mechanical models. In particular, I have attempted to follow the development of each model with specific spectroscopic examples which utilize the basic models as foundations to understand the behavior of real chemical systems. My experience is that the methodology works better than simply talking about quantum mechanics first, and then following with a discussion of spectroscopy, as though the two topics are not related.

Also toward that end, I have included a great deal of the applications of group theory into the text. While group theory is often the bailiwick of inorganic chemistry, I find that it is also very useful in the descriptions of molecular vibrations, molecular orbitals, selection rules, and other topics that are typically discussed in a course in physical chemistry.

It is my sincere hope that by feathering these two topics into the discussion of quantum chemistry that students will not simply get bogged down in the minutia of complex equations and math, but rather have the chance to see the “big picture.”

And, as always, I wish all students who study physical chemistry all of the best in their endeavors. May the expectation value of your experience be satisfaction!

CHAPTER OVERVIEW

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, ones 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.

1.1: 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.

$$\begin{aligned} F &= ma \\ &= m\frac{dv}{dt} \\ &= m\frac{d^2x}{dt^2} \end{aligned}$$

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

$$p = mv$$

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

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

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

$$\begin{aligned}\frac{d}{dt}H &= \frac{dx}{dt}\left(-\frac{dU}{dx}+\frac{dU}{dx}\right) \\ &= \frac{dx}{dt}(0) \\ &= 0\end{aligned}$$

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.

1.2: 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 ($\mathbf{u}$ and $\mathbf{v}$) in three-dimensional space can be described as a linear combination of basis vectors in the x, y and z directions ($\mathbf{i}$, $\mathbf{j}$ and $\mathbf{k}$, respectively.)

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

The inner product of two vectors $\mathbf{u}$ and $\mathbf{v}$ is given the symbol $\langle\mathbf{u} \mid v\rangle$. 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

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

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 u indicates the magnitude of the vector $\mathbf{u}$ and α is the angle formed between the two vectors $\mathbf{u}$ and $\mathbf{v}$. 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 $\alpha/2$ 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.

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

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.

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

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

In the case of vectors, $\mathbf{i}$, $\mathbf{j}$ and $\mathbf{k}$ 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 $\mathbf{e}_1, \mathbf{e}_2 \ldots \mathbf{e}_N$ by the following relationship

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

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

$$\delta_{\mathrm{ij}} = \left|\begin{array}{ll}1 & \mathrm{if\,i}=\mathrm{j}\\ 0 & \mathrm{if\,i}\neq\mathrm{j}\end{array}\right.$$

Similarly, functions $(f_1(x), f_2(x)\ldots f_N(x))$ can form an orthonormal set if

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

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**.

1.3: Classical Description of a Wave on a String

The mathematics used in solving quantum mechanical problems follow be 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

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

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

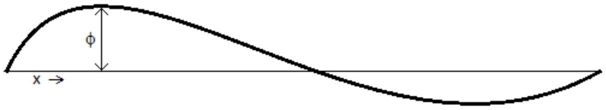

Figure 1.3.1

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

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

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:

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

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

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 $X(0) = 0$ 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,

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

Or

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

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.

$$\begin{gathered} X_n(x) = A_n\sin\left(\frac{n\pi x}{a}\right) \\ n = 1, 2, 3... \end{gathered}$$

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

a := 1　　　x := 0, 0.02.. a　　　n := 1, 2.. 4

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

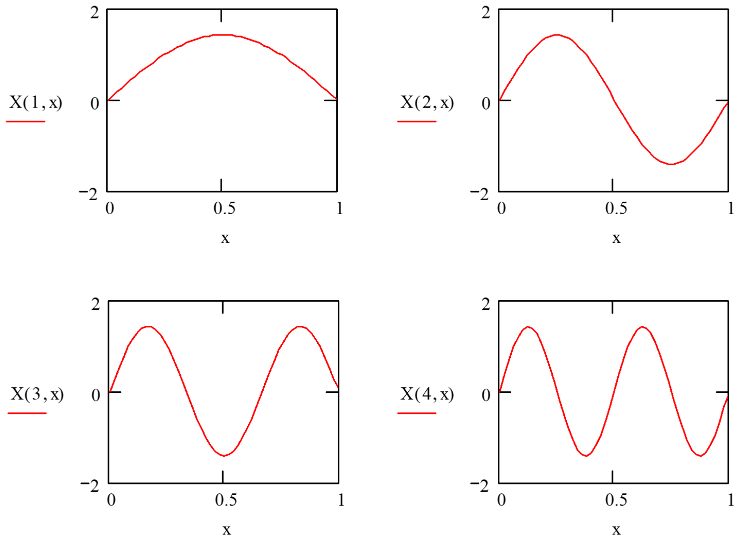

Figure 1.3.2

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

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

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

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

Substitution into the above expression yields

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

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:

$$A_n^2 \int_{x=0}^{x=a} \sin^2\left(\frac{n\pi\, x}{a}\right) dx A_n^2 \left[\frac{x}{2} - \frac{\sin\left(\frac{2n\pi\, x}{a}\right)}{4\left({}^{n\pi}\!/_{a}\right)}\right]_{x=0}^{x=a}$$

$$= A_n^2 \left[\frac{a}{2} - 0 - 0 + 0\right]$$

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

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

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

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

form an orthonormal set of functions. The 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

$$\delta_{nm} = \left| \begin{array}{l} 1 if n = m \\ 0 if n \neq m \end{array} \right.$$

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 special solutions and is given by $k = \frac{n\pi}{a}$. 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 \sigma such that

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

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, σ is a phase shift in time. For a given choice of $t = 0$, σ 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.

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

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

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

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.

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!

1.4: 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 20^{th} 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**.

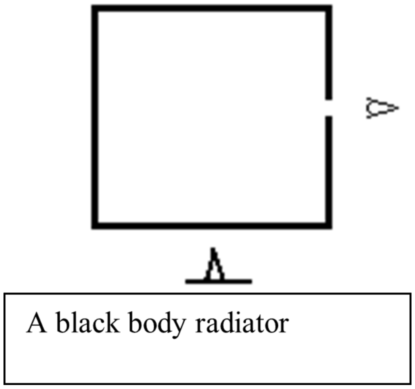

Figure 1.4.1

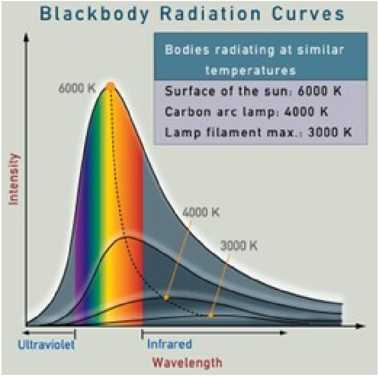

Figure 1.4.2

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 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

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

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.

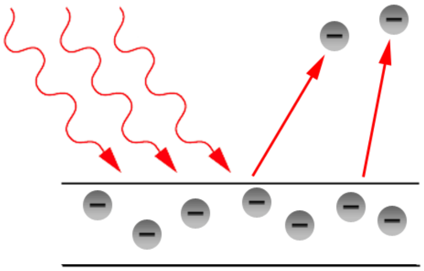

Figure 1.4.3

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. ($E_{photon} = h\nu$)

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.

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

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

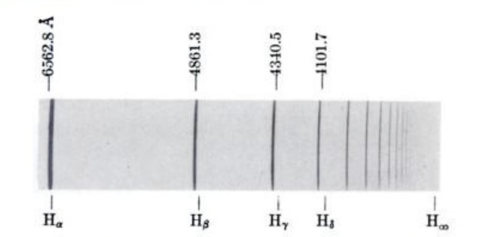

Figure 1.4.4

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 $G = 3647.053\overset{\circ}{A}$, or the series limit, and $n = 3, 4, 5, \ldots$.

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 $R_H = 109677.581 cm^{-1}$. Also, $n_l < n_u$ and either value must obey $n = 1, 2, 3, \ldots$.

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.

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[1] M. Planck, "On the Law of Distribution of Energy in the Normal Spectrum," Annalen der Physik, vol. 4, p. 553, 1901. W310W9405

[2] A. Einstein, "On a Heuristic Viewpoint Concerning the Production and Transformation of Light," Annalen der Physik, vol. 17, pp. 132-148, 1905. W310W9405

[3] J. J. Balmer, "Hinweis auf die Spektrallinien des Wasserstoffs," Annalen der Physik und Chemie, vol. 25, pp. 80-85, 1885. W310W9405

[4] C. Davisson and L. Germer, "Diffraction of Electrons by a Crystal of Nickel," Physical Review, vol. 30, pp. 705-740, 1927. W310W9405

[5] N. Bohr, "On the Constitution of Atoms and Molecules, Part I," Philosphical Magazine, vol. 26, pp. 1-24, 1913. W310W9405

[6] J. Baggot, The Meaning of Quantum Theory, New York: Oxford Science Publications, 1992, p. 28.W310W9405

1.5: On Superposition and the Weirdness of Quantum Mechanics

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 a or b (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 though 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:

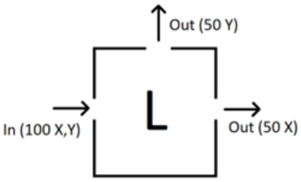

Figure 1.5.1

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

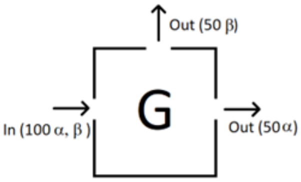

Figure 1.5.2

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

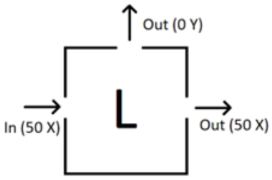

Figure 1.5.3

demonstrating that the property is indeed repeatable. The same behavior is observed using the Greek box, in that previously measured a electrons will always exit the a 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 a electrons afterward. The apparatus for testing for this kind of correlation might look as follows:

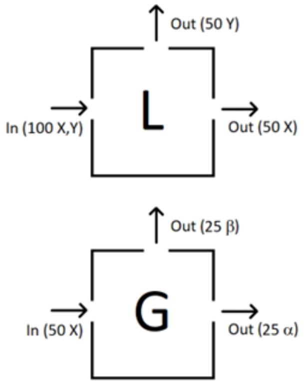

Figure 1.5.4

As is suggested in the diagram, the outcome of the Greek measurement does not show any preference for a or b for previously measured X electrons. The outcome for measuring a 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 a aperture output of the Greek box and run that through a Latin box. The box arrangement for this experiment would look as follows:

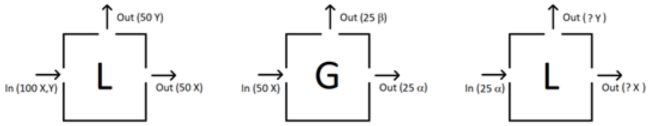

Figure 1.5.5

What do you expect for the percentages of electrons leaving the Latin box apertures? As it turns out, half of the a 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:

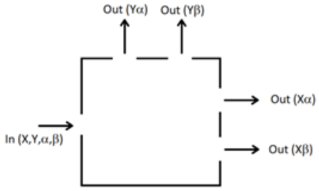

Figure 1.5.6

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.

Figure 1.5.7

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 – ant 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. Consier 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.

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:

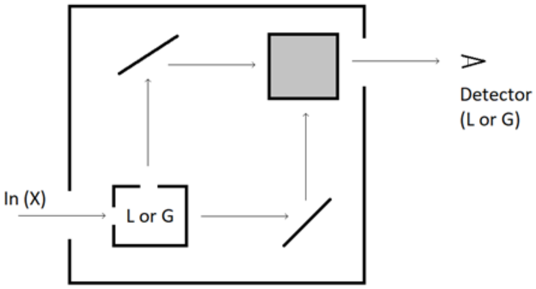

Figure 1.5.8

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

1. Sort the X electrons using a Latin box, and measure the Latin property at the exit

2. Sort the X electrons using a Latin box, and measure the Greek property at the exit
3. Sort the X electrons using a Greek box, and measure the Greek property at the exit
4. 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% a, 50% b
III	100% X	Greek	Greek	50% a, 50% b
IV	100% X	Greek	Latin	???

Let’s consider the results individually.

Experiment I

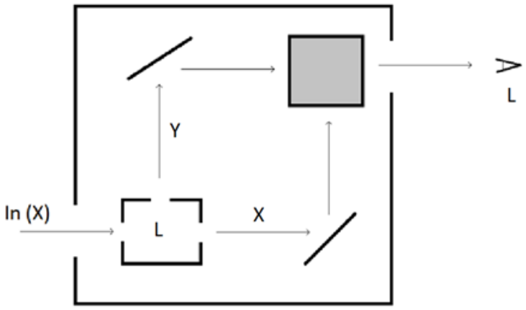

Figure 1.5.9

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

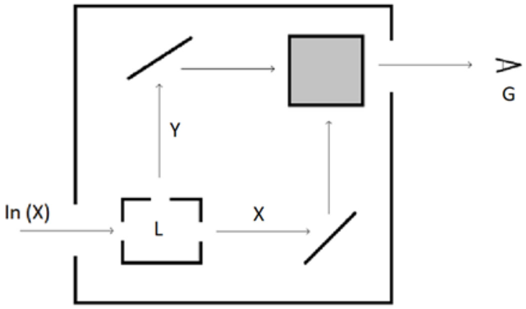

Figure 1.5.10

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% a and 50% b electrons to be detected.

Experiment III

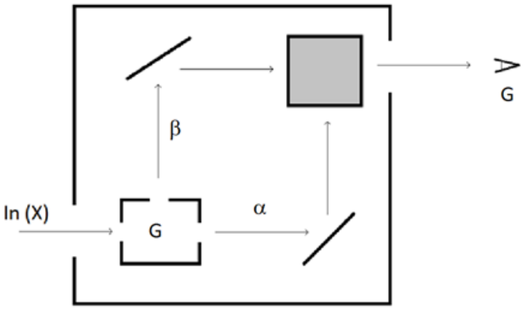

Figure 1.5.11

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

Experiment IV

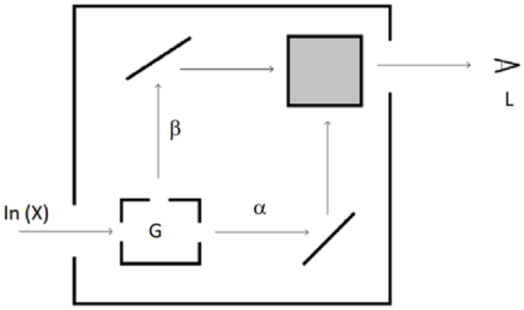

Figure 1.5.12

In this configuration, one might expect half of the incident X electrons to exit the sorter along the a path, and when detected, half will be X, and half will be Y. Similarly for those electrons that travel along the b 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 a and b paths inside the box. This setup might look something like what is depicted in the diagram below.

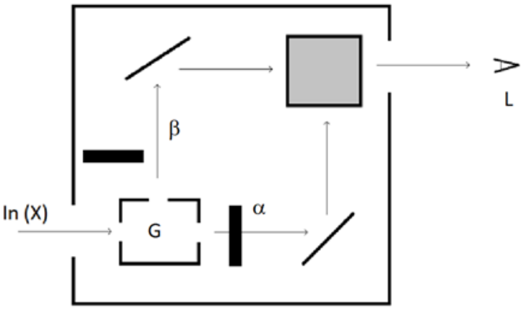

Figure 1.5.13

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

Experiment	a-path	b-path		
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 a-path or the b-path?

If the a-path is open (experiments A and B) we detect electrons at the exit, but the intensity is reduced by 50% if the b-path is blocked (Experiment B). This result is consistent with the interpretation that half of the electrons take the a-path and half take the b-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 b-path. And further, we can conclude that they are not simply taking the a-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 descript 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 supposition allows us to extend our understanding beyond simple stating 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 if 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.

1.6: References

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1.7: Vocabulary and Concepts

acceleration

basis set

black body radiation

correlated

eigenfunction

eigenvalue

force

Fourier coefficients

Hamiltonian

kinetic energy

Kronecker Delta

linear combinations

mass

momentum

normalization constant

normalize

normalized

orthogonality

orthonormal

position

potential energy

superposition

superposition theorem

velocity

wavefunctions

1.8: 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) is given by

$$h=x^2$$

a. At what point on the surface (what value of x) will the sphere have the maximum kinetic energy?
b. What will the potential energy be at the point you specified in a?
c. If the sphere begins at rest at position x = -1.00 m, what is its potential energy?
d. 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.

   a. Calculate the magnitudes of vectors **u** and **v**.
   b. Find expressions for vectors $\mathbf{e_1}$ and $\mathbf{e_2}$ which are unit vectors parallel to u and v respectively.
   c. Are the vectors u and v orthogonal? Demonstrate this mathematically.
   d. Consider a vector $\mathbf{w}=3\mathbf{i}-6\mathbf{j}$. find values for c_1 and c_2 in order to express w as a linear combination of $\mathbf{e_1}$ and $\mathbf{e_2}$.
   e. $\mathbf{w}=c_1\mathbf{e}_1+c_2\mathbf{e}_2$

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

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

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

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

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

b. Show that

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

c. Show that

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

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.

Metal	Work Function (eV)
Al	4.08
Fe	4.5
Co	5.0
Cu	4.7

Metal	Work Function (eV)
Ag	4.73
Au	5.1
Na	2.28
K	2.3
Cs	2.1

a. Calculate the energy of a photon of this energy in
    i. J
    ii. kJ/mol
    iii. eV
b. Of the elements in the table to the left, which (if any) would produce photoelectrons if light of $\lambda = 488\ nm$ 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 $\lambda = 488\ nm$?
d. What is the longest wavelength of light that will produce photoelectrons from the surface of silver?

CHAPTER OVERVIEW

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.

2.1: Background

At the beginning of the 1900 s, 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.

2.2: 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 $\Psi(\mathbf{r}, \mathrm{t})$ that depends on the coordinates of the particle $(\mathbf{r})$ and the time (t). This function, called the wavefunction has the important property that

$$\mathbf{\Psi}^{*}(\mathbf{r}, \mathrm{t})\mathbf{\Psi}(\mathbf{r}, \mathrm{t})\mathrm{dxdydz}$$

is the probability of finding the particle within the infinitesimally small volume element dxdydz 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 Â. 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

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

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 smooth [1] 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 2.2.1

Consider a particle of mass m in box of length a that is prepared such that it's 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.

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

The total probability will be given by the following integral.

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

Note that the final probability is unitless!

[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.

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	**r**
$\hat{p}$	Momentum	$-i\hbar\frac{d}{dx}$	$-i\hbar\vec{\nabla}$
$\hat{H}$	Energy	$\hat{T}+\hat{U}$	
$\hat{T}$	Kinetic	$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$	$-\frac{\hbar^2}{2m}\nabla^2$

	Physical Observable	One Dimension	Three Dimensions
$\hat{U}$	Potential	U(x)	U($\mathbf{r}$)

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-behaved [2] 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

[2] A well-behaved function is one that is normalizable and continuous over the relevant space of the problem.

✓ Example 2.2.1

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

Solution

For an operator $\hat{A}$ to be Hermitian, the following relationship must hold (for wellbehaved 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 $d(uv)=udv+vdu$ and integrating by parts. Using this approach

$$\int udv=uv-\int vdu$$

Making the substitutions that

$$\begin{aligned}u&=g^{*}\\dv&=\frac{d}{dx}fdx\end{aligned}$$

it should be clear that

$$\begin{aligned}du&=\frac{d}{dx}g^{*}dx\\v&=f\end{aligned}$$

So

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

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 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 5^{th} 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.

2.3: 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 $\mathrm{x}=0$ and $\mathrm{x}=a$. 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 $(\mathrm{x}<0$ and $\mathrm{x}>\mathrm{a})$ and zero every place 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 $\mathrm{x}=0$ and $\mathrm{x}=a$ since the infinite potential energy precludes the particle from ever existing outside of the limits of $\mathrm{x}=0$ and $\mathrm{x}=a$.

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

Figure 2.3.1

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 $\psi(\mathrm{x})$ 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 $\psi(\mathrm{x})$ 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 $\lambda = \mathrm{h}/\mathrm{p}$, 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.

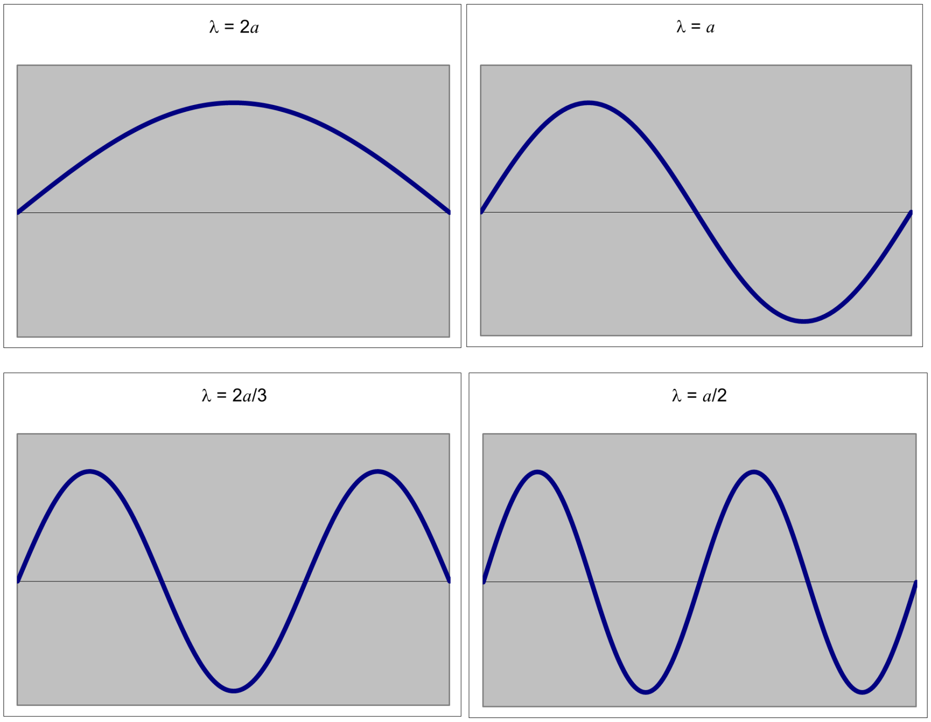

Figure 2.3.2

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.

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

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

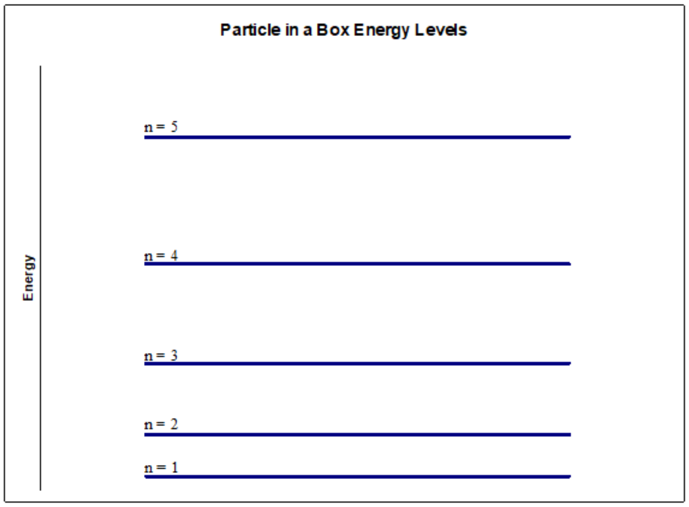

Figure 2.3.3

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 if 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 $\mathrm{B}=0$ 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 $\mathrm{A}=0$ and the other is to make $\mathrm{k}=0$. Both are trivial solutions and unimportant (but fun to mention in class!) The other way to force the function to 0 at $\mathrm{x}=\mathrm{a}$ is to insure that the sine function is zero by forcing

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

where n is an integer $(\mathrm{n}=1,2,3\ldots)$, since the sine function crosses zero every $\mathrm{n}\pi$ 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 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

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

Solving for A yields

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

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.

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

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

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 produced 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

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

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 $\alpha = \dfrac{n\pi}{a}$

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

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

✓ Example 2.3.1

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:

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

Therefore the wavefunction is normalized!

2.4: 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 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:

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

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 the relationship

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

The expectation value for the property associated with operator Â 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, $\frac{a}{2}$ 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 $\text{n} = 2$ 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 $\langle \mathrm{x}\rangle$, $\langle \mathrm{x}^2\rangle$, $\langle \mathrm{p}\rangle$ and $\langle \mathrm{p}^2\rangle$. Two of those quantities we already know from the previous sections.

The variance in x (σ_x^2)

To calculate $\langle \mathrm{x}^2\rangle$, 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 $\alpha = \dfrac{n\pi}{a}$ and noting that $\cos(2\mathrm{n}\pi\mathrm{x}) = 1$ and $\sin(2\mathrm{n}\pi\mathrm{x}) = 0$ for any value of n, we see that

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

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.

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

The variance in $p\left(\sigma_p^2\right)$

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

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

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

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

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

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

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

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

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

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

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

For momentum, the variance is given by

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

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

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

If the end result of the commutator operating on $\mathrm{f(x)}$ 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.

$$[\hat{\mathrm{A}}, \hat{\mathrm{A}}] = 0$$
$$\left[\hat{\mathrm{A}}, \hat{\mathrm{A}}^{\mathrm{n}}\right] = 0$$

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

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

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

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

Theorem 2.4.1

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.

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

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

$$d(uv)=vdu+udv$$

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.

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

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.)

2.5: 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

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

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 $\Psi(\mathrm{x})$ 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 $\langle \mathrm{E} \rangle$.

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

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

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

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

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

Completeness

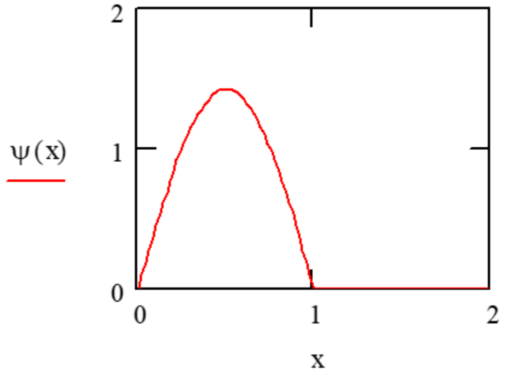
Imagine the following scenario. A quantum mechanical particle of mass m in a onedimensional box of length a is prepared such that its wavefunction is given by $\psi_1(\mathrm{x})$. Instantaneously, the length of the box increases to $2a$. The particle is no longer in an eigenstate of the new system. 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.

$a := 1$

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

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



$n := 1, 2 .. 15$

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

$$c(n) := \int_{0}^{2\cdot a} \psi(x)\cdot\phi(n,x)\,dx$$

$c(n) =$

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

$m := 7$

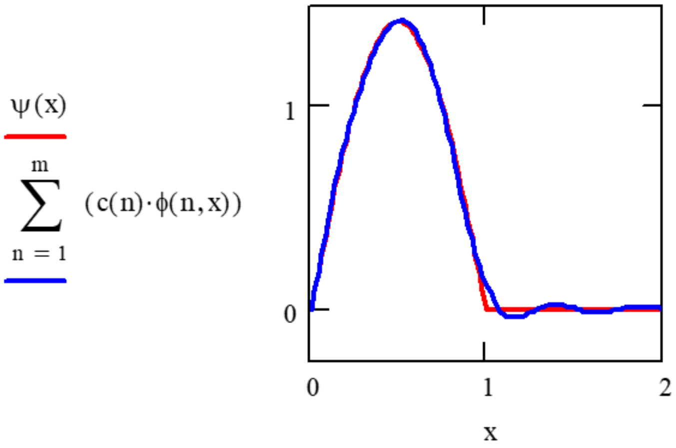


Figure 2.5.1

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?)

2.6: 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

$$\begin{aligned}&\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}+\right)X(x)Y(y)Z(z) = -k^2X(x)Y(y)Z(z) \\ &Y(y)Z(z)\frac{d^2}{dx^2}X(x)+X(x)Z(z)\frac{d^2}{dy^2}Y(y)+X(x)Y(y)\frac{d^2}{dz^2}Z(z) = -k^2X(x)Y(y)Z(z)\end{aligned}$$

Dividing both sides by $\mathrm{X(x)Y(y)Z(z)}$ 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.

$$\begin{aligned}\frac{1}{X(x)}\frac{d^2}{dx^2}X(x)=-k_x^2\\ \frac{1}{Y(y)}\frac{d^2}{dy^2}Y(y)=-k_y^2\\ \frac{1}{Z(z)}\frac{d^2}{dz^2}Z(z)=-k_z^2\end{aligned}$$

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!

$$\begin{aligned}X(x)&=\sqrt{\frac{2}{a}}\sin\left(\frac{n_x\pi x}{a}\right) \quad n_x=1,2,3,\ldots\\ Y(y)&=\sqrt{\frac{2}{b}}\sin\left(\frac{n_y\pi y}{b}\right) \quad n_y=1,2,3,\ldots\\ Z(z)&=\sqrt{\frac{2}{c}}\sin\left(\frac{n_y\pi z}{c}\right) \quad n_z=1,2,3,\ldots\end{aligned}$$

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

$$\begin{aligned}E&=E_x+E_y+E_z\\ &=\left(\frac{n_x^2h^2}{8ma^2}\right)+\left(\frac{n_y^2h^2}{8mb^2}\right)+\left(\frac{n_z^2h^2}{8mc^2}\right)\end{aligned}$$

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.

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

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

$$\mathrm{E}_{\text{tot}}=\mathrm{E}_{\text{elec}}+\mathrm{E}_{\text{vib}}+\mathrm{E}_{\text{rot}}$$

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

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

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.)

Level	n_X	n_y	n_z	$E/\left(h^2/8ma^2\right)$	Degeneracy
1	1	1	1	3	1
2	1	1	2	6	3
3	1	2	1	6	3
4	2	1	1	6	3
5	1	2	2	9	3
6	2	1	2	9	3
7	2	2	1	9	3
8	1	1	3	11	3
9	1	3	1	11	3
10	3	1	1	11	3
11	2	2	2	12	1
12	1	2	3	14	6
13	2	3	1	14	6
14	3	2	1	14	6
15	1	3	2	14	6
16	3	2	1	14	6
17	2	1	3	14	6

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 sp^3 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.

Theorem 2.6.1

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 $\hat{A}$.

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

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

$$\begin{aligned}\hat{\mathrm{A}}\left(\mathrm{c}_1 \mathrm{f}+\mathrm{c}_2 \mathrm{~g}\right) & =\mathrm{c}_1 \hat{\mathrm{A}} f+\mathrm{c}_2 \hat{\mathrm{A}} g \\ & =a \mathrm{c}_1 \mathrm{f}+a \mathrm{c}_2 \mathrm{~g} \\ & =a\left(\mathrm{c}_1 \mathrm{f}+\mathrm{c}_2 \mathrm{~g}\right)\end{aligned}$$

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

$$V(x,y)=\left|\begin{array}{ll}\infty & \text{for } x^2+y^2\neq a^2\\ 0 & \text{for } x^2+y^2=a^2\end{array}\right.$$

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

$$V(r,\theta)=\left|\begin{array}{ll}\infty & \text{for } r\neq a\\ 0 & \text{for } r=a\end{array}\right.$$

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 is it a constant $(r=a.)$

So after a trivial rearrangement, we see

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

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

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

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!

$$\frac{d}{d\theta}Ae^{im_l\theta}=iAm_le^{im_l\theta}$$

and

$$\frac{d}{d\theta}iAm_le^{im_l\theta}=-Am_l^2e^{im_l\theta}$$

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.

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

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

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

And the energies are given by

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

2.7: 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 $\mathrm{C}=\mathrm{C}$ 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:

$$E_n = \frac{n^2 h^2}{8 m a^2}$$

where $n = 1, 2, 3 \ldots$, h is Plank's constant $\left(h = 6.63 \times 10^{-34} \mathrm{Js}\right)$, m is the mass of an electron $\left(m_\mathrm{e} = 9.11 \times 10^{-31} \text{ kg}\right)$ and a is the length of the box $\left(a = 1.529 \times 10^{-9} \text{ m}\right)$.

The energy levels will be filled with the 12π 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.

$$\begin{aligned} E_6 &= \frac{6^2\left(6.63 \times 10^{-34} \mathrm{Js}\right)^2}{8\left(9.11 \times 10^{-31} \text{ kg}\right)\left(1.529 \times 10^{-9} \text{ m}\right)^2} = 9.288 \times 10^{-19} \text{ J} \\ E_7 &= \frac{7^2\left(6.63 \times 10^{-34} \mathrm{Js}\right)^2}{8\left(9.11 \times 10^{-31} \text{ kg}\right)\left(1.529 \times 10^{-9} \text{ m}\right)^2} = 1.2642 \times 10^{-18} \text{ J} \end{aligned}$$

So the energy of excitation will be $3.354 \times 10^{-19} \text{ J}$. 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.

2.8: Entanglement and Schrödinger'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 Erin 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 p-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 $\mathrm{m_s} = -\frac{1}{2}$.

$$\beta^{+} \longleftarrow \pi_0 \longrightarrow \beta^{-}$$

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

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

which allows for the possibility that either particle is spin up or spin down to be equally lightly. But the spins of the two particles are intimately coupled to one another. If the electron $(\beta^-)$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

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

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

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

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.

2.9: References

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

2.10: Vocabulary and Concepts

commute

equation of motion

Hamiltonian

Heisenberg Uncertainty Principle

Kinetic Energy

orthogonal

spooky action at a distance

Superposition Principle

wavefunction

2.11: Problems

1. Consider the functions $f(x) = A\left(1 - x^2\right)$ and $g(x) = 3x^3 - x$.
    - a. Find a value for A such that $f(x)$ is normalized on the interval $-1 \leq x \leq 1$.
    - b. Are the functions $\mathrm{f(x)}$ and $\mathrm{g(x)}$ orthogonal over the interval $-1 \leq \mathrm{x} \leq 1$?
2. 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.
    - a. $\mathrm{e^x}$ $\quad 0 \leq x \leq \infty$
    - b. $\mathrm{e^{-x}}$ $\quad 0 \leq x \leq \infty$
    - c. $1/\mathrm{x}$ $\quad -\infty \leq \mathrm{x} \leq \infty$
    - d. $\mathrm{e^{i\theta}}$ $\quad 0 \leq x \leq 2\pi$
    - e. $x(1-x)$ $\quad 0 \leq x \leq 1$
3. Consider the following operators. Determine whether or not they are Hermitian.
    - a. $\mathrm{d/dx}$
    - b. $i\ \mathrm{d/dx}$
    - c. $\mathrm{d^2/dx^2}$
    - d. $i\ \mathrm{d^2/dx^2}$
4. Consider an operator $\hat{\mathrm{A}}$ and associated set of eigenfunctions ϕ_{n} that satisfies

$$\hat{A}\phi_{\mathrm{n}} = a_{\mathrm{n}}\phi_{\mathrm{n}}$$

Show that if the operator is Hermitian that the eigenvalues a_{n} must be real-valued.

5. Consider the data in the table.
    - a. Calculate $\langle x\rangle$ and $\left\langle x^2\right\rangle$.
    - b. Calculate σ_x^2 for the data set.
    - c. Does $\sigma_x^2 = \left\langle x^2\right\rangle - \langle x\rangle^2$? If not, what is the difference?
6. Consider a particle of mass m in a rectangular solid box with edge lengths given by $a = \mathrm{a}$, $b = 2\mathrm{a}$, $c = 2\mathrm{a}$. Find the degeneracies of the first 10 energy levels for the system.

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

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 $\psi(x) = \mathrm{Ax}(a - x)$.
    - a. Find a value of A that normalizes the wavefunction.
    - b. Find the expectation values for x and x^2 ($\langle x\rangle$ and $\langle x^2\rangle$).
    - c. Find the expectation values for p and $\mathrm{p^2}$ ($\langle \mathrm{p}\rangle$ and $\langle \mathrm{p^2}\rangle$).
    - d. 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.
    - e. Find the value of $\sigma_x\sigma_p$. Does it exceed $\frac{\hbar}{2}$?
8. Consider a particle of mass m in a box of length a. The system is prepared such that the wavefunction is given by $\psi(\mathrm{x}) = \mathrm{Ax^2}(a - \mathrm{x})$.
    - a. Find a value of A that normalizes the wavefunction.
    - b. What are the units on the wavefunction?
    - c. Find $\langle x\rangle$.

d. Is $\langle\mathrm{x}\rangle=a/2$? Why or why not?

9. Consider the following pairs of operators and determine whether or not the operators commute.
   a. $\mathrm{d}/\mathrm{dx}, \mathrm{d}^2/\mathrm{dx}^2$
   b. $\mathrm{x}, \mathrm{d}^2/\mathrm{dx}^2$
   c. $\mathrm{x}, \int dx$

10. Consider a particle of mass m in a box of length a for which the wavefunction is given by

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

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

   a. Show that the wavefunction $\Psi(\mathrm{x})$ is normalized.
   b. Graph the wavefunction $\Psi(\mathrm{x})$.
   c. What is the expectation value for energy $\langle\mathrm{E}\rangle$ for the system?
   d. What is the most likely energy to be measured for the system?

11. Consider benzene $(\mathrm{C}_6\mathrm{H}_6)$ as modeled using the free-electron model.
   a. Using a $\mathrm{C}-\mathrm{C}$ bond length of $\mathrm{r}_{\mathrm{cc}}=0.139\ \mathrm{nm}$, calculate the circumference of the ring and its radius.
   b. Based on the model, what are the degeneracies of the four lowest energy levels?
   c. 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.
   d. How does the value you found in part c compare to the observed band-origin of the $A_{1\mathrm{g}}\rightarrow\mathrm{B}_{1\mathrm{u}}$ transition of benzene $(\lambda=215\ \mathrm{nm})$?

CHAPTER OVERVIEW

3: An Introduction to Group Theory

Many problems in chemistry can be simplified based on the symmetry of molecules and/or the symmetries of atomic and molecular orbitals. Since this course will deal mostly in the mathematical models used to describe molecular motions (rotations and vibration) and the orbitals needed to describe the electronic structure of atoms and molecules, some introduction to the mathematics of symmetry is useful. The concepts discussed in this chapter will be used through the text to demonstrate how symmetry can be used to simplify the descriptions of atomic and molecular behavior.

3.1: Overview

Group Theory is the mathematical theory associated with the mathematical properties of groups. In chemistry, group theory is the mathematics of symmetry. A **group** (G) is a set of elements $(A, B$, etc.) that can be associated through a mathematical operation (sometimes referred to as a **multiplication operation**, eg. $A * B$) and satisfying the following criteria:

1. The group must have an **identity element** (E) such that for each element A in the group, $A * E = E * A = A$. (It can be proven that for a given group and multiplication operation, the identity element is unique.)
2. Each element A in the group must have an **inverse** (A^{-1}) that is also a member of the group and that satisfies the criterion $A * A^{-1} = A^{-1} * A = E$. (It can be proven that each element has one and only one inverse.)
3. The group must be **closed** under multiplication. That means that for any pair of elements in the group A and B for which $A * B = C$, C must also be a member of the group.

Note that the multiplication operation need not be **commutative**. The order of multiplication may matter. There is no guarantee that $A * B = B * A$. Many groups that satisfy this property are called **abelian** groups.

The set of numbers 1 and –1 form an abelian group under the normal operation of simple multiplication. A simple **group multiplication table** table can be constructed for this group.

	1	-1
1	1	-1
-1	-1	1

Clearly, the identity element in this group is 1 since multiplication by 1 gives the same number back. Also, both members happen to be their own inverse since

$$1 * 1 = 1 \text{ and } (-1) * (-1) = 1$$

3.2: Group Theory in Chemistry

In Chemistry, group theory is useful in understanding the ramifications of symmetry within chemical bonding, quantum mechanics and spectroscopy. The group elements we are concerned with are **symmetry operations**.

Symbol	Operation	Description	Element	Mathematical example
E	identity	This is the “don’t do anything to it” operation	E.	$E(x, y, z) = (x, y, z)$
C_n	Proper rotation	This is an operation in which the object is rotated about an axis by an angle of $\frac{2\pi}{n}$ radians. The axis will be referred to as the “C_n axis”.	C_n. The axis with the largest value of n is designated the “principle rotation axis” and the z-axis is always assigned as lying along the **principle rotation axis**.	$C_4(x, y, z) = (y, -x, z)$ $C_2(x, y, z) = (-x, -y, z)$ Etc.
σ	Reflection plane	This operation involves reflection of the object through a mirror plane.	σ_v, σ_d or σ_h. σ_v and σ_d contain the principle rotation axis, whereas σ_h planes are perpendicular to the principle rotation axis.	$\sigma_v(x, y, z) = (-x, y, z)$ (for reflection through the yz plane) $\sigma_h(x, y, z) = (x, y, -z)$ $\sigma_d(x, y, z) = (y, x, z)$
i	Inversion center	This operation involves reflection trough a point.	i. The inversion center (if it exists) will always be located at the center of mass of a molecule.	$i(x, y, z) = (-x, -y, -z)$
S_n	Improper rotation	This operation involves a rotation through a C_n axis followed by reflection by a σ_h plane.	S_n.	

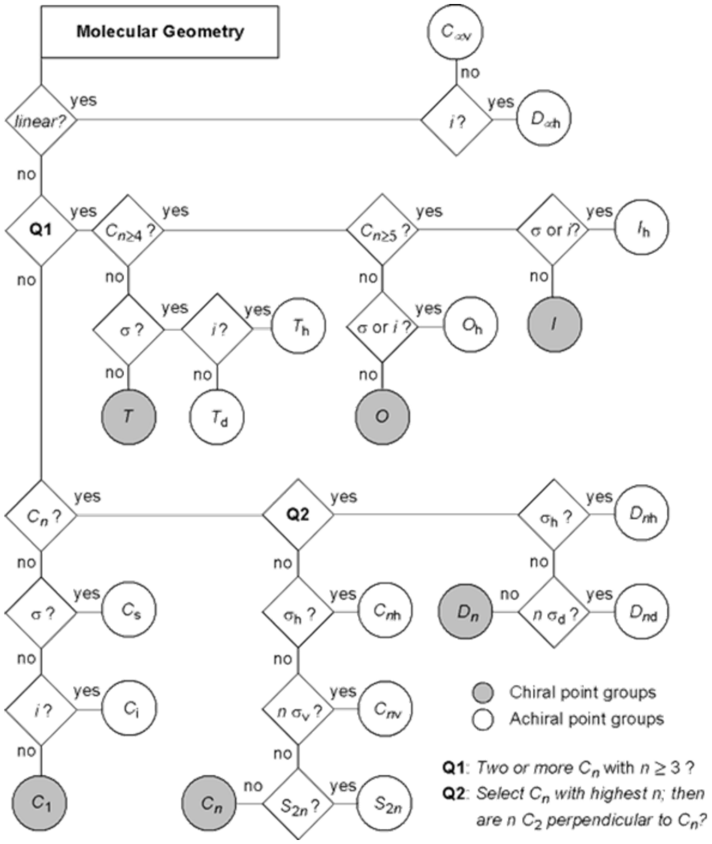


Figure 3.2.1

A symmetry operation is a geometrical manipulation that leaves an object in a geometry that is indistinguishable from that which it had before the manipulation. There are five important types of symmetry operations with which we are concerned. Each type of operation has an associated **symmetry element**. Using standardized notation, these operations and elements can be summarized as follows.

A given molecule may have several of the above symmetry elements. The particular combination will define a group, and that group can be given a named based on the type of symmetry elements it contains. Further, all of the convenient wavefunctions that describe the vibrations, rotations and molecular orbitals of the molecule will be eigenfunctions of the symmetry elements, forcing some very useful mathematical properties upon the wavefunctions.

A case study: the symmetry of a tennis racket

A tennis racquet has all of the same symmetry elements as a water molecule or a formaldehyde molecule. Let's identify these symmetry elements and write out a group multiplication table for the group to which that particular set belongs.

The most obvious symmetry element is always the identity element (E). Every object possesses this symmetry element. Some objects are so asymmetrical that this is the only symmetry element they possess. Certainly, a tennis racquet possesses the symmetry element **E**.

The next most useful element to examine is the reflection plane. An object may or may not possess this type of symmetry. A tennis racquet has two vertical (σ_v) reflection planes. One is in the plane of the strings and the other is perpendicular to the face of the racquet. This happens often that an object has more than one of a given type of symmetry element. For our purposes, we will designate the plane that is perpendicular to the face of the racquet as σ_v and the one that is parallel to the face of the racquet as σ_v'.

A tennis racquet possesses neither an inversion center (i) nor an improper rotation axis (S_n).

The set of symmetry elements that the object does possess (E, C_2, σ_v and σ_v') define a group that goes by the label C_{2v}. Any object that has these and only these symmetry elements is said to have C_{2v} symmetry. It is easy to demonstrate that the set of symmetry elements that define C_{2v} define a group.

3.3: Determining the Point Group for a Molecule- the Schoenflies notation

The first step in determining the point group for a molecule is to determine the structure of the molecule. Once this is done, identify all of the symmetry elements the molecular structure possesses. Once this has been accomplished, you can use the preceding flowchart to determine the correct point group using the **Scheonflies notation** system.

✓ Example 3.3.1

Determine the point group for a methane molecule.

Solution

A methane molecules has tetrahedral symmetry. It contains the following symmetry elements: E, 4 C_3 (one each along a C-H bond) axes, 6 σ planes (one each containing the carbon and a pair of hydrogen atoms), 3 C_2 axes (each on bisecting an HCH bond angle.) It also has 3 S_4 axes (each one co-linear with a C_2 axis.) The molecule belongs to the point group T_d, as can be discerned from the following analysis.

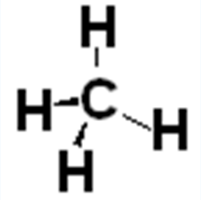


Figure 3.3.1

1. Is the molecular Linear? No
2. Does the molecule have two or more $C_{n\geq 3}$ axes? Yes
3. Does the molecule have a $C_{n\geq 4}$ axis? No
4. Does the molecule have any σ planes? Yes
5. Does the molecule have an inversion center? No

The molecule belongs to the T_d Point Group.

✓ Example 3.3.2

Determine the point group for CH_3Cl.

Solution

Chloromethane has the same tetrahedral shape as methane, but belongs to the point group C_{3v}. The molecule has the following symmetry elements: E, C_3 (along the C-Cl bond axis) and 3 σ_v planes (each containing the chlorine and carbon atoms plus one hydrogen atom. The classification of the molecule goes as follows:

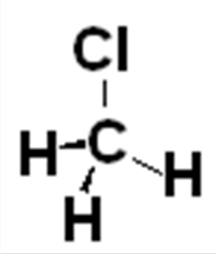


Figure 3.3.2

1. Is the molecule linear? No
2. Does the molecule have two or more $C_{n\geq 3}$ axes? No
3. Does the molecule have a C_n axis? Yes
4. Are there n C_2 axes perpendicular to the principle axis? No
5. Does the molecule have a σ_h plane? No
6. Does it have n σ_v planes? Yes

The molecule belongs to the C_{3v} point group.

✓ Example 3.3.3

Determine the point group for benzene.

Solution

Benzene has a planar geometry and belongs to the point group D$_{6h}$. The molecule possesses the following symmetry elements: E, C_6, 6 C_2, 6 σ_v, σ_h and i. The classification of the molecule goes as follows:

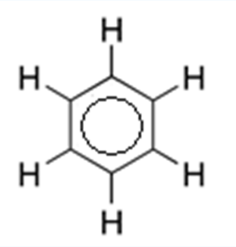


Figure 3.3.3

1. Is the molecule linear? No
2. Does the molecule have two or more $C_{n \geq 3}$ axes? No
3. Does the molecule have a C_n axis? (n = 6 for benzene) Yes
4. Are there n C_2 axes perpendicular to the principle axis? Yes
5. Does the molecule have a σ_h plane? Yes

The molecule belongs to the point group D_{6h}

✓ Example 3.3.4

Classify ethane by its point group.

Solution

Ethene has a planar geometry. The molecule possesses the following symmetry elements: E, 3 C_2, 3 σ, and i. The classification of the molecule goes as follows:

1. Is the molecule linear? No
2. Does the molecule have two or more $C_{n \geq 3}$ axes? No
3. Does the molecule have a C_n axis? Yes $(n = 2)$
4. Are there n C_2 axes perpendicular to the principle axis? Yes
5. Does the molecule have a σ_h plane? Yes

The molecule belongs to the D_{2h} point group.

✓ Example 3.3.5

Classify the isomers of dichloroethene by their point groups.

Solution

Dichloroethene has three isomers. All of them have a planar geometry. The cis- and gem- isomers have the following symmetry elements: E, C_2, and $2\sigma_v$. (The 1,1- (or gem-) isomer has the same elements as the cis- isomer.) The classification of the molecule goes as follows:

1. Is the molecule linear? No
2. Does the molecule have two or more $C_{n \geq 3}$ axes? No
3. Does the molecule have a C_n axis? Yes $(n = 2)$
4. Are there nC_2 axes perpendicular to the principle axis? No
5. Does the molecule have a σ_h plane? No

6. Does the molecule have $n\sigma_v$ planes? Yes

The cis-isomer belongs to the C_{2v} point group.

The trans-isomer has the following symmetry elements: E, C_2, σ_h, and i. The classification of the molecule goes as follows:

1. Is the molecule linear? No
2. Does the molecule have two or more $C_{n\geq3}$ axes? No
3. Does the molecule have a C_n axis? Yes $(n = 2)$
4. Are there nC_2 axes perpendicular to the principle axis? No
5. Does the molecule have a σ_h plane? Yes

The trans-isomer belongs to the C_{2h} point group.

3.4: Multiplication Operation for Symmetry Elements

Multiplication is fairly simple when it comes to symmetry operations. One simply applies the operations from right to left. Going back to the tennis racket example, it is fairly simple to visualize each symmetry element. To show this, it is useful to construct a group multiplication table. To do this, it is useful to pick a corner of the object and imagine where it is transported under a pair of sequential operations. Then imagine what operation will affect the same transformation directly. By applying them pairwise, one can generate the group multiplication table:

$\boldsymbol{C_{2v}}$	E	C_2	σ_v	σ_v'
E	E	C_2	σ_v	σ_v'
C_2	C_2	E	σ_v'	σ_v
σ_v	σ_v	σ_v'	E	C_2
σ_v'	σ_v'	σ_v	C_2	E

What should jump right out from this multiplication table is that the group C_{2v} 1) is abelian (actually, this will become clear after the term is defined) and 2) has the property that each element happens to be its own inverse! For some objects (such as a three-legged stool or an ammonia molecule) this will not be the case.

3.5: More Definitions- Order and Class

An important definition is the **order** of a group. The order (h) is simply the number of symmetry elements in the group. For the C_{2v} point group, the order is $h = 4$.

Another important concept defines the number of **classes** of operations a point group contains. Two operations (A and B) belong to the same class if there is a third operation (C) in the group that relates them by the **similarity transform**

$$C^{-1}AC = B$$

According to this definition, the operations A and B are said to be **complementary**. A complete set of complementary operations within a group defines a **class**. This will be demonstrated later, using the C_{3v} point group operations.

In the case of the C_{2v} point group, no two elements are in the same class. This has some very important ramifications for the point group. A group for which this the case is said to be an **abelian group**. Not all point groups will have this property however.

3.6: Representations

A **representation** is any mathematical construct that will reproduce the group multiplication table. In general, there are an infinite number of representations possible for a given group, however, most of them will be related through simple relationships, and thus can be constructed from (or reduced to) other representations. Those that cannot be reduced to linear combinations of other representations are called **irreducible representations**. The irreducible representations are particularly useful as they can be used to predict the mathematical properties of any function that is an eigenfunction of all of the symmetry elements of a group. The number of classes of operations always gives the number of irreducible representations. Each irreducible representation can be labeled as Γ_i.

To construct a representation for a group, one must assign each operation a mathematical element. For the C_{2v} point group, we can get away with using either 1 or –1 for each element. (This is a consequence of each operation belonging to its own class.) The simplest representation can be constructed by assigning each symmetry element as 1. The group multiplication table will hold, as can be seen below.

C_{2v}	**1**	**1**	**1**	**1**
1	1	1	1	1
1	1	1	1	1
1	1	1	1	1
1	1	1	1	1

Note that each product gives a value that corresponds to the correct element. For example, we let C_2 = 1 and σ_v = 1. The product of C_2 *σ_v yields σ'_v. And since the value we assigned σ'_v= 1 . . and $1 * 1 = 1$ . . everything worked. This particular representation seems pretty trivial since it has to work for any multiplication table that can ever be written! In fact, every point group has this type of representation. Since 1 gives all of the elements of this representation, this is called the **totally symmetric representation**.

Another representation (Γ_2) can be constructed in which E and C_2 are represented by a 1 and σ_v and $\sigma'_v$are represented by –1. In this case, the multiplication table looks as follows:

C_{2v}	**1**	**1**	**-1**	**-1**
1	1	1	-1	-1
1	1	1	-1	-1
-1	-1	-1	1	1
-1	-1	-1	1	1

It should be clear again (or easily enough verified) that this has the same pattern as the group multiplication table.

Two other representations can be constructed in this manner (with all of the elements given as either 1 or –1). Together with the first representation, these can be summarized as in the following table.

C_{2v}		**E**	C_2	σ_v	σ'_v
Γ_1	A_1	1	1	1	1
Γ_2	A_2	1	1	-1	-1
Γ_3	B_1	1	-1	1	-1
Γ_4	B_2	1	-1	-1	1

These irreducible representations (Γ_i) go by a standardized set of naming rules. First, the irreducible representations are all singly degenerate (no two-by-two or three-by-three matrices were needed for the representations) so all of the irreducible representations are given the symbol A or B. A is used if the representation is symmetric (1) with respect to the principle rotation axis (C_2) and B if it is antisymmetric (-1) with respect to the principle axis. The subscript is 1 if the representation is symmetric with respect to the σ_v reflection plane, and 2 if the representation is antisymmetric with respect to this plane of reflection. If an irreducible representation requires a set of two-by-two matrices, the representation is designated E, and three-by-three matrix irreducible representations are labeled T.

We'll discuss more on the difference between a reducible and irreducible representation later. First, lets work through a slightly more difficult point group. The C_{3v} point group is not abelian and requires matrices for some of the irreducible representations.

The Symmetry of a Triangular Pyramid: a more complex point group

An example of a point group that requires two-by-two matrix elements for the irreducible representations is the C_{3v} point group. This point group (which describes the symmetry elements of an ammonia molecule or a pyramid with an equilateral triangular base) consists of the symmetry elements E, C_3, C_3' (or C_3^2), σ_v, $\sigma_v'$and σ_v''.

In the figure to the left, the C_3 axis runs perpendicular to the base of the pyramid (you are looking straight down on the top of the pyramid) and the C_3 operation might correspond to a clockwise rotation of the figure about that axis. The C_3' axis is the same as the C_3 axis, but the C_3' operation corresponds to a *counter*clockwise rotation by $2\pi/3$ radians. Note that this operation is equivalent to performing the C_3 operation twice (hence the alternative notation of C_3^2.) The σ_v, $\sigma_v'$and σ_v'' elements are reflection planes that lie perpendicular to the base, but each containing one edge of the pyramid. The reader is left to imagine the identity element.

If the corners of the base of the pyramid are labeled for convenience, the effect of each symmetry operation can be represented as follows.

$$
\begin{array}{ll}
E * (1,2,3) = (1,2,3) & \sigma_v * (1,2,3) = (1,3,2) \\
C_3 * (1,2,3) = (3,1,2) & \sigma_v' * (1,2,3) = (3,2,1) \\
C_3^2 * (1,2,3) = (2,3,1) & \sigma_v” * (1,2,3) = (2,1,3)
\end{array}
$$

Following these permutations, it is possible to construct the group multiplication table. The group multiplication table for this group (C_{3v}) looks as follows:

$\boldsymbol{C_{3v}}$	**E**	$\boldsymbol{C_3}$	$\boldsymbol{C_3^2}$	$\boldsymbol{\sigma_v}$	$\boldsymbol{\sigma_v'}$	$\boldsymbol{\sigma_v''}$
E	E	C_3	C_3^2	σ_v	$\boldsymbol{\sigma_v'}$	σ_v''
$\boldsymbol{C_3}$	C_3	C_3^2	E	σ_v''	σ_v	$\boldsymbol{\sigma_v'}$
$\boldsymbol{C_3^2}$	C_3^2	E	C_3	$\boldsymbol{\sigma_v'}$	σ_v''	σ_v
$\boldsymbol{\sigma_v}$	σ_v	$\boldsymbol{\sigma_v'}$	σ_v''	E	C_3	C_3^2
$\boldsymbol{\sigma_v'}$	$\boldsymbol{\sigma_v'}$	σ_v''	σ_v	C_3^2	E	C_3
$\boldsymbol{\sigma_v''}$	σ_v''	σ_v	$\boldsymbol{\sigma_v'}$	C_3	C_3^2	E

From this information, it is possible to separate the operations into classes. Note, for example that $(\sigma_v)^{-1} = \sigma_v$ and $(\sigma_v')^{-1} = \sigma_v'$ and $(\sigma_v'')^{-1} = \sigma_v''$. Using these relationships, the similarity transforms of C_3 involving these operations all yield C_3^2.

$$
\begin{array}{c}
(\sigma_v)^{-1} * C_3 * \sigma_v = (\sigma_v * C_3) * \sigma_v = \sigma_v'' * \sigma_v = C_3^2 \\
(\sigma_v')^{-1} * C_3 * \sigma_v' = (\sigma_v' * C_3) * \sigma_v' = \sigma_v * \sigma_v' = C_3^2 \\
(\sigma_v'')^{-1} * C_3 * \sigma_v'' = (\sigma_v'' * C_3) * \sigma_v'' = \sigma_v' * \sigma_v'' = C_3^2
\end{array}
$$

Similarly, the similarity transforms on C_3^2 using these operations all yield C_3.

$$
\begin{array}{c}
(\sigma_v)^{-1} * C_3^2 * \sigma_v = (\sigma_v * C_3^2) * \sigma_v = \sigma_v' * \sigma_v = C_3 \\
(\sigma_v')^{-1} * C_3^2 * \sigma_v' = (\sigma_v' * C_3^2) * \sigma_v' = \sigma_v'' * \sigma_v' = C_3 \\
(\sigma_v'')^{-1} * C_3^2 * \sigma_v'' = (\sigma_v'' * C_3^2) * \sigma_v'' = \sigma_v * \sigma_v'' = C_3
\end{array}
$$

This is sufficient to indicate that the operations C_3 and C_3^2 belong to the same class. However, to show that these are the only two operations in this class. Consider the similarity transforms based on the operators E, C_3 and C_3^2 on C_3 :

$$(E)^{-1} * C_3 * E = (E * C_3) * E = E * C_3 = C_3$$
$$(C_3)^{-1} * C_3 * C_3 = (C_3^2 * C_3) * C_3 = E * C_3 = C_3$$
$$(C_3^2)^{-1} * C_3 * C_3^2 = (C_3 * C_3) * C_3^2 = C_3^2 * C_3^2 = C_3$$

The fact that the result of a similarity transform on either C_3 or C_3^2 never results in σ_v, σ_v'or σ_v'', is a consequence of the proper rotation operations belonging to a different class than the reflection planes. In fact, there are three classes of operations for this point group. This implies that there are three irreducible representations for this point group.

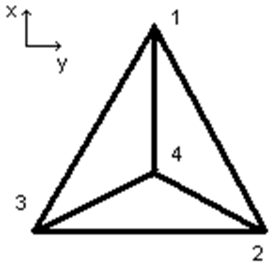


Figure 3.6.1

Another useful approach is to use matrix operators to affect the changes to the object caused by the symmetry operation. The choice of matrix operators depends on the basis set of functions being used to model the system. In this case, we will use position vectors of the corners of the bas of the pyramid. Other choices of basis might be the atomic orbitals on the atoms in a molecule. This is a very convenient choice when the task of constructing symmetry-adapted linear combinations of atomic orbitals for the purpose of modeling molecular orbitals. But I digress . . .

Consider the position vectors of the corners of the base of our trigonal pyramid. They can be specified by indicating the (x, y, z) coordinates if the origin is located in the plane of the base along the axis where all of the symmetry elements intersect.

Corner	**x**	**y**	**z**
1	0	$\frac{1}{\sqrt{3}}$	0
2	1/2	$-\frac{1}{2\sqrt{3}}$	0
3	-1/2	$-\frac{1}{2\sqrt{3}}$	0
4	0	0	h

Only corners 1, 2 and 3 will be important since none of the symmetry elements moves the fourth corner! Assuming unit length for the base edges and a height of h for the pyramid, the following table gives the (x, y, z) coordinates for each of the four corners.

From the previous discussion, we have already determined the effects of each of the symmetry operations.

$$\begin{array}{ll} E * (1,2,3) = (1,2,3) & \sigma_v * (1,2,3) = (1,3,2) \\ C_3 * (1,2,3) = (3,1,2) & \sigma_v' * (1,2,3) = (3,2,1) \\ C_3^2 * (1,2,3) = (2,3,1) & \sigma_v'' * (1,2,3) = (2,1,3) \end{array}$$

The task now is to construct matrix representations for each of the symmetry operations that will affect the above stated changes when matrix multiplication is used as the operation.

The identity element is easy. It will be the 3x3 identity matrix given by

$$E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

This is easily confirmed since

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

for any choice of x, y and z. The other operations are a little trickier, but not too hard. It can be shown that the matrix that affects a rotation of α radians about the z-axis is given by

$$\begin{pmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

So that the resultant of this operation is given by

$$\begin{pmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x\cos\alpha - y\sin\alpha \\ x\sin\alpha + y\cos\alpha \\ z \end{pmatrix}$$

For a rotation of $2\pi/3$ radians, it is useful to note the following.

$$\cos(2\pi/3) = -1/2$$

$$\sin(2\pi/3) = \sqrt{3}/2$$

So the transformation of corner 1 of the pyramid is accomplished as follows for the C_3 operation.

$$\begin{pmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} 0 \\ 1/\sqrt{3} \\ 0 \end{pmatrix} = \begin{pmatrix} -1/2 \\ -1/2\sqrt{3} \\ 0 \end{pmatrix}$$

The operation has transformed corner 1 into corner 3. It is also easily shown that the operator matrix also transforms corner 2 into corner 1, and corner 3 into corner 2. This is just as expected according to the expression shown above:

$$C_3 * (1,2,3) = (3,1,2)$$

Additionally, the matrix must satisfy the multiplication table relationship of $C_3 * C_3 = C_3^2$.

$$\begin{pmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

This is the rotation matrix for a rotation of $-2\pi/3$ radians. Hence, the product worked out as expected since the C_3^2 operation is equivalent to the rotation of $-2\pi/3$ radians.

The matrix representations for the σ_v planes can be worked out by one of two methods. One is to set up the matrix equation for how a point is transformed. The other is by using the group multiplication table to generate a matrix as the product of two other operations in the group for which the matrix has already been established.

To demonstrate these methods, recall from above that the σ_v operation exchanges corners 2 and 3. The matrix for this operation must satisfy the following expression:

$$\begin{pmatrix} R_{11} & R_{12} & R_{13} \\ R_{21} & R_{22} & R_{23} \\ R_{31} & R_{32} & R_{33} \end{pmatrix}\begin{pmatrix} 1/2 \\ -1/2\sqrt{3} \\ 0 \end{pmatrix} = \begin{pmatrix} -1/2 \\ -1/2\sqrt{3} \\ 0 \end{pmatrix}$$

The matrix that will affect this transformation is:

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Now, using the group multiplication table, we can generate $\sigma_v'$and σ_v'' by the relationships

$$\sigma_v * C_3^2 = \sigma_v'$$

$$\sigma_v * C_3 = \sigma_v''$$

or

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 1/2 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \sigma_v'$$

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 1/2 & \sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \sigma_v \text{”}$$

The set of matrices can now be used as a representation of the group. However, these matrices can be seen as a reproducible representation of the group since they are in block-diagonal form.

$$E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} C_3 = \begin{pmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} C_3^2 = \begin{pmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\sigma_v = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \sigma_v' = \begin{pmatrix} 1/2 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \sigma_v \text{”} = \begin{pmatrix} 1/2 & \sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

This representation can be broken down into two simpler representations. The first consists only of the lower right block of each of the matrices above. This yields the totally symmetric representation. The other is a representation of 2x2 matrices that are made from the upper left block of each of the matrices above. There is one other irreducible representation for the C_{3v} point group. It is given in the table below without derivation, but it is easy to demonstrate that it satisfies the group multiplication table.

C_{3v}			**E**	**C$_3$**
Γ_1	A_1	1	1	1
Γ_2	A_2	1	1	1
Γ_3	E	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix}$	$\begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}$

C_{3v}		σ_v	σ_v'	σ_v''
Γ_1	A_1	1	1	1
Γ_2	A_2	-1	-1	-1
Γ_3	E	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}$	$\begin{pmatrix} 1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix}$

3.7: The "Great Orthogonality Theorem"

One thing that is important about irreducible representations is that they are orthogonal. This is the property that makes group theory so very useful in chemistry, because orthogonality makes integrals zero. It's always easier to do the integrals when orthogonality tells us the result will be zero before doing any complicated math!

The **Great Orthogonality Theorem** (GOT) can be stated:

$$\sum_R [\Gamma_i(R)_{mn}]\,[\Gamma_j(R)_{m'n'}]^* = \frac{h}{\sqrt{l_i l_j}}\delta_{ij}\delta_{mm'}\delta_{nn'}$$

(Any theorem with that many subscripts must have something truly useful to say!) In this notation, $\Gamma_i(R)_{mn}$ indicates the row m, column n element of the i^{th} irreducible representation for symmetry operation R. The m and n are needed since not all irreducible representations are made up of just 1 and –1. Many irreducible representations need to use matrices to represent each symmetry element. For these cases, l_i gives the dimension of the matrices used in the Γ_i. In our example of the C_{2v} point group, all irreducible representations have $l = 1$, so the GOT can be stated more simply (for this point group specifically) as

$$\sum_R [\Gamma_i(R)]\,[\Gamma_j(R)]^* = h\delta_{ij}$$

Consider applying this statement to the A_2 and B_1 irreducible representations (Γ_2 and Γ_3) for the C_{2v} point group.

$$\begin{aligned}\textstyle\sum_R [\Gamma_2(R)]\,[\Gamma_3(R)]^* &= \Gamma_2(E)\Gamma_3(E)+\Gamma_2(C_2)\Gamma_3(C_2)+\Gamma_2(\sigma_v)\Gamma_3(\sigma_v)+\Gamma_2(\sigma_v')\Gamma_3(\sigma_v')\\ &= (1)(1)+(1)(-1)+(-1)(1)+(-1)(-1)\\ &= 1-1-1+1\\ &= 0\end{aligned}$$

Similarly, considering using the GOT on just Γ_4 (the B_2 irreproducible representation) yields the following

$$\begin{aligned}\textstyle\sum_R [\Gamma_4(R)]\,[\Gamma_4(R)]^* &= \Gamma_4(E)\Gamma_4(E)+\Gamma_4(C_2)\Gamma_4(C_2)+\Gamma_4(\sigma_v)\Gamma_4(\sigma_v)+\Gamma_4(\sigma_v')\Gamma_4(\sigma_v')\\ &= (1)(1)+(-1)(-1)+(-1)(-1)+(1)(1)\\ &= 1+1+1+1\\ &= 4\end{aligned}$$

Recall that the order of the group (h) is 4 because there are four symmetry elements in the group.

In the case of the C_{3v} point group, there is a 2x2 matrix representation. Consider the upper right member of each of the $\Gamma_3(E)$ matrices (row 1, column 2) and apply the GOT to these elements along with the elements of $\Gamma_1(A_1)$.

$$\begin{aligned}\textstyle\sum_R [\Gamma_1(R)]\,[\Gamma_3(R)_{12}] &= (1)(0)+(1)(\sqrt{3}/2)+(1)(-\sqrt{3}/2)+(1)(0)+(1)(-\sqrt{3}/2)+(1)(\sqrt{3}/2)\\ &= 0\end{aligned}$$

Similarly, applying the GOT to the row 1, column 1 elements of $\Gamma_3(E)$ we see

$$\begin{aligned}\textstyle\sum_R [\Gamma_3(R)_{11}]\,[\Gamma_3(R)_{11}] &= (1)^2+(-1/2)^2+(-1/2)^2+(-1)^2+(1/2)^2+(1/2)^2\\ &= 3 = 6/2 = h/l_3\end{aligned}$$

Now tell me . . isn't that truly a ***Great* Orthogonality Theorem** ? (Now how much would you pay?) Once we introduce the concept of *character*, we will restate the GOT in terms of class characters.

3.8: Character and Character Tables

Most summaries of group theory do not give the full matrix specifications for each irreducible representation in each important point group. Rather, a very useful quantity is defined, called the **character**. An important property that elements of the same class will share is that they have the same character. As such, it is only necessary to show the character once for each class of operations in the group.

The character of an element is given by the sum of the diagonal elements of the matrix used to represent the symmetry operation.

$$\chi_i(R) = \sum_m \Gamma_i(R)_{mm}$$

C_{3v}	E	C_3	s_v
A_1	1	1	1
A_2	1	1	-1
E	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \cos(2\pi/3) & -\sin(2\pi/3) \\ \sin(2\pi/3) & \cos(2\pi/3) \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

To evaluate the characters of each of the classes within each irreproducible representation, we need only generate a representation for one operation within each class. The three irreducible representations for some characteristic operators in each class can be expressed as follows:

Using the expressions above, the character table for the C_{3v} group can be expressed as

C_{3v}	E	$2\,C_3$	$3\,\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

Note that the character of the identity element is always given as the dimension of the matrices used in the irreducible representation.

$$\chi_i(E) = l_i$$

The GOT can be expressed in terms of characters.

$$\sum_R \chi_i(R)\chi_j(R) = h\delta_{ij}$$

This statement has a number of important and useful properties and consequences. One relationship deals with the sum of the squares of the characters of the identity elements.

$$\sum_i \left[\chi_i(E)\right]^2 = h$$

These expressions can be used to find and verify the characters for other point groups. For example, consider the partial character table for the point group C_{4v}.

A typical kind of exam or quiz question might be to fill in the missing values. In this case, all of the values are missing! So let's tackle the problem based on what we know from definitions, and complete the problem by using of the GOT.

C_{4v}	E	$2\,C_4$	C_2	$2\,\sigma_v$	$2\,\sigma_d$
A_1					
A_2					

C_{4v}	E	$2\ C_4$	C_2	$2\ \sigma_v$	$2\ \sigma_d$
B_1					
B_2					
E					

First off, the order of the group is $h = 8$. Second, every group has a totally symmetric representation. This is the A_1 representation and has members that are all 1. Let’s fill that in (using red for clarity.)

C_{4v}	E	$2\ C_4$	C_2	$2\ \sigma_v$	$2\ \sigma_d$
A_1	1	1	1	1	1
A_2					
B_1					
B_2					
E					

Additionally, we can fill in the column for the identity element. All of the A and B representations are singly degenerate, and the E representation is doubly degenerate. So using the expression

$$\sum_i [\chi_i(E)]^2 = h$$

That yields the following (shown in *red*):

C_{4v}	E	$2\ C_4$	C_2	$2\ \sigma_v$	$2\ \sigma_d$
A_1	1	1	1	1	1
A_2	1				
B_1	1				
B_2	1				
E	2				

And it clearly satisfies

$$\begin{aligned}\sum_i [\chi_i(E)]^2 &= (1)^2 + (1)^1 + (1)^2 + (1)^1 + (2)^2 \\ &= 8 = h\end{aligned}$$

Now using the definition that A representations have a character of 1 for the (are symmetric with respect to) the principle rotation axis and B representations have a character of –1 for (or are antisymmetric with respect to) the principle axis rotation. Thus, we can fill in

C_{4v}	E	$2\ C_4$	C_2	$2\ \sigma_v$	$2\ \sigma_d$
A_1	1	1	1	1	1
A_2	1	1			
B_1	1	-1			
B_2	1	-1			
E	2	?			

But should we do about the character of the C_4 operation under the irreducible doubly degenerate representation E? One solution comes from another important consequence of the GOT. This can be stated as

$$\sum_i \chi_i(R_m)\chi_i(R_n) = h\delta_{mn}$$

Using this relationship, we can solve for the character of the C_4 operation under the E irreducible representation.

$$\begin{aligned} \textstyle\sum_i \chi_i(E)\chi_i(C_4) &= \textstyle\sum_i \chi_i(E)\left[2\chi_i(C_4)\right] \\ &= 2(1)(1)+2(1)(1)+2(1)(-1)+2(1)(-1)+2(2)x=0 \end{aligned}$$

The only value of *x* that will satisfy this expression is *x* = 0. We can enter this value and also apply the definitions that the A_1 and B_1 representations are symmetric with respect to the σ_v operation and the A_2 and B_2 representations are antisymmetric with respect to σ_v.

C_{4v}	**E**	**2 C_4**	C_2	**2 σ_v**	**2 σ_d**
A_1	1	1	1	1	1
A_2	1	1		-1	
B_1	1	-1		1	
B_2	1	-1		-1	
E	2	0		?	

Again, the question mark can be removed as above.

$$\begin{aligned} \textstyle\sum_i \chi_i(E)\chi_i(\sigma_v) &= \textstyle\sum_i \chi_i(E)\left[2\chi_i(\sigma_v)\right] \\ &= 2(1)(1)+2(1)(-1)+2(1)(1)+2(1)(-1)+2(2)x=0 \end{aligned}$$

Once again, as luck would have it, the only value of *x* that satisfies the equation is *x* = 0. Now, we can apply the GOT to the representations for A_1, and A_2 to generate an equation with two unknowns to determine the characters of C_2 and σ_d for representations A_2 and B_1. We can solve it because we know *x* and *y* can only be 1 or –1. (These are the only values possible for singly degenerate representations.)

$$\begin{aligned} \textstyle\sum_R \chi_i(R)\chi_j(R) &= \chi_1(E)\chi_2(E)+2\chi_1(C_4)\chi_2(C_4)+\cdots \\ &= (1)(1)+2(1)(1)+(1)x+2(1)(-1)+2(1)y=0 \\ &= 1+x+2y=0 \end{aligned}$$

C_{4v}	**E**	**2 C_4**	C_2	**2 σ_v**	**2 σ_d**
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
B_1	1	-1		1	
B_2	1	-1		-1	
E	2	0		0	

The only combination that works is $x = 1$ and $y = -1$. The character table now looks as follows:

Completion of the rest of the character table is left as an exercise.

3.9: Direct Products

The intensity of a transition in the spectrum of a molecule is proportional to the magnitude squared of the transition moment matrix element.

$$\text{Intensity } \propto \left| \int (\psi')^{*} \vec{\mu}\, (\psi") \, d\tau \right|^{2}$$

By knowing the symmetry of each part of the integrand, the symmetry of the product can be determined as the **direct product** of the symmetries of each part $(\psi')^{*}$, $(\psi")$ and μ. This is helpful, since the integrand must not be antisymmetric with respect to any symmetry elements or the integral will vanish by symmetry. Before exploring that concept, let's look at the concept of direct products.

This is a concept many people have seen, in that the integral of an odd function over a symmetric interval, is zero. Recall what it means to be an "odd function" or an "even function.

Symmetry	definition	Integrals
Even	$f(-x) = f(x)$	$\int_{-a}^{a} f(x)dx = 2\int_{0}^{a} f(x)dx$
Odd	$f(-x) = -f(x)$	$\int_{-a}^{a} f(x)dx = 0$

Consider the function $f(x) = \left(x^{3} - 3x\right) e^{-x^{2}}$. A graph of this function looks as follows:

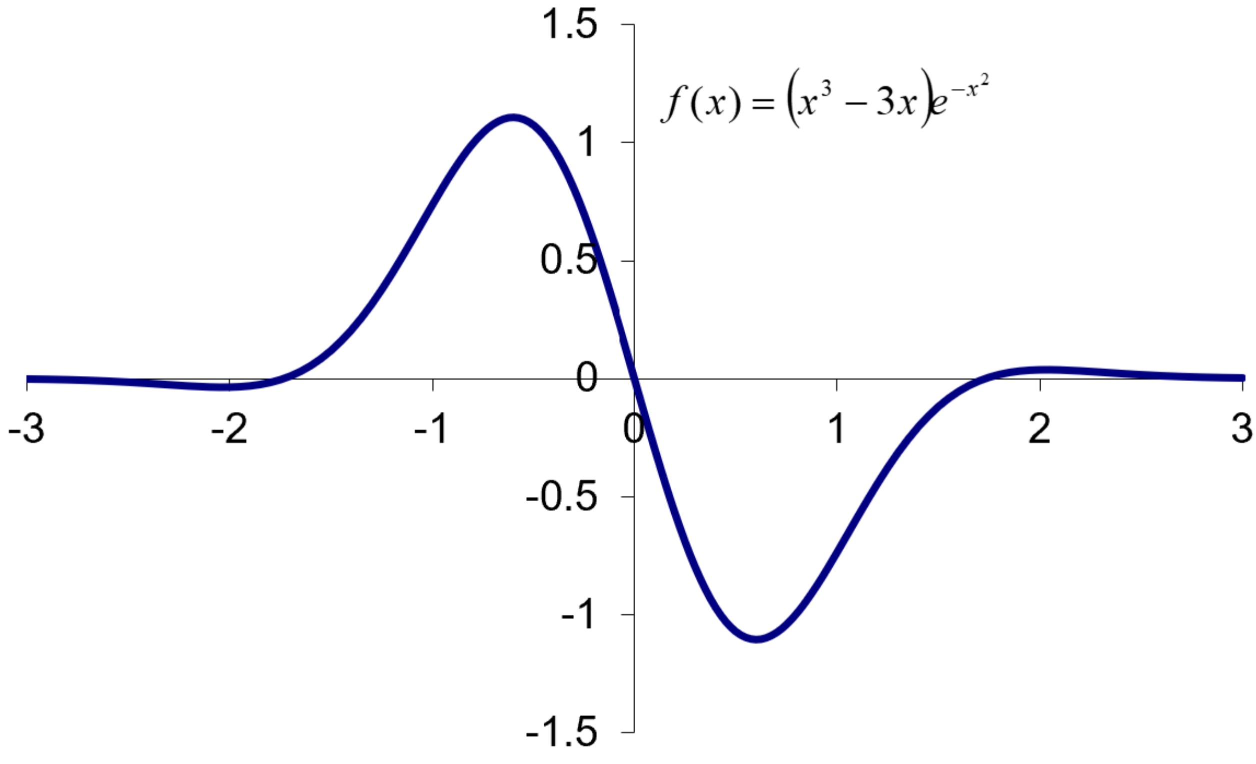


Figure 3.9.1

One notes that the area under the curve on the side of the function for which $x > 0$ has exactly the same magnitude but opposite sign of the area under the other side of the graph. Mathematically,

$$\begin{aligned} \int_{-a}^{a} f(x)dx &= \int_{-a}^{0} f(x)dx + \int_{0}^{a} f(x)dx \\ &= -\int_{0}^{a} f(x)dx + \int_{0}^{a} f(x)dx = 0 \end{aligned}$$

It is also interesting to note that the function *f(x)* can be expressed as the product of two functions, one of which is an odd function ($x^3 - 3x$) and the other which is an even function (e^{-x^2}). The result is an odd function. By determining the symmetry of the function as a product of the eigenvalues of the functions with respect to the inversion operator, as discussed below, one can derive a similar result.

The even/odd symmetry is an example of inversion symmetry. Recall that the inversion operator (in one dimension) affects a change of sign on x.

$$\hat{i}\, f(x) = f(-x)$$

“Even” and “odd” functions are eigenfunctions of this operator, and have eigenvalues of either +1 or –1. For the function used in the previous example,

$$f(x) = g(x)h(x)$$

where

$$g(x) = x^3 - 3x \text{ and } h(x) = e^{-x^2}$$

Here, $g(x)$ is an odd function and $h(x)$ is an even function. The product is an odd function. This property is summarized for any $f(x) = g(x)h(x)$, in the following table.

g(x)	h(x)	f(x)	ig(x)=__g(x)	ih(x)=__h(x)	if(x)=__f(x)
even	even	even	1	1	1
even	odd	odd	1	-1	-1
odd	odd	even	-1	-1	1

Note that the eigenvalue (+1 or –1) is simply the character of the inversion operation for the irreducible representation by which the function transforms! In a similar manner, any function that can be expressed as a product of functions (like the integrand in the transition moment matrix element) can be determined as the direct product of the irreducible representations by which each part of the product transforms.

Consider the point group C_{2v} as an example. Recall the character table for this point group.

C_{2v}	E	C_2	σ_v	σ_v ’			
A_1	1	1	1	1	z		$x^2 - y^2$, z^2
B_2	1	-1	-1	1	y	R_x	yz
B_1	1	-1	1	-1	x	R_y	xz
A_2	1	1	-1	-1		R_z	xy

The direct product of irreducible representations can by the definition

$$\chi_{prod}(R) = \chi_i(R) \otimes \chi_j(R)$$

So for the direct product of B_1 and B_2, the following table can be used.

C_{2v}	E	C_2	σ_v	σ_v ’
B_1	1	-1	1	-1
B_2	1	-1	-1	1
$B_1 \otimes B_2$	1	1	-1	-1

The product is actually the irreducible representation given by A_2 ! As it turns out, the direct product will always yield a set of characters that is either an irreducible representation of the group, or can be expressed as a sum of irreducible representations. This suggests that a multiplication table can be constructed. An example (for the C_{2v} point group) is given below.

Studying this table reveals some useful generalizations. Two things in particular jump from the page. These are summarized in the following tables.

	A	B
A	A	B
B	B	A

	1	2
1	1	2
2	2	1

C_{2v}	A_1	A_2	B_1	B_2
A_1	A_1	A_2	B_1	B_2
A_2	A_2	A_1	B_2	B_1
B_1	B_1	B_2	A_1	A_2
B_2	B_2	B_1	A_2	A_1

This pattern might seem obvious to some. It stems from the idea that

*symmetric*symmetric = symmetric*

*symmetric*antisymmetric = antisymmetric*

*antisymmetric*antisymmetric = symmetric*

Noting that A indicates that an irreducible representation is *symmetric* with respect to the C_2 operation and B indicates that an irreducible representation is *antisymmetric* . . and that the subscript 1 indicates that an irreducible representation is *symmetric* with respect to the σ_v operation, and that a subscript 2 indicates that an irreducible representation is *antisymmetric* . . the rest seems to follow! Some point groups have irreducible representations use subscripts g/u or primes and double primes. The g/u subscript indicates symmetry with respect to the inversion (i) operator, and the prime/double prime indicates symmetry with respect to a σ plane (generally the plane of the molecule for planar molecules).

This method works well for singly degenerate representations. But what does one do for products involving doubly degenerate representations? As an example, consider the C_{3v} point group.

C_{3v}	E	2 C_3	$3\sigma_v$		
A_1	1	1	1	z	
A_2	1	1	-1		R_z
E	2	-1	0	(x, y)	(R_x, R_y)

Consider the direct product of A_2 and E.

C_{3v}	E	2 C_3	3 σ_v
A_2	1	1	-1
E	2	-1	0
$A_2 \otimes E$	2	-1	0

This product is clearly just the E representation. Now one other example – Consider the product $E \otimes E$.

C_{3v}	E	2 C_3	$3\sigma_v$
E	2	-1	0
E	2	-1	0
$E \otimes E$	4	1	0

To find the irreducible representations that comprise this reducible representation, we proceed in the same manner as determining the number of vibrational modes belonging to each symmetry.

$$\begin{aligned} N_{A_1} &= \frac{1}{6}[(1)(4)+2(1)(1)+3(1)(0)] = 1 \\ N_{A_2} &= \frac{1}{6}[(1)(4)+2(1)(1)+3(-1)(0)] = 1 \\ N_E &= \frac{1}{6}[(2)(4)+2(-1)(1)+3(0)(0)] = 1 \end{aligned}$$

This allows us to build a table of direct products. Notice that the direct product always has the total dimensionality that is given by the product of the dimensions.

C_{3v}	A_1	A_2	E
A_1	A_1	A_2	E
A_2	A_2	A_1	E
E	E	E	$A_1 + A_2 + E$

The concepts developed in this chapter will be used extensively in the discussions of vibrational, rotational and electronic degrees of freedom in atoms and molecules.

3.10: Vocabulary and Concepts

abelian

abelian group

character

class

closed

commutative

complementary

direct product

Great Orthogonality Theorem

group

group multiplication table

Group Theory

identity element

inverse

irreducible representations

multiplication operation

order

principle rotation axis

representation

Scheonflies notation

similarity transform

symmetry element

symmetry operations

totally symmetric representation

3.11: Problems

1. Find the symmetry elements and point groups for the following molecules
   a. SF_4
   b. $CHCl_3$
   c. Pyridine
   d. Naphthalene
   e. ICl_5
   f. PCl_5

2. Consider diazine, which has three isomers. Determine which isomer(s) has/have C_{2v} symmetry and which has/have D_{2h} symmetry.
3. Complete the following character table.

	E	2 A	2 B	C	3 D	3 F
A_1	1	1	1	1	1	1
A_2	1	1	1	1	-1	-1
B_1			1			
B_2	1	-1	1	-1	-1	1
E_1			1			
E_2			-1			

4. Complete the following direct product table.

C_{4h}	A_g	B_g	E_g	A_u	B_u	E_u
A_g	A_g	B_g	E_g	A_u	B_u	E_u
B_g	B_g					
E_g	E_g		$A_g+B_g+E_g$			$A_u+B_u+E_u$
A_u	A_u			A_g		
B_u	B_u					
E_u	E_u					

5. Consider the following group multiplication table. Separate the operations into classes.

	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	B	E	F	C	D
B	B	E	A	D	F	C
C	C	D	F	E	A	B
D	D	F	C	B	E	A
F	F	C	D	A	B	E

6. Demonstrate that the A_2, B_1, B_2 and E irreducible representations are orthogonal to the A_1 irreducible representation under the point group C_{4v}.

7. A point group has 8 operations which fall into five classes. How many irreducible representations will it have? How many will be singly degenerate? How many will be doubly degenerate?

CHAPTER OVERVIEW

4: The Harmonic Oscillator and Vibrational Spectroscopy

One of the four important problems in quantum mechanics that can be solved analytically is that of the Harmonic Oscillator. This problem is very important to chemists as it provides the model for vibrating molecules and explains what we see in infrared and Raman spectra of molecules. In this chapter we will develop the problem, discuss the limitations of the simple problem and how we deal with them, and the applications of the conclusions to molecular spectroscopy and the measurement of molecular properties.

4.1: The Potential Energy Surface for a Diatomic Molecule

5.2: The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the MoleculeConsider the **potential energy surface** for a diatomic molecule. The functional form can be seen in the following graph.

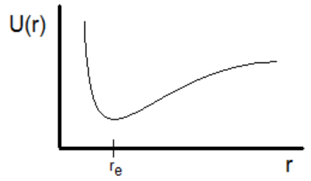


Figure 4.1.1

In the surface, it is easy to see the “hard wall” on the left side, where the repulsive force between atoms is strong (which is why the curve is so steep) and the “soft wall” on the right side of the well, where the restorative force of the chemical bond exists. The bond length at the potential minimum is indicated by r_e, the equilibrium bond length.

The function can be expressed as a Taylor series expansion. For convenience, we can define $x = (r - r_e)$. We will also define the zero of energy to be the bottom of the potential well. Given these definitions and the Taylor expansion about $x = 0$ which can be expressed by

$$U(x) = U(0) + \frac{d}{dx}U(x)\bigg|_{x=0}(x) + \frac{1}{2}\frac{d^2}{dx^2}U(x)\bigg|_{x-0}(x^2) + \frac{1}{6}\frac{d^3}{dx^3}U(x)\bigg|_{x-0}(x^3) + \cdots$$

We can evaluate these terms qualitatively based on the above diagram and the definitions provided above. The first two terms of the expansion are zero, by the choice of the zero of energy and because the derivative is zero at the potential minimum. The third and fourth terms are simplified by making the following substitutions

$$\frac{d^2}{dx^2}U(x)\bigg|_{x-0} \equiv k \text{ and } \frac{d^3}{dx^3}U(x)\bigg|_{x-0} \equiv \gamma$$

The new function can be rewritten as

$$U(x) = \frac{1}{2}k\,x^2 + \frac{1}{6}\gamma\,x^3 + \cdots$$

And if the series is truncated at the x^2 term, it yields the familiar Harmonic Oscillator potential energy function that corresponds to a Hook’s Law oscillator.

$$U(x) = \frac{1}{2}k\,x^2$$

Transforming to Center of Mass Coordinates

Consider a diatomic molecule that can be modeled as two masses (m_1 and m_2) attached by a spring that has a force constant k. The location of atom 1 is z_1 and that of atom 2 is z_2. The equilibrium length of the spring is r_e.

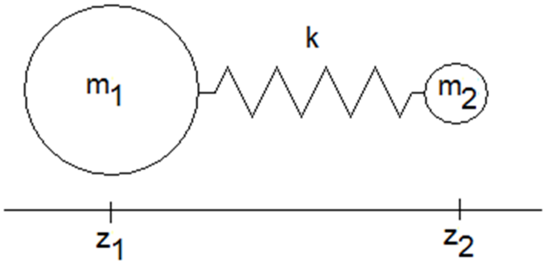


Figure 4.1.2

The force acting on either atom can be expressed in two ways.

$$F = ma$$

and

$$F = -kx$$

where m is either m_1 or m_2 and x is the displacement from the equilibrium distance, given by

$$x = (z_2 - z_1 - r_e)$$

The force acting on atom 1 is in the opposite direction of that acting on atom 2. This suggests two equations that will govern the motion of atom 1 and atom 2 respectively.

$$m_1 \frac{d^2}{dt^2} z_1 = k\left(z_2 - z_1 - r_e\right) \quad \text{and} \quad -m_2 \frac{d^2}{dt^2} z_2 = k\left(z_2 - z_1 - r_e\right)$$

Dividing both equations by the masses yields the following pair of equations.

$$\frac{d^2}{dt^2} z_1 = \frac{k}{m_1}\left(z_2 - z_1 - r_e\right) \quad \text{and} \quad -\frac{d^2}{dt^2} z_2 = \frac{k}{m_2}\left(z_2 - z_1 - r_e\right)$$

Add these two equations yields

$$\frac{d^2}{dt^2} z_1 - \frac{d^2}{dt^2} z_2 = \left(\frac{1}{m_1} + \frac{1}{m_2}\right) k\left(z_2 - z_1 - r_e\right)$$

The term $\left(\frac{1}{m_1} + \frac{1}{m_2}\right)$ has important significance, as it is the reciprocal of the reduced mass.

$$\left(\frac{1}{m_1} + \frac{1}{m_2}\right) = \frac{m_1 + m_2}{m_1 m_2} = \frac{1}{\mu}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

The reduced mass is introduced as a consequence of moving to center of mass coordinates. It is the mass of a single object that would move with the same frequency of oscillation were it attached to a fixed point by a spring of the same force constant. It is important to note that μ has units of mass. Also, in the limit that m_1 and m_2 have the same value (let's call it m_1)

$$\begin{aligned} \mu &= \frac{m_1 m_1}{m_1 + m_1} \\ &= \frac{m_1^2}{2m_1} = \frac{m_1}{2} \end{aligned}$$

This result makes a great deal of sense because for equal masses, the motion of the molecule will involve equal and opposite motions of the two atoms relative to the center of mass (which will be the middle of the bond.) Thus, a single mass oscillating with the same frequency is moving relative to a distance that is in the middle of the spring. Hence, the mass will have to be half of the mass of one of the atoms, or the frequency would be different.

The other important limit is when one mass is significantly larger than the other. Consider what happens when $m_1 >> m_2$

$$\begin{aligned} \mu &= \frac{m_1 m_2}{m_1 + m_2} \\ &\approx \frac{m_1 m_2}{m_1} = m_2 \end{aligned}$$

This result makes a great deal of sense because if one mass is significantly larger than the other, it will be the light atom that undergoes the larger motion. In the limit that $m_1 = \infty$, the center of mass is located at z_1 and the heavy atom becomes a fixed point in the motion.

The next task is to simplify things further by introducing a mass-weighted coordinate, Z.

$$Z \equiv \frac{m_1 z_1 + m_2 z_2}{m_1 + m_2}$$

This expression gives the location of the center of mass of the molecule. The utility of this substitution is found in taking the difference of the two equations

$$m_1 \frac{d^2}{dt^2} z_1 = k\left(z_2 - z_1 - r_e\right) \quad \text{and} \; -m_2 \frac{d^2}{dt^2} z_2 = k\left(z_2 - z_1 - r_e\right)$$

which yields

$$\begin{aligned} m_1 \frac{d^2}{dt^2} z_1 + m_2 \frac{d^2}{dt^2} z_2 &= 0 \\ \frac{d^2}{dt^2}\left(m_1 z_1 + m_2 z_2\right) &= 0 \end{aligned}$$

Dividing both sides by $(m_1 + m_2\ )$ yields

$$\begin{aligned} \left(\frac{1}{m_1 + m_2}\right) \frac{d^2}{dt^2}\left(m_1 z_1 + m_2 z_2\right) &= 0 \\ \frac{d^2}{dt^2}\left(\frac{m_1 z_1 + m_2 z_2}{m_1 + m_2}\right) &= 0 \end{aligned}$$

Finally, making the substitution for the center of mass

$$\frac{d^2}{dt^2} Z = 0$$

which tells us that the center of mass of the system does not move in time.

4.2: Solving the Schrödinger Equation

It is convenient to make the substitution that

$$x = (z_2 - z_1 - r_e)$$

This allows us to write the Hamiltonian for the system then as

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

where μ is the reduced mass given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

k is the force constant of the bond and x is defined by

$$x = (r - r_e)$$

as previously state. The Schrödinger equation is then given by

$$\left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2\right)\psi(x) = E\psi(x)$$

Energy Levels

The boundary conditions require that the square of the wavefunction must have a finite area below it in order to ensure that the wavefunction is normalizable. The only way this happens is if the following conditions are met

$$\lim_{x\to\pm\infty}\psi(x) = 0$$

The resulting energy levels are the set of eigenvalues that correspond to the functions that satisfy the above stated boundary condition. These energies have values given by

$$E_v = \hbar\sqrt{\frac{k}{\mu}}\,(v + 1/2) \qquad v = 0, 1, 2, 3, \ldots$$

Notice how the use of the boundary conditions is what leads to the instruction of quantized energies.

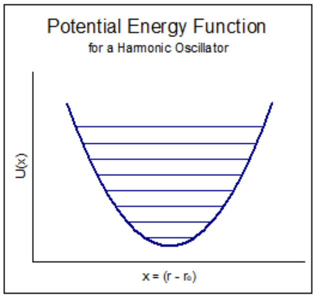


Figure 4.2.2

The resulting energy levels are evenly spaced with increasing energy. The actual spacing is determined by the physical characteristics of a given molecule, namely the reduced mass and the force constant.

Spectroscopic Constants and Force Constants

Vibrational spectroscopy is often done using units of cm^{-1}. Energies expressed in terms of this unit are called **term values**. The termvalue is given as the energy divided by Planck's constant and the speed of light (E/hc). Standard notation uses the symbol G_v to indicate the term value for vibrational energy. G_v is given by

$$G_v = \frac{E_v}{hc} = \omega_e(v + \frac{1}{2})$$

where

$$\omega_e = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

The vibrational constant w_e can be determined experimentally for specific molecules. Consider the following values for various molecules.

Molecule	$\omega_e (cm^{-1})$	**k (N/m)**	μ **(kg)**
$^1H^{35}Cl$	2989.74	516	1.627×10^{-27}
$^1H^{79}Br$	2649.67	412	1.652×10^{-27}
$^1H^{127}I$	2309.5	314	1.660×10^{-27}
$^{19}F^{19}F$	916.64	347	1.577×10^{-26}
$^{16}O^{16}O$	1580.93	1177	1.328×10^{-26}
$^{14}N^{14}N$	2359.61	3116	1.163×10^{-26}

Two important points can be made from this data. First, a typical force constant for a single bond is on the order of a couple hundred N/m. Secondly, multiple bonds lead to significantly larger force constants. This is not too surprising since the force constant gives a measure of the stiffness of the bond.

The Wavefunctions

The wavefunctions for the harmonic oscillator are determined by solving the Schrödinger equation. As stated before, the only wavefunctions that obey the boundary conditions have eigenvalues given by

$$E_v = \hbar\sqrt{\frac{k}{\mu}}(v + {}^1\!/_2)$$

where $v = 0, 1, 2, 3, \ldots$ The wavefunctions themselves can be determined by solving the differential equation using a power-series solution. In the end, we find that the resulting function involve a set of **orthogonal polynomials** known as the **Hermite Polynomials**. We will discuss some properties of this important set of functions before discussing the wave functions themselves.

Hermite Polynomials

The **Hermite polynomials** are a set of orthogonal polynomials. Like all sets of orthogonal polynomials, they have 1) a generator formula, 2) an orthogonality relationship and 3) a (or several) recursion relations that relate one function in the series to others.

The Hermite polynomials can be generated using the following function

$$H_v(y) = (-1)^v e^{y^2} \frac{d^v}{dy^v} e^{-y^2}$$

Using this function, the first few Hermite polynomials can be generated.

v	$H_v(y)$
0	1
1	2y
2	$4y^2 - 2$

Further members of the set of functions can be generated using one of the important recursion relations.

$$H_{v+1}(y) = 2yH_v(y) - 2vH_{v-1}(y)$$

Using this function, we can generate a longer list of Hermite polynomials without having to take so many derivatives.

v	$H_v(y)$
0	1
1	$2y$
2	$4y^2-2$
3	$8y^3-12y$
4	$16y^4-48y^2+12$
5	$32y^5-160y^3+120y$
	Etc.

Another important relationship between these functions is that

$$\frac{d}{dy}H_v(y) = 2vH_{v-1}(y)$$

In addition to these relationships, the Hermite polynomials have an important orthogonality relationship.

$$\int_{-\infty}^{\infty} H_v(y)H_{v'}(y)e^{-y^2}\,dy = v!2^v\sqrt{\pi}\delta_{vv'}$$

The Hermite polynomials also have important symmetry properties. Each function in the set is an eigenfunction of the **inversion operator**. The inversion operator is a symmetry operator that is defined by the operation (in one dimension)

$$\hat{i}\,f(x) = f(-x)$$

Functions that are eigenfunctions of this operator can be classified as being either **even function** or **odd function**.

Even	$f(-x) = f(x)$
Odd	$f(-x) = -f(x)$

Even functions are **symmetric** eigenfunctions of the inversion operator and odd functions are **antisymmetric** eigenfunctions as their eigenvalues are +1 and -1 respectively. Even and odd functions also have important properties when integrated over symmetric intervals.

Even	$\int_{-a}^{a} f(x)dx = 2\int_{0}^{a} f(x)dx$
Odd	$\int_{-a}^{a} f(x)dx = 0$

These properties can greatly simplify integration involving these types of functions!

The Harmonic Oscillator Wavefunctions

The wavefunctions for the Harmonic Oscillator have three important parts: 1) a normalization constant, 2) a Hermite polynomial and 3) an exponential function that insures the orthogonality of the wavefunctions.

$$\psi_v(x) = N_v H_v\left(\alpha\frac{1}{2}x\right)e^{-\alpha x^2/2}$$

where

$$\alpha = \sqrt{k\cdot\mu} \text{ and } N_v = \sqrt{\frac{\sqrt{\alpha/\pi}}{2^v\cdot v!}}$$

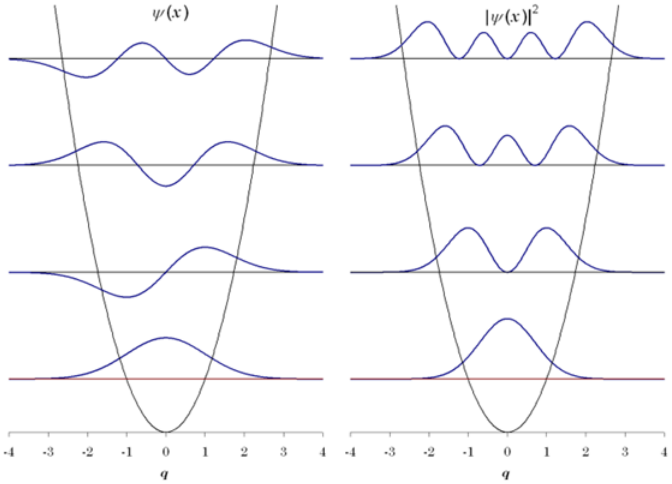


Figure 4.2.3

Expectation Values

The simplicity of the wavefunctions makes the calculation of expectation values very simple for the harmonic oscillator problem.

Position

The expectation value of position can be determined solely based on symmetry arguments. Recall that harmonic oscillator wavefunctions are either even or odd functions. The symmetry of the products of even or odd functions can be summarized as follows.

	even	odd
even	even	odd
odd	odd	even

It is easy to recognize this multiplication table as arising from taking the products of the eigenvalues of the functions with respect to the inversion operator.

	1	-1
1	1	-1
-1	-1	1

These results will be used to demonstrate that the expectation value of position is the same for all of the stationary wavefunction. Consider the integral required to calculate this value.

$$\langle x\rangle = \int_{-\infty}^{\infty} \psi_v \cdot x \cdot \psi_v dx$$

The wavefunction ψ_v is either an even or odd function depending only on whether v is even or odd. Since the $\hat{x}$ operator is itself an odd function (always), there are only two possibilities for the total symmetry of the integrand.

ψ_v	**x**	ψ_v	**Integrand Symmetry**
even	odd	even	odd
odd	odd	odd	odd

The pattern emerges due to the fact that the product of even and odd function produces a resulting function according to the following symmetry multiplication table.

Regardless of whether the wavefunction is an even or odd function, the product

$\psi_v \cdot x \cdot \psi_v$

is always an odd function. And as we have seen before, the integral of an odd function over any symmetric interval is zero by symmetry.

Therefore, the expectation value of x, $\langle x \rangle$, is always 0 for any eigenstate of the harmonic oscillator. The means that $\langle r \rangle = r_e$, the equilibrium bond length.

Momentum

The evaluation of the expectation value of momentum can be made following the same symmetry arguments. In order to do this, one must consider the effect of taking a derivative of a function.

Consider the following even function

$$f(x) = 4x^2 - 2$$

The first derivative of this function is given by

$$\frac{d}{dx} f(x) = 8x$$

which is an odd function. The derivative of this function

$$\frac{d}{dx} 8x = 8$$

yields an even function. The following set of properties will hold for the symmetries of functions and their derivatives.

$f(x)$	$\frac{d}{dx} f(x)$
even	odd
odd	even

As such, the symmetry of the integrand for the calculation of the expectation value of momentum

$$\int_{-\infty}^{\infty} \psi_v \hat{p} \psi_x dx$$

must always be an odd function, since the $\hat{p}$ takes the first derivative of the wavefunction.

ψ_v	$p \cdot \psi_v$	**Integrand Symmetry**
even	odd	odd
odd	even	odd

The result is that the expectation value of momentum, $\langle p \rangle$, must also be 0 for any eigenstate of the harmonic oscillator problem. Again, this can be reasoned by noting that half of the time the momentum measured will be in the direction of the bond stretching, and the other half of the time in the direction of the bond being compressed. On average, these two circumstances will cancel, yielding an average value of $\langle p \rangle = 0$.

Energy

As with any eigenstate, the expectation value of energy $\langle E \rangle$ is easy to calculate. Recall that the wavefunctions were determined to be eigenfunctions of the Hamiltonian.

$$\hat{H} \psi_v = E_v \psi_v$$

As such, The expectation value of energy is trivially easy to find for a system in an eigenstate.

$$\begin{aligned}\langle E\rangle &= \int_{-\infty}^{\infty} \psi_v \hat{H} \psi_v dx \\ &= \int_{-\infty}^{\infty} \psi_v E_v \psi_v dx \\ &= E_v \int_{-\infty}^{\infty} \psi_v \psi_v dx \\ &= E_v\end{aligned}$$

since the wavefunctions are normalized. The expectation value of energy is always an eigenvalue of the Hamiltonian for a system that is in an eigenstate of the Hamiltonian.

Tunneling

One of the curious consequences of quantum mechanics can be seen in the form of **tunneling**. This odd behavior becomes possible whenever the square of the wavefunction extends beyond a classical barrier to the motion of the particle r molecule. In the case of the harmonic oscillator, this is seen as possible since the squared wavefunction extends beyond the classical turning points of the oscillation.

The classical turning point is defined as the point in the motion where all energy has been converted from kinetic energy to potential energy. At this point, the motion switches direction as potential energy is converted back into kinetic energy. Since there is a non-zero value of the squared wavefunction beyond this point for all eigenstates, there is a non-zero probability of measuring the position of the system to lie beyond these classical turning points. And then if there is a new potential well accessible if the system tunnels through the classical barrier, there is a non-zero probability of finding the system in that well, meaning that the system may have changed states completely!

This result is another example of the bizarreness of quantum mechanics. If one were to consider a classical ball that is thrown against the wall at the front of the classroom, one expects that the ball will return to the thrower after bouncing off the wall every time. But for a quantum mechanical ball, there is a non-zero possibility of finding the ball on the other side of the wall! If this were to be the case, the ball would have been said to have tunneled through the wall.

The probability for this happening is proportional to that fraction of the area under the squared wavefunction curve that lies beyond the classical barrier. This probability will be decreased for heavier objects as the fraction of wavefunction beyond the classical barrier will be smaller.

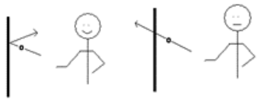


Figure 4.2.4

4.3: Strengths and Weaknesses

Keeping in mind that the harmonic oscillator model is an approximate model, it should not come as a surprise that there are a number of shortcomings to it.

The harmonic oscillator does not place any constraints on bond length. At the short bond length side of the potential, there is nothing in the model to prevent the bond length from becoming zero or even negative (implying that it is possible for one atom to pass through the other in a molecule. Additionally, the harmonic oscillator does not allow for molecular dissociation as the potential energy just keeps increasing with increasing bond length. None the less, the harmonic oscillator model works quite well for small displacements from the equilibrium bond length.

The Morse Potential

One improved form of a potential energy function was provided by Phillip Morse (Morse, 1929). The Morse potential is given by the following function

$$U(r) = D_e \left(1 - e^{-\beta(r-r_e)}\right)^2$$

where D_e is the dissociation energy of the molecule. While this function still allows for negative bond lengths, it does allow for molecular dissociation at long bond lengths.

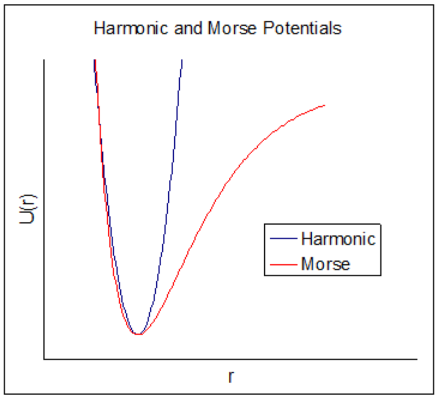


Figure 4.3.1

The force constant for the Morse potential is determined by evaluating the second derivative of the potential energy function at the potential minimum.

$$k = \frac{d^2}{dr^2} U(r) \Big|_{r=r_e}$$

Based on the expression given above for the Morse potential, the following result is obtained.

$$k = 2D_e\beta^2$$

Anharmonicity

A solution to the Schrödinger equation using the Morse potential produces an additional constant in the energy expression for vibrational energy.

$$G_v = \omega_e(v + 1/2) - \omega_e x_e (v + 1/2)^2$$

The new constant, $\omega_e x_e$, is called an **anharmonicity constant**, as it accounts for deviation from the harmonic potential. For a more general potential energy function, the expression for the vibrational term value can be expressed as a longer power series in $(v + ½)$.

$$G_v = \omega_e(v + 1/2) - \omega_e x_e (v + 1/2)^2 + \omega_e y_e (v + 1/2)^3 + \cdots$$

For well-behaved molecules, the magnitude of the anharmonicity constants decreases with increasing order in $(v + ½)$. Thus, the series can be truncated at some point and will provide an adequate model for the purposes of fitting experimental data.

4.4: Vibrational Spectroscopy Techniques

Infrared and Raman spectroscopy are two experimental methods that are commonly used by chemists to measure vibrational frequencies (ω_e). Infrared spectroscopy generally involves direct absorption whereas Raman spectroscopy involves scattering of light.

Infrared Spectra

Infrared spectroscopy is a commonly used technique in the identification of molecular compounds. It is also a very convenient technique to use in determining molecular force constants, since the spectrum records vibrational frequencies.

Based on the results of the harmonic oscillator problem, the selection rules for an infrared spectrum are determined to be

$$\Delta v = \pm 1$$

That means that as a molecule absorbs or emits a single infrared photon (meaning the electronic state of the molecule does not change) the vibrational quantum number can go up or down (depending on absorption or emission) by one quantum. For a typical experiment, the theory predicts a single band in the spectrum of a molecule, and that band will be centered at a frequency equal to ω_e for the molecule.

A schematic diagram of a typical infrared absorption spectroscopy experiment is shown below. The light is produced at the source (typically an incandescent light bulb or a glowbar), passes through the sample where some of the light can be absorbed, and then the monochrometer (which is typically either a grating or an interferometer) which is used to distinguish between the various frequencies of light, and finally the light is detected by a detector. Plotting detected intensity as a function of frequency produces the spectrum.

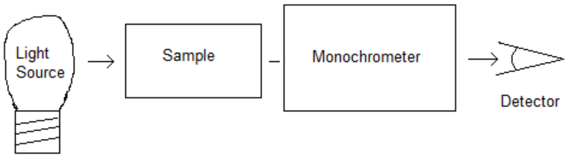


Figure 4.4.1

Determining a Force Constant

Consider the experimentally determined we value for carbon monoxide (CO.) The spectrum shows a strong absorption at $2143\ cm^{-1}$ due to CO. Using this value for ω_e (it is actually a little off due to anharmonicity), the force constant can be determined for the molecule.

$$\omega_e = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

Using a value of 1.14×10^{-26} kg for the reduced mass of the molecule, the force constant is found to be 1856 N/m. The literature value for this force constant is $1860\ cm^{-1}$. Given that this calculation did not treat anharmonicity, the agreement is pretty good!

Progressions in Electronic Spectra

Electronic transition in diatomic molecules which can be observed in the visible and ultraviolet regions of the spectrum can have a great deal of vibrational structure as the molecule is free to vibrate in both the upper and lower states. Figure $4.4.2$ shows vibrational progressions in the emission spectrum of AlBr near 2800 Å (Fleming & Mathews, 1996).

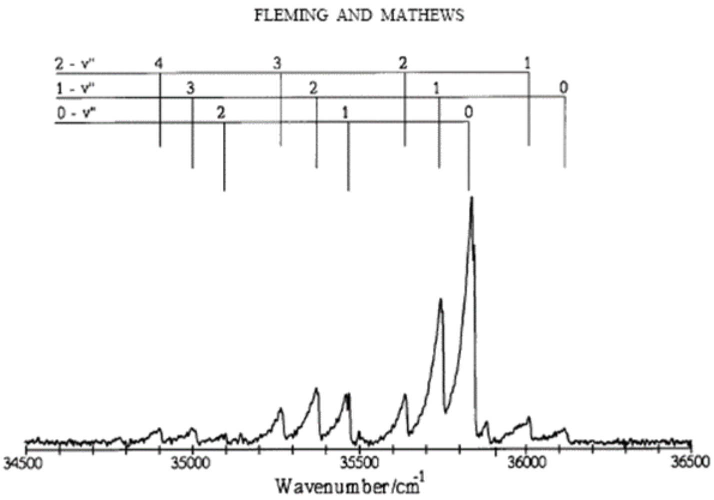


Figure 4.4.2: A-X transition of AlBr near 2800 Å.

These progressions can be analyzed to provide dissociation energies for the electronic states involved in the transition.

If the vibrational energy function is truncated at the $\omega_e x_e$ level (as predicted by the Morse potential) the vibrational term value will reach a maximum value at some value of v. Any further vibrational excitation is predicted to lower the molecular energy. This is actually the **dissociation limit**. Therefore, the maximum value of v for a bound state (v_{max}) is the largest value of v for which the vibrational energy spacing is positive. The dissociation energy of the molecule is then given by the sum of vibrational energy spacings from $v = 0$ to $v = v_{max}$.

Determining a Dissociation Energy

To find the value of the dissociation energy, it is convenient to define the difference between successive vibrational terms as

$$\Delta G_{v+1/2} \equiv G_{v+1} - G_v$$

Using the expression for G_v as predicted by the Morse potential,

$$\begin{aligned} \Delta G_{v+1/2} = &\ \omega_e(v+3/2) - \omega_e x_e(v+3/2)^2 - \omega_e(v+1/2) - \omega_e x_e(v+1/2)^2 \\ &= \omega_e(v+3/2-v-1/2) - \omega_e x_e\left(v^2+3v+9/4-v^2-v-1/4\right) \\ &= \omega_e - \omega_e x_e(2v+2) \\ &= \omega_e - 2\omega_e x_e(v+1) \end{aligned}$$

This suggests that a set of values of $\Delta G_{v+1/2}$ vs. $(v+1)$ should yield a straight line with a slope equal to -2ω_e x_e and an intercept equal to ω_e. And v_{max} is determined by setting $\Delta G_{v+\frac{1}{2}}$ to zero and solving for v (Figure 4.4.3).

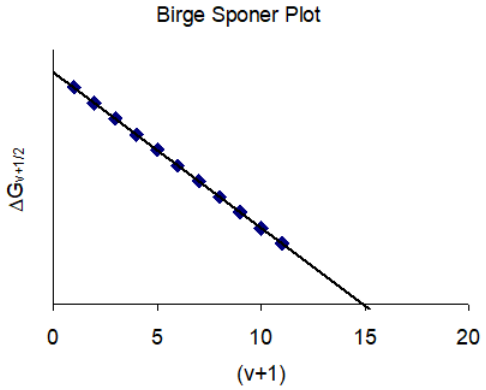


Figure 4.4.3: Birge-Sponer method to determine the dissociation energy of a molecule from the vibrational spacings.

The **Birge-Sponer method** (Gaydon, 1946) can be used to determine the sum of vibrational spacings, and thus the dissociation of a molecule. The method involves plotting $\Delta G_{v+\frac{1}{2}}$ vs. $(v+1)$. The dissociation energy is taken as the area under the curve.

Vibrations of Polyatomic Molecules

Nonlinear molecules have $3N-6$ vibrational degrees of freedom, where N is the number of atoms in the molecule. Thus, a triatomic molecule such as water has three vibrational degrees of freedom. These account for the three vibrational modes of water (symmetric stretch, bend and antisymmetric stretch.)

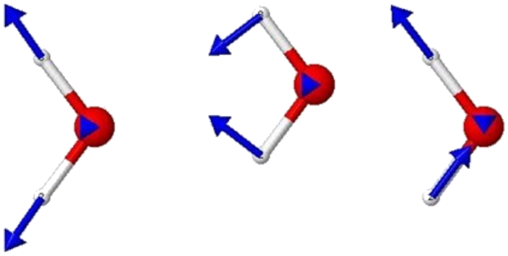


Figure 4.4.4

Each mode will have a characteristic frequency. If each mode is treated as a harmonic oscillator, the total vibrational energy is given by

$$G = \sum_{i=1}^{3N-6} \omega_i (v_i + 1/2)$$

where ω_i is the frequency of the i^{th} vibrational mode, and v_i is the quantum number indicating the number of quanta of the i^{th} mode excited. If anharmonicity is to be included, the expression becomes

$$G = \sum_{i=1}^{3N-6} \omega_i (v_i + 1/2) - \sum_{i=1}^{3N-6} \sum_{j=1}^{3N-6} x_{ij} (v_i + 1/2)(v_j + 1/2)$$

where x_{ij} is the anharmonicity term that couples the vibrational modes.

4.5: Group Theory Considerations

Group theory provides a powerful set of tools for predicting and interpreting vibrational spectra. In this section, we will consider how Group Theory helps us to understand these important phenomena.

Transformation of Axes and Rotations

It is possible to determine the symmetry species or irreducible representation by which each of the three Cartesian coordinate axes transform. This is useful, particularly in determining selection rules in spectroscopy, as the components of a molecule's dipole moment will transform as these axes. The rotations are also useful in understanding the rotational selection rules.

Recall the character table for the C_{2v} point group.

$\boldsymbol{C_{2v}}$	E	$\boldsymbol{C_2}$	$\boldsymbol{\sigma_v}$	$\boldsymbol{\sigma_v}$ '
$\boldsymbol{A_1}$	1	1	1	1
$\boldsymbol{A_2}$	1	1	-1	-1
$\boldsymbol{B_1}$	1	-1	1	-1
$\boldsymbol{B_2}$	1	-1	-1	1

It is useful to determine how each axis (x, y and z) is transformed under each symmetry operation. Once this is done, it will be easy to determine the representation that transforms the axis in this way. A table might be useful. Recalling our designation of the σ_v operation as reflection through the xz plane, it can be shown easily that the axes transform as follows:

$\boldsymbol{C_{2v}}$	E	$\boldsymbol{C_2}$	$\boldsymbol{\sigma_v}$	$\boldsymbol{\sigma_v}$ '
x	x	-x	x	-x
y	y	-y	-y	y
z	z	z	z	z

The z-axis is unchanged by any of the symmetry operations. Another way of saying this is that the z-axis is symmetric with respect to all of the operations. (In this point group, all of the symmetry elements happen to intersect on the z-axis, which is why it is unchanged by any of the symmetry operations.) The conclusion is that the z-axis transforms with the A_1 representation.

The other axes can be described the same way. Note that the x-axis is symmetric with respect to the σ_v operation and the E operation. (Everything is symmetric with respect to the E operation, oddly enough.) The x-axis is antisymmetric, however, with respect to the σ_v ' and C_2 operations. The results for all axes can be summarized in the character table.

$\boldsymbol{C_{2v}}$	E	$\boldsymbol{C_2}$	$\boldsymbol{\sigma_v}$	$\boldsymbol{\sigma_v}$ '	
$\boldsymbol{A_1}$	1	1	1	1	z
$\boldsymbol{A_2}$	1	1	-1	-1	
$\boldsymbol{B_1}$	1	-1	1	-1	x
$\boldsymbol{B_2}$	1	-1	-1	1	y

Rotations about the x, y and z axes can be characterized in a similar fashion. Consider the angular momentum vector for each rotation and how it transforms. Such a vector can be constructed using he right-hand rule. If the fingers on your right hand point in the direction of the rotation, your thumb points in the direction of the angular momentum vector.

Rotation about the z-axis (R_z) is symmetric with respect to the operations E and C_2, but antisymmetric with respect to operations σ_v and σ_v '. Rotation about the x-axis is symmetric with respect to E and C_2. Clearly, this operation transforms as the irreducible representation A_2. Rotation about the x-axis and y-axis can also be characterized as following the properties of the B_2 and B_1 representations respectively. As such, the character table for C_{2v} can be augmented to include this information.

C_{2v}	E	C_2	σ_v	σ_v ’		
A_1	1	1	1	1	z	
A_2	1	1	-1	-1		R_z
B_1	1	-1	1	-1	x	R_y
B_2	1	-1	-1	1	y	R_x

Another interpretation of the transformation of the x, y and z-axes is that the representations that indicate the symmetries of these axes in the point group also indicate how the p_x, p_y and p_z orbitals transform. The set of d orbital wavefunctions can also be used. These transformations are generally given in another column in the character table. (This information is also useful for calculating polarizabilities, and hence selection rules for Raman transitions!)

C_{2v}	E	C_2	σ_v	σ_v ’			
A_1	1	1	1	1	z		x^2 -y^2, z^2
A_2	1	1	-1	-1		R_z	xy
B_1	1	-1	1	-1	x	R_y	xz
B_2	1	-1	-1	1	y	R_x	yz

Characterizing Vibrational Modes

Vibrational wave functions describing the normal modes of vibrations will be eigenfunctions of the symmetry properties of the group. As such, group theory can be quite useful in determining the vibrational selection rules needed to predict infrared spectra.

The number of vibrational degrees of freedom for a molecule is given by ($3N-6$) if the molecule is non-linear and ($3N-5$) if it is linear. In these expressions, N is the number of atoms in the molecule. One way to think of these numbers is that it takes 3N Cartesian coordinates (an x, y and z variable) for each atom in the molecule to fully specify the structure of a molecule. As such, 3N is the total number of degrees of freedom.

Since the molecule can translate through space in the x, y or z directions, three (3) degrees of freedom belong to translation. One can also think of these three degrees of freedom being the three Cartesian coordinates needed to specify the location of the center of mass of the molecule – or for the translation of the center of mass of the molecule.

For non-linear molecules, rotation can occur about each of the three Cartesian axes as well. So three (3) degrees of freedom belong to rotation for non-linear molecules. Linear molecules only have rotational degrees of freedom about the two axes that are perpendicular to the molecular axis (which remember is the C axis – and thus the z-axis.) So linear molecules only have two (2) rotational degrees of freedom.

The sum of the irreducible representations by which the vibrational modes transform can be found fairly easily using group theory. The first step is to determine how the three Cartesian axes transform under the symmetry operations of the point group. As an example, let’s use water (H_2O), which belongs to the C_{2v} point group since it is familiar. Later, we will work though a more complex example.

Consider the character table for the C_{2v} point group.

C_{2v}	E	C_2	σ_v	σ'_v			
A_1	1	1	1	1	z		x^2-y^2, z^2
A_2	1	1	-1	-1		R_z	xy
B_1	1	-1	1	-1	x	R_y	xz
B_2	1	-1	-1	1	y	R_x	yz

The sum of the representations by which the axes transform will be given by $B_1+B_2+A_1$.

C_{2v}		E	C_2	σ_v	σ_v ’	
Γ_1	A_1	1	1	1	1	z
Γ_2	B_1	1	-1	1	-1	x
Γ_3	B_2	1	-1	-1	1	y
Γ_{xyz}	$A_1+B_1+B_2$	3	-1	1	1	

The reducible representation (Γ_{xyz}) is then multiplied by the representation generated by counting the number of atoms in the molecule that remain unmoved by each symmetry element. This representation for water is generated as follows:

C_{2v}	E	C_2	σ_v	σ_v ’
O	✓	✓	✓	✓
H_1	✓	-	-	✓
H_2	✓	-	-	✓
$\Gamma_{unmoved}$	3	1	1	3

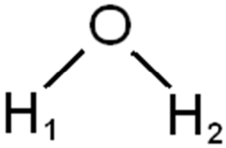


Figure 4.5.1

The reducible representation that describes the transformation of the Cartesian coordinates of each of the atoms in the molecule are given by the product of $\Gamma_{xyz} \cdot \Gamma_{unmoved}$ as shown in the following table.

C_{2v}	E	C_2	σ_v	σ_v ’
Γ_{xyz}	3	-1	1	1
$\Gamma_{unmoved}$	3	1	1	3
$\Gamma_{total}=\Gamma_{xyz} \cdot \Gamma_{unmoved}$	9	-1	1	3

Note that the order of Γ_{total} is given by $3N$. This is the sum of representations needed to describe the transformation of each of the Cartesian coordinates for each atom. f the representation for the Cartesian coordinates (Γ_{xyz}) is subtracted from Γ_{total}, the remainder describes the sum of representations by which the rotations and vibrations transform, and this result should be of order ($3N-3$). Let’s see . . .

C_{2v}	E	C_2	σ_v	σ_v ’
Γ_{total}	9	-1	1	3
Γ_{xyz}	3	-1	1	1
$\Gamma_{vib+rot}$	6	0	0	2

So far, so good. Now let’s subtract the sum of the representations by which the rotations transform. The remainder of this operation should be of order ($3N-6$) and give the sum of irreducible representations by which the vibrations transform.

C_{2v}	E	C_2	σ_v	σ_v ’
$\Gamma_{vib+rot}$	6	0	0	2

C_{2v}	E	C_2	σ_v	σ_v ’
Γ_{rot}	3	-1	-1	-1
Γ_{vib}	3	1	1	3

C_{2v}	E	C_2	σ_v	σ_v ’
A_1	1	1	1	1
A_1	1	1	1	1
B_2	1	-1	-1	1
Γ_{vib}	3	1	1	3

A quick calculation shows that this result is generated by the sum of $A_1 + A_1 + B_2$. To see this, we can use the Great Orthogonality Theorem. (I told you it was *great*!) In this case, the number of vibrational modes that transform as the i^{th} irreducible representation is given by the relationship

$$N_i = \frac{1}{h}\sum_R \chi_i(R)\chi_{vib}(R)$$

For the A_1 representation, this sum looks as follows.

$$\begin{aligned} N_{A_1} &= \frac{1}{h}\left(\chi_{A_1}(E)\cdot\chi_{vib}(E)+\chi_{A_1}(C_2)\cdot\chi_{vib}(C_2)+\chi_{A_1}(\sigma_v)\cdot\chi_{vib}(\sigma_v)+\chi_{A_1}(\sigma_v^{'})\cdot\chi_{vib}(\sigma_v^{'})\right) \\ &= \frac{1}{4}((1)\cdot(3)+(1)\cdot(1)+(1)\cdot(1)+(1)\cdot(3)) \\ &= \frac{1}{4}(8) \\ &= 2 \end{aligned}$$

The result for the A_2 representation should come to zero since no vibrational modes transform as A_2. For the A_2 representation, this sum looks as follows.

$$\begin{aligned} N_{A_2} &= \frac{1}{4}((1)\cdot(3)+(1)\cdot(1)+(-1)\cdot(1)+(-1)\cdot(3)) \\ &= \frac{1}{4}(0)=0 \end{aligned}$$

For B_1 and B_2 the sum looks as follows:

$$\begin{aligned} N_{B_1} &= \frac{1}{4}((1)\cdot(3)+(-1)\cdot(1)+(1)\cdot(1)+(-1)\cdot(3)) \\ &= \frac{1}{4}(0)=0 \\ N_{B_2} &= \frac{1}{4}((1)\cdot(3)+(-1)\cdot(1)+(-1)\cdot(1)+(1)\cdot(3)) \\ &= \frac{1}{4}(4)=1 \end{aligned}$$

Let’s see if that makes sense! Consider the three normal-mode vibrations in water. These (the symmetric stretch, the bend and the antisymmetric stretch) can be depicted as follows:

It is fairly simple to show that the symmetric stretch and the bending mode both transform as the A_1 representation. Similarly, the antisymmetric stretching mode transforms as the B_2 representation. (Note that we have chosen the *xz* plane (or the σ_v plane) to lie perpendicular to the molecule!)

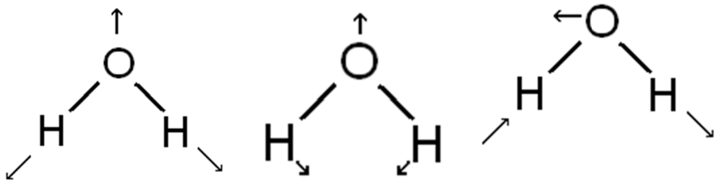


Figure 4.5.2

Example 4.5.1

Find the symmetries of the normal vibrational modes of ammonia.

Solution

Recall the character table for the C_{3v} point group:

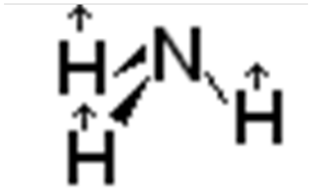
C_{3v}	E	2 C_3	3 \sigma		
A_1	1	1	1	z	
A_2	1	1	-1		R_z
E	2	-1	0	x, y	R_x, R_y

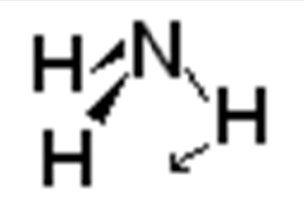
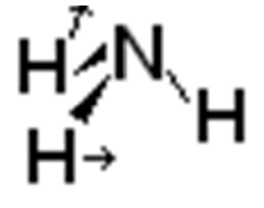
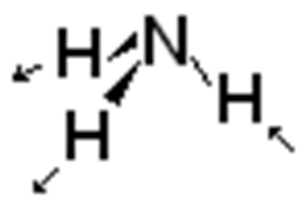
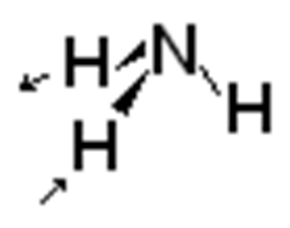
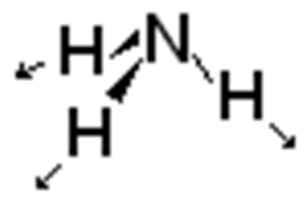
The representation for Γ_{total} can be found in the same way as before. Once we have Γ_{total}, Γ_{vib} is determined as before.

C_{3v}	E	2 C_3	$3\sigma_v$
Γ_{xyz}	3	1	1
$\Gamma_{unmoved}$	4	1	2
Γ_{total}	12	1	2

C_{3v}	E	2 C_3	$3\sigma_v$
Γ_{total}	12	1	2
Γ_{xyz}	3	1	1
Γ_{rot}	3	0	-1
Γ_{vib}	6	0	2

The GOT can be used to find how many modes of each symmetry are present.

Mode		Freq. (cm^{-1})	Sym.
Umbrella		1139	A_1

Mode		Freq. (cm^{-1})	Sym.
Bend	 	1765	E
Antisym. Str.	 	3464	E
Sym. Str.		3534	A_1

$$
\begin{aligned}
N_{A_1} &= \frac{1}{6}[(1)\cdot(6)+2(1)\cdot(0)+3(1)\cdot(2)] \\
&= \frac{1}{6}(12)=2 \\
N_{A_2} &= \frac{1}{6}[(1)\cdot(6)+2(1)\cdot(0)+3(-1)\cdot(2)] \\
&= \frac{1}{6}(0)=0 \\
N_{E} &= \frac{1}{6}[(2)\cdot(6)+2(-1)\cdot(0)+3(0)\cdot(2)] \\
&= \frac{1}{6}(12)=2
\end{aligned}
$$

So there are two (2) A_1 modes and two (2) doubly degenerate E modes of vibration. These can be summarized in the table to the right.

✓ Example 4.5.2: The vibrational modes of SF_4

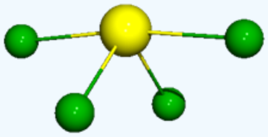


Figure 4.5.3

Solution

SF_4 is an example of a molecule with a "see saw" geometry. It belongs to the point group C_{2v} like water. Let's find the symmetries of the normal modes of vibration using group theory. First, we must generate Γ_{total}.

C_{2v}	E	C_2	σ_v	σ_v'
Γ_{xyz}	3	-1	1	1
$\Gamma_{unmoved}$	5	1	3	3
Γ_{total}	15	-1	3	3

C_{2v}	E	C_2	σ_v	σ_v'
Γ_{total}	15	-1	3	3
Γ_{xyz}	3	-1	1	1
Γ_{rot}	3	-1	-1	-1
Γ_{vib}	9	1	3	3

Now, subtract Γ_{xyz} and Γ_{rot} to generate Γ_{vib} as shown above.

So this implies that there are nine degrees of freedom due to vibration. This is the result we expect since for the 5-atom non-linear molecule, (3N-6) = 9. To generate the number of vibrational modes that transform as the A_1 irreducible representation, the follow expression must be evaluated.

$$\begin{aligned} N_{A_1} &= \frac{1}{h}(\chi_{A_1}(E)\cdot\chi_{vib}(E)+\chi_{A_1}(C_2)\cdot\chi_{vib}(C_2)+\chi_{A_1}(\sigma_v)\cdot\chi_{vib}(\sigma_v)+\chi_{A_1}(\sigma_v')\cdot\chi_{vib}(\sigma_v')) \\ &= \frac{1}{4}((1)\cdot(9)+(1)\cdot(1)+(1)\cdot(3)+(1)\cdot(3)) \\ &= \frac{1}{4}(16) \\ &= 4 \end{aligned}$$

Similarly,

$$\begin{aligned} N_{A_2} &= \frac{1}{4}((1)\cdot(9)+(1)\cdot(1)+(-1)\cdot(3)+(-1)\cdot(3)) \\ &= \frac{1}{4}(4)=1 \\ N_{B_1} &= \frac{1}{4}((1)\cdot(9)+(-1)\cdot(1)+(1)\cdot(3)+(-1)\cdot(3)) \\ &= \frac{1}{4}(8)=2 \\ N_{B_2} &= \frac{1}{4}((1)\cdot(9)+(-1)\cdot(1)+(-1)\cdot(3)+(1)\cdot(3)) \\ &= \frac{1}{4}(8)=2 \end{aligned}$$

So there should be 4 vibrational modes of A_1 symmetry, 1 of A_2 symmetry and two each of B_1 and B_2 symmetry. A calculation of the structure and vibrational frequencies in SF_4 at the B3LYP/6-31G(d) level of theory^1 yields the following.

Mode	Freq. (cm^{-1})	Symmetry	Mode	Freq. (cm^{-1})	Symmetry
1	189	A_1	6	584	A_1
2	330	B_1	7	807	B_2
3	436	A_2	8	852	B_1
4	487	A_1	9	867	A_1
5	496	B_2			

The calculation also allows for the simulation of the infrared spectrum of SF_4.

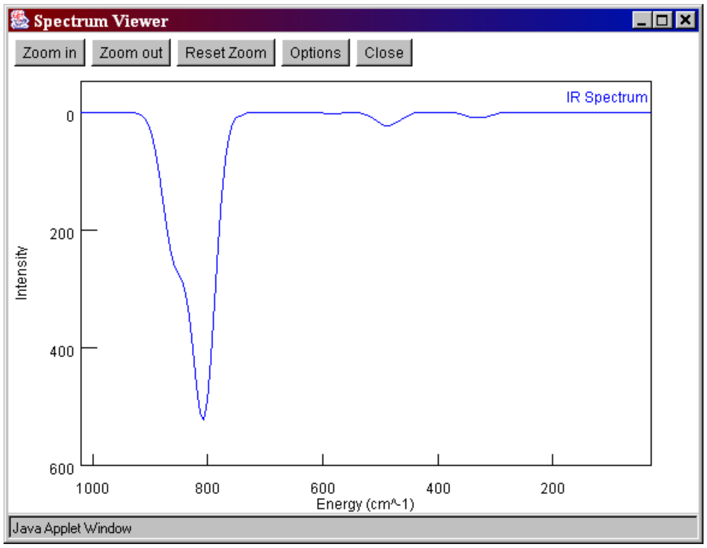


Figure 4.5.4

What would be exceptionally useful is if group theory could help to identify which vibrational modes are active – or if any are inactive. Fortunately, it can! (And *now* how much would you pay?) The tools for determining selection rules depend on direct products.

Intensity

Group theory provides tools to calculate when a spectral transition will have zero intensity, and this will not be seen. In this section, we will se how group theory can help to determine the **selection rules** that govern which transitions can and cannot be see.

$$\text{Intensity} \propto \left|\int (\psi')^* \vec{\mu}\, (\psi")\, d\tau\right|^2$$

The intensity of a transition in the spectrum of a molecule is proportional to the magnitude squared of the transition moment matrix element.

By knowing the symmetry of each part of the integrand, the symmetry of the product can be determined as the **direct product** of the symmetries of each part (\psi’) *, (\psi”) and \mu. This is helpful, since the integrand must not be antisymmetric with respect to any symmetry elements or the integral will vanish by symmetry. Before exploring that concept, lets look at the concept of direct products.

This is a concept many people have seen, in that the integral of an odd function over a symmetric interval, is zero. Recall what it means to be an “odd function” or an “even function.

Symmetry	definition	Intensity
Even	$f(-x) = f(x)$	$\int_{-a}^{a} f(x)dx = 2\int_{0}^{a} f(x)dx$

Symmetry	**definition**	**Intensity**
Odd	$f(-x) = -f(x)$	$\int_{-a}^{a} f(x)dx = 0$

Consider the function $f(x) = \left(x^3 - 3x\right) e^{-x^2}$. A graph of this function looks as follows:

One notes that the area under the curve on the side of the function for which $x > 0$ has exactly the same magnitude but opposite sign of the area under the other side of the graph. Mathematically,

$$\begin{aligned} \int_{-a}^{a} f(x)dx &= \int_{-a}^{0} f(x)dx + \int_{0}^{a} f(x)dx \\ &= -\int_{0}^{a} f(x)dx + \int_{0}^{a} f(x)dx = 0 \end{aligned}$$

It is also interesting to note that the function *f(x)* can be expressed as the product of two functions, one of which is an odd function ($x^3 - 3x$) and the other which is an even function (e^{-x^2}). The result is an odd function. By determining the symmetry of the function as a product of the eigenvalues of the functions with respect to the inversion operator, as discussed below, one can derive a similar result.

The even/odd symmetry is an example of inversion symmetry. Recall that the inversion operator (in one dimension) affects a change of sign on *x*.

$$\hat{i} f(x) = f(-x)$$

“Even” and “odd” functions are eigenfunctions of this operator, and have eigenvalues of either +1 or –1. For the function used in the previous example,

$$f(x) = g(x)h(x)$$

where

$g(x) = x^3 - 3x$ and $h(x) = e^{-x^2}$

Here, $g(x)$ is an odd function and $h(x)$ is an even function. The product is an odd function. This property is summarized for any $f(x) = g(x)h(x)$, in the following table.

g(x)	**h(x)**	**f(x)**	***i*g(x)=__g(x)**	***i*h(x)=__h(x)**	***i*f(x)=__f(x)**
even	even	even	1	1	1
even	odd	odd	1	-1	-1
odd	odd	even	-1	-1	1

Note that the eigenvalue (+1 or –1) is simply the character of the inversion operation for the irreducible representation by which the function transforms! In a similar manner, any function that can be expressed as a product of functions (like the integrand in the transition moment matrix element) can be determined as the direct product of the irreducible representations by which each part of the product transforms.

Consider the point group C_{2v} as an example. Recall the character table for this point group.

C_{2v}	**E**	C_2	σ_v	σ_v ’			
A_1	1	1	1	1	z		x^2 -y^2, z^2
A_2	1	1	-1	-1		R_z	xy
B_1	1	-1	1	-1	x	R_y	xz
B_2	1	-1	-1	1	y	R_x	yz

The direct product of irreducible representations can by the definition

$$\chi_{prod}(R) = \chi_i(R) \cdot \chi_j(R)$$

So for the direct product of B_1 and B_2, the following table can be used.

$\boldsymbol{C_{2v}}$	**E**	$\boldsymbol{C_2}$	$\boldsymbol{\sigma_v}$	$\boldsymbol{\sigma_v}$ **'**
$\boldsymbol{B_1}$	1	-1	1	-1
$\boldsymbol{B_2}$	1	-1	-1	1
$\boldsymbol{B_1 \otimes B_2}$	1	1	-1	-1

The product is actually the irreducible representation given by A_2 ! As it turns out, the direct product will always yield a set of characters that is either an irreducible representation of the group, or can be expressed as a sum of irreducible representations. This suggests that a multiplication table can be constructed. An example (for the C_{2v} point group) is given below.

$\boldsymbol{C_{2v}}$	$\boldsymbol{A_1}$	$\boldsymbol{A_2}$	$\boldsymbol{B_1}$	$\boldsymbol{B_2}$
$\boldsymbol{A_1}$	A_1	A_2	B_1	B_2
$\boldsymbol{A_2}$	A_2	A_1	B_2	B_1
$\boldsymbol{B_1}$	B_1	B_2	A_1	A_2
$\boldsymbol{B_2}$	B_2	B_1	A_2	A_1

Studying this table reveals some useful generalizations. Two things in particular jump from the page. These are summarized in the following tables.

	A	B					1	2
A	A	B				1	1	2
B	B	A				2	2	1

This pattern might seem obvious to some. It stems from the idea that

*symmetric*symmetric = symmetric*

*symmetric*antisymmetric = antisymmetric*

*antisymmetric*antisymmetric = symmetric*

Noting that A indicates an irreducible representation is *symmetric* with respect to the C_2 operation and B indicates that the irreducible representation is *antisymmetric* . . and that the subscript 1 indicates that an irreducible representation is *symmetric* with respect to the σ_v operation, and that a subscript 2 indicates that the irreducible representation is *antisymmetric* . . the rest seems to follow! Some point groups have irreducible representations use subscripts g/u or primes and double primes. The g/u subscript indicates symmetry with respect to the inversion (*i*) operator, and the prime/double prime indicates symmetry with respect to a σ plane (generally the plane of the molecule for planar molecules).

This method works well for singly degenerate representations. But what does one do for products involving doubly degenerate representations? As an example, consider the C_{3v} point group.

$\boldsymbol{C_{3v}}$	**E**	**2** $\boldsymbol{C_3}$	**3**$\boldsymbol{\sigma_v}$		
$\boldsymbol{A_1}$	1	1	1	z	
$\boldsymbol{A_2}$	1	1	-1		R_z
E	2	-1	0	(x, y)	(R_x, R_y)
$\boldsymbol{C_{3v}}$	**E**	**2** $\boldsymbol{C_3}$	**3**$\boldsymbol{\sigma_v}$		
$\boldsymbol{A_2}$	1	1	-1		
E	2	-1	0		

C_{3v}	E	2 C_3	$3\sigma_v$		
$A_2 \otimes$ E	2	-1	0		

Consider the direct product of A_2 and E.

This product is clearly just the E representation. Now one other example – Consider the product $E \otimes E$.

C_{3v}	E	2 C_3	$3\sigma_v$
E	2	-1	0
E	2	-1	0
$E \otimes E$	4	1	0

To find the irreducible representations that comprise this reducible representation, we proceed in the same manner as determining the number of vibrational modes belonging to each symmetry.

$$\begin{aligned} N_{A_1} &= \frac{1}{6}[(1)(4)+2(1)(1)+3(1)(0)]=1 \\ N_{A_2} &= \frac{1}{6}[(1)(4)+2(1)(1)+3(-1)(0)]=1 \\ N_E &= \frac{1}{6}[(2)(4)+2(-1)(1)+3(0)(0)]=1 \end{aligned}$$

This allows us to build a table of direct products. Notice that the direct product always has the total dimensionality that is given by the product of the dimensions.

C_{3v}	A_1	A_2	E
A_1	A_1	A_2	E
A_2	A_2	A_1	E
E	E	E	A_1+A_2+E

Now that we have a handle on direct products, we can move on to selection rules.

Selection Rules

According to quantum mechanics, transitions will only be allowed (have non-zero intensity) if the squared magnitude of the transition moment ($|\int \psi' * \vec{\mu}\psi" \, d\tau|^2$) is not zero. If the integral vanishes by symmetry, obviously the transition moment will have zero magnitude and the transition is **forbidden** and will not be seen. In order to determine if the integral vanishes by symmetry, it is necessary to determine the symmetry by which the dipole moment operator transforms.

This ($\vec{\mu}$) is a vector operator and can be decomposed into x, y and z components. As such, the transition moment is also a vector property that can have x-, y- and/or z-axis components. Clearly, it will be important to determine how the three axes transform. Fortunately, this information is contained in character tables! Consider the following two point groups, C_{3v} and C_{2v}.

C_{3v}	E	2 C_3	$3\sigma_v$		
A_1	1	1	1	z	
A_2	1	1	-1		R_z
E	2	-1	0	(x,y)	(R_x,R_y)

C_{2v}	E	C_2	σ_v	σ_v '		
A_1	1	1	1	1	z	

C_{2v}	E	C_2	σ_v	σ_v ’		
A_2	1	1	-1	-1		R_z
B_1	1	-1	1	-1	x	R_y
B_2	1	-1	-1	1	Y	R_x

In the case of C_{2v}, it is clear that the x-, y- and z-axes transform as the B_1, B_2 and A_1 irreducible representations respectively. In the case of C_{3v}, the z-axis transforms as A_1, but the x- and y-axes come as a pair and transform as the E irreducible representation. It will always require two axes to complete the basis for a doubly degenerate representation.

Under the C_{2v} point group, any vector quantity will transform as the sum of A_1 +B_1 +B_2 as we saw for Γ_{xyz} before. Further, one can say that the x-axis component transforms as B_1, the y-axis component as B_2 and the z-axis component as A_1. By a similar token, under the C_{3v} point group, a vector quantity transforms as the sum of $A_1 + E$. The z-axis component transforms as A_1 and the x- and y-axis components come as a pair that transform by the E representation. All that is needed to complete the picture is to determine the symmetries of the upper and lower state wave functions.

Infrared Active Transitions

In order for a spectral transition to be allowed by electric dipole selection rules, the transition moment integral must not vanish.

$$\int \psi'^{*} \vec{\mu} \psi" \, d\tau$$

This can be determined by using the irreducible representations by which the two wavefunctions transform and the three components of the transition moment operator, which will be x, y and z.

$$\int \Gamma_{\psi'} \Gamma_{\vec{\mu}} \Gamma_{\psi"} \, d\tau$$

If the direct product of the integrand does not contain at least a component of the totally symmetric irreducible representation, the integral will vanish by symmetry.

✓ Example 4.5.3

The three vibrational modes of H_2 O transform by A_1 (symmetric stretch), A_1 (bend) and B_2 (antisymmetric stretch.) Will the symmetric stretch mode be infrared active?

Solution

For the symmetric stretch, which transforms as A_1, the transition moment integrand will be have symmetry properties determined by the product

$$\psi' \begin{pmatrix} x \\ y \\ z \end{pmatrix} \psi" \qquad A_1 \begin{pmatrix} B_1 \\ B_2 \\ A_1 \end{pmatrix} A_1$$

where one of the irreducible representations from the set in the middle of the product may be used. (They are the irreducible representations by which the x, y and z axes transform.) In this case, the z-axis must be used.

$$A_1 \cdot A_1 \cdot A_1 = A_1$$

This is the only component that will not vanish.When the z-axis component must be used to make the transition moment operator not vanish, the transition is said to be a parallel transition. Transition moments that lie along axis perpendicular to the z-axis are said to be perpendicular transitions. Parallel and Perpendicular Transitions often have very different selection rules and thus very different band contours.

Another Method

Another method that can be used to see if a mode is infrared active is to take the direct product of the irreducible representations of the wavefunction, and use Γ_{xyz} for the transition moment. If the resulting product has a component that is totally symmetric, the mode will be infrared active.

✓ Example 4.5.4

Is the antisymmetric stretch mode of water predicted to be infrared active?

Solution

This mode transforms as the B_2 irreducible representation. Γ_{xyz} is given by

$$\Gamma_{xyz} = B_1 + B_2 + A_1$$

So:

C_{2v}	E	C_2	σ_{xz}	σ_{yz}
B_2	1	-1	-1	1
Γ_{xyz}	3	-1	1	1
Γ_{prod}	3	1	-1	1

The resulting reducible representation will have a component of the totally symmetric irreducible representation.

$$A_1 \cdot \Gamma_{prod} = (1)(3) + (1)(1) + (1)(-1) + (1)(1) = 4$$

So the A_1 irreducible representation appears once in the product reducible representation. In fact, the component that does not vanish is due to the presence of B_2 in Γ_{xyz}. Hence, the transition is predicted to be a perpendicular $\perp$ transition, since the transition moment lies along the y-axis.

✓ Example 4.5.5

Will the E modes in NH_3 be infrared active?

Solution

In the C_{3v} point group, Γ_{xyz} is given by $A_1 + E$

C_{3v}	E	2 C_3	3 σ_v
E	2	-1	0
Γ_{xyz}	3	0	1
Γ_{prod}	6	0	0

Γ_{prod} clearly has the totally symmetric irreducible representation as a component.

$$A_1 \cdot \Gamma_{prod} = (1)(6) + 2(1)(0) + 3(1)(0) = 6$$

In fact, it is the E component of Γ_{xyz} that makes this transition allowed (and so it is a perpendicular ($\perp$) transition.

C_{3v}	E	2 C_3	3 σ_v
E	2	-1	0
E	2	-1	0
Γ_{prod}	4	1	0

$$A_1 \cdot \Gamma_{prod} = (1)(4) + 2(1)(1) + 3(1)(0) = 6$$

Vibrational Raman Spectra

Vibrational Raman spectroscopy is often used as a complementaR_y method to infrared spectroscopy. The selection rules for Raman spectroscopy can be determined in much the same way, except that a polarizability integral must be used. The polarizability operator can be expressed as a 3x3 tensor of the form

$$\alpha = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix}$$

This tensor is symmetric along the diagonal, and the elements transform in the same ways as the functions x^2, y^2, z^2, xy, xz and yz.

Example 4.5.6

What are the vibrational mode symmetries for the molecule H_2CCH_2 which transforms as the D $_{2h}$ point group? Which modes will be infrared active? Which will be Raman active?

Solution

Set up the vibrational analysis table in the usual manner.

D_{2h}	E	C_2(z)	C_2(y)	C_2(x)	i	σ_{xy}	σ_{xz}	σ_{yz}		
A_g	1	1	1	1	1	1	1	1		$x^2, \; y^2, \; z^2$
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x	yz
A_u	1	1	1	1	-1	-1	-1	-1		
B_{1u}	1	1	-1	-1	-1	-1	1	1	z	
B_{2u}	1	-1	1	-1	-1	1	-1	1	y	
B_{3u}	1	-1	-1	1	-1	1	1	-1	x	
$\boldsymbol{\Gamma_{xyz}}$	3	-1	-1	-1	-3	1	1	1		
Γ_{rot}	3	-1	-1	-1	3	-1	-1	-1		

D_{2h}	E	C_2(z)	C_2(y)	C_2(x)	i	σ_{xy}	σ_{xz}	σ_{yz}
Γ_{xyz}	3	-1	-1	-1	-3	1	1	1
Γ_{unm}	6	0	0	2	0	6	2	0
Γ_{tot}	18	0	0	-2	0	6	2	0
Γ_{xyz}	3	-1	-1	-1	-3	1	1	1
	15	1	1	-1	3	5	1	-1
Γ_{rot}	3	-1	-1	-1	3	-1	-1	-1
Γ_{vib}	12	2	2	0	0	6	2	0

Decomposing to the individual components:

D_{2h}	E	C_2(z)	C_2(y)	C_2(x)	i	σ_{xy}	σ_{xz}	σ_{yz}	sum	#(h)
$A_g \cdot \Gamma_{vib}$	(1)(12)	(1)(2)	(1)(2)	(1)(0)	(1)(0)	(1)(6)	(1)(2)	(1)(0)	24	3

D_{2h}	E	C_2(z)	C_2(y)	C_2(x)	i	σ_{xy}	σ_{xz}	σ_{yz}	sum	#(h)
$B_{1g} \cdot \Gamma_{vib}$	(1)(12)	(1)(2)	(-1)(2)	(-1)(0)	(1)(0)	(1)(6)	(-1)(2)	(-1)(0)	16	2
$B_{2g} \cdot \Gamma_{vib}$	(1)(12)	(-1)(2)	(1)(2)	(-1)(0)	(1)(0)	(-1)(6)	(1)(2)	(-1)(0)	8	1
$B_{3g} \cdot \Gamma_{vib}$	(1)(12)	(-1)(2)	(-1)(2)	(1)(0)	(1)(0)	(-1)(6)	(-1)(2)	(1)(0)	0	0
$A_u \cdot \Gamma_{vib}$	(1)(12)	(1)(2)	(1)(2)	(1)(0)	(-1)(0)	(-1)(6)	(-1)(2)	(-1)(0)	8	1
$B_{1u} \cdot \Gamma_{vib}$	(1)(12)	(1)(2)	(-1)(2)	(-1)(0)	(-1)(0)	(-1)(6)	(1)(2)	(1)(0)	8	1
$B_{2u} \cdot \Gamma_{vib}$	(1)(12)	(-1)(2)	(1)(2)	(-1)(0)	(-1)(0)	(1)(6)	(-1)(2)	(1)(0)	16	2
$B_{3u} \cdot \Gamma_{vib}$	(1)(12)	(-1)(2)	(-1)(2)	(1)(0)	(-1)(0)	(1)(6)	(1)(2)	(-1)(0)	16	2

So

$$\Gamma_{vib} = 3A_g + 2B_{1g} + B_{2g} + A_u + B_{1u} + 2B_{2u} + 2B_{3u}$$

Of these, the 6 gerade modes will be Raman active, and the five B_{nu} modes ($n = 1, 2, 3$) will be infrared active. The A_u mode will be dark.

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1. Calculation performed using Gaussian 98 (http://www.gaussian.com/) using the WebMO (http://www.webmo.net/) web-based interface.

4.6: References

Fleming, P. E., & Mathews, C. W. (1996). A Reanalysis of the $A^1\Pi$ –X 1 $^1\Sigma$ +Transition of AlBr. Journal of Molecular Spectroscopy, 175(1), 31-36. doi:10.1006/jmsp.1996.0005

Gaydon, A. G. (1946). The determination of dissociation energies by the birge-sponer extrapolation. Proceedings of the Physical Society, 58(5), 525-537.

Meyer, C. F., & Levin, A. A. (1929). Physical Review A, 34, 44.

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4.7: Vocabulary and Concepts

anharmonicity constant

direct product

even function

Hermite polynomials

odd function

potential energy surface

Taylor series

term values

tunneling

4.8: Problems

1. For each molecule, calculate the reduced mass (in kg) and the force constant for the bond (in N/m).

Molecule	ω_e **(cm $^{-1}$)**	μ **(kg)**	**k (N/m)**
$^{1}H^{79}Br$	2648.975		
$^{35}Cl_2$	559.72		
$^{12}C^{16}O$	2169.81358		
$^{69}Ga^{35}Cl$	365.3		

2. The typical carbonyl stretching frequency is on the order of 1600-1900 cm^{-1}. Why is this value smaller than the value of ω_e for CO given in the table above?

3. The first few Hermite polynomials are given below.

v	$\boldsymbol{H_v(y)}$
0	1
1	$2y$
2	$4y^2-2$

$$H_{v+1}(y) = 2yH_v(y) - 2vH_{v-1}(y)$$

   a. Use the recursion relation to generate the functions H_3 (y) and H_4 (y).
   b. Demonstrate that the first three Hermite polynomials (H_0 (y), H_1 (y) and H_2 (y)) form an orthogonal set.

4. The Morse Potential function is given by

$$U(x) = D_e\left(1-e^{-\beta x}\right)$$

where $x = (r - r_e)$.

   a. Find an expression for the force constant of a Morse Oscillator bond by evaluating
   b. For $^{1}H^{35}Cl$, $D_e = 7.31 \times 10^{-19} J$ and $\beta = 1.8 \times 10^{10} m^{-1}$. Use your above expression to evaluate k for the bond in HCl.
   c. On what shortcoming of the Harmonic Oscillator model does the Morse Potential improve? What shortcoming does the Morse model share with that of a Harmonic Oscillator?

5. The following data are observed in the vibrational overtone spectrum in $^{1}H^{35}Cl$ (Meyer & Levin, 1929).

$v' \leftarrow v''$	$\tilde{\nu}_{obs}$ (cm^{-1})
$1 \leftarrow 0$	2885.9
$2 \leftarrow 0$	5666.8
$3 \leftarrow 0$	8347.0
$4 \leftarrow 0$	10923.1
$5 \leftarrow 0$	13396.5

From these data, calculate a set of $\Delta G_{v+\frac{1}{2}}$ values. Fit these results to the form

$$\Delta G_{v+\frac{1}{2}} = \omega_e - 2\,\omega_e x_e (v+1)$$

to determine values for ω_e and $\omega_e x_e$ for HCl.

6. The following wavenumber frequencies are reported for the band origins for the $1-v$" bands in an electronic transition of a diatomic molecule. Using the Birge-Sponer method, determine the dissociation energy of the molecule in its ground electronic state.

v"	**Wavenumber (cm^{-1})**	$\Delta G_{v+\frac{1}{2}}$ (cm^{-1})
	19586.9	
	19522.3	
	19504.8	
	19465.9	
	19418.3	
	19375.1	
	19323.2	
	19275.7	
	19223.8	
	19167.6	
	19111.4	
	19050.9	
	18990.4	
	18925.6	
	18860.7	
	18795.9	
	18722.4	
	18653.3	
	18579.8	
	18506.3	
27	18428.5	
	18342.1	
	18259.9	
	18177.8	
	18091.5	
	17996.3	
	17909.8	
	17814.8	
	17719.7	
	17624.6	

CHAPTER OVERVIEW

5: The Rigid Rotor and Rotational Spectroscopy

One of the most powerful tools for elucidating molecular structure is the analysis of rotationally resolved molecular spectra. These can be observed in the microwave, infrared, and visible/ultraviolet regions of the spectrum. The **rigid rotor** (or rigid rotator) problem provides the idealized model that chemists use to describe the rotational motion of a molecule. In this chapter, we will explore the quantum mechanical model of a rotating body, and apply the results to lay the foundation for an understanding of the rotational structure in molecular spectra. We'll look at the shortcomings of the model when applying it to real molecules (which as we saw in the previous chapter, do not have rigid bonds!) and apply these results to the interpretation of pure rotational spectra (generally found in the microwave region of the spectrum) and rotationvibration spectra (accounting for the rotational structure that is observed in infrared spectra of molecules.)

5.1: Spherical Polar Coordinates

The description of a rotating molecule in Cartesian coordinates would be very cumbersome. The problem is actually much easier to solve in **spherical polar coordinates**. Consider a particle that is located in space at some arbitrary point (x,y,z). In spherical polar coordinates, the position of a particle is also described by three variables, namely r, θ, and ϕ. These variables are defined according to the diagram. The distance from the origin to the point is specified by r. θ gives the angle formed by the position vector of the point and the positive z-axis. ϕ give the angle of rotation from the positive x-axis of the projection of the position vector into the xy plane. The ranges of possible values for r, θ and ϕ are given by

$$\begin{gathered}0 \leq r \leq \infty \\ 0 \leq \theta \leq \pi \\ 0 \leq \phi \leq 2\pi\end{gathered}$$

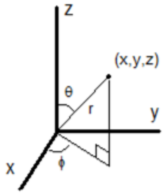

Figure 5.1.1

The coordinates of any point can be transformed from spherical polar coordinates to Cartesian coordinates using the following equations.

$$\begin{gathered}x = r \sin\theta \cos\phi \\ y = r \sin\theta \sin\phi \\ z = r \cos\theta\end{gathered}$$

The coordinates can be transformed from Cartesian coordinates to spherical polar coordinates by these equations.

$$\begin{gathered}r = \sqrt{x^2 + y^2 + z^2} \\ \theta = \tan^{-1}\left(\frac{y}{x}\right) \\ \phi = \cos^{-1}\left(\frac{z}{\sqrt{x^2 + y^2 + z^2}}\right)\end{gathered}$$

5.2: Potential Energy and the Hamiltonian

Since there is no energy barrier to rotation, there is no potential energy involved in the rotation of a molecule. All of the energy is kinetic energy. This simplifies the writing of the Hamiltonian.

In Cartesian coordinates, the Hamiltonian can be written

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

In spherical polar coordinates, the Hamiltonian can be written

$$\begin{aligned}\hat{H} &= -\frac{\hbar^2}{2\mu}\nabla^2 \\ &= -\frac{\hbar^2}{2\mu}\left(\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\end{aligned}$$

For the rigid rotor problem, r is taken to be a constant, simplifying the operator.

$$\hat{H} = -\frac{\hbar^2}{2\mu r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

The expression $\mu \mathrm{r}^2$ is the **moment of inertia** for the molecule. This value shows up often in problems involving the rotation of a molecule.

$$I = \mu r^2$$

While the expression for the Hamiltonian in spherical polar coordinates looks considerably more cumbersome than the Hamiltonian expressed in Cartesian coordinates, it will still be simpler to solve the problem describing the rotation of a molecule.

5.3: Solution to the Schrödinger Equation

The time-independent Schrödinger equation can be written as follows.

$$\hat{H}\psi(\theta,\phi) = E\psi(\theta,\phi)$$
$$-\frac{\hbar^2}{2\mu r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\psi(\theta,\phi) = E\psi(\theta,\phi)$$

Since the Hamiltonian can be expressed as a sum of operators, one in θ and the other in ϕ, it follows that the wavefunction should be able to be expressed as a product of two functions.

$$\psi(\theta,\phi) = \Theta(\theta)\Phi(\phi)$$

Making this substitution, the equation becomes

$$-\frac{\hbar^2}{2\mu r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\Theta(\theta)\Phi(\phi) = E\Theta(\theta)\Phi(\phi)$$

With minimal rearrangement, the following result can be derived

$$\frac{\Phi(\phi)}{\sin\theta}\frac{d}{d\theta}\sin\theta\frac{d}{d\theta}\Theta(\theta) + \frac{\Theta(\theta)}{\sin^2\theta}\frac{d^2}{d\phi^2}\Phi(\phi) = -\frac{2\mu r E}{\hbar^2}\Theta(\theta)\Phi(\phi)$$

And dividing both sides by $\Theta(\theta)\Phi(\phi)$ produces

$$\left(\frac{1}{\Theta(\theta)\sin\theta}\frac{d}{d\theta}\sin\theta\frac{d}{d\theta}\Theta(\theta)\right) + \left(\frac{1}{\Phi(\phi)\sin^2\theta}\frac{d^2}{d\phi^2}\Phi(\phi)\right) = -\frac{2\mu r^2 E}{\hbar^2}$$

This expression suggests that the sum of two functions, one only in θ and the other only in ϕ, when added together, yields a constant. As the two variables θ and ϕ are independent of one another, the only way this can be true is if each equation is itself equal to a constant.

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\sin\theta\frac{d}{d\theta}\Theta(\theta) = -\lambda_1^2\Theta(\theta)$$
$$\frac{1}{\sin^2\theta}\frac{d^2}{d\phi^2}\Phi(\phi) = -\lambda_2^2\Phi(\phi)$$

where λ_1 and λ_2 are constants of separation (the form of which is chosen for convenience) which satisfy the following relationship.

$$\begin{aligned}-\lambda_1^2 - \lambda_2^2 &= -\lambda^2 \\ &= -\frac{2\mu r^2 E}{\hbar^2}\end{aligned}$$

Rotation in the xy plane $(\theta = \pi/2)$

We'll tackle the equation in ϕ first. One way to picture this part of the equation is that it describes the rotation of a molecule in the xy plane only (defined by $\theta = \pi/2$.) Given this constraint, it is clear that the $\sin^2(\theta)$ term becomes unity, since $\sin(\pi/2) = 1$. The problem then becomes

$$\frac{d^2}{d\phi^2}\Phi(\phi) = -\frac{2\mu r^2 E}{\hbar^2}\Phi(\phi)$$

If a substitution is made for the constants on the right-hand side of the equation,

$$-m_l^2 = -\frac{2\mu r^2 E}{\hbar^2}$$

we get

$$\frac{d^2}{d\phi^2}\Phi(\phi) = -m_l^2\Phi(\phi)$$

which should look like a familiar problem. Instead of using sine and cosine functions this time though, we will use an imaginary exponential function instead.

$$\Phi(\phi) = A_{m_l}e^{im_l\phi}$$

The boundary condition for this problem is that the function $\Phi(\phi)$ must be single valued. Therefore

$$\Phi(\phi) = \Phi(\phi + 2\pi)$$

So

$$A_{m_l}e^{im_1\phi} = A_{m_1}e^{im_l(\phi+2\pi)}$$

Dividing both sides by A_{m_l} and expressing the second exponential as a product yields

$$\begin{aligned} e^{im_l\phi} &= e^{im_l\phi}e^{im_l2\pi} \\ 1 &= e^{im_l2\pi} \end{aligned}$$

Using the Euler relationship

$$e^{i\alpha} = \cos\alpha + i\sin\alpha$$

we see that

$$1 = \cos(2m_l\pi) + i\sin(2m_l\pi)$$

In order for this to be true, the sine term must vanish and the cosine term must become unity. This is true if m_l is an integer, either positive or negative and including zero.

$$m_l = \ldots, -2, -1, 0, 1, 2, \ldots$$

Energy Levels

As such, the energy of a rigid rotator limited to rotation in the xy plane is given by

$$E_{m_l} = \frac{m_l^2\hbar^2}{2\mu r^2} \qquad m_l = 0, \pm1, \pm2, \ldots$$

It is important to note that these functions are doubly degenerate for any non-zero value of m_l as there are always two values of m_l that yield the same energy.

Normalization

The wavefunctions can be normalized in the usual way.

$$\begin{aligned} \int_0^{2\pi}\left(A_{m_l}e^{im_l\phi}\right)^*\left(A_{m_l}e^{im_l\phi}\right)d\phi = 1 \\ &= A_{m_l}^2\int_0^{2\pi}e^{-im_l\phi}e^{im_l\phi}d\phi \\ &= A_{m_l}^2\int_0^{2\pi}d\phi \\ &= A_{m_l}^2[\phi]_0^{2\pi} \\ &= 2\pi A_{m_l}^2 \\ \sqrt{\frac{1}{2\pi}} &= A_{m_l} \end{aligned}$$

As was the case with the particle in a box problem, the normalization factor does not depend on the quantum number. The wavefunctions can be expressed

$$\Phi(\phi) = \sqrt{\frac{1}{2\pi}} e^{im_l \phi} \quad m_l = 0, \pm 1, \pm 2, \ldots$$

Rotation in three dimensions

We are now ready to tackle the more complicated problem of rotation in three dimensions. Recall the Schrödinger equation as was previously written.

$$\frac{\Phi(\phi)}{\sin\theta} \frac{d}{d\theta} \sin\theta \frac{d}{d\theta} \Theta(\theta) + \frac{\Theta(\theta)}{\sin^2\theta} \frac{d^2}{d\phi^2} \Phi(\phi) = -\frac{2\mu r E}{\hbar^2} \Theta(\theta) \Phi(\phi)$$

We already know the form of the solutions for the $\Phi(\phi)$ part of the equation. However, due to the $1/\sin^2\theta$ term in the Φ equation, it is possible that the solution to the Θ part of the equation will introduce a new constraint on the quantum number m_i.

Energy Levels

The only well-behaved functions (functions that satisfy all of the boundary conditions) have energies given by

$$E_l = \frac{l(l+1)\hbar^2}{2\mu r^2} \quad l = 0, 1, 2, \ldots$$

The quantum number l indicated the angular momentum. m_l is the z-axis component of angular momentum. The z-axis is treated differently than the $\mathtt{x}$ - or y-axes due to the unique manner in which the z-axis is treated in the choice of the spherical polar coordinate system (since θ is taken as the angle of the position vector with the positive z-axis.) Also, as will be shown later, the operator $\hat{L}_z$, the z-axis angular momentum component operator, has a special relationship with the Hamiltonian (as does the squared angular momentum operator, $\hat{L}^2$.)

Degeneracy

The interpretation of the quantum number m_l is that it gives the magnitude of the z-axis component of the angular momentum vector. And since no vector can have a component with a magnitude greater than that of the vector itself, the constraint on m_l that is introduced by this solution is

$$|m_l| \leq l$$

so for a given value of l, there are $(2l+1)$ values of $\mathrm{m_l}$ that fit the constraint. And since the energy expression does not depend on m_l, it is clear that each energy level has a degeneracy that is given by $(2l+1)$. That can be demonstrated as in the diagram below for an angular momentum vector of magnitude $2(l=2)$.

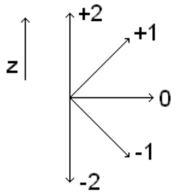

Figure 5.3.1

As can be seen in the diagram, there are five possible values of $m_l, +2, +1, 0, -1$ and -2. These five values correspond to the $(2l+1)$ degeneracy predicted for a state with total angular momentum given by $l = 2$ (and therefore $2l+1 = 5$). When we see the wavefunctions in more detail, there will be a new reason for this constraint on the quantum number m_l.

Wavefunctions

For convenience, we'll first look at the solutions where $m_l = 0$. The wavefunctions under this constraint have two parts, a normalization constant and a Legendre polynomial in $\cos(\theta)$. The Legendre polynomials are another set of orthogonal polynomials, similar to the Hermite polynomials that occur in the solution to the harmonic oscillator problem. The Legendre polynomials can be generated by the following relationship

$$P_l(x) = \frac{1}{2^l l!} \frac{d^l}{dx^l} \left(x^2 - 1\right)^l$$

The first few Legendre polynomials are given below.

l	$\mathbf{P}_l(\mathbf{x})$	$\mathbf{P}_l(\cos\theta)$
0	1	1
1	x	$\cos(\theta)$
2	$\frac{1}{2}\left(3x^2-1\right)$	$\frac{1}{2}\left[3\cos^2(\theta)-1\right]$
3	$\frac{1}{2}\left(5x^3-3x\right)$	$\frac{1}{2}\left[5\cos^3(\theta)-3\cos(\theta)\right]$

A recursion relation for the Legendre Polynomials is given by

$$(l+1)P_{l+1}(x)=(2l+1)xP_l(x)-lP_{l-1}(x)$$

When $m_l=0$, the spherical harmonic function $Y_l^m(\theta,\phi)=\Theta(\theta)\Phi(\phi)$ becomes just $\Theta(\theta)$, since the ϕ dependence disappears. The $\Theta(\theta)$ part of the wavefunctions are given by

$$\Theta(\theta)=\left[\frac{(2l+1)}{2}\right]^{\frac{1}{2}}P_l(\cos\theta)$$

The functions are slightly different for $m_l\neq 0$. In this case, the functions involve a set of functions that are related to the Legendre Polynomials called the associated Legendre polynomials. These functions are generated from the Legendre polynomials via the following relationship.

$$P_l^{|m_l|}(x)=(-1)^{|m_l|}\left(1-x^2\right)^{\backslash m_l//2}\frac{d^{|m_l|}}{dx^{|m_l|}}P_l(x)$$

Note that for any value of $|m_l|>l$, the derivative of $\mathrm{P}_l(\mathrm{x})$ vanishes.

$$\frac{d^{|m_l|}}{dx^{|m_l|}}P_l(x)=0\quad\text{for }|m_l|>l$$

And this is the origin of the constraint on m_l.

The associated Legendre polynomials depend on both l and m_l. Also, given the $|m_l|$ dependence, the sign of m_l does not matter. (The only place that the sign of m_l matter is in the $\Phi(\phi)$ function.) The first few associated Legendre Polynomials are given in the table below.

I	$\lvert\boldsymbol{m_l}\rvert$	$\mathbf{P}^{\lvert m\rvert}(\mathbf{x})$	$\mathbf{P}^{\lvert m\rvert}(\cos\theta)$
0	0	1	1
1	0	x	$\cos(\theta)$
	1	$\left(1-\mathrm{x}^2\right)^{\frac{1}{2}}$	$\sin(\theta)$
2	0	$\frac{1}{2}\left(3\mathrm{x}^2-1\right)$	$\frac{1}{2}\left(3\cos^2(\theta)-1\right)$
	1	$3\mathrm{x}\left(1-\mathrm{x}^2\right)^{\frac{1}{2}}$	$3\cos(\theta)\sin(\theta)$
	2	$3\left(1-\mathrm{x}^2\right)$	$3\sin^2(\theta)$

5.4: Spherical Harmonics

The rigid rotor problem was solved using the Schrödinger equation

$$-\frac{\hbar^2}{2\mu r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\psi(\theta,\phi)=E\psi(\theta,\phi)$$

As it turns out, the solutions to this equation are very important in a number of areas in chemistry and physics. The eigenfunctions are known as the **spherical harmonics** $\left(Y_l^{m_l}(\theta,\phi)\right)$ and they appear in every problem that has spherical symmetry. The Spherical Harmonics satisfy the relationship

$$\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)Y_l^{m_l}(\theta,\phi)=\hbar^2 l(l+1)Y_l^{m_l}(\theta,\phi)$$

Each function $Y_l^{m_l}(\theta,\phi)$ has three parts: 1) a normalization constant, 2) an associated Legendre polynomial in $\cos(\theta)$, and 3) an imaginary (for $m_l \neq 0$) exponential in ϕ.

$$Y_l^{m_l}(\theta,\phi)=\left[\frac{(2l+1)\,(l-|m_l|)}{4\pi\,(l+|m_l|)}\right]^{\frac{1}{2}}P_l^{|m_l|}(\cos\theta)e^{im_l\phi}$$

The first few Spherical harmonics are shown in the table below.

$\boldsymbol{I}$	$\boldsymbol{m_I}$	$Y_l^{m_l}(\theta,\phi)$
0	0	$\sqrt{\frac{1}{4\pi}}$
1	0	$\sqrt{\frac{3}{4\pi}}\cos(\theta)$
	±1	±1
2	±1	$\sqrt{\frac{5}{16\pi}}\left(3\cos^2(\theta)-1\right)$
	0	$\sin(\theta)\cos(\theta)e^{\pm i\phi}$
	±2	$\sqrt{\frac{15}{32\pi}}\sin^2(\theta)e^{\pm 2i\phi}$

Notice the $(2l+1)$ degeneracy in these functions, due to the $(2l+1)$ values of m_l for each value of l. Also, it is useful to not that these functions all have l angular nodes (values of θ that cause the wavefunction to vanish.) For the $l=1$ wavefunctions, these nodes occur at $\theta=\pi/2$ for $m_l=0$ and at $\theta=0$ for $m_l=\pm1$. The number of nodes in each wavefunction is a useful property to know when discussing how these functions related to the radial wavefunction in the Hydrogen atom.

5.5: Angular Momentum

The Spherical Harmonics are involved in a number of problems where **angular momentum** is important (including the Rigid Rotor problem, the H-atom problem and anything else where spherical symmetry is involved.) Angular momentum is a vector quantity that is given by the cross product of position and momentum.

$$\overrightarrow{\mathbf{L}} = \overrightarrow{\mathbf{r}} \times \overrightarrow{\mathbf{p}}$$

This quantity can be calculated from the following determinant.

$$\begin{aligned} \overrightarrow{\mathbf{L}} = \overrightarrow{\mathbf{r}} \times \overrightarrow{\mathbf{p}} &= \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} \\ &= (yp_z - zp_y)\,\mathbf{i} + (zp_x - xp_z)\,\mathbf{j} + (xp_y - yp_x)\,\mathbf{k} \end{aligned}$$

Substituting the operators for the components of linear momentum, the operators that correspond to the three components of angular momentum are

$$\begin{aligned} \widehat{L_x} &= -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \\ \widehat{L_y} &= -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \\ \widehat{L_z} &= -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \end{aligned}$$

These can be used to determine the square of the angular momentum, which is given by the dot product of $\overrightarrow{\mathbf{L}}$ with itself.

$$\overrightarrow{\mathbf{L}} \cdot \overrightarrow{\mathbf{L}} = L^2 = L_x^2 + L_y^2 + L_z^2$$

Similarly, the operator for the square of the angular momentum is given by

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

In spherical polar coordinates, the angular momentum operators are given by the expressions

$$\begin{aligned} \hat{L}_x &= -i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right) \\ \hat{L}_y &= -i\hbar\left(-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right) \\ \hat{L}_z &= -i\hbar\frac{\partial^2}{\partial\phi^2} \end{aligned}$$

And the angular momentum squared operator is given by

$$\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

For the Rigid-Rotator problem, it is interesting to note that the Hamiltonian is very closely related to the angular momentum squared operator.

$$\begin{aligned} \hat{H} &= -\frac{\hbar^2}{2\mu r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \\ &= \frac{1}{2I}\hat{L}^2 \end{aligned}$$

The eigenfunctions of the $\hat{L}^2$ operator are the Spherical Harmonics, $Y_l^{m_1}(\theta,\phi)$. These functions have the important properties that

$$\hat{H} Y_l^{m_l}(\theta,\phi) = \frac{\hbar^2 l(l+1)}{2\mu r^2} Y_l^{m_l}(\theta,\phi)$$
$$\hat{L}^2 Y_l^{m_l}(\theta,\phi) = \hbar^2 l(l+1) Y_l^{m_l}(\theta,\phi)$$
$$\hat{L}_z Y_l^{m_l}(\theta,\phi) = \hbar m_l Y_l^{m_l}(\theta,\phi)$$

Seeing as the spherical harmonics are eigenfunctions of all three of these operators, what is implied about the commutator of these two operators?

There are important relationships between the angular momentum operators. Each of the operators corresponding to the components of angular momentum commutes with the $\hat{L}^2$ operator, but they do not commute with one another. This implies that one can measure the squared angular momentum and only one component of angular momentum. This is generally taken as the z-axis component of angular momentum as the z-axis has special properties due to the manner in which the spherical polar coordinates have been defined.

$$\left[\hat{L}^2, \hat{L}_x\right] = \left[\hat{L}^2, \hat{L}_y\right] = \left[\hat{L}^2, \hat{L}_z\right] = 0$$
$$\left[\hat{L}_x, \hat{L}_y\right] \neq 0; \left[\hat{L}_y, \hat{L}_z\right] \neq 0; \left[\hat{L}_x, \hat{L}_z\right] \neq 0$$

The commutators involving two components of angular momentum are particularly interesting. Consider the commutator between and $\hat{L}_x$ and $\hat{L}_y$.

$$\left|\hat{L}_x, \hat{L}_y\right| = \hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x$$

Let’s define each term separately and then take the difference.

$$\begin{aligned}\hat{L}_x\hat{L}_y &= (-i\hbar)^2 \left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\\ &= -\hbar^2 \left(y\frac{\partial}{\partial z} z\frac{\partial}{\partial x} - y\frac{\partial}{\partial z} x\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} z\frac{\partial}{\partial x} + z\frac{\partial}{\partial y} x\frac{\partial}{\partial z}\right)\end{aligned}$$

The second, third and fourth terms are easy to simplify as the derivatives do not affect the x or z variables. The first term, however, requires some application of the chain rule.

$$\hat{L}_x\hat{L}_y = -\hbar^2\left(\left\{y\frac{\partial}{\partial x} + yz\frac{\partial^2}{\partial x\partial z}\right\} - xy\frac{\partial^2}{\partial z^2} - z^2\frac{\partial^2}{\partial x\partial y} + xz\frac{\partial^2}{\partial y\partial z}\right)$$

Similarly,

$$\begin{aligned}\hat{L}_y\hat{L}_x &= (-i\hbar)^2\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\\ &= -\hbar^2\left(z\frac{\partial}{\partial x} y\frac{\partial}{\partial z} - z\frac{\partial}{\partial x} z\frac{\partial}{\partial y} - x\frac{\partial}{\partial z} y\frac{\partial}{\partial z} + x\frac{\partial}{\partial z} z\frac{\partial}{\partial y}\right)\\ &= -\hbar^2\left(zy\frac{\partial^2}{\partial x\partial z} - z^2\frac{\partial^2}{\partial x\partial y} - xy\frac{\partial^2}{\partial z^2} + \left\{x\frac{\partial}{\partial y} + xz\frac{\partial^2}{\partial z\partial y}\right\}\right)\end{aligned}$$

Taking the difference will cancel all of the second derivative terms, leaving only the first derivative terms behind.

$$\begin{aligned}\hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x &= -\hbar^2\left(y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right)\\ &= i\hbar\hat{L}_z\end{aligned}$$

Similarly, it can be shown that

$$\left[\hat{L}_y, \hat{L}_z\right] = i\hbar\hat{L}_x$$
$$\left[\hat{L}_z, \hat{L}_x\right] = i\hbar\hat{L}_y$$

5.6: Application to the Rotation of Real Molecules

While the spherical harmonics are the wavefunctions that describe the rotational motion of a rigid rotator, the names of the quantum numbers are changed to reflect the type of angular momentum encountered in the problem. The quantum number l and m_l should be familiar as these are the ones used in the hydrogen atom problem to describe the orbital angular momentum. However, for rotational motion, these are replaced by J and $\mathrm{M_J}$. The energy levels of the rigid rotator are therefore given by

$$E_J = J(J+1)\frac{\hbar^2}{2\mu r^2}$$

And since $\mathrm{M_J}$ does not appear in the energy level expression, each level has a $(2\,\mathrm{J}+1)$ degeneracy. The spacings between energy levels increases with increasing J due to the $\mathrm{J(J+1)}$ dependence (which has a $\mathrm{J^2}$ term.) This pattern is shown in the diagram below.

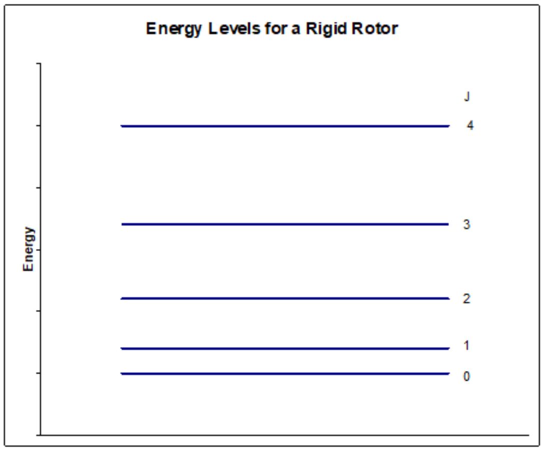

Figure 5.6.1

For spectroscopic measurements, the rotational energy (given the symbol F_J) is often expressed in spectroscopic units, such as $\mathrm{cm^{-1}}$. Also, a spectroscopic constant, B, is used to describe the energy level stack.

$$F_J = \frac{E_J}{hc} = BJ(J+1)$$

where the spectroscopic constant B is given by

$$B = \frac{h}{8\pi^2 c\mu r^2}$$

Thus, by knowing the value of μ, the reduced mass, and measuring the value of B, the rotational constant, one can determine the value of r, the bond length. This is the utility of rotational spectroscopy - it gives us detailed information about molecular structure!

Centrifugal Distortion

As we know, since they vibrate, real molecules do not have rigid bonds. So it is no surprise to learn that the Rigid Rotor is really just a limiting ideal model, much like the ideal gas law describes limiting ideal behavior.

Real molecules, especially when rotating with very high angular momentum, will tend to stretch. In other words, the average bond length will increase with increasing J. And given the inverse relationship between B and bond length(r), it is not surprising that the effective B value is smaller at higher levels of J. In fact, this centrifugal distortion problem is well treated by introducing a "distortion constant" D such that

$$F_J = BJ(J+1) - D[J(J+1)]^2$$

Naturally, one would expect the distortion constant to be small in the case of a strong, inflexible bond, but larger if the bond is weaker. The approximation of Kraitzer suggests that the distortion constant is determined to a good approximation by

$$D \approx \frac{4B^3}{\omega_e^2}$$

For a well behaved molecule, he distortion constant D is always smaller in magnitude than B. Some molecules require several distortional constants to yield a reasonable description of their rotational energy level stack. If additional constants are needed, they are introduced as coefficients in a power series of $\mathrm{J(J+1)}$.

$$\mathrm{F_J = BJ(J+1) - D[J(J+1)]^2 + H[J(J+1)]^3 + \ldots}$$

The power series is truncated at a point that yields a good fit to experimental observations for a given molecule.

5.7: Spectroscopy

The experimental determination of spectroscopic rotational constants provides a very precise set of data describing molecular structure. To see how experimental measurements inform the determination of molecular structure, let’s examine what is to be expected in the pure rotational spectrum of a molecule first.

Microwave Spectroscopy

The rotational selection rule in microwave absorption spectra is

$$\Delta \mathrm{J} = +1$$

(Selection rules are discussed in more detail in a later section.) The pattern of lines predicted to be observed in a microwave spectrum (a pure rotational spectrum of a mole) can be derived by taking differences in rotational energy levels.

$$\begin{aligned} \tilde{\upsilon}_J &= F_{J+1} - F_J \\ F_{J+1} - F_J &= B(J+1)(J+2) - BJ(J+1) \\ &= B\left(J^2+3J+2\right) - B\left(J^2+J\right) \\ &= B\left(J^2+3J+2-J^2-J\right) \\ &= B(2J+2) \\ &= 2B(J+1) \end{aligned}$$

This suggests that a pure microwave spectrum should consist of a series of lines that are evenly spaces, the spacing between which is $2\ \mathrm{B}$. It also suggests that a plot of the line frequency divided by $(\mathrm{J}+1)$ should yield a straight and horizontal line,

$$\frac{\tilde{\upsilon}_J}{(J+1)} = 2B$$

The inclusion of distortion yields a slightly different conclusion.

$$\begin{aligned} F_{J+1} - F_J \quad &= B(J+1)(J+2) - D[(J+1)(J+2)]^2 - BJ(J+1) + D[J(J+1)]^2 \\ &= B\left(J^2+3J+2-J^2-J\right) - D\left[\left(J^2+3J+2\right)^2 - \left(J^2+J\right)^2\right] \\ &= B(2J+2) - D\left(J^4+6J^3+13J^2+12J+4-J^4-2J^3-J^2\right) \\ &= 2B(J+1) - D\left(4J^3+12J^2+12J+4\right) \\ &= 2B(J+1) - 4D(J+1)^3 \end{aligned}$$

$$\frac{\tilde{\upsilon}_J}{(J+1)} = 2B - 4D(J+1)^2$$

This suggests that a plot of $\frac{\tilde{\upsilon}_J}{(J+1)}$ vs. $(J+1)^2$ should yield a straight line with slope -4D and intercept $2\ \mathrm{B}$.

Consider the following set of data for the microwave spectrum of $^{12}\mathrm{C}^{16}\mathrm{O}$ (Lovas & Krupenie, 1974).

A plot of $\frac{\tilde{\upsilon}_J}{J+1}$ vs. J yields a plot as the following.

J	$\tilde{\upsilon}_\mathrm{J}\ (\mathrm{cm}^{-1})$
0	3.84503
1	7.68992
2	11.53451
3	15.37867
4	19.22223
5	23.06506

J	$\tilde{v}_J\ (\mathrm{cm}^{-1})$
6	26.90701

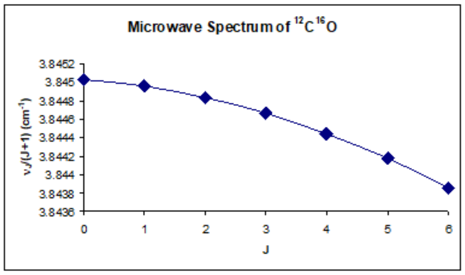

Figure 5.7.1

Clearly, this is not a horizontal line. The conclusion is that centrifugal distortion is not negligible for this molecule. Including distortion suggests that the plot that should be considered would involve $\frac{\tilde{v}_J}{(J+1)}$ vs. $(\mathrm{J}+1)^2$. This yields the following:

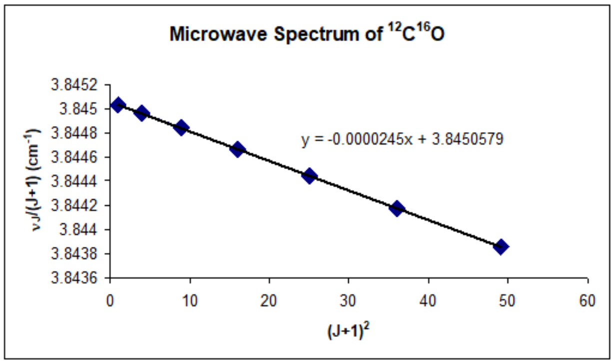

Figure 5.7.2

This does yield a straight line! From the fit, one calculates a B value of $1.92253\ \mathrm{cm}^{-1}$ and a D value of $0.00000612\ \mathrm{cm}^{-1}$.

Calculating a Bond Length from Spectroscopic Data

Spectroscopic data (and microwave data in particular) provides extremely high precision information from which bond lengths can be determined. Based on the above data and the masses of carbon-12 (12.00000 amu) and oxygen-16 (15.99491463 amu) (Rosman & Taylor, 1998) a reduced mass for $^{12}\mathrm{C}^{16}\mathrm{O}$ can be calculated as

$$\mu = \frac{m_C m_O}{m_C + m_O} = 6.85621\mathrm{amu} = 1.1385 \times 10^{-26}\ \mathrm{kg}$$

Recalling the expression for the rotational constant B

$$B = \frac{h}{8\pi^2 c \mu r^2}$$

The bond length is given by

$$r = \sqrt{\frac{h}{8\pi^2 c \mu B}}$$

Using the data from above, one calculates a bond length for CO to be $r = 1.1312\text{Å}$. This value is actually the average value of the bond length in the $v = 0$ level. The literature value for the equilibrium bond length (the bond length at the potential minimum) is given by $r_e = 1.128323\text{Å}$ (Bunker, 1970) which is slightly shorter (as is to be expected.) The extrapolation of data to determine values at the potential minimum is discussed in a later section.

Rotation-Vibration Spectroscopy

Each vibrational level in a molecule will have a whole stack of rotational energy levels. As such, vibrational transitions will also show rotational fine structure. This fine structure can be analyzed to determine very precise values for molecular structure in much the same ways microwave data for the pure rotational spectrum can be. One method for analyzing this data is that of **combination differences** although direct fitting of the data will give better results mathematically. Before beginning a discussion of combination differences, however, it is necessary to discuss **selection rules**.

Selection Rules and Branch Structure

Selection rules are determined for spectroscopic transitions as those transitions for which the **transition moment** integral does not vanish. This is because the observed intensities of spectroscopic transitions are proportional to the squared magnitude of the transition moment. The transition moment integral is given by

$$\int (\psi')^{*} \vec{\mu} (\psi'') \, d\tau$$

and so the intensities of transitions are given by

$$\text{Int.} \propto \left| \int (\psi')^{*} \vec{\mu} (\psi'') \, d\tau \right|^{2}$$

where a single prime (’) indicates the upper state of the transition and a double prime (") indicates the lower state. The operator $\vec{\mu}$ corresponds to the change in the electric dipole moment of the molecule as it undergoes a transition from a state described by ψ " to one described by ψ ’. Other operators may be used in this expression (magnetic dipole, electric quadrupole, etc.) but these lead to significantly weaker transitions (by a factor of 10^6 or more!) When the electric dipole operator is used, the transitions for which the transition moment is not zero are said to be **allowed transitions**, while all others are said to be **forbidden transitions** by electric dipole selection rules. Since other types of transitions are so weak by comparison, a transition that is said to be allowed or forbidden is assumed to mean by electric dipole selection rules unless specifically stated otherwise.

The selection rules for vibrational transitions are

$$\Delta \mathrm{v} = \pm 1$$

For closed-shell molecules (molecules where all of the electrons are paired), the rotational selection rules are

$$\Delta \mathrm{J} = \pm 1$$

$\Delta \mathrm{J} = 0$ is possible for some open-shell molecules, but his topic will be discussed in more detail in Chapter 7.

The rotational fine structure of a transition can be separated into branches according to the specific change in the rotational quantum number J.

ΔJ	
$+1$	R-branch
0	Q-branch
-1	P-branch

In Raman spectroscopy (which is an inelastic light scattering process rather than the direct absorption or emission of a photon, and thus follows different selection rules) O- and S-Branches can be observed with $\Delta \mathrm{J} = -2$ and $+2$ respectively.

The spectrum of possible branches and transitions that can be observed for all possible molecules can be quite daunting (and take an entire graduate level course in molecular spectroscopy just to scratch the surface!) For the purposes of this discussion, we will limit ourselves for the time being to just closed-shell molecules for which P- and R-branches can be observed.

Consider the following energy level diagram depicting the rotational energy levels in two different states. The diagram shows the expected branch structure for a closed shell molecule. Notice that the transition lines get longer with increasing J in the R-branch, but shorter with increasing J in the P-branch. The largest difference in transition energy is for successive lines in the spectrum is that between the R_0 and P_1 lines. The **band origin** $(\tilde{v}_0)$ will lie between these two lines, and is at the energy difference between the $J' = 0$ and $J" = 0$, the two non-rotating levels in the two vibrational levels. Also notice that the rotational energy spacings in the upper state are smaller than those in the lower state. This is do to a smaller B value in the upper state $(\mathrm{v} = 1)$, which has a larger average bond length than the $v = 0$ level.

Energy Level Diagram

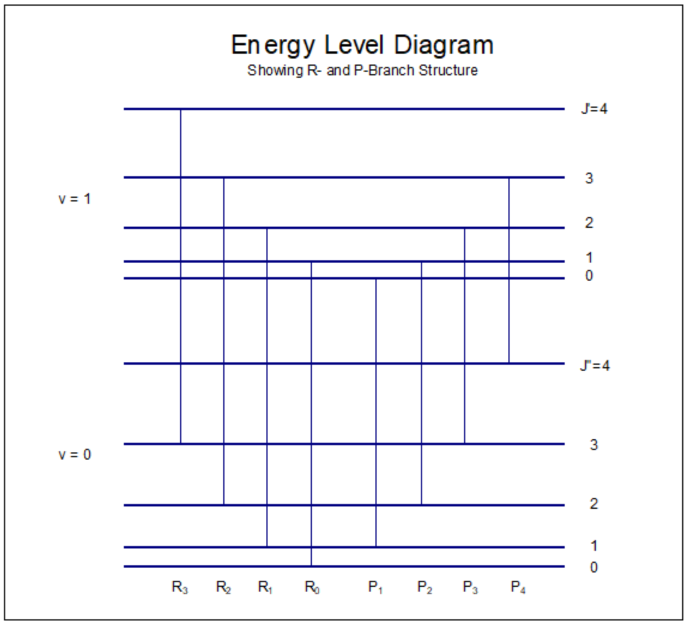

Figure 5.7.3

Combination Differences

Consider the following partial energy level diagram:

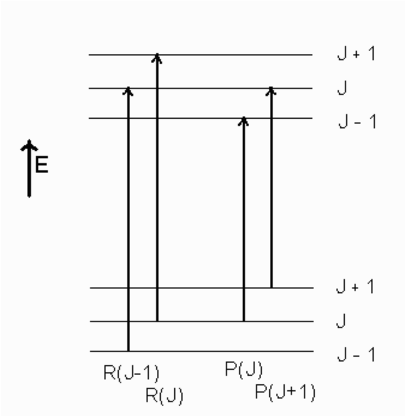

Figure 5.7.4

It is clear that since the $\mathrm{R(J)}$ and $\mathrm{P(J)}$ transitions share a common lower rotational level (F_J), the energy difference between the $R(J)$ and $P(J)$ transitions gives the energy difference between the $\mathrm{F_{J+1}}$ and $\mathrm{F_{J-1}}$ in the upper state of the transition. Similarly, the difference between F_{J+1} and F_{J-1} in the lower state is given by $R(J-1) - P(J+1)$. Thus, by taking differences of transition energies in the proper combination, dependence on one of the states can be eliminated. Also, the difference $\Delta_2\,\mathrm{F(\,J)}$ can be found. This difference is defined by:

$$\Delta_2\,\mathrm{F(\,J)} \equiv \mathrm{F_{J+1} - F_{J-1}}$$

Using the rigid rotator model,

$$F_J = BJ(J+1)$$

an expression for $\Delta_2 F(J)$ can be easily derived:

$$\begin{aligned}\Delta_2 \mathrm{F}(\mathrm{J}) &= \mathrm{B}(\mathrm{J}+1)(\mathrm{J}+2)-\mathrm{B}(\mathrm{J}-1)(\mathrm{J}) \\ &= \mathrm{B}\left(\mathrm{J}^2+3\,\mathrm{J}+2\right)-\mathrm{B}\left(\mathrm{J}^2-\mathrm{J}\right) \\ &= \mathrm{B}(4\,\mathrm{J}+2) \\ &= 4\,\mathrm{B}\left(J+\frac{1}{2}\right)\end{aligned}$$

Thus the value of $\Delta_2\,\mathrm{F}(\mathrm{J})$ that can be found for either the upper or lower states by combination differences from the energies of the spectral lines, can be used to find the spectroscopic constant B.

$$\frac{\Delta_2 F(J)}{\left(J+\frac{1}{2}\right)}=4B$$

And the $\Delta_2\,\mathrm{F}(\mathrm{J})$ values are determined by the combination differences

$$\begin{gathered}\Delta_2 F'(J)=R(J)-P(J) \\ \Delta_2 F''(J)=R(J-1)-P(J+1)\end{gathered}$$

were the single prime (") refers to the upper state and the double prime (") refers to the lower state.

For most molecules, the rotational distortion constants are not negligible. In this case, the rotational term values are given by

$$\mathrm{F}(\mathrm{J})=\mathrm{BJ}(\mathrm{J}+1)-\mathrm{DJ}^2(\mathrm{J}+1)^2+\mathrm{HJ}^3(\mathrm{J}+1)^3+\ldots$$

Neglecting terms of higher order than $\mathrm{DJ}^2(\mathrm{J}+1)^2$ (since these terms are small for most molecules) the combination differences relationship can be derived as

$$\begin{aligned}\Delta_2 \mathrm{F}(\mathrm{J}) &= \mathrm{B}(\mathrm{J}+1)(\mathrm{J}+2)-\mathrm{D}(\mathrm{J}+1)^2(\mathrm{J}+2)^2-\mathrm{B}(\mathrm{J}-1)(\mathrm{J})+\mathrm{D}(\mathrm{J}-1)^2(\mathrm{J})^2 \\ &= \mathrm{B}\left[\left(\mathrm{J}^2+3\,\mathrm{J}+2\right)-\left(\mathrm{J}^2-\mathrm{J}\right)\right]-\mathrm{D}\left[\left(\mathrm{J}^2+2\,\mathrm{J}+1\right)\left(\mathrm{J}^2+4\,\mathrm{J}+4\right)-\left(\mathrm{J}^2-2\,\mathrm{J}+1\right)\mathrm{J}^2\right] \\ &= \mathrm{B}(4\,\mathrm{J}+2)-\mathrm{D}\left(\mathrm{J}^4+4\,\mathrm{J}^3+4\,\mathrm{J}^2+2\,\mathrm{J}^3+8\,\mathrm{J}^2+8\,\mathrm{J}+\mathrm{J}^2+4\,\mathrm{J}+4-\mathrm{J}^4+2\,\mathrm{J}^3-\mathrm{J}^2\right) \\ &= 4\,\mathrm{B}\left(J+\frac{1}{2}\right)-\mathrm{D}\left(8\,\mathrm{J}^3+12\,\mathrm{J}^2+12\,\mathrm{J}+4\right) \\ &= 4\,\mathrm{B}\left(J+\frac{1}{2}\right)-8\mathrm{D}\left(\mathrm{J}^3+\frac{3}{2}\,\mathrm{J}^2+\frac{3}{2}\,\mathrm{J}+\frac{1}{2}\right)\end{aligned}$$

It would be convenient if the term involving D could be factored. Recognizing that

$$\left(J+\frac{1}{2}\right)^3=\mathrm{J}^3+\frac{3}{2}\,\mathrm{J}^2+\frac{3}{4}\,\mathrm{J}+\frac{1}{8}$$

the "cube" can be "completed" by

$$\begin{aligned}\Delta_2 \mathrm{F}(\mathrm{J}) &= 4\,\mathrm{B}\left(J+\frac{1}{2}\right)-8\mathrm{D}\left(\mathrm{J}^3+\frac{3}{2}\,\mathrm{J}^2+\frac{3}{4}\,\mathrm{J}+\frac{1}{8}+\frac{3}{4}\,\mathrm{J}+\frac{3}{8}\right) \\ &= 4\,\mathrm{B}\left(J+\frac{1}{2}\right)-8\mathrm{D}\left(J+\frac{1}{2}\right)^3-8\mathrm{D}(\frac{3}{4}\,\mathrm{J}+\frac{3}{8}) \\ &= 4\,\mathrm{B}\left(J+\frac{1}{2}\right)-8\mathrm{D}\left(J+\frac{1}{2}\right)^3-\mathrm{D}(6\,\mathrm{J}+3) \\ &= 4\,\mathrm{B}\left(J+\frac{1}{2}\right)-8\mathrm{D}\left(J+\frac{1}{2}\right)^3-6\mathrm{D}\left(J+\frac{1}{2}\right) \\ &= [4\,\mathrm{B}-6\mathrm{D}]\left(J+\frac{1}{2}\right)-8\mathrm{D}\left(J+\frac{1}{2}\right)^3\end{aligned}$$

And by dividing through by $\left(J+\frac{1}{2}\right)$

$$\frac{\Delta_2 F(J)}{\left(J+\frac{1}{2}\right)}=[4\,\mathrm{B}-6\mathrm{D}]-8\mathrm{D}\left(J+\frac{1}{2}\right)^2$$

So using the spectral data, a plot of

$$\frac{\mathrm{R(J)-P(J)}}{\left(J+\frac{1}{2}\right)} \text{ vs. } \left(J+\frac{1}{2}\right)^2$$

or

$$\frac{\mathrm{R(J-1)-P(J+1)}}{\left(J+\frac{1}{2}\right)} \text{ vs. } \left(J+\frac{1}{2}\right)^2$$

should yield straight lines with slopes of $8\mathrm{D}$ and an intercept of $(4\,\mathrm{B}-6\mathrm{D})$ for the upper and lower states respectively.

Additional Spectroscopic Constants

Since each vibrational level has a different average bond length (increasing with increasing vibrational quantum number for a well-behaved electronic state,) the rotational constant has a dependence on the vibrational quantum number v.

$$B_v=B_e-\alpha_e\left(v+\frac{1}{2}\right)+\gamma_e\left(v+\frac{1}{2}\right)^2+\ldots$$

where B_e is the equilibrium value of the rotational constant (and the constant from which $\mathrm{r_e}$ is derived), α_e and γ_e are constants that describe how rotation and vibration are coupled in a molecule. Usually this power series in $\left(\mathrm{v}+\frac{1}{2}\right)$ can be truncated at the α_e term (unless data for a great many vibrational levels are known.)

Similarly, the distortional term can be expanded in a power series in $\left(\mathrm{v}+\frac{1}{2}\right)$.

$$D_v=D_e-\beta_e\left(v+\frac{1}{2}\right)+\ldots$$

For most molecules, β_e is not determined within experimental uncertainty unless a great many vibrational levels have been included in the fit.

A typical methodology would be to determine $\mathrm{B_v}$ for all of the vibrational levels for which data exists. (A single vibration-rotation band analysis provides two values, one for the upper state and one for the lower state.) Then the B_v values are fit to the functional form given by

$$B_v=B_e-\alpha_e\left(v+\frac{1}{2}\right)+\gamma_e\left(v+\frac{1}{2}\right)^2+\ldots$$

truncating the power series so as to include the minimum number of adjustable parameters as are needed to yield a good fit to the data. This process yields a value for $\mathrm{B_e}$ which can then be used to calculate r_e. These values can then be compared to those found in the literature (if such a value has been measured) or reported in the literature if it has not yet been measured! A similar approach is used for the distortional term(s).

Line Intensity in Rotational Structure

One element that we have not discussed in the subject of rotational spectroscopy (or the rotational fine structure in vibration-rotation spectroscopy) is the intensities of the spectral lines. The intensity will be determined by two factors: 1) the population of the originating state (lower state in absorption and upper state in emission spectra) which is well described for a thermalized sample by a **Maxwell-Boltzmann distribution**, and 2) the **line strength**, which is determined by the quantum mechanical relationship between the upper and lower states of the transition.

The Maxwell-Boltzmann Distribution

The Maxwell-Boltzmann distribution of energy level populations will be achieved by any system that is in thermal equilibrium (usually implying that a sufficient number of molecular collisions occur for a gas phase sample, or that all of the parts of a sample are in thermal contact with one another in condensed phase samples) to ensure thermal uniformity throughout the sample. The distribution is given by the following expression:

$$\frac{N_i}{N_{tot}} = \frac{d_i e^{-E_i/kT}}{q}$$

where $\frac{N_i}{N_{\text{tot}}}$ is the fraction of molecules in the i^{th} quantum state, that has and energy given by E_i and a degeneracy given by d_i. The term kT is the Boltzmann constant times the temperature on an absolute scale. The denominator, q, is a partition function, which is part of a normalization factor. The partition function is given by

$$q = \sum_i d_i e^{-E_i/kT}$$

In the case of rotational energy levels for closed-shell molecules, the subscript I can be replaced by the rotational quantum number J.

$$q_{rot} = \sum_J d_J e^{-E_J/kT}$$

In this expression, the rotational energy level degeneracies are always given by $(2J+1)$ and the rotational energy levels (if treated as rigid rotor levels) are given by $hcBJ(J+1)$. Thus the expression for the rotational partition function, qrot, is given by

$$q_{rot} = \sum_J (2J+1) e^{-hcBJ(J+1)/kT}$$

It is handy to note that $\frac{hc}{kT}$ has a value of approximately $206\ \text{cm}^{-1}$ at room temperature. When the energy E_i exceeds approximately $10 \cdot \text{kT}$, the exponential term becomes negligibly small.

Focusing on the numerator of the Maxwell-Boltzmann expression, it is clear that the effect of increasing J is mixed in the expression. As J increases, the degeneracy increases (having the effect of increased fractional population in the level) but also the exponential term gets smaller due to the higher energy (having the effect of a decreased fractional population in the energy level.) A plot of factional population as a function of J (for HCl at 298 K) is shown below.

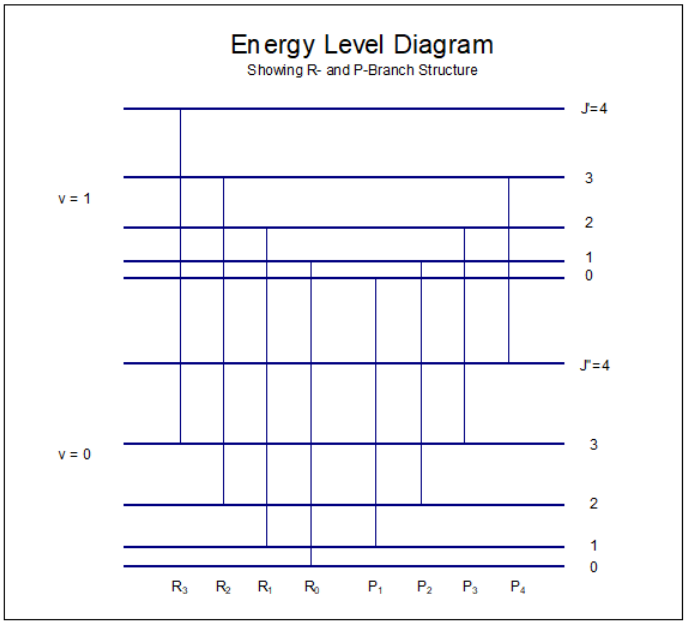

Figure 5.7.5

Note that at low values of J, the fractional population increases with increasing J, to a point. Eventually, the exponential term takes over and the population is extinguished. The J value (J_{max}) at which this changeover occurs is a function of the rotational constant

B and the temperature, and can be determined by solving the following expression for J.

$$\frac{d}{dJ}(2J+1)e^{\frac{-hcBJ(J+1)}{kT}}=0$$

The result is

$$J_{\max}=\sqrt{\frac{kT}{2Bhc}}-\frac{1}{2}$$

The intensity pattern is plainly visible in the rotation-vibration spectrum of HCl. A simulated spectrum of the 1-0 band of $H^{35}Cl$ is shown below, clearly showing the P- and R-branch structure, and the large gap between where the band origin can be found.

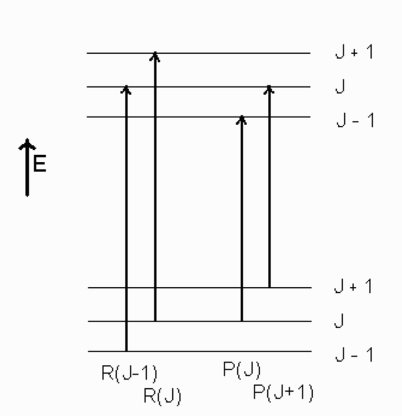

Figure 5.7.6

Line Strength Considerations

The second major consideration in spectral line intensity is the **line strength**. This is determined by the squared magnitude of the transition moment integral.

$$\text{Int.}\propto\left|\int(\psi')^{*}\vec{\mu}\,(\psi'')\,d\tau\right|^{2}$$

The rotational contribution, often called the rotational line strength, to this expression is a **HönlLondon factor**. For closed shell diatomic molecules, the Hönl-London factors are given by

$$\begin{aligned}\mathrm{S_J}&=\mathrm{J}+1 &&(\text{for R-branch lines})\\ \mathrm{S_J}&=\mathrm{J} &&(\text{for P-branch lines})\end{aligned}$$

A good way to think of these expressions is to view them as **branching ratios**. They indicate the relative fraction of molecules in a given level that will undergo an R-branch transition compared to what fraction will undergo a P-branch transition. The molecules the lower state must "decide" to undergo either an R-branch transition or a P-branch transition. The relative fraction of each type of "decision" is the branching ratio.

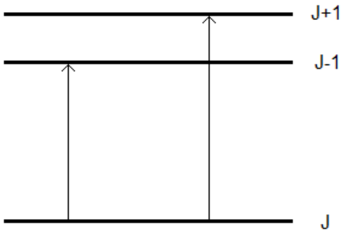

Figure 5.7.7

Notice that the sum of these two expressions gives the total degeneracy of the rotational level. Given this relationship, it should be clear that the fractions of molecules undergoing each type of transition are given by

$$F_R = \frac{J+1}{2J+1} \quad \text{and} \quad F_P = \frac{J}{2J+1}$$

For open shell molecules, the expressions can be quite a bit more complex, but that is a topic for a more detailed course on molecular spectroscopy. However, some of the details of rotational structure of open shell molecules will be discussed in Chapter 8, as the electronic portion of the molecular wavefunction can affect the rotational structure profoundly.

5.8: References

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5.9: Vocabulary and Concepts

allowed transitions

angular momentum

combination differences

forbidden transitions

Hönl-London factor

Legendre polynomial

line strength

Maxwell-Boltzmann distribution

moment of inertia

rigid rotor

selection rules

spherical harmonics

spherical polar coordinates

transition moment

5.10: Problems

1. Consider the data given in the table for lines found in the pure rotational spectrum of ${}^{12}\mathrm{C}^{16}\mathrm{O}$. Determine an approximate value for B and assign the spectrum (the lower → upper state rotational quantum numbers for each line.) Make a graph of $\frac{\tilde{v}_J}{(J+1)}$ vs. $(J+1)^2$ and determine

line	$\tilde{v}\ (\mathrm{cm}^{-1})$
1	3.84503319
2	7.68991907
3	11.5345096
4	15.378662
5	19.222223
6	23.065043

the best fit line. Use these results to determine B and D for the molecule. Compare your results to those found in the NIST Webbook of Chemistry for the ground electronic state of CO.

2. Consider the following data for the rotation-vibration spectrum of $\mathrm{H}^{35}\mathrm{Cl}$.
    a. Using the differences in frequency, assign the location of the band origin and assign the P - and R-branches accordingly.
    b. Using combination differences, fir the data to find B’, D’, B" and D’.
    c. Use your results to find B_{e}, α_{e} and De_{e}.
    d. Based on your value of B_e, find a value for r_e for the molecule.
    e. Compare your results to those found in the NIST Webbook of Chemistry.

line	Freq. $\left(\mathbf{cm}^{-1}\right)$	$\Delta\tilde{v}$
1	3085.62	
2	3072.76	
3	3059.07	
4	3044.88	
5	3029.96	
6	3014.29	
7	2997.78	
8	2980.90	
9	2963.24	
10	2944.89	
11	2925.78	
12	2906.25	
13	2865.09	
14	2843.65	
15	2821.49	
16	2798.78	
17	2775.79	

line	Freq. $(\mathbf{cm}^{-1})$	$\Delta\tilde{v}$
18	2752.03	
19	2727.75	
20	2703.06	
21	2677.73	
22	2651.97	
23	2625.74	
24	2599.00	

3. A recursion formula for the Legendre Polynomials is given by

$$(l+1)P_{l+1}(x) = (2l+1)xP_l(x) - lP_{l-1}(x)$$

Based on $P_0(x) = 1$ and $P_1(x) = x$ find expressions for $P_2(x)$ and $P_3(x)$.

4. The function describing the $l = 1,\ \mathrm{m}_l = 0$ spherical harmonic is $Y_1^0(\theta, \phi) = \sqrt{\frac{3}{4\pi}}\cos(\theta)$
   a. Show that this function is normalized. To do this, you must use the limits on θ and ϕ of $0 \leq \theta \leq \pi$, and $0 \leq \phi \leq 2\pi$. Also, for the angular part of the Laplacian, $d\tau = \sin(\theta) d\theta d\phi$
   b. Using plane polar graph paper (or a suitable graphing program) plot the square of the function from problem 2 in the yz plane (which gives a cross-section of the probability function for the particular spherical harmonic.) Does the shape look familiar?
5. Based on the given bond-length data, calculate values for the rotational constants for the following molecules:

Molecule	Bond Length $(\mathrm{\mathring{A}})$
$\mathrm{H^{35}Cl}$	1.2746
$\mathrm{H^{79}Br}$	1.4144
$\mathrm{H^{127}I}$	1.6092

6. The spacing between lines in the pure rotational spectrum of BN is $3.31\ \mathrm{cm}^{-1}$. From this, find B and calculate the bond length ($\mathrm{r_{BN}}$) in the BN molecule.
7. From your result in problem 6, calculate the frequencies of the first 4 lines in the pure rotational spectrum of BN.

CHAPTER OVERVIEW

6: The Hydrogen Atom

The hydrogen atom problem was one that was very perplexing to the pioneers of quantum theory. While its quantized nature was evident from the known atomic emission spectra, there were no models that could adequately describe the patterns seen in the spectra.

6.1: Older Models of the Hydrogen Atom

Two of the most important (historically) models of the hydrogen atom and it's energy levels/spectra were proved by Johannes Balmer, a high school teacher, and Niels Bohr, a Danish physicist. Balmer's model was a completely empirical fit to existing data for the emission spectrum of hydrogen, whereas Bohr provided an actual theoretical underpinning to the form of the model which Balmer derived. In this section, we will discuss the development and ramifications of these two models.

Balmer's Formula

Balmer (Balmer, 1885) was the first to provide an empirical formula that gave a very good fit to the data, but offered no theoretical reasoning as to why the formula had the simple form it did. Balmer felt, however, that despite the lack of a theoretical foundation, such a simple pattern could not be the result of an "accident".

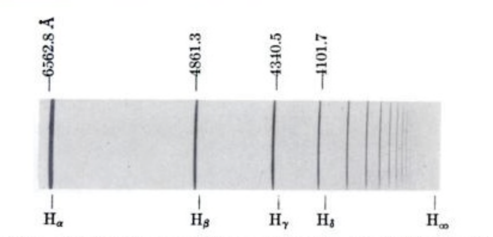

Figure 6.1.1

Balmer suggested the formula

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

to calculate the wavelengths (λ) of the lines in the visible emission spectrum of hydrogen. In this formula, $G = 3647.053$ Å, which is the series limit (depicted as H_∞ in the figure above.) Balmer considered this to be a "fundamental constant" for hydrogen and fully expected other elements to have similar fundamental constants.

In modern terms, Balmer's formula has been extended to describe all of the emission lines in the spectrum of atomic hydrogen.

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

where n_l and n_u are integers with $n_l < n_u$. R_H is the Rydberg constant for hydrogen and has the value

$$R_H = 109677\ cm^{-1}$$

The job of subsequent investigators was to provide a theory that explained the form of the Rydberg Equation shown above and to correctly predict the value of the Rydberg Constant.

This model describes all known series of emission lines in the spectrum of atomic hydrogen. Each series is characterized by the lower state quantum number. The following table summarizes the names of these series.

n_l	Name	Region
1	Lyman	Vacuum Ultraviolet
2	Balmer	Visible/Ultraviolet
3	Paschen	Near Infrared
4	Brachen	Infrared
5	Pfund	Far Infrared

The Bohr Model

Niels Bohr (Bohr, 1913) was the first person to offer a successful quantum theory of the hydrogen atom in his 1913 paper. He was later awarded the Nobel Prize in Physics in 1922 for his contributions to the understanding of atomic structures (as well as many other significant contributions.) And while the Bohr model has significant shortcomings in terms of providing the best description of a hydrogen atom, it still provides the basis (a “solar system model”) for how many people view atoms today.

Bohr’s model was mostly an extension of the Rutherford model of an atom, in which electrons exist in a cloud surrounding a dense, positively charged nucleus. The Bohr model suggested a possible structure to this cloud in an attempt to give an explanation of the empirical formula presented by Balmer. The strength of the Bohr model is that it does provide an accurate prediction not only of the form of Balmer’s formula, but also of the magnitude of the Rydberg constant that appears in the formula.

Bohr’s approach was to balance the electrostatic attractive force between an electron and a positively charged nucleus, with the centrifugal force the electron feels as it orbits the nucleus in a circular orbit. He derived these orbits by making the assumption that the angular momentum of an orbiting electron is an integral multiple of $\hbar$.

While successful in predicting the form of the Rydberg Equation and the magnitude of R_H, the Bohr model presented some difficulty. First, it ignored the reality that a charged particle orbiting another (oppositely) charged nucleus would see its orbit decay over time, eventually colliding with the nucleus. This clearly does not happen with hydrogen! Also, the Bohr model was not extendable to larger atoms. Quantum mechanics would have to address these problems, while also providing the kind of explanations for the Rydberg Equation provided by Bohr.

6.2: The Quantum Mechanical H-atom

As is so often the case for quantum mechanical systems, the story of the hydrogen atom begins with writing down the Hamiltonian describing the system.

The Potential Energy and the Hamiltonian

The time-independent Schrödinger equation has the following form.

$$\hat{H}\psi\left(r,\theta,\phi\right) = E\psi\left(r,\theta,\phi\right)$$

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2 + U(r)\right]\psi(r,\theta,\phi) = E\psi(r,\theta,\phi)$$

where m is the reduced mass for the electron/nucleus system. The Laplacian operator has the form

$$\begin{aligned}\nabla^2 &= \left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\\ &= \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\\ &= \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}+\frac{1}{r^2}\hat{L}^2\end{aligned}$$

The potential energy is given by the electrostatic attraction of the electron to the nucleus.

$$U\left(r\right) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

where Z is the charge on the nucleus in electron charges (also given by the atomic number), e is the charge on an electron and ε_0 is the vacuum permittivity.

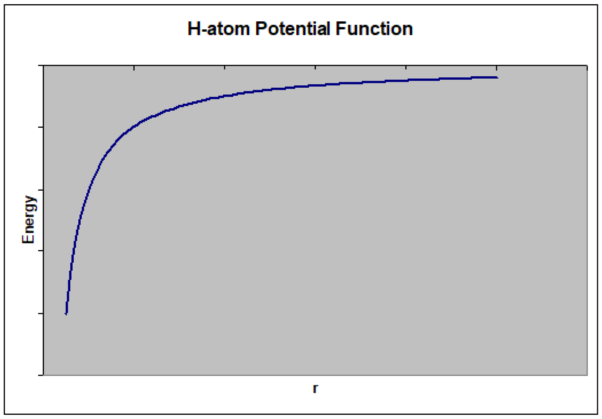

Figure 6.2.1

The $\frac{1}{r}$ dependence means that the electrostatic attraction diminishes as the distance between the electron and the nucleus is increased. The potential energy approaches zero as r goes to ∞, at which point the atom ionizes.

Putting this all together allows the Hamiltonian to be expressed as

$$\hat{H} = -\frac{\hbar^2}{2\mu r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}-\frac{Ze^2}{4\pi\varepsilon_0 r}+\frac{1}{2\mu r^2}\hat{L}^2$$

The wavefunctions can be expressed as a product of a radial part and an angular part since the CityplaceHamilton is separable into these two parts.

$$\psi\left(r,\theta,\phi\right) = R(r)Y_l^{m_l}\left(\theta,\phi\right)$$

The angular part of the function, $Y_l^{m_l}\left(\theta,\phi\right)$ are the spherical harmonics and are eigenfunctions of the $\hat{L}^2$ operator. Substitution into the Schrödinger equation yields

$$Y_l^{m_l}(\theta,\phi)\left(-\frac{\hbar^2}{2\mu r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}-\frac{Ze^2}{4\pi\varepsilon_0 r}\right)R(r)+\frac{R(r)}{2\mu r^2}\hat{L}^2 Y_l^{m_l}(\theta,\phi)=ER(r)Y_l^{m_l}(\theta,\phi)$$

Since the spherical harmonics are eigenfunctions of the $\hat{L}^2$ operator, the following substitution can be made.

$$\hat{L}^2 Y_l^{m_l}(\theta,\phi)=\hbar^2 l(l+1)Y_l^{m_l}(\theta,\phi)$$

After making this substitution and dividing both sides by $Y_l^{m_l}(\theta,\phi)$, we get

$$\left(-\frac{\hbar^2}{2\mu r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}-\frac{Ze^2}{4\pi\varepsilon_0 r}\right)R(r)+\frac{\hbar^2 l(l+1)}{2\mu r^2}R(r)=ER(r)$$

However, since l shows up in the equation in which we are solving for the radial wavefunctions $R(r)$, it is not to be unexpected that the solution to the radial part of the equation will place new constraints on the quantum number l. In fact, the radial wavefunctions themselves depend on l and a **principle quantum number** number n.

The Energy Levels

Applying the boundary condition that the radial wavefunction $R(r)$ must vanish as $r\rightarrow\infty$, the only wavefunctions that behave properly have the following eigenvalues

$$E_n=-\frac{\mu Z^2 e^4}{2\hbar^2(4\pi\varepsilon_0)^2}\frac{1}{n^2}\qquad n=1,2,3,\ldots$$

Notice also that this expression vanishes as n approaches ∞, which is the ionization limit of the atom. Also, since the energy expression depends only on n (and not on l and m_l) it is expected that there will be a great deal of degeneracy in the wavefunctions.

Taking differences between two energies levels (to derive an expression for the energy differences that can be observed in the spectrum of hydrogen), it is seen that

$$E_{n'}-E_{n"}=-\frac{\mu Z^2 e^4}{2\hbar^2(4\pi\varepsilon_0)^2}\left(\frac{1}{n'^2}-\frac{1}{n"^2}\right)=\frac{\mu Z^2 e^4}{2\hbar^2(4\pi\varepsilon_0)^2}\left(\frac{1}{n"^2}-\frac{1}{n'^2}\right)$$

which is exactly the form of the Rydberg Equation. Now dividing both sides by hc in order to convert from energy units to wavenumber units

$$\begin{aligned}\frac{E_{n'}-E_{n"}}{hc}&=\frac{\mu Z^2 e^4}{(hc)2\hbar^2(4\pi\varepsilon_0)^2}\left(\frac{1}{n"^2}-\frac{1}{n'^2}\right)\\&=109677.581\ cm^{-1}\left(\frac{1}{n"^2}-\frac{1}{n'^2}\right)\end{aligned}$$

using the reduced mass for the hydrogen atom and a nuclear charge of +1. So this model also predicts the correct value for the **Rydberg constant** R_H.

The Rydberg Constant for Heavier Nuclei

The expression for the Rydberg constant is

$$R_H=\frac{\mu e^4}{(hc)2\hbar^2(4\pi\varepsilon_0)^2}$$

which has a value of $R_H=109677.581\ cm^{-1}$. In this expression, μ is the reduced mass of the electron-proton system in the hydrogen atom. But what happens when the mass of the nucleus is extremely large? First, consider the reduced mass.

$$\mu=\frac{m_e m_N}{m_e+m_N}$$

Where m_e is the mass of an electron and m_N is the mass of the nucleus. In the case that the nuclear mass is extremely large compared to the mass of an electron, the total mass is approximately equally to the mass of the nucleus.

$$(m_e+m_N)\approx m_N$$

In this case, the reduced mass becomes

$$\begin{aligned}\mu &= \frac{m_e m_N}{m_e + m_N} \\ &\approx \frac{m_e m_N}{m_N} = m_e\end{aligned}$$

And the Rydberg constant expression comes to

$$\begin{aligned}R_\infty &= \frac{m_e e^4}{(hc)2\hbar^2(4\pi\varepsilon_0)^2} \\ &= 109737.316\ cm^{-1}\end{aligned}$$

where R_∞ indicates the Rydberg constant for an infinite mass nucleus atom. It is this value that is usually found in tables of physical constants.

But for lighter atoms, such as hydrogen, the value of the Rydberg constant deviates form this value. In fact, hydrogen shows the largest deviation for any atom, given that it has the lightest nucleus. Compared to experimental precision, this deviation is important (even for atoms where the mass of an electron is only 1×10^{-6} times that of the nucleus!) if one hopes to fit data to experimental precision.

To address this problem, we look back to the expression for the Rydberg constant for an arbitrary mass nucleus, R_M.

$$\begin{aligned}R_M &= \frac{\mu e^4}{(hc)2\hbar^2(4\pi\varepsilon_0)^2} \\ &= \left(\frac{m_N}{m_e + m_N}\right)\frac{m_e e^4}{(hc)2\hbar^2(4\pi\varepsilon_0)^2} = \left(\frac{m_N}{m_e + m_N}\right) R_\infty\end{aligned}$$

Clearly as the mass of the nucleus (m_N) becomes larger, the value of R_M will approach that of R_∞ asymptotically.

The Wavefunctions

The hydrogen atom wavefunctions $\psi(r, \theta, \phi)$ can be expressed as a product of radial and angular functions.

$$\psi_{nlm_l}(r, \theta, \phi) = R_{nl}(r)\, Y_l^{m_l}(\theta, \phi)$$

The angular part is simply the spherical harmonics that were described in Chapter 5, depend on the quantum numbers l and m_l. More details of how the spherical harmonics are generally presented as H-atom angular functions is discussed in section 3.i. The radial part of the wave functions, $R_n^l(\theta, \phi)$ will be described in a later section.

The Angular Part of the Wavefunctions

Each orbital wave function can be designated with a letter than indicates the value of l as assigned in the following table.

l	**Designation**
0	s
1	p
2	d
3	f

The angular parts of the wavefunctions are given by the spherical harmonics. After taking linear combinations to eliminate the imaginary part of the wave functions, the familiar shapes of s, p, d and f orbitals are generated. For example, the p_x and p_y orbitals are generated as linear combinations of the p_{-1} and p_1 orbitals.

$$p_x = \frac{1}{\sqrt{2}}\left(Y_1^1 - Y_1^{-1}\right) \propto \sin\theta\cos\phi$$

$$p_y = \frac{1}{i\sqrt{2}}\left(Y_1^1 + Y_1^{-1}\right) \propto \sin\theta\sin\phi$$

Similar linear combinations are used to generate the $d_{x^2-y^2}$, d_{xy}, d_{yz} and d_{xz} functions.

$$d_{z^2} = Y_2^0$$

$$d_{xz} = -\frac{1}{\sqrt{2}}\left(Y_2^1 - Y_2^{-1}\right) \quad d_{yz} = -\frac{1}{i\sqrt{2}}\left(Y_2^1 + Y_2^{-1}\right)$$

$$d_{xy} = -\frac{1}{\sqrt{2}}\left(Y_2^2 - Y_2^{-2}\right) \quad d_{x^2-y^2} = -\frac{1}{i\sqrt{2}}\left(Y_2^2 + Y_2^{-2}\right)$$

There are multiple choices for how to take linear combinations to generate the f orbital functions (the best choice being determined by the geometry of the complex in which an f-orbital containing atom exists), so these are rarely shown in textbooks! The tables below give the angular parts of s, p and d hydrogen atom orbitals. The linear combinations shown above have been used to eliminate the imaginary parts of the wave functions. The result is what is usually plotted for the shapes of these orbitals.

l	**Orbital**	$Y_l^{m_l}(\theta, \phi)$
0	s	$\sqrt{\frac{1}{4\pi}}$
1	p_x	$\sqrt{\frac{3}{4\pi}}\sin(\theta)\cos(\phi)$
	p_y	$\sqrt{\frac{3}{4\pi}}\sin(\theta)\sin(\phi)$
	p_z	$\sqrt{\frac{3}{4\pi}}\cos(\theta)$

l	**Orbital**	$Y_l^{m_l}(\theta, \phi)$
2	d_{z^2}	$\sqrt{\frac{5}{16\pi}}\left(3\cos^2(\theta) - 1\right)$
	d_{xz}	$\sqrt{\frac{15}{16\pi}}\sin(\theta)\cos(\theta)\sin(\phi)$
	d_{yz}	$\sqrt{\frac{15}{16\pi}}\sin(\theta)\cos(\theta)\cos(\phi)$
	d_{xy}	$\sqrt{\frac{15}{64\pi}}\sin^2(\theta)\sin(2\phi)$
	$d_{x^2-y^2}$	$\sqrt{\frac{15}{64\pi}}\sin^2(\theta)\cos(2\phi)$

These functions generate the familiar angular parts of the hydrogen atom wavefunctions. Some depictions are shown in the figure below.

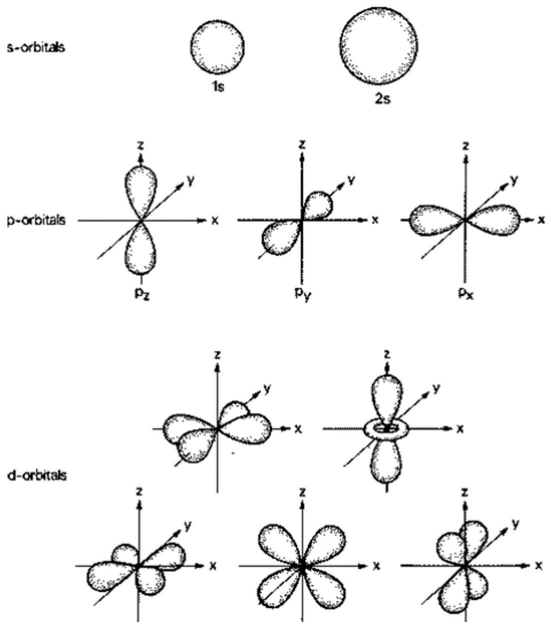

Figure 6.2.2

The Radial Part of the Wavefunctions

The radial part of the wavefunction has three parts. 1) a normalization constant, 2) an associated Laguerre Polynomial and 3) an exponential part that ensures the wavefunction vanishes as $r \to \infty$. The associated Laguerre polynomials are derived from the Laguerre polynomials (much like the associated Legendre Polynomials were from the Legendre polynomials.) The Laguerre polynomials can be derived from the expression

$$L_n(x) = \frac{e^x}{n!} \frac{d^n}{dx^n} x^n e^{-x}$$

The first few Laguerre polynomials are given by

n	L_n (x)
0	1
1	$-x+1$
2	$\frac{1}{2}(x^2-4x+2)$
3	$\frac{1}{6}(-x^3+9x^2-18x+6)$

A recursion formula for these functions is given by

$$L_{n+1}(x) = (2n+1-x)L_n(x) - n^2 L_{n-1}(x)$$

The associated Laguerre polynomials can be generated using the expression

$$L_n^\alpha(x) = \frac{d^\alpha}{dx^\alpha} L_n(x)$$

This expression is used to generate an associated Laguerre polynomial of degree $n-\omega$ and order ω. The functions of interest to the hydrogen atom radial problem are the associate Laguerre polynomials of degree $n-l-1$ and order $2l+1$. It can be shown that these functions can be generated from the relationship

$$L_{n+l}^{2l+1}(x) = \sum_{k=0}^{n-l-1} (-1)^{k+1} \frac{[(n+l)!]^2}{(n-1-l-k)!\,(2l+1+k)!k!} x^k$$

Note that when $n-l-1$ is less than zero, the functions vanish. This leads to the restriction on the quantum number *l* that comes from the solutions to the radial part of the problem.

$$l \leq n-1$$

The first few associated Laguerre polynomials that appear in the hydrogen atom wavefunctions are shown below.

n	l		$L_{n+l}^{2l+1}(x)$	# nodes
1	0	$L_1^1(x)$	-1	0
2	0	$L_2^1(x)$	$-2!(2-x)$	1
	1	$L_3^3(x)$	$-3!$	0
3	0	$L_3^1(x)$	$-3!(3-3x-½x^2)$	2
	1	$L_4^3(x)$	$-4!(4-x)$	1
	2	$L_5^5(x)$	$-5!$	0

Notice that if $(2l+1)$ exceeds $(n+l)$, the derivative causes the function to go to zero, as was the case for the associated Legendre Polynomials when m_l exceeds l. This provides the constraint on *l* that was expected to be found in the solution to the radial part given that *l* shows up in the equation to be solved.

$$l \leq n-1$$

Typically, x is replaced by a new function in r, ρ. ρ is defined as follows:

$$\rho = \left(\frac{2Zr}{na_0}\right)$$

where a_0 is the Bohr radius. The overall expression for the radial wavefunction is given as follows:

$$R_{nl}(r) = -\left[\frac{(n-l-1)!}{2n[(n+l)!]^3}\right]^{1/2} \left(\frac{Z}{na_0}\right)^{l+3/2} r^l L_{n+l}^{2l+1}\left(\frac{2Zr}{na_0}\right) e^{-r/na_0}$$

The first several radial wavefunctions are given below.

n	l		$R_n^l(\rho)$
1	0	1s	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\frac{Zr}{a_0}}$
2	0	2s	$\left(\frac{Z}{2a_0}\right)^{3/2} (2-\rho)\, e^{-\rho/2}$
	1	2p	$\frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{3/2} \rho e^{-\rho/2}$
3	0	3s	$\frac{2}{27}\left(\frac{Z}{3a_0}\right)^{3/2} (27-18\rho+2\rho^2)\, e^{-\rho}$
	1	3p	$\frac{1}{27}\left(\frac{2Z}{3a_0}\right)^{3/2} (6\rho-\rho^2)\, e^{-\rho/3}$
	2	3d	$\frac{4}{27\sqrt{10}}\left(\frac{Z}{3a_0}\right)^{3/2} \rho^2 e^{-\rho/3}$

where $\rho = Zr/a_0$. a_0 is the Bohr radius, which has a value of $5.29177249 \times 10^{-11}$ m.

✓ Example 6.2.1

What is the expectation value of *r* for the electron if it is in the 1s subshell of an H atom?

Solution

The expectation value can be found from

$$\langle r \rangle = \int_0^\infty \psi_{1s}^* \cdot r \cdot \psi_{1s} \, r^2 dr$$

Where $r^2 dr$ comes from the r portion of the volume element $dx\ dy\ dz$ after it has been transformed into spherical polar coordinates.

Substituting the wavefunction from above yields

$$\langle r \rangle = \int_0^\infty \left[2 \left(\frac{1}{a_0} \right)^{\frac{3}{2}} e^{-\frac{r}{a_0}} \right] r \left[2 \left(\frac{1}{a_0} \right)^{\frac{3}{2}} e^{-\frac{r}{a_0}} \right] r^2 dr$$

This expression simplifies to

$$\langle r \rangle = 4 \left(\frac{1}{a_0} \right)^3 \int_0^\infty r^3 \left[e^{-\frac{2r}{a_0}} \right] dr$$

A table of integrals shows

$$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$$

Substituting the above integral into the general form results in

$$\begin{aligned} \langle r \rangle &= 4 \left(\frac{1}{a_0} \right)^3 \left(\frac{6}{\left(\frac{2}{a_0} \right)^4} \right) \\ &= \frac{24}{16} \left(\frac{1}{a_0^3} \right) \left(a_0^4 \right) \\ &= \frac{3}{2} a_0 \end{aligned}$$

Example 6.2.2

What is the most probable value of r for the electron in a hydrogen atom in a 1s orbital?

Solution

The most probable value of r will be found at the maximum of the function

$$P(r) = r^2 [R(r)]^2$$

This can be found by taking the derivative and setting it equal to zero. First, let’s find the probability function

$$P(r) = r^2 \left[2 \left(\frac{1}{a_0} \right)^{\frac{3}{2}} e^{-\frac{r}{a_o}} \right]^2 = \frac{4}{a_0^3} r^2 e^{-\frac{2r}{a_0}}$$

At the maximum, the derivative is zero.

$$\frac{d}{dr} P(r) = 0$$

So

$$\frac{d}{dr} \left[\frac{4}{a_o^3} r^2 e^{-\frac{2r}{a_0}} \right] = \frac{4}{a_3^3} \left(2r\, e^{-\frac{2r}{a_0}} - \frac{2}{a_0} r^2 e^{-\frac{2r}{a_0}} \right) = 0$$

After dividing both sides by $\frac{4}{a_0^3}$, and placing the right-hand term on the other side of the equals sign, this simplifies to

$$2r\, e^{-\frac{2r}{a_0}} = \frac{2}{a_0} r^2 e^{-\frac{2r}{a_0}}$$

This is further simplified by dividing both sides by $e^{-\frac{2r}{a_0}}$:

$$2r = \frac{2}{a_0}\, r^2$$

The rest of the algebra is straight forward (actually, all of the algebra was straight-forward, but who is counting?)

$$r = a_0$$

Nodes

A hydrogen atom wavefunction can have nodes in either the orbital (angular) part of the wavefunction or the radial part. The total number of nodes is always given by $n – 1$. The number of **angular nodes** is always given by l. The number of radial nodes, therefore, is determined by both *n* and *l*. Consider the following examples.

Nodes

	radial	angular	total
1s	0	0	0
4d	2	1	3
5f	1	3	4
2d		-	-
2p	0	1	1

Notice that it is impossible to form a 2d wavefunction as it violates the relationship that

$$l \leq n – 1$$

causing the radial wavefunction to vanish. This is easy to see as the combination of $n = 2$ and $l = 3$ implies that there are -1 radial nodes, which is clearly impossible.

Shells, Subshells and Orbitals

It is convenient to name the different subdivisions of the electronic structure of a hydrogen atom. The subdivisions are based on the quantum numbers n, l and m_l. A **shell** is characterized by the quantum number n. (Examples: the n=2 shell or the n=4 shell.) A **subshell** is characterized by both the quantum number n and l. (Examples: the 2s subshell or the 3d subshell.) An **orbital** is characterized by the quantum number n, l, and m_l . (Examples: the $2p_0$ orbital or the 5f1 orbital.) It should be noted that an orbital can also be constructed from a linear combination of other orbitals! (Example: the $2p_x$ orbital or the $3d_{xy}$ orbital.)

Degeneracy

The hydrogen atom wavefunctions have high degeneracies since the energy of a given level depends only on the principle quantum number n. As such, all wavefunctions with the same value of n will have the same eigenvalue to the Hamiltonian, and are degenerate. Recall the following relationships:

$$l \leq n - 1 \text{ and } m_l \leq l$$

These relationships can be used to fill in the following table that indicates the degeneracies of the hydrogen atom energy levels.

Subshell	**n**	$\boldsymbol{l}$	$\boldsymbol{m_l}$	$\boldsymbol{m_s}$		
					orbital	**total**
1s	1	0	0	$+\frac{1}{2}, -\frac{1}{2}$	1	2
2s	2	0	0	$+\frac{1}{2}, -\frac{1}{2}$	4	8
2p		1	+1, 0, -1	$+\frac{1}{2}, -\frac{1}{2}$		
3s	3	0	0	$+\frac{1}{2}, -\frac{1}{2}$	9	18
3p		1	+1, 0, -1	$+\frac{1}{2}, -\frac{1}{2}$		

Subshell	**n**	l	m_l	m_s		
3d		2	+2, +1, 0, -1, -2	$+\frac{1}{2}, -\frac{1}{2}$		
4s	4	0	0	$+\frac{1}{2}, -\frac{1}{2}$	16	32
4p		1	+1, 0, -1	$+\frac{1}{2}, -\frac{1}{2}$		
4d		2	+2, +1, 0, -1, -2	$+\frac{1}{2}, -\frac{1}{2}$		
4f		3	+3, +2, +1, 0, -1, -2, -3	$+\frac{1}{2}, -\frac{1}{2}$		

It is clear that the total degeneracy of a shell is given by $2n^2$.

The Overall Wavefunctions

The total wavefunction, including both angular and radial parts, for hydrogen-like atoms is given by

$$\Psi_{nlm_l} = R_{nl}\left(r\right) Y_l^{m_l}\left(\theta, \phi\right)$$

The first few hydrogen atom orbital wavefunctions are given in the table below.

Shell	**Subshell**	m_l	**Wavefunction**	
1	1s	0	ψ_{100}	$\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho}$
2	2s	0	ψ_{200}	$\frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \left(2-\rho\right) e^{-\rho/}$
	2p	0	ψ_{210}	$\frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \rho e^{-\rho/2} \cos(\theta$
		±1	$\psi_{21\pm1}$	$\frac{1}{\sqrt{64\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \rho e^{-\rho/2} \sin(\theta$

6.3: Rydberg Spectra of Polyelectronic Atoms

To a very good approximation, the electronic spectra of highly excited atoms look a lot like the spectrum of hydrogen. These highly excited states of atoms are called "Rydberg States" and to a good approximation, the excited electron in a Rydberg state "feels" the nucleus of the atom as a point charge. As this occurs, the atom comes to be in a state that looks much like a state in a hydrogen-like atom, with a heavy nucleus that has $a+1$ charge (the residual ion if the excited electron is removed).

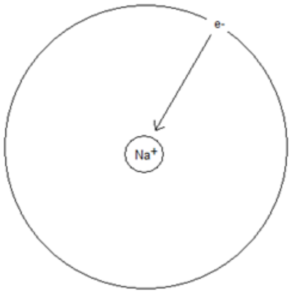

Figure 6.3.1

In cases such as this, the energy levels of the excited electron can almost be treated using the Rydberg formula proposed by Balmer, and with the correct Rydberg constant (R_M) and nuclear charge. The formula does not work perfectly, but can be forced to fit the data by introducing a "fudge factor."

Approximating a Hydrogen-like Atom

Scientists like to force the descriptions of real systems in terms of the limiting ideal cases with slight perturbations. In the case of real atoms, there are two common ways that this is typically done. One is to fudge the nuclear charge and the other is to fudge on the principle quantum number.

Shielding and Effective Nuclear Charge

One "fudges" the nuclear charge by noting that the excited electron will not "see" the inner core ion as a point charge with $a+1$ charge. Instead, it will feel the full charge of the nucleus, but shielded by the electrons that remain in the ion. Thus, the **effective nuclear charge** (Z^*) can be used.

$$\tilde{\nu} = (Z^*)^2 R_M \left(\frac{1}{n_l^2} - \frac{1}{n_u^2} \right)$$

where Z^*, the effective nuclear charge, is defined by

$$Z^* = Z - \sigma$$

where σ is the **shielding constant** and is determined by adding the effects of each of the inner electrons. The trouble with this approach is that the degree of shielding is dependent on the excitation level of the excited electron. The shielding constant σ should reach a limiting value for highly excited Rydberg states of the atom.

Quantum Defect and the Effective Principal Quantum Number

Another approach is to "fudge" on the principle quantum number of the excited electron. The utility of using this method is that there is only one electron to treat, rather than a slew of electrons in the core ion, the shielding of each will be variable. In this method, the **effective principal quantum number** n^* is defined as

$$n^* = n - \delta$$

where δ is the **quantum defect**. The quantum defect has the useful property that it reaches a constant value for electrons in atoms at high levels of excitation.

The ionization potential

The ionization potential of an atom I defined by the enthalpy change at 0 K for the following reaction

$$M \leftarrow M^+ + e^- \qquad \Delta H = IP$$

If one pictures ionization as a series of excitations of the electron to be removed through a set of Rydberg states, one can deduce the ionization potential of an atom. (This is how atomic spectroscopy is used to determine highly accurate ionization potentials.)

Using the effective principle quantum number n^*, the energy levels can be expressed as

$$\frac{E}{hc} = \frac{IP}{hc} - \frac{R_M}{(n^*)^2}$$

Consider the Rydberg series in ^{23}Na, the first few levels of which is given below. For Na, the Rydberg constant can be calculated

$$\begin{aligned} R_{Na} &= \left(\frac{m_{Na}}{m_e + m_{Na}}\right) R_\infty \\ &= \left(\frac{3.81763 \times 10^{-26} kg}{9.109 \times 10^{-31} kg + 3.81763 \times 10^{-26} kg}\right) (109737.316\ cm^{-1}) \\ &= 109734.698\ cm^{-1} \end{aligned}$$

Based on a guess of the ionization potential, an effective principle quantum number can be calculated for each level from

$$n^* = \sqrt{\frac{R_{Na}}{IP - E}}$$

From n^*, one can calculate the quantum defect (δ) and adjust the guess of the ionization potential until Σ becomes constant for large n.

$IP =$	$41449.48 cm^{-1}$		$R_{Na} =$	$109734.7\ cm^{-1}$
Level	n	δ	$n*$	Energy (cm^{-1})
3p	3	0.883	2.117	16956.17
4p	4	0.867	3.133	30266.99
5p	5	0.862	4.138	35040.38
6p	6	0.860	5.140	37296.32
7p	7	0.858	6.142	38540.18
8p	8	0.858	7.142	39298.35
9p	9	0.857	8.143	39794.48
10p	10	0.857	9.143	40136.80
11p	11	0.857	10.143	40382.92
12p	12	0.857	11.143	40565.78
13p	13	0.857	12.143	40705.34
14p	14	0.856	13.144	40814.27
15p	15	0.856	14.144	40900.91
16p	16	0.857	15.143	40970.97
17p	17	0.857	16.143	41028.41

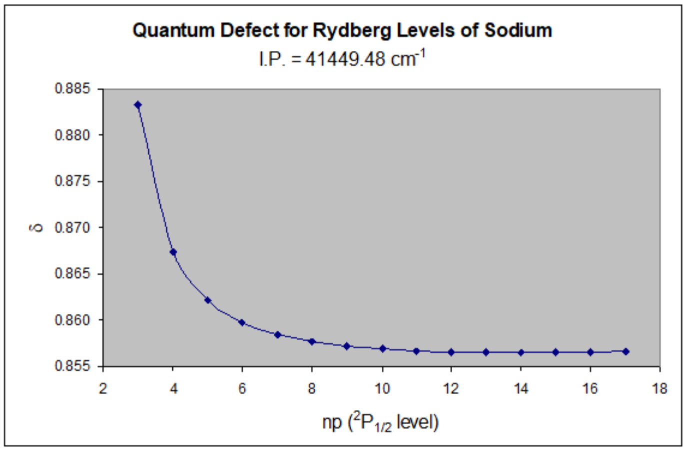

Figure 6.3.2

This method is extremely sensitive and can be used to determine very precise values of ionization potentials for atoms. The above result is 5.145 eV, whereas the literature value for the ionization potential of sodium is 5.139 eV (Webelements). The slightly large value determined from this data is a consequence of only using a limited number of excited levels, and not the highest energy levels, which behave most Rydberg-like. A close examination of the data actually reveals that there is some curvature to the δ vs n curve at high values of n. Since the curve is actually increasing at the larger values of n, it is an indication that the guess for the ionization potential is slightly high – a fact that is consistent with the literature value!

6.4: References

Balmer, J. J. (1885). Notiz über die Spectrallinien des Wasserstoffs. Annalen der Physik und Chemie, 25, 80-85.Bohr, N. (1913). On the Constitution of Atoms and Molecules, Part I. Philosophical Magazine, 26, 1-24.Webelements. (n.d.). Retrieved November 19, 2009, from http://webelements.com/sodium/atoms.html

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6.5: Vocabulary and Concepts

angular nodes

effective nuclear charge

effective principle quantum number

orbital

principle quantum number

quantum defect

Rydberg constant

shell

shielding constant

subshell

6.6: Problems

1. Calculate the finite-mass Rydberg constant (R_M) for
   a. H
   b. D
   c. $_7N$
   d. $_{11}Na$
2. The 1s orbital wavefunction for hydrogen is given by

$$\psi_{1s} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-\frac{r}{a_0}}$$

a. Show that this wavefunction is normalized.
b. Find the expectation value of r in units of a_0 (the Bohr Radius.)

3. Show that the 2s wavefunction for hydrogen is
   a. Normalized
   b. An eigenfunction of the Hamiltonian. (What is the eigenvalue?)
4. The Laguerre Polynomial $L_1(x)$ is given by

$$L_1\left(x\right) = -x+1$$

The Associated Laguerre polynomials are generated from the relationship

$$L_n^\alpha\left(x\right) = \frac{d^\alpha}{dx^\alpha} L_n(x)$$

   a. Show that the Associated Laguerre polynomials $L_1^0\left(x\right) = -x+1$, $L_1^1\left(x\right) = -1$, and $L_1^2\left(x\right) = 0$. (In fact, $L_1^\alpha\left(x\right) = 0$ for any choice of $\alpha > 1$.)
   b. Given that the Associated Laguerre polynomials used in the radial wavefunctions of the Hydrogen atom problem are $L_{n+l}^{2l+1}(x)$, derive a relationship between n and l that ensure that $L_{n+l}^{2l+1}\left(x\right) \neq 0$.

5. Using the Laguerre polynomials $L_2\left(x\right) = \frac{1}{2}\left(x^2-4x+2\right)$ and $L_1\left(x\right) = -x+1$, show that

$$\frac{d}{dx}L_n\left(x\right) = \frac{d}{dx}L_{n-1}\left(x\right) - L_{n-1}(x)$$

6. Sketch the radial wavefunctions for the 1s, 2s, 2p, 3s, 3p, and 3d orbital wavefunctions of Hydrogen.
7. Determine the number of nodes in each of the following hydrogen atom orbital wavefunctions:

wavefunction	Total nodes	Angular nodes	Radial nodes
2s			
3p			
5d			
6f			

8. Determine the ionization potential for $_3He^+$.
   a. Find R_{He} for the He-3 isotope.
   b. Use the relationship

$$IP = Z^2 R_M \left(\frac{1}{(1)^2} - \frac{1}{(\infty)^2}\right)$$

9. Based on the following data, find the ionization energy of Rb, using the fact that at high excitation, the quantum defect (δ) becomes constant.

n (for the $np \leftarrow 5s$ transition)	Wavenumber (cm^{-1})
5	12578.950
6	23715.081
7	27835.02
8	29834.94
9	30958.91
10	31653.85
11	32113.55
12	32433.50
13	32665.03
14	32838.02
15	32970.66
16	33074.59
17	33157.54
18	33224.83
19	33280.13
20	33326.13

CHAPTER OVERVIEW

7: Approximate Methods

The previous chapters all dealt with problems that can be solved analytically. However, there are many problems that are of chemical interest that cannot be solved exactly. For these problems, we must employ some methods that will approximate a correct and complete solution. Two such methods will be discussed in this chapter.

7.1: Perturbation Theory

Often times, a system represents only a small difference from an exactly solvable system. In these instances, **perturbation theory** can be used to describe the system. To use perturbation theory, one must separate the Hamiltonian into two parts: one for which the solution is known ($\hat{H}^{(0)}$) and the other part which will represent the perturbation to the system ($\hat{H}^{(1)}$).

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}$$

The solution for the unperturbed system is known.

$$\hat{H}^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$$

The energy levels and wavefunctions for the perturbed system are determined by applying a series of corrections (referred to as first order, second order, etc.)

$$E_n = E_n^{(o)} + E_n^{(1)} + E_n^{(2)} + \ldots$$

$$\psi_n = \psi_n^{(o)} + \psi_n^{(1)} + \psi_n^{(2)} + \ldots$$

Oftentimes only the first and second order corrections are needed to give a reasonable description of the system. The first order correction to the energy is given by

$$E_n^{(1)} = \int \psi_n^{(0)}\hat{H}^{(1)}\psi_n^{(0)}\,d\tau$$

The second order correction to the energy depends on the first order correction to the wavefunctions.

$$E_n^{(2)} = \int \psi_n^{(0)}\hat{H}^{(1)}\psi_n^{(1)}\,d\tau$$

The formula for generating the first order corrections to the wavefunctions is given by

$$\psi_n^{(1)} = \sum_{i\neq n}\psi_i^{(0)}\frac{\int \psi_i^{(0)}\hat{H}^{(0)}\psi_n^{(0)}\,d\tau}{E_n^{(0)} - E_i^{(0)}}$$

Substitution into the expression for $E_n^{(2)}$ yields

$$E_n^{(2)} = \sum_{i\neq n}\frac{\left|\int \psi_n^{(0)}H^{(1)}\psi_n^{(0)}\,d\tau\right|^2}{E_n^{(0)} - E_1^{(0)}}$$

7.2: Variational Method

The **variational method** is based on the Variational principle which says that a wavefunction that is not the true wavefunction will always yield a value for the energy that is greater than the true ground state energy of the system. This principle can be proven using the superposition theorem that was previously discussed.

Theorem 7.2.1: Variational Method

Assume a trial wavefunction $\psi(x)$ describing a particle in a box, that can be expressed as a linear combination of the normal particle in a box wavefunctions.

$$\psi(x) = \sum_n c_n \phi_n(x)$$

Assuming $\psi(x)$ is normalized, the expectation value of energy $\langle E \rangle$ is obtained from the expression

$$\langle E \rangle = \int \psi(x)\, \hat{H}\, \psi(x)\, d\tau$$

Substituting the expression for $\psi(x)$ from above

$$\langle E \rangle = \int \left(\sum_m c_m \phi_m \right) \hat{H} \left(\sum_n c_n \phi_n \right) d\tau$$

Noting that

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

Substitution yields

$$\langle E \rangle = \int \left(\sum_m c_m \phi_m \right) \left(\sum_n c_n E_n \phi_n \right) d\tau$$

Gathering terms, one obtains

$$\begin{aligned} \langle E \rangle &= \int \left(\sum_m \sum_n c_m c_n E_n \phi_m \phi_n \right) d\tau \\ &= \sum_m \sum_n c_m c_n E_n \int (\phi_m \phi_n)\, d\tau \\ &= \sum_m \sum_n c_m c_n E_n \delta_{mn} \end{aligned}$$

The Kronecker delta will destroy one of the summations since it will pick out only one value to be non-zero.

$$\begin{aligned} \langle E \rangle &= \sum_m \sum_n c_m c_n E_n \delta_{mn} \\ &= \sum_n c_n^2 E_n \end{aligned}$$

Thus if any components of the linear combination have a non-zero contribution ($c_n \neq 0$ for $n > 1$) the expectation value has to be larger than E_1.

The Variational principle can be used to determine reasonable trial wavefunctions (Ψ) based on a set of approximate wavefunctions (ϕ_n). This is done by assuming the trial wavefunction can be expressed as a linear combination of the approximate wavefunctions

$$\Psi = \sum_n c_n \phi_n$$

and then determining the contribution to the trial function by minimizing the energy with respect to the coefficients (c_n) in the expansion.

$$\frac{\partial}{\partial c_n}\langle E\rangle = 0$$

This will produce n equations with n unknown values of c_n which can be simultaneously solved to yield the optimal values of c_n. This methodology is used to a great extent in computational chemistry methods.

Example 7.2.1

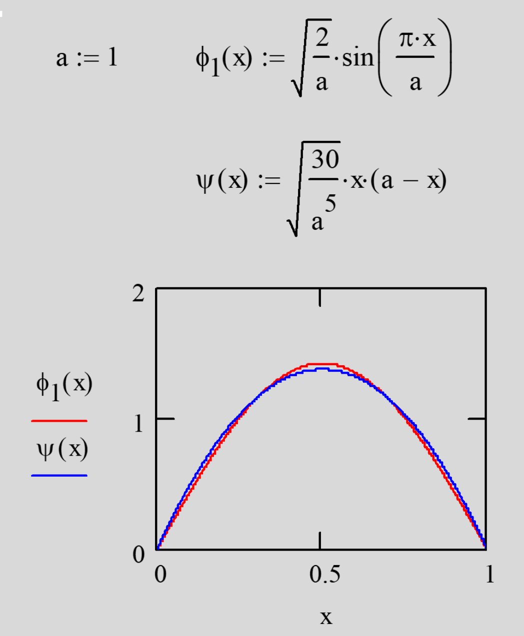
What is $\langle E\rangle$ for a system with the following wavefunction that approximates ψ_1 (x) for a particle in a box?

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

Solution

The wavefunction is a reasonable, but not perfect, approximation of the $n = 1$ level of a particle in a box.

$$\phi_1(x) = \sqrt{\frac{2}{a}} \cdot \sin\left(\frac{\pi \cdot x}{a}\right)$$



$$a := 1 \qquad \phi_1(x) := \sqrt{\frac{2}{a}}\cdot\sin\left(\frac{\pi\cdot x}{a}\right)$$

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

Figure 7.2.1

The expectation value of energy is found in the usual manner.

$$\begin{aligned}\langle E\rangle &= \int_0^a \psi\,\hat{H}\,\psi\,d\tau \\ &= -\frac{\hbar^2}{2m}\,\frac{30}{a^5}\int_0^a \left(ax - x^2\right)\frac{d^2}{dx^2}\left(ax - x^2\right)dx = -\frac{15\hbar^2}{ma^5}\int_0^a \left(ax - x^2\right)(-2)\,dx \\ &= \frac{30\hbar^2}{ma^5}\left[\frac{ax^2}{2} - \frac{x^3}{3}\right]_0^a = \frac{30\hbar^2}{ma^5}\left(\frac{a^3}{6}\right) \\ &= \frac{5\hbar^2}{ma^2}\end{aligned}$$

This result is slightly larger than $\frac{h^2}{8ma^2}$ since $\frac{5}{(2\pi)^2} = 0.127$ and $\frac{1}{8} = 0.125$.

> In the variational method, an approximate form of a wave function can be used

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7.3: Vocabulary and Concepts

perturbation theory

variational method

7.4: Problems

1. Consider a particle of mass m in a box defined between $x = 0$ and $x = a$, that is prepared in the $n = 1$ state. If the wavefunction is approximated by

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

a. Show that the expectation value of $\langle E \rangle$ exceeds E_1 for a particle in a box.
b. By what percentage does the approximate energy exceed that of the $n = 1$ energy?

CHAPTER OVERVIEW

8: Polyelectronic Atoms

One of the shortcomings of Bohr’s model of the hydrogen atom was that it was not extensible to atoms that had more than one electron. The newly emerging quantum mechanics was hoped to do a better job. Unfortunately, while the hydrogen atom problem is solvable analytically, issues arise when an attempt is made to solve the problem for atoms with multiple electrons. Regardless, the first step in deriving this theory, then, is writing the Hamiltonian for the System.

8.1: Potential Energy and the Hamiltonian

The potential energy of a poly electronic atom is all electrostatic in nature. There are attractive forces between electrons and the nucleus and repulsive forces between the electrons themselves. For simplicity, we will consider the helium atom first, which has a nucleus with a charge of +2 electron charges and two electrons with -1 charges each.

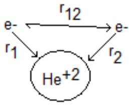

Figure 8.1.1

The Hamiltonian for this system will have kinetic energy terms for both electrons and three terms to describe the potential energy in the system. The attractive forces will lead to negative contributions to the potential energy and the repulsive (electron-electron) force will contribute a positive value to the potential energy. In atomic units, this yields

$$\hat{H} = \hat{T}_1 + \hat{T}_1 - \frac{2}{r_1} - \frac{2}{r_2} + -\frac{1}{r_{12}}$$

The $-\frac{1}{r_{12}}$ (electron-electron repulsion term) makes the problem unseparable into terms that relate only to a single electron. This creates a three body problem, which cannot be solved analytically.

The Orbital Approximation

The way we deal with this problem is to simply ignore the electron-electron repulsion term in the solution, and treat it phenomenologically after the fact. This is known as the **orbital approximation**, as it allows for the separation of the Hamiltonian into two terms, one of which deals in electron 1 and the other in electron 2.

$$\begin{aligned} \hat{H}_{tot} &= \hat{T}_1 - \frac{2}{r_1} + \hat{T}_2 - \frac{2}{r_2} \\ &= \hat{H}_1 + \hat{H}_2 \end{aligned}$$

This is also the approximation that allows us to write electronic configurations for polyelectronic atoms. In the electronic configuration, we assume that each electron has a hydrogen-like wavefunction.

8.2: The Aufbau Principle

The **aufbau principle**(German for “building up” principle), or building up principle, suggests that we can construct a description of an atom my adding subatomic particles one at a time, moving through the periodic table until we reach the element of interest.

Under this description, a carbon atom (atomic number 6) is similar to a boron (atomic number 5) atom, but with one additional proton and some additional neutrons in the nucleus and one additional electron added to the electron cloud.

Electronic Configurations

Consider carbon, which is atomic number 6. Most chemists advanced to a level to which they are prepared to take a course in physical chemistry can construct an electronic configuration for ${}_6C$.

$${}_6C\colon [He]2s^2 2p^2$$

Or for ${}_{23}V$, one would write

$${}_{23}V\colon [Ar]4s^2 3d^3$$

It is a curious thing that that the 4s subshell fills before the 3d subshell, since in atomic hydrogen, the 3d subshell has a lower energy. However, in polyelectronic atoms, (specifically for K and Ca) the 4s subshell is actually lower in energy than the 3d subshell. As such, according to the aufbau principle, it is the 4s subshell that fills first of the two.

However, it is important to note that the relative energies of the subshells change with changing nuclear charge and differing numbers of electrons. For example, in Sc, it is the 4s electrons that are higher in energy than the 3d electron. As such, the 4s electrons are the first to be removed when the atom is ionized.

Shells, Subshells, Orbitals and Spin

It is useful to develop some nomenclature to describe the different combinations of quantum numbers that describe the different wavefunctions for the electrons in an atom. In order to do this, we need ot define a few terms that will come in handy later.

i. **shell**– characterized by the principle quantum number n
ii. **subshell**– characterized by n and the angular momentum quantum number *l*
iii. **orbital**– characterized by n, *l* and the azimuthal quantum number m_l.

In addition to shells, subshells and orbitals, electrons have spin. The spin quantum number of an electron is $\mathbf{s} = \frac{1}{2}$. But generally electrons are described as being “spin up” or “spin down” based on the value of the z-axis component of the spin, m_s. m_s can take values of $+\frac{1}{2}$ and $-\frac{1}{2}$. Each orbital can hold two electrons. If there are two electrons in the orbital, the spins must be pairs such that one is “spin up” and the other is “spin down.”

8.3: Orbital Diagrams

Orbital diagrams are handy to depict electronic configurations without having to resort to just quantum numbers. In an orbital diagram, each orbital is depicted using a box or a line and electrons are depicted with arrows pointing either up or down depending on the value of m_s.

8.4: Angular Momentum Coupling

Any system that has more than one source of angular momentum will be subject to coupling between those forms of angular momentum. For example, consider the emission from an excited hydrogen atom, for which the electron is in the 2p subshell the atom emits a photon as the electron relaxes to be in the ground 1s subshell. In fact, this transition is doubled as two lines can be observed if viewed at high enough resolution.

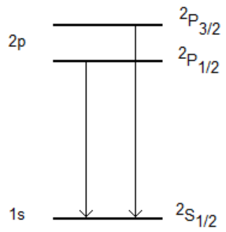

Figure 8.4.1

The transition is depicted in the above energy level diagram. The upper (2p) state is shown to be split into two components, one labeled $^2P_{3/2}$ and one $^2P_{1/2}$. The lower state has only one component, labeled $^2S_{1/2}$. Part of the job of quantum mechanics will be to describe this splitting. The explanation comes in the form of angular momentum coupling.

There are two sources of **angular momentum** in the electronic wavefunction of the atom: the orbital angular momentum $(l = 1)$ and the electron spin angular momentum $(s = \frac{1}{2})$. These angular momenta can couple to yield a total angular momentum $J = \frac{3}{2} \; or \; \frac{1}{2}$. The resultant angular momentum can be determined by the two angular momentum vectors adding in parallel of antiparallel. The result is to split the state into two components.

Term Symbols

Angular momentum in atoms can be summarized using a **term symbol**. The term symbol will indicate a number of different types of angular momentum such as the total orbital angular momentum, total spin angular momentum and the total (spin + orbit) angular momentum. In the limit that **Russell-Saunders coupling** (which will be described in detail shortly) provides a a good description of the atom, the term symbol used will be of the form

$$^{(2S+1)}L_J$$

where S is the total spin angular momentum and $(2S+1)$ is the spin degeneracy, L is the total orbital angular momentum, and J gives the total of the spin-orbit angular momentum. (The convention will be followed that lower-case letters are used to indicate one-electron properties and upper-case letters are used to describe total atom properties.)

L and S must be calculated using vectoral sums of the single-electron angular momenta (whether orbital or spin.) The vectoral sums can yield several values depending on the angle between the vectors. The possible magnitudes of the resultant vectors will be quantized, with the range of magnitudes being given by a **Clebsch series**. Consider the addition of the angular momentum vectors for two electrons in $p(l = 1)$ subshells.

$$\begin{aligned} \mathbf{L} &= \boldsymbol{l}_1 \oplus \boldsymbol{l}_2 \\ &= l_1 + l_2, l_1 + l_2 - 1, l_1 + l_2 - 2, \ldots, |l_1 - l_2| \end{aligned}$$

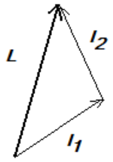

Figure 8.4.2

As such, the possible values of **L** for a p^2 configuration are

$$\begin{aligned}\mathbf{L} &= \boldsymbol{l}_1 \oplus \boldsymbol{l}_2 \\ &= 1 \oplus 1 \\ &= 2,\ 1,\ 0\end{aligned}$$

As in the case of one-electron orbital angular momenta, the total orbital angular momentum is signified using a letter. The following table shows which letters are used.

One-electron		Total Atom	
l	Designation	**L**	Designation
0	s	0	S
1	p	1	P
2	d	2	D
3	f	3	F
4	g	4	G

The possible values of $\boldsymbol{S}$, are given by $s_1 \oplus s_2$. (For all electrons, $\mathbf{1}s = \frac{1}{2}$.)

$$\boldsymbol{S} = \boldsymbol{s}_1 \oplus \boldsymbol{s}_2 = \frac{1}{2} \oplus \frac{1}{2}$$

So the possible values of $(2\boldsymbol{S}+1)$ are 3 and 1. In other words, both triplet and singlet states arise from a p^2 configuration.

However, not all possible combinations of $\boldsymbol{L}$ and $(2\boldsymbol{S}+1)$ are possible. In fact, only those values that arise from distinguishable combinations of **miscrostate** quantum number combinations are possible.

The Microstate Method

The number of distinguishable microstates for a given electronic configuration is given by

$$\frac{G!}{N!(G-N)!}$$

where G is the number of spin-orbit states possible for a single electron and N is the number of electrons. For a p^2 configuration, $G=6$ and $N=2$. So the number of microstates is given by

$$\frac{6!}{2!\cdot 4!} = \frac{6\cdot 5\cdot 4\cdot 3\cdot 2\cdot 1}{(2\cdot 1)\cdot(4\cdot 3\cdot 2\cdot 1)} = 15$$

So there are 15 possible microstates possible. Each microstate will be characterized by a value of m_l and m_s for each electron under consideration. A complete set of microstates for a p^2 configuration is shown in the table below. m_l and m_s are indicated for electrons 1 and 2 in the atom. Notice that only distinguishable combinations are shown!

			$\boldsymbol{m_L}$	$\boldsymbol{m_S}$	**Designation**		
	1	**2**	**1**	**2**			
1	+1	+1	$+\frac{1}{2}$	$-\frac{1}{2}$	+2	0	^1D
2	+1	0	$+\frac{1}{2}$	$+\frac{1}{2}$	+1	+1	^3P
3	+1	0	$+\frac{1}{2}$	$-\frac{1}{2}$	+1	0	^1D
4	+1	-1	$+\frac{1}{2}$	$+\frac{1}{2}$	0	+1	^3P
5	+1	-1	$+\frac{1}{2}$	$-\frac{1}{2}$	0	0	^1D

			m_L	m_S	Designation		
6	+1	0	$-\frac{1}{2}$	$+\frac{1}{2}$	+1	0	^3P
7	+1	0	$-\frac{1}{2}$	$-\frac{1}{2}$	+1	-1	^3P
8	+1	-1	$-\frac{1}{2}$	$+\frac{1}{2}$	0	0	^3P
9	+1	-1	$-\frac{1}{2}$	$-\frac{1}{2}$	0	-1	^3P
10	0	0	$+\frac{1}{2}$	$-\frac{1}{2}$	0	0	^1S
11	0	-1	$+\frac{1}{2}$	$+\frac{1}{2}$	-1	+1	^3P
12	0	-1	$+\frac{1}{2}$	$-\frac{1}{2}$	-1	0	^1D
13	0	-1	$-\frac{1}{2}$	$+\frac{1}{2}$	-1	0	^3P
14	0	-1	$-\frac{1}{2}$	$-\frac{1}{2}$	-1	-1	^3P
15	-1	-1	$+\frac{1}{2}$	$-\frac{1}{2}$	-2	0	^1D

The “Designation” column in the above table is really for bookkeeping only. For example, it should be noted that there are two miscrostates that yield m_L = +1, m_S = 0. One has been designated ^1D and the other ^3P. In fact, the wavefunctions needed to describe these term symbol components require linear combinations of both microstates.

The resulting microstates for a p^2 configuration are ^1D, ^3P and ^1S. The methodology for determining this from the table of microstates is as follows:

1. Find the largest value of m_L and the largest value of m_S that corresponds to that value.
2. From these, find L and S for the term symbol.
3. Mark combinations of m_L and m_S that match the pattern for a given term symbol.
4. Repeat from step 1 for remaining microstates. Keep repeating until there are no microstates left.

It is very important to approach this process methodically or errors will occur in determining microstate-term symbol correlations.

Utilizing this methodology to work through the above table, we start with the largest value for m_L which is +2. The largest value of m_S that goes with it is 0. This indicates $\boldsymbol{L}$ and $\boldsymbol{S}$ values of 2 and 1 respectively. $\boldsymbol{L}=2$ indicates a D state. $\boldsymbol{S}=0$ indicates that $(2\boldsymbol{S}+1)=1$ (or a singlet state.) So the resulting term is ^1D. This will have components of $m_L=+2,\ +1,\ 0,\ -1,\ -2$. Each will have m_S = 0. This accounts for five of the microstates.

The largest value of m_L for the remaining microstates is $m_L=+1$. the largest value of m_S that goes with $m_L=+1$ is $m_S=+1$. This correlates to $\boldsymbol{L}=1$, $S=1$ or a ^3P state. There are nine combinations of microstates for this term symbol, one each for each combination of $m_L=+1,\ 0,\ -1$ and $m_S=+1,\ 0,\ -1$.

After these combinations are marked, the only remaining combination is $m_L=0$, $m_S=0$, which corresponds to a ^1S state.

The number of microstates used for a given term symbol can be determined from $(2L+1)$ and $(2S+1)$, the orbital and spin degeneracies respectively. Consider the following table. Notice that the total of $(2L+1)(2S+1)$ is the same as the number of original microstates.

	$(2L+1)$	$(2S+1)$	$(2L+1)(2S+1)$
^1D	5	1	5
^3P	3	3	9

	$(\boldsymbol{2L+1})$	$(\boldsymbol{2S+1})$	$(\boldsymbol{2L+1})(\boldsymbol{2S+1})$
${}^1S$	1	1	1
		Total	15

Spin-Orbit Coupling

The one thing that has not been determined from the microstates themselves is the total angular momentum $\boldsymbol{J}$, which is given by the vectoral sum of $\boldsymbol{L}$ and $\boldsymbol{S}$. $\boldsymbol{J}$ values must be determined for each term separately. This coupling of spin and orbit angular momenta will split the term states further.

$$J = L \oplus S$$

	L	**S**	**J**	**Terms**
${}^1D$	2	0	2	${}^1D_2$
${}^3P$	1	1	2, 1, 0	${}^3P_2$, ${}^3P_1$, ${}^3P_0$
${}^1S$	0	0	0	${}^1S_0$

Again, the values of the spin-orbit degeneracies, given by (2J+1) can be used to determine if the coupling scheme has been done properly.

	J	**(2J+1)**
${}^1D_2$	2	5
${}^3P_2$	2	5
${}^3P_1$	1	3
${}^3P_0$	0	1
${}^1S_0$	0	1
	Total	15

Again, notice that the total matches the original number of microstates.

The Hole Rule

When dealing with a subshell that is more than half filled, it is oftentimes easier (or at least less tedious) to employ the **hole rule**. The hole rule involves treating electron holes rather than the electrons themselves. Consider ${}_6C$ and ${}_8O$ as an example of complementary atoms. Carbon has a p^2 configuration and oxygen a p^4 configuration. (Added together, that makes a p^6 configuration, which closes the p-subshell and is why the two atoms are complementary.)

For each microstate in the p^2 system, there exists one in the p^4 system that when added together would complete the p-subshell. An example is shown below.

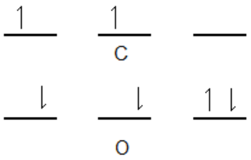

Figure 8.4.3

This relationship ensures that the exact same symmetry relationships hold for the p^4 system as for the p^2 system. Hence, the term symbols that arise from a p^4 system are ${}^1D$, ${}^3P$ and ${}^1S$. With spin-orbit coupling, the 3P will split into three components, ${}^3P_0$, ${}^3P_1$ and ${}^3P_2$. Of these, ${}^3P_2$ will have the lowest energy according to Hund's rule 3b, as these terms arise from a system where the subshell is more than half filled.

Hund’s Rules

Hund’s rules are used to determine the lowest energy state within the manifold of states generated from a given electronic configuration. The rules can be summarized as follows:

1. The lowest energy state will be the one with the largest value of **S**.
2. For multiple states with the same largest value of **S**, the lowest energy state will have the largest value of **L**.
3. For states with the same values of **L** and **S**, the lowest energy state will have
    a. The smallest value of **J**, if the term arises from an electronic configuration in which the subshell is less than half filled
    b. The largest value of **J**, if the term arises from an electronic configuration in which the subshell is more than half filled

For the case of a p^2 configuration, the largest value of **S** generated is **S** = 1, for the ${}^3P$ state. And within this state, the lowest energy term will be ${}^3P_0$, since p^2 corresponds to a subshell that is less than half filled.

✓ Example 8.4.1: Nonequivalent Electrons

Determine the term symbols that arise from the p^3 configuration of ${}_7$ N.

Solution

Consider a carbon atom in an excited state where the electronic configuration is given by

${}_6C$: [He] 2s ^{2} 2p^1 3p^1

This is an example of a pp configuration (which is different than a p^2 configuration since the two electrons have different values of the principle quantum number n. In this case, a number of microstate combinations become distinguishable that would not be before. A complete set of microstates for a pp configuration is given in the table below. In this case, since the electrons are not equivalent, it is possible for both to be in orbitals where m_l = +1 with $m_s = +\frac{1}{2}$ since they are in different subshells.

			m_L	m_S	Designation		
	2p	**3p**	**2p**	**3p**			
1	+1	+1	$+\frac{1}{2}$	$+\frac{1}{2}$	+2	+1	${}^3D$
2	+1	+1	$+\frac{1}{2}$	$-\frac{1}{2}$	+2	0	${}^3D$
3	+1	+1	$-\frac{1}{2}$	$+\frac{1}{2}$	+2	0	${}^1D$
4	+1	+1	$-\frac{1}{2}$	$-\frac{1}{2}$	+2	-1	${}^3D$
5	+1	0	$+\frac{1}{2}$	$+\frac{1}{2}$	+1	+1	${}^3D$
6	+1	0	$+\frac{1}{2}$	$-\frac{1}{2}$	+1	0	${}^3D$
7	+1	0	$-\frac{1}{2}$	$+\frac{1}{2}$	+1	0	${}^1D$
8	+1	0	$-\frac{1}{2}$	$-\frac{1}{2}$	+1	-1	${}^3D$
9	+1	-1	$+\frac{1}{2}$	$+\frac{1}{2}$	0	+1	${}^3D$
10	+1	-1	$+\frac{1}{2}$	$-\frac{1}{2}$	0	0	${}^3D$
11	+1	-1	$-\frac{1}{2}$	$+\frac{1}{2}$	0	0	${}^1D$

			m_L	m_S	Designation		
12	+1	-1	$-\frac{1}{2}$	$-\frac{1}{2}$	0	-1	^3D
13	0	+1	$+\frac{1}{2}$	$+\frac{1}{2}$	+1	+1	^3P
14	0	+1	$+\frac{1}{2}$	$-\frac{1}{2}$	+1	0	^3P
15	0	+1	$-\frac{1}{2}$	$+\frac{1}{2}$	+1	0	^1P
16	0	+1	$-\frac{1}{2}$	$-\frac{1}{2}$	+1	-1	^3P
17	0	0	$+\frac{1}{2}$	$+\frac{1}{2}$	0	+1	^3S
18	0	0	$+\frac{1}{2}$	$-\frac{1}{2}$	0	0	^3S
19	0	0	$-\frac{1}{2}$	$+\frac{1}{2}$	0	0	^1S
20	0	0	$-\frac{1}{2}$	$-\frac{1}{2}$	0	-1	^3S
21	0	-1	$+\frac{1}{2}$	$+\frac{1}{2}$	-1	+1	^3D
22	0	-1	$+\frac{1}{2}$	$-\frac{1}{2}$	-1	0	^3D
23	0	-1	$-\frac{1}{2}$	$+\frac{1}{2}$	-1	0	^1D
24	0	-1	$-\frac{1}{2}$	$-\frac{1}{2}$	-1	-1	^3D
25	-1	+1	$+\frac{1}{2}$	$+\frac{1}{2}$	0	+1	^3P
26	-1	+1	$+\frac{1}{2}$	$-\frac{1}{2}$	0	0	^3P
27	-1	+1	$-\frac{1}{2}$	$+\frac{1}{2}$	0	0	^1P
28	-1	+1	$-\frac{1}{2}$	$-\frac{1}{2}$	0	-1	^3P
29	-1	0	$+\frac{1}{2}$	$+\frac{1}{2}$	-1	+1	^3P
30	-1	0	$+\frac{1}{2}$	$-\frac{1}{2}$	-1	0	^3P
31	-1	0	$-\frac{1}{2}$	$+\frac{1}{2}$	-1	0	^1P
32	-1	0	$-\frac{1}{2}$	$-\frac{1}{2}$	-1	-1	^3P
33	-1	-1	$+\frac{1}{2}$	$+\frac{1}{2}$	-2	+1	^3D
34	-1	-1	$+\frac{1}{2}$	$-\frac{1}{2}$	-2	0	^3D
35	-1	-1	$-\frac{1}{2}$	$+\frac{1}{2}$	-2	0	^1D

			m_L	m_S	**Designation**		
36	-1	-1	$-\frac{1}{2}$	$-\frac{1}{2}$	-2	-1	^3D

In this example, there are more term symbols generated due to the fact that the electrons are not in the same subshell. The resulting term symbols are ^3D, ^3P, ^3S, ^1P, ^1P and ^1S. As such, this set of microstates includes some combinations of m_l and m_s which would not be possible if the two electrons were in the same subshell.

8.5: The Pauli Exclusion Principle

One explanation as to why the differences between the term symbols that arise from a p^2 configuration relative to a pp configuration is the **Pauli Exclusion principle**. The usual statement of the Pauli Exclusion Principle is that no two electrons in an atom can have the same set of four quantum numbers n, l, m_l and m_s. Another explanation is to simply announce that

Electrons are Fermions!

This approach is useful if you happen to know the properties of Fermions, but does not provide much insight if you do not.

A **Fermion** is a particle with half-integral spin. An obvious example (according to the statement above) is an electron which has $\boldsymbol{s}=\dfrac{1}{2}$. Other examples include protons and neutrons and fluorine-19 nuclei (all with $\boldsymbol{I}=\dfrac{1}{2}$), aluminum-27 nuclei ($\boldsymbol{I}=\dfrac{5}{2}$) etc. Fermions have the property that the total wavefunction of a system containing two equivalent fermions must change sign if the two particles are exchanged.

The other type of particle is called a **Boson**. This is a particle with integral spin. Examples of bosons include deuterium nuclei or nitrogen-14 nuclei (both with $\boldsymbol{I}=1$) or helium-4 nuclei ($\boldsymbol{I}=0$). A system containing two equivalent bosons must have a wavefunction that does not change sign for the exchange of two equivalent bosons.

$$\begin{aligned}\Psi(1,2)=-\Psi(2,1) \qquad &\text{(for fermions)}\\ \Psi(1,2)=\Psi(2,1) \qquad &\text{(for bosons)}\end{aligned}$$

In order to explore the properties of these types of particles, it is useful to define an operator that exchanges two equivalent particles (1 and 2).

$$\begin{aligned}\hat{O}\Psi(1,2)&=\Psi(2,1)\\ \hat{O}\psi_m(1)\psi_n(2)&=\psi_m(2)\psi_n(1)\end{aligned}$$

In the limit that spin and orbital wavefunctions are separable (the total wavefunction can be expressed as the product of a spin function and an orbital function)

$$\Psi_{tot}=\psi_{orbital}\psi_{spin}$$

both the spin and orbital functions must be eigenfunctions of the electron exchange operator. We shall explore the properties of this operation on spin wavefunction to explore the difference between single and triplet spin wavefunctions as derived from a pp pr p^2 configuration.

Consider how the microstates shown in Table 1 behave under the exchange operation.

$$\begin{aligned}\hat{O}\Psi_1&=\hat{O}\alpha(1)\alpha(2)=\alpha(2)\alpha(1)=\Psi_1\\ \hat{O}\Psi_2&=\hat{O}\alpha(1)\beta(2)=\alpha(2)\beta(1)=\Psi_3\\ \hat{O}\Psi_3&=\hat{O}\beta(1)\alpha(2)=\beta(2)\alpha(1)=\Psi_2\\ \hat{O}\Psi_4&=\hat{O}\beta(1)\beta(2)=\beta(2)\beta(1)=\Psi_4\end{aligned}$$

Wavefunctions Ψ_1 and Ψ_4 are eigenfunctions of $\hat{O}$. Wavefunctions Ψ_2 and Ψ_3 are not eigenfunctions of $\hat{O}$, but they are clearly related to one another through the electron exchange operation as the operation converts one into the other. The relationship suggests that linear combinations of Ψ_2 and Ψ_3 can be taken in order to construct spin wavefunctions that are eigenfunctions of $\hat{O}$. One linear combination is symmetric (eigenvalue = +1) and the other is be antisymmetric (eigenvalue = -1). The correct, normalized linear combinations are as follows.

$$\begin{aligned}\Psi_s&=\frac{1}{\sqrt{2}}(\Psi_2+\Psi_3)=\frac{1}{\sqrt{2}}(\alpha(1)\beta(2)+\beta(1)\alpha(2))\\ \Psi_a&=\frac{1}{\sqrt{2}}(\Psi_2-\Psi_3)=\frac{1}{\sqrt{2}}(\alpha(1)\beta(2)-\beta(1)\alpha(2))\end{aligned}$$

Under the electron exchange operator, these linear combinations behave as follows.

$$\hat{O}\Psi_s = \hat{O}\left[\frac{1}{\sqrt{2}}(\alpha(1)\beta(2)+\beta(1)\alpha(2))\right] = \frac{1}{\sqrt{2}}(\alpha(2)\beta(1)+\beta(2)\alpha(1)) = \Psi_s$$

$$\hat{O}\Psi_a = \hat{O}\left[\frac{1}{\sqrt{2}}(\alpha(1)\beta(2)-\beta(1)\alpha(2))\right] = \frac{1}{\sqrt{2}}(\alpha(2)\beta(1)-\beta(2)\alpha(1)) = -\Psi_a$$

So Ψ_s is symmetric with respect to electron interchange and Ψ_a is antisymmetric with respect to electron interchange. Noting that Ψ_1 and Ψ_4 are natural symmetric eigenfunctions of the exchange operator, it is easy to group the spin wavefunctions into triplet and singlet components according to symmetry with respect to the operator $\hat{O}$. The summary of these results is shown in the table below.

		Wavefunction		S	M_S
Triplet	Symmetric	Ψ_1	$\alpha(1)\alpha(2)$		+1
		Ψ_s	$\frac{1}{\sqrt{2}}(\alpha(1)\beta(2)+\beta(1)\alpha(2))$		0
		Ψ_4	$\beta(1)\beta(2)$		-1
Singlet	Antisymmetric	Ψ_a	$\frac{1}{\sqrt{2}}(\alpha(1)\beta(2)-\beta(1)\alpha(2))$		0

It can be seen that there are three components of the triplet spin wavefunction and only one component to the singlet function, as implied by the names “triplet” and “singlet.” More importantly, it is clear that to generate the ground state wavefunction for the atom, one *must* include contributions from paired electron spin functions (Ψ_s). So the statement of Hund’s rule that maximizing the number of electrons with the same value of m_s attains the lowest energy state is clearly incorrect, as it excludes the necessary component with $M_S = 0$.

For equivalent electrons (electrons in the same subshell, or the p^2 case) the symmetric spin wavefunction set (the triplet functions) must take antisymmetric orbital function (P). The singlet spin function, which is antisymmetric to electron exchange, must take a symmetric orbital function (D or S.) As such, the three term symbols generated are ^1D, ^3P and ^1S. If the electrons are not equivalent, as is the case in a pp configuration, all combinations of the triplet and singlet spin functions with D, P and S orbital functions are possible and the resulting terms are ^3D, ^3P, ^3S, ^1D, ^1P and ^1S.

The ^3D, ^1P and ^3S functions are not possible in the p^2 case, as these would require microstates that are either duplicates of other microstates, or microstates that involve two electrons in the same orbital with the same value of m_s. The latter is a clear violation of the Pauli Exclusion Principle since both electrons would then have the same values of n, l, m_l and m_s.

8.6: Atomic Spectroscopy

The complex spectra of atoms can be understood using term symbols, as they contain all of the symmetry and quantum number values needed. The selection rules for systems that are well described by **Russell-Saunders coupling** are

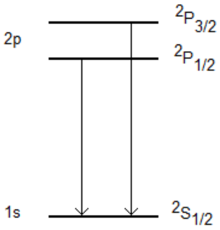

Figure 8.6.1

$$\Delta S = 0$$

$$\Delta L = 0,\ \pm 1 \text{ (but not } 0 \leftrightarrow 0)$$

$$\Delta J = 0,\ \pm 1 \text{ (but not } 0 \leftrightarrow 0)$$

Consider a $^2P \leftarrow ^2S$ transition. An energy level diagram for such a transition is shown to the right.

The selection rules predict two lines will be observed in the spectrum. The splitting between the lines will be related to the spin-orbit coupling constant in the upper state. Note that for this transition, $\Delta S =$ and $\Delta L = +1$. (In spectroscopy recall that changes are always calculated as the upper state value minus the lower state value as in $\Delta L = L' - L"$). The two lines predicted have $\Delta J = 0$ and $+1$ as depicted in the diagram.

Things get more complex for larger values of L and S. For example, consider the transition between a ^3D state and a ^3P state (with the ^3D state as the upper state and both states increasing in energy with increasing J.)

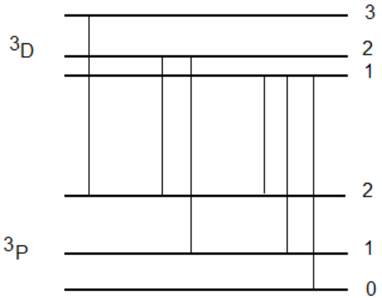

Figure 8.6.2

For this transition, six lines are predicted. The pattern formed by the lines can vary based on the relative values of the spin-orbit coupling constants in each level. In general, the upper state will have the lower spin-orbit coupling constant, as electronic excitation quenches spin-orbit coupling.

Landé Interval Rule

The **Landé Interval Rule** describes the magnitude of the splittings in a term manifold. For example, it is predicted that the splitting pattern in a 3P state is

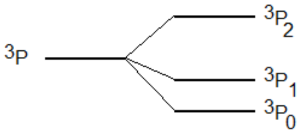

Figure 8.6.3

The splitting between the $^3P_2$ level and the $^3P_1$ level is twice as large as that between the $^3P_1$ component and the $^3P_0$ component. In general, the Landé Interval Rule can be stated

$$E_{J+1} - E_J = hcA(J+1)$$

where A is the **spin-orbit splitting constant** for the level. The Landé Interval Rule works well for small splittings, where the spin-orbit interaction can be treated as a perturbation to the Hamiltonian. There will generally be small deviations from the interval rule, especially when relativistic effects become important. The Landé Interval can be used to interpret the complex splitting patterns that can be seen in some atomic spectra.

The Deslandres Table

A very useful tool that can be used in spectroscopy is the **Deslandres table**. In such a table, transitions are arranged according to upper and lower state combinations in such a way as to accentuate the differences in energy between quantum levels. For example, consider the following energy level diagram for ^3D–^3P transition, where the six transitions have been labeled a-f for convenience.

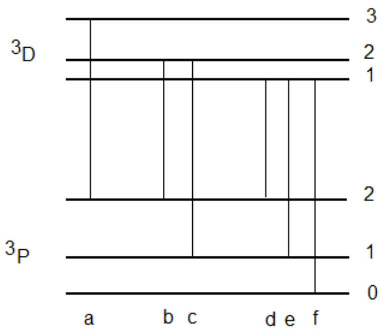

Figure 8.6.4

Looking at the diagram, it should be clear that the difference in energy between lines b and c must be identical to that between lines d and e, since both differences give the difference in energy between the $J = 2$ and $J = 1$ components of the ^3P level. Similarly, the difference in energy between lines b and d must be equal to that between lines c and e, as that is the difference in energy between the $J = 2$ and $J = 1$ levels in the ^3D state.

A Deslandres table summarizes the information in the energy level diagram and also incorporates the values of the measured lines in the spectrum. Symbolically, the Deslandres table for the above transition would look as follows

		^3D				
		3	3A’	2	2A’	1
^3P	2	a	$a-b$	b	$b-d$	d
	2A”			$c-b$		$e-d$
	1	–		c	$c-e$	e
	A”					$f-e$
	0	–		–		f

The table contains not only the line frequencies, but also the differences between them. It is the constancy of differences that confirms the assignment of the spectrum.

Example 8.6.1

consider the following data for a ^3D–^3P transition. Assign the lines and calculate the spin-orbit coupling constants for both the upper and lower states based on your assignments.

Line	Freq (cm^{-1})
1	18492.74

Line	Freq (cm^{-1})
2	18511.98
3	18525.82
4	18540.84
5	18542.36
6	18545.06

The stick spectrum (simulated spectrum, with transitions indicated as sticks instead of lines with a definite line shape and without intensity data indicated) looks as follows.

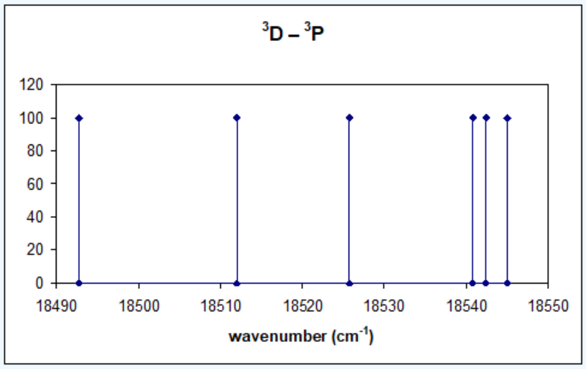

Figure 8.6.5

Solution

It would be difficult to assign the spectrum simply based on the pattern seen above. In some cases, the spectral pattern can be quite complex! A couple of things can be inferred, however, based on the energy level diagram above.

The smallest energy transition is for ${}^3D_1 – {}^3P_2$ and

the largest energy transition is either ${}^3D_1 – {}^3P_0$ or ${}^3D_2 – {}^3P_1$ (depending on the relative magnitudes of the spin-orbit splittings.)

Based on these observations, we can assign the 18492.74 line.

If 18545.06 cm^{-1} is the ${}^3D_1 – {}^3P_0$ transition, then the difference should be 3A”. This predicts a lower level spin-orbit-coupling constant of A” = 17.44 cm^{-1}. And there must be a line at 18527.62 cm^{-1}. But there is no such line! Hence, the highest energy transition is not the ${}^3D_1 – {}^3P_0$ transition. It must be the ${}^3D_2 – {}^3P_1$ transition instead!

If the $18542.36\ cm^{-1}$ line is the ${}^3D_1 – {}^3P_0$ transition, a value of $A” = 16.54\ cm^{-1}$ is predicted. This predicts a line at $18525.82\ cm^{-1}$ which does exist! (This is idealized theoretical data for demonstration purposes. The Landé interval rule does not always hold as strongly as that.)The difference between the ${}^3D_2 – {}^3P_1$ transition and the ${}^3D_1 – {}^3P_1$ transition is 19.24 cm^{-1}. In order to maintain a constant set of differences, there must be a line at 18511.98 cm^{-1}, which there is. This is assigned as the ${}^3D_2 – {}^2P_2$ transition.The only remaining line is 18540.84 cm^{-1}, which is assigned as the ${}^3D_3 – {}^3P_2$ transition. The final Deslandres table looks as follows.

		^3D				
		3	3A’	2	2A’	1
^3P	2	18540.84	28.86	18511.98	19.24	18492.74
	2A”			33.08		33.08
	1	--		18545.06	19.24	18525.82
	A”					16.54
	0	--		--		18542.36

In conclusion, angular momentum coupling schemes can be used to describe the states in a polyelectronic atom. These states can be used to predict the spectroscopy of these systems. In the next chapter, we will apply a number of the principles developed in this chapter in order to understand the electronic structure of diatomic molecules. This has important ramifications on both spectroscopy and bonding in these molecules, and also forms a foundation for how we think about electronic structure in larger molecules.

8.7: Vocabulary and Concepts

angular momentum

aufbau principle

Boson

Clebsch series

Deslandres table

Fermion

hole rule

Hund’s rules

Landé Interval Rule

miscrostate

orbital

orbital approximation

Pauli Exclusion principle

Russell-Saunders coupling

shell

spin-orbit splitting constant

subshell

term symbol

8.8: Learning Objectives

After mastering the material covered in this chapter, one will be able to:

1. Describe the Orbital Approximation and explain how it leads to differences for polyelectronic atoms relative to the Hydrogen atom results.
2. Utilize the Aufbau principle to determine the ground electronic state electronic configuration for a polyelectronic atom, taking into account any important consequences of
    a. the Pauli Exclusion Principle
    b. Hund’s Rules of Maximum Multiplicity
3. Construct an orbital diagram depicting an electronic configuration, including using such a diagram to predict important properties of the ground (or any) electronic state configuration of an atom. These properties may include
    a. Paramagnetism or diamagnetism
    b. Total spin multiplicity or the number of total spin multiplicities associated with a given electronic configuration.
4. Use Russell-Saunders angular momentum coupling to determine the term symbols that arise for a given electronic configuration. Especially, one should be able to predict the lowest-energy term-state that arises from an electronic configuration consistent with Hund’s Rules.
5. Employ electron exchange symmetry rules to construct symmetry-adapted linear combinations of spin functions that can be used to satisfy the Pauli Exclusion Principle by creating total wavefunctions that are antisymmetric with respect to the exchange of equivalent electrons.
6. Construct energy-level diagrams for term states that are consistent with Russell-Saunders coupling and the Lande Interval Rule.
    a. Use these diagrams to predict the structure of electronic transition spectra involving these states.
    b. Organize the data into a Deslandres Table to aid in the conformation of assignments and the calculation of spin-orbit coupling constants.

8.9: Problems

1. Write a table of microstates and predict the term simple that arise for N with an electronic configuration of [He] $2s^2 2p^3$. Which is predicted to be the ground electronic state?
2. On the planet Zorg, electrons can exist in ζ orbitals, with $l = \frac{3}{2}$ (and so $m_l = +\frac{3}{2},\ +\frac{1}{2},\ -\frac{1}{2},\ -\frac{3}{2}$). All other rules apply (2 electrons per orbital, Hund's Rules, etc.)
    a. How many microstates arise from a ζ^2 configuration?
    b. Write a table of microstates for the ζ^2 configuration. What term symbols arise from this set of microstates?
3. Using the accepted conventions, draw an orbital diagram for the d electrons in V.
    a. What is the predicted ground state term?
    b. How many additional microstates contribute to the term?
4. Consider a ${}^3P$–${}^3P$ transition (in which both states increase in energy with increasing J.)
    a. Draw an energy level diagram for the transition and predict the component transitions.
    b. consider the following values: $A" = 12.3\ cm^{-1}$, $A' = 8.4\ cm^{-1}$ and the ${}^3P_1 - {}^3P_0$ transition occurs at $12459.3\ cm^{-1}$. Based on these complete a Deslandres table describing all of the component transitions and the spin-orbit spacings in the ${}^3P - {}^3P$ transition.

CHAPTER OVERVIEW

9: Molecules

Quantum mechanics can be used to predict a large number of properties, especially those related to electronic spectroscopy, for diatomic molecules. A number of the concepts discussed in this chapter can be expanded to explain a great deal of the behavior of polyatomic molecules as well.

9.1: Potential Energy and the Hamiltonian

The first task of applying quantum mechanics to a problem is writing the Hamiltonian. This requires deriving an expression for potential energy. Consider as an example, the simplest diatomic molecule, H_2^+.

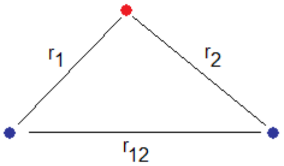

Figure 9.1.1

In the above diagram, the blue dots indicate protons and the red dot, an electron. There will be attractive forces between the electron and protons 1 and 2 (separated by r_1 and r_2 respectively) and a repulsive force between the two protons, separate by a distance r_{12}. In atomic units, the Hamiltonian can be written

$$\hat{H} = \hat{T}_1 + \hat{T}_2 + \hat{T}_e - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r_{12}}$$

where T_1, T_2 and T_e indicate the kinetic energies of protons 1 and 2 and the electron, respectively. As was the case in the helium atom, the H_2^+ molecule involves a three body problem which cannot be solved analytically. As such, an approximation must be made in order to proceed.

9.2: The Born-Oppenheimer Approximation

The **Born-Oppenheimer approximation** (Born & Oppenheimer, 1927) is made in order to simplify the problem in the case of a molecule. This approximation is based on the relative masses (and therefore the relative speeds) of the heavy nuclei compared to the light electron. It says that if the nuclei move (such as due to molecular vibration) that the electron(s) will react to a change in the potential energy field instantaneously. As such, the internuclear distance (r_{12}) can be fixed, and the wave function for the electron optimized. If the nuclear coordinates are fixed, the Hamiltonian becomes

$$\hat{H} = \hat{T}_e - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r_{12}}$$

and the value of $\frac{1}{r_{12}}$ becomes a constant.

There are many cases where the Born-Oppenheimer approximation breaks down, such as Renner-Teller interactions and Jahn-Teller interactions which involve strong coupling between vibrational motion of a molecule and the electronic state. For the purposes of this text, we will stick to examples where the Born-Oppenheimer approximation is reasonable.

The Born-Oppenheimer approximation makes it possible to calculate a number of properties for molecules. Below is an example of a potential energy surface of O_2 calculated using molecular modeling software at the HF/6-31G(d) level of theory. Basically, the program optimizes the wavefunctions describing the molecular orbitals based on a fixed internuclear separation. After populating the resultant orbitals with electrons, a total molecular energy is generated. After repeating this process at several different internuclear separation values, the curve can be constructed.

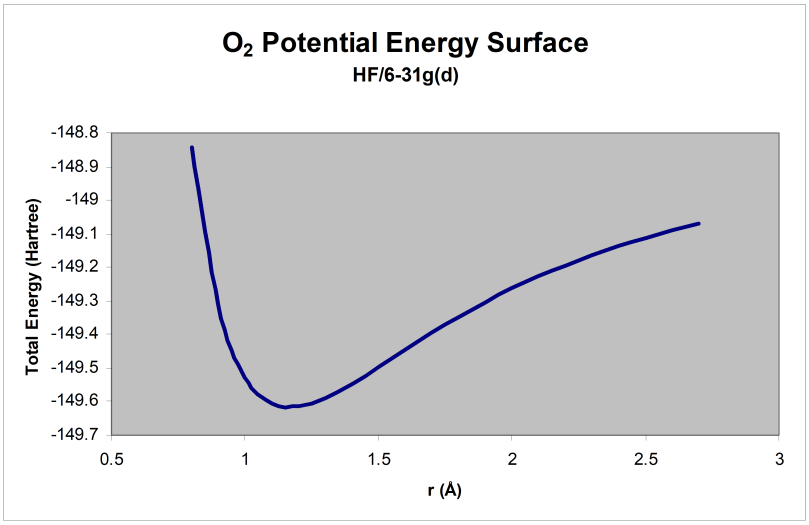

Figure 9.2.1

Such calculations are based entirely on the electronic structure of the molecule. As such, some insight into the nature of molecular orbitals and their wavefunctions is needed to proceed.

9.3: Molecular Orbital Theory

There are a number of ways to describe the electronic structure in diatomic molecules and the wavefunctions that are needed for the descriptions. **Molecular Orbital theory** provides one such example. There are many ways to describe molecular orbitals. One of the most commonly used is the method of using **linear combinations of atomic orbitals** (LCAO).

Linear Combinations of Atomic Orbitals (LCAO)

Consider a wavefunctions derived from the Schrödinger equation that can be expressed as linear combinations of the 1s orbitals centered on each atom. The wavefunction can then be written

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = c_1(1s_1) + c_2(1s_2)$$

In this expression, r_1 and r_2 are the coordinates (position vectors) for nuclei 1 and 2. $1s_1$ an $1s_2$ refer to the 1s orbitals centered on nuclei 1 and 2 respectively. Due to the symmetry of the molecule, the magnitudes of c_1 and c_2 must be the same.

$$c_1 = c_2 = c$$

In order to be normalized, the wave function must satisfy

$$\begin{aligned} 1 &= c^2 \int (1s_1 + 1s_2)(1s_1 + 1s_2)\, d\tau \\ &= c^2 \int 1s_1 1s_1 d\tau + 2c^2 \int 1s_1 1s_2 d\tau + c^2 \int 1s_2 1s_2 d\tau \end{aligned}$$

The first and the third integrals in this expression are unity due to the fact that the 1s orbitals are themselves normalized. This the expression becomes

$$\begin{aligned} 1 &= 2c^2 + 2c^2 \textstyle\int 1s_1 1s_2 d\tau \\ &= 2c^2 \left(1 + \textstyle\int 1s_1 1s_2 d\tau\right) \end{aligned}$$

The integral in this expression $\int 1s_1 1s_2 d\tau$ does not vanish due to orthogonality as we have seen in other examples, since the wavefunctions are centered in different locations. The magnitude of the integral, therefore, depends on the degree to which the two orbitals overlap one another. The **overlap integral** is commonly given the symbol S. The magnitude of the normalization constant for the molecular wavefunction will depend intimately on the magnitude of this overlap.

$$1 = 2c^2 (1 + S)$$

Solving for c, the following results

$$c = [2(1+S)]^{\frac{1}{2}}$$

And the wavefunction can be written as

$$\psi(r_1, r_1) = \frac{1}{[2(1+S)]^{1/2}}(1s_1 + 1s_2)$$

The value of the overlap integral S will depend on the size of the orbitals and also the internuclear separation. The above wavefunction is an example of a **bonding orbital** as the value of the overlap S will be positive. Positive overlap is a stabilizing condition and acts to hold a molecule together. But just as a linear combination can be constructed from the sum of the 1s orbitals on the two H atoms, one can also be constructed from the difference.

$$\psi(r_1, r_1) = c\,(1s_1 - 1s_2)$$

This wavefunction will have **negative overlap** and thus produce an **antibonding orbital** which, if populated, has the effect of destabilizing the molecule.

The Expectation Value for Energy

The energies of these bonding and antibonding orbitals can be calculates from the following expressions

$$\begin{aligned}\langle E\rangle &= \frac{\int\psi^*\hat{H}\,\psi\,d\tau}{\int\psi^*\,\psi\,d\tau}\\ &= \frac{\int(c_1 1s_1+c_2 1s_2)\,\hat{H}\,(c_1 1s_1+c_2 1s_2)\;d\tau}{\int(c_1 1s_1+c_2 1s_2)\,(c_1 1s_1+c_2 1s_2)\;d\tau} = \frac{c_1^2H_{11}+2c_1c_2H_{12}+c_2^2H_{22}}{c_1^2+2c_1c_2S+c_2^2}\end{aligned}$$

In this expression, H_{11} and H_{22} are the **Coulomb integrals** defined by

$$H_{ii}=\int 1s_i\;\hat{H}\,1s_i\,d\tau$$

It can be easily shown that $H_{11}=H_{22}$ by symmetry. The other type of integral (besides S, the overlap integral which has already been discussed) is H_{12}, called the **exchange integral**.

$$H_{ij}=\int 1s_i\,\hat{H}\,1s_j\,d\tau$$

The energy of the wavefunction is minimized by use of the variational principle. Specifically, the coefficients c_1 and c_2 must be chosen so as to minimize the energy of the wavefunction. This is done by differentiating the energy expression and setting it equal to zero (since the derivative will be zero at the minimum.) For simplicity, the expression is rearranged so that implicit differentiation is easier to see.

$$E\left(c_1^2+2c_1c_2S+c_2^2\right)=c_1^2H_{11}+2c_1c_2H_{12}+c_2^2H_{22}$$

Differentiation of this expression with respect to c_1 and c_2 yields two expressions which can be used to find the two unknowns, c_1 and c_2.

$$\begin{aligned}E\left(2c_1+2c_2S\right)+\frac{\partial E}{\partial c_1}\left(c_1^2+2c_1c_2S+c_2^2\right)&=2c_1H_{11}+2c_2H_{12}\\ E\left(2c_2+2c_1S\right)+\frac{\partial E}{\partial c_2}\left(c_1^2+2c_1c_2S+c_2^2\right)&=2c_2H_{22}+2c_1H_{12}\end{aligned}$$

Since $\frac{\partial E}{\partial c_1}=0$ at the minimum, the second terms on the left sides of the above equations vanish. (How nice of them!)

$$\begin{aligned}E\left(2c_1+2c_2S\right)&=2c_1H_{11}+2c_2H_{12}\\ E\left(2c_2+2c_1S\right)&=2c_2H_{22}+2c_1H_{12}\end{aligned}$$

These expressions can be rearranged.

$$\begin{aligned}c_1\left(E-H_{11}\right)+c_2\left(SE-H_{12}\right)&=0\\ c_1\left(H_{12}-SE\right)+c_2\left(E-H_{22}\right)&=0\end{aligned}$$

So long as the Coulomb, Exchange and Overlap integrals can be determined, the coefficients can be as well. The non-trivial solution for c_1 and c_2 can be found from the determinant of the matrix shown below being set to zero.

$$\begin{vmatrix}H_{11}-E & SE-H_{12}\\ H_{12}-SE & E-H_{22}\end{vmatrix}=0$$

It can be shown (although it will not be shown here) that

$$H_{ii}=E(1s)+J$$

where $E(1s)$ is the energy of a 1s orbital in hydrogen and J is an expression that depends on internuclear distance (r), given by

$$J=e^{-2r}\left(1+\frac{1}{r}\right)$$

Similarly, H_{ij} can be determined from

$$H_{ij}=E(1s)S+K$$

where K is given by

$$K = \frac{S}{r} - e^{-r}(1+r)$$

Notice that the expressions for both J and K vanish as r approaches ∞. Given these substitutions, the determinant equation becomes

$$\begin{vmatrix} E_{1s}+J+E & E_{1s}+K-SE \\ E_{1s}S+K-SE & E_{1s}+J+E \end{vmatrix} = 0$$

Or

$$(E_{1s}+J+E)^{\,2} - (E_{1s}+K-SE)^{\,2} = 0$$

Being quadratic in E, this expression yields two solutions for the energy. One will give the energy of the bonding orbital and the other will be the energy of the antibonding orbital. (Now how much would you pay?) These energies are given by the expressions

$$E_{bonding} = E_{1s} + \frac{J+K}{1+S}$$

and

$$E_{antibonding} = E_{1s} + \frac{J-K}{1-S}$$

The following diagrams show the radial wavefunctions (across the z-axis of the molecule) for both the bonding and antibonding combinations of 1s orbitals. The graph on the left shows the value of the wavefunction, while the one on the right shows the square of the wavefunction. Note the node in the middle of the molecule in the antibonding orbital!

The following figures show the axial wavefunction for the

$$\psi = 1s_A + 1s_B$$

bonding and the

$$\psi = 1s_A - 1s_B$$

antibonding orbitals (on the left) and the corresponding squared axial wavefunctions on the right.

Bonding:

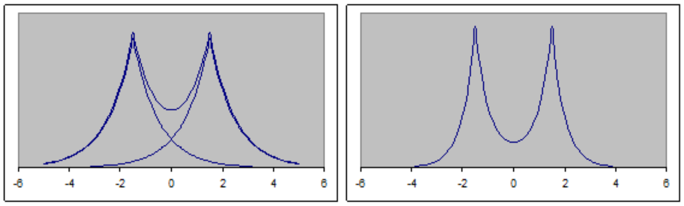

Figure 9.3.1

Antibonding:

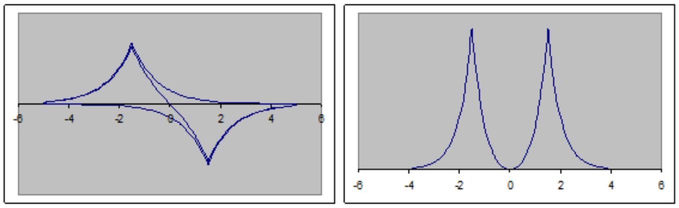

Figure 9.3.2

These orbitals are easy to visualize and understand based on a pictorial approach of linear combinations of orbitals as well. In the pictorial approach, the emphasis is on the sign of the function in the overlap region.

Bonding and Antibonding Orbitals Constructed from s Orbitals

The combination of 1s orbitals can be visualized in the following diagram

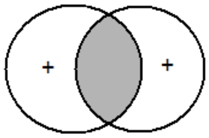

Figure 9.3.3

In this diagram, depicting the symmetric overlap to two 1s orbitals, it can be seen that the region of overlap will have a positive value (as it is given by the product of two positive numbers. This is an example of a s orbital since it is cylindrically symmetric about the internuclear axis.

Just as the symmetric combination can be depicted, the antisymmetric combination is also easy to generate.

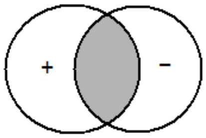

Figure 9.3.4

In this depiction, it should be clear that the region of overlap has a negative value. Another way to think about this is that the wavefunction must change sign as it crosses from left to right. This implies a node between the nuclei!

As stated before, the positive overlap depicted in the first orbital is a stabilizing condition, and the negative overlap in the second is destabilizing. This can be depicted in an orbital diagram.

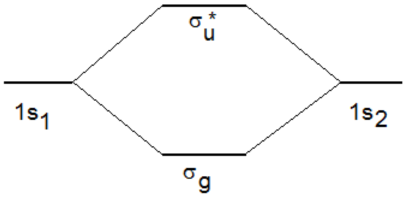

Figure 9.3.5

In this diagram, the atomic orbitals on the separated atoms are shown on the far right and left, and the orbitals in the middle column are the molecular orbitals that arise from the linear combination of the atomic orbitals. σ_g indicates the bonding orbital and σ_u^* indicates the antibonding orbital resulting from the symmetric and antisymmetric combinations of the 1s orbitals. The subscripts g and u state for **gerade** and **ungerade** respectively. Gerade is a German word meaning even, which ungerade means odd. Specifically, these terms (and subscripts) are used to indicate the symmetry of a function with respect to inversion. The g/u symmetry can be determined by drawing an arrow through the middle of a picture of a molecular orbital. If the arrow ends in a point with the opposite sign, the wavefunction is ungerade. However, it must be noted that this symmetry applies only to homonuclear diatomic molecules (and other molecules that possess an inversion center symmetry elements.) More will be discussed about molecular symmetry in later chapters.

Bonding and Antibonding Orbitals constructed from p Orbitals

Bonding and antibonding σ orbitals can be constructed from p-orbitals that are aligned on axis. In the diagram below, the upper picture indicates an antibonding orbital while the lower image is a bonding orbital.

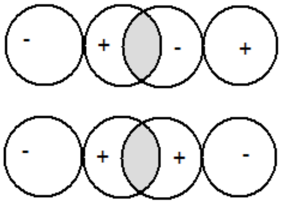

Figure 9.3.6

In addition to σ orbitals, π orbitals can also be constructed.

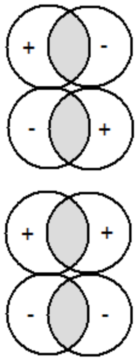

Figure 9.3.7

Clearly the π-bonding orbital is ungerade, while the π-antibonding orbital is gerade (if an inversion center exists within the molecule. It is also important to note that π-type overlap is smaller than \sigma-overlap, due to the need to get two nuclei so close together for strong overlap of the p orbitals in a π orientation. As such, the π orbitals are less stabilizing or destabilizing relative to the atomic orbital energies.

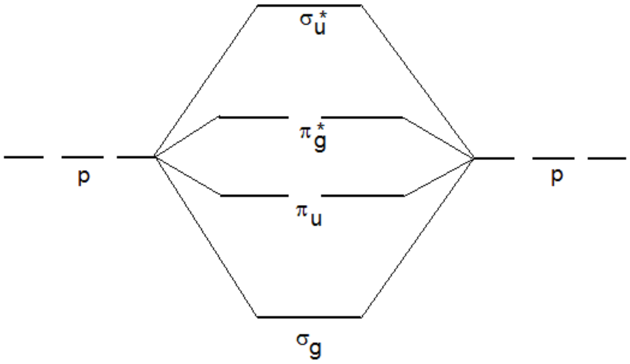

Figure 9.3.8

The σ boding and antibonding orbitals will be formed by the symmetric and antisymmetric combinations of the p_z orbitals on the separated atoms, whereas the π orbitals will be formed from the p_x and p_y orbitals from the separated atoms.

Electronic Configurations

Electronic configurations can be written for molecules just as they can be for atoms. Instead of being numbered by the principle quantum number, however, molecular orbitals are numbered sequentially from the lowest energy orbital of a certain symmetry. Consider the following list of electronic configurations for homonuclear diatomic molecules formed using the first ten elements.

Molecule	Electronic Configuration	Bond Order	Electronic State
H_2	$(1\sigma_g)^2$	1	${}^1\Sigma_g^+$
He_2	$(1\sigma_g)^2(1\sigma_u^*)^2$	0	unbound

Molecule	Electronic Configuration	Bond Order	Electronic State
Li_2	$KK(2\sigma_g)^2$	1	$^1\Sigma_g^+$
Be_2	$KK(2\sigma_g)^2(2\sigma_u^*)^2$	0	unbound
B_2	$KK(2\sigma_g)^2(2\sigma_u^*)^2(3\sigma_g)^2$	1	$^1\Sigma_g^+$
C_2	$KK(2\sigma_g)^2(2\sigma_u^*)^2(3\sigma_g)^2(1\pi_u)^2$	2	$^3\Sigma_g^-$
N_2	$KK(2\sigma_g)^2(2\sigma_u^*)^2(3\sigma_g)^2(1\pi_u)^4$	3	$^1\Sigma_g^+$
O_2	$KK(2\sigma_g)^2(2\sigma_u^*)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g^*)^2$	2	$^3\Sigma_g^-$
F_2	$KK(2\sigma_g)^2(2\sigma_u^*)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g^*)^4$	1	$^1\Sigma_g^+$
Ne_2	$KK(2\sigma_g)^2(2\sigma_u^*)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g^*)^4(3\sigma_u^*)^2$	0	unbound

In this table, the older shell notation is used to indicate a filling of the inner shell electrons, $(1\sigma_g)^2(1\sigma_u^*)^2$. These are given the symbol KK.

Bond Order

The bond order of a molecule is determined by adding the number of electrons in boding orbitals, subtracting the number of electrons in antibonding orbitals and dividing the result by 2 (since there are two electrons per orbital.)

$$\text{Bond Order } = \frac{\#bonding - \#antibonding}{2}$$

The larger the bond order, the stronger a chemical bond is predicted to be. Also, since strong bonds are short bonds, the larger the bond order, the shorter a bond is predicted to be.

Ionization of a molecule may have a profound affect on the bond order, and therefore the bond length. Consider the molecule c_2 that has an electronic configuration given by

$$c_2 : KK(2\sigma_g)^2(2\sigma_u^*)^2(3\sigma_g)^2(1\pi_u)^2$$

The addition of an electron to for c_2^- will require the electron to go into the 1_{pu} bonding subshell. This will have the effect of strengthening the bond (since it increases the bond order.) Removal of an electron to form c_2^+ would weaken the bond since it involves the removal of a bonding electron.

Paramagnetism

While the bond order of oxygen (O_2) is correctly predicted by a Lewis Structure, the Lewis structure fails to predict that the molecule will be **paramagnetic**. Paramagnetism is a property of a molecule or atom that occurs when the system has unpaired electrons. These electrons each have a small magnetic moment which can align with an external magnetic field, lowering the energy of the atom or molecule. As such, the atom or molecule will be attracted to a magnetic field.

Photograph showing liquid oxygen being trapped in a magnetic field due to its paramagnetic nature.

Figure 9.3.9

Oxygen, which has an electronic configuration given by

$$\begin{aligned} \mathrm{O}_2: \quad & (1\sigma_\mathrm{g})^2(1\sigma_\mathrm{u}{}^*)^2(2\sigma_\mathrm{g})^2(2\sigma_\mathrm{u})^2(3\sigma_\mathrm{g})^2(1\pi_\mathrm{u})^4(1\pi_\mathrm{g})^2 \\ & \mathrm{KK}(2\sigma_\mathrm{g})^2(2\sigma_\mathrm{u})^2(3\sigma_\mathrm{g})^2(1\pi_\mathrm{u})^4(1\pi_\mathrm{g})^2 \end{aligned}$$

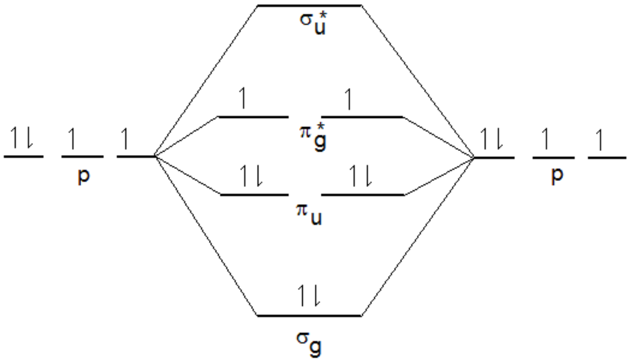

Figure 9.3.10

It is clear that there are two unpaired electrons. This is a property that cannot be predicted based on the Lewis Structure!

9.4: Hund's coupling cases (a) and (b)

There are clearly sources of angular momentum in a molecule due to orbital and spin considerations. But unlike atoms, molecules can also have angular momentum contributions from molecular rotation. There are many ways to describe the coupling of these different types of angular momentum. This text will focus on two specific cases, Hund’s coupling cases a and b.

Hund’s case (a)

In **Hund’s case (a)** coupling, the orbital and spin angular momenta are strongly coupled to the internuclear axis of the molecule. This defines the quantum number Λ and Σ, which are the internuclear axis projections of L and S. The sum of Λ and Σ give the total electronic angular momentum along the internuclear axis, Ω.

$$\Lambda+\Sigma=\Omega$$

Ω is then coupled to the end-over-end rotational angular momentum of the molecule (R) to give J, the total angular momentum.

$$J=\Omega+R$$

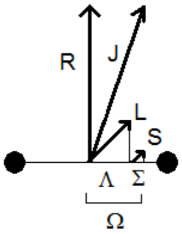

Figure 9.4.1

For a molecule that is well described by Hund’s case (a) coupling, that is in a $^1\Pi$ electronic state, the lowest value of J possible is $J=1$. The one unit of angular momentum comes from the orbital part of the wave function, so $J=1$ actually describes a non-rotating molecule $(R=0)$!

Hund’s case (a) does a good job of describing molecules which exhibit moderate spin-orbit coupling. If the coupling is extremely strong, another case (case (c), for example) is needed to describe the molecule’s properties.

Hund’s case (b)

Hund’s case (b) is slightly different from case (a) in that the spin angular momentum is uncoupled from the internuclear axis. As such, in Hund’s case (b) coupling, the quantum numbers Σ and Ω are undefined. In this case, the end-over-end rotation (R) of the molecule couples with Λ to produce N, which describes the sum of rotation plus orbital angular momentum.

$$N=\Lambda+R$$

N can then couple with S to give J, the total angular momentum.

$$J=N+S$$

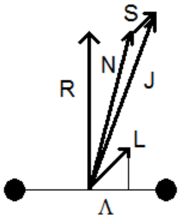

Figure 9.4.2

Singlet states, with $S=0$, are always well described by Hund’s case (b) coupling. Hund’s case (b) is a good description for molecules where spin-orbit coupling is weak (or immeasurably small.)

In the section describing the rotation of molecules as rigid rotators, the quantum number J was used to describe the total angular momentum due to rotation. This is consistent with both Hund's cases (a) and (b) for molecules in ${}^1\Sigma$ states, where $\Lambda = 0$ and $S = 0$ (implying where appropriate that $\Sigma = 0$ as well.)

9.5: Diatomic Term Symbols

A term symbol for a diatomic molecule contains a great deal of information about symmetry properties of the wavefunction which describes the electronic state. The symmetry properties are closely related to the values of the quantum numbers which specify the wavefunction. The pattern used to assign a symbol to a value for a quantum number is very similar to the pattern used for atomic systems. The major difference is that the quantum numbers must reflect the cylindrical symmetry of diatomic molecules rather than the spherical symmetry of atoms.

Quantum Number	One Electron		Many Electrons	
	Atom (l)	Molecule (λ)	Atom (L)	Molecule (Λ)
0	s	σ	S	Σ
1	p	π	P	Π
2	d	δ	D	Δ
3	f	ϕ	F	Φ

Just as there is a $(2l+1)$ degeneracy in the spherical wavefunctions, there is also an important degeneracy pattern in the wavefunctions of diatomic molecules. Σ and σ states are singly degenerate whereas all other are doubly degenerate. Why this is should become apparent as we develop the united atom method for decomposing spherical symmetry to cylindrical symmetry.

λ or Λ	Wavefunction Symmetry		Degeneracy
0	σ	Σ	1
1	π	Π	2
2	δ	Δ	2
3	ϕ	Φ	2

There are three methods commonly used to derive terms symbols for diatomic molecules. All of the methods are based on determining the quantum number Λ and the total spin quantum number. In the case of homonuclear diatomic molecules, the inversion symmetry is also important.

Σ states have another important symmetry designation. Σ states can have either + or - symmetry depending on whether or not the state is symmetric with respect to reflection through a plane containing the internuclear axis. Symmetric states are designated as Σ^+ state and antisymmetric ones are Σ^-. Π, Δ and all other states with $L \neq 0$ are doubly degenerate as they have both + and - components.

There is always an odd number of S states generated for the United Atom method or the Separated Atom method. They will come in pairs of Σ^+, Σ^- and the odd remaining state will have +/- symmetry as determined by the **Wigner-Witmer rule**. For this, one must consider the associated atomic state (using either the United Atom or the Separated Atom method). The +/- symmetry is determined by whether the indicated sum is even or odd according to the following table.

Method	Sum	Value	Parity
United Atom	$L+\sum l_i$	even	+
		odd	-
Separated Atom	$L_A+\sum l_A+L_B+\sum l_B$	even	+
		odd	-

United Atom Method

Think of the molecule as an atom with the same number of electrons. The atom will have spherical symmetry. The task is to reduce the spherical symmetry of the atomic wavefunction to the cylindrical symmetry of the diatomic molecule. In this case, the z-axis of the unified atom becomes the internuclear axis of the molecule. Thus, the quantum numbers will transform as

$$\begin{aligned} M_L &\rightarrow \Lambda \\ S &\rightarrow \Lambda \end{aligned}$$

✓ Example 9.5.1

What molecular terms are predicted for the OH radical?

Solution

The unified atom with the same number of electrons as OH is fluorine. The ground state designation for atomic fluorine is ^2P. For this state, $L = 1$ and so m_L can be -1, 0 or +1. The only values of m_L are 0 and 1. Therefore, the predicted terms will be Σ and Π. The multiplicity will be the same as the unified atom ($S = \frac{1}{2}$). The Σ state will be symmetric with respect to reflection though a plane containing the z-axis since

$$L + \sum l_i$$

is even for fluorine. So the expected terms are

$$^2\Sigma^+ \text{ and } ^2\Pi.$$

As it turns out, the ground state of OH is $^2\Pi$. The only way to confirm the ground state, however, is to use the molecular orbital method.

Separated Atom Method

A second method for determining molecular term symmetries is the separated atom method. This method is similar to the atomic term symbol method of writing out an exhaustive list of microstates and then accounting for each one. The quantum numbers which are important are determined from the sums of the z-component quantum numbers of the atomic wavefunctions. Thus, the values of Λ which are possible will be given by all possible combinations of m_L. Values of the same magnitude are then paired to make the two degenerate components for any values of $\Lambda > 0$.

✓ Example 9.5.2

What molecular terms arise for HLi, formed from a ground state hydrogen atom and a ground state lithium atoms?

Solution

The ground state of lithium is ^2S. For this set of atoms, we can construct the following table to combine values of m_L to form values of Λ and values of S as well.

	H (^2S)	**Li (^2S)**	**Λ and S**
M_L	0	0	0
S	$\frac{1}{2}$	$\frac{1}{2}$	1, 0

It is clear that the only value of Λ that can be generated from these separated atom states is $\Lambda = 0$, or a Σ state. The sum of $L_A + L_B + \Sigma l_A + \Sigma l_B$ is given by $0 + 0 + 0 + 0 = 0$, which is even. Hence, the Σ state has Σ^+ symmetry. So the resulting states are $^1\Sigma_g^+$ and $^3\Sigma_g^+$. The ground state of Li_2 is $^1\Sigma_g^+$, but this can only be confirmed by the use of the molecular orbital method.

✓ Example 9.5.3

What molecular terms are predicted for the OH radical?

Solution

The ground state atomic term for O is ^3P and that for H is ^2S. The following table shows the possible combinations of m_L to form Λ and the combinations of S which form the familiar Clebcsh series of resultant S values.

	H (^2S)	**O (^3P)**	**Λ and S**
M_L	0	+1, 0, -1	+1, 0, -1
S	$\frac{1}{2}$	1	$\frac{3}{2}$, $\frac{1}{2}$

The combination of a P term and an S term gives one Π ($\Lambda = \pm 1$) and one $\Sigma (\Lambda = 0)$ term. The sum $L_A + L_B + \Sigma l_A + \Sigma l_B$ is given by $1 + 0 + 4 + 0$ and is clearly odd. Therefore, the Σ state will be of Σ^- symmetry. The spin quantum numbers which are possible are $\frac{3}{2}$ and $\frac{1}{2}$. Therefore, the possible term symbols are $^4\Pi$, $^4\Sigma^-$, $^2\Pi$ and $^2\Sigma^-$. (The ground state of the OH radical happens to be of $^2\Pi$ symmetry, but again, this can only be confirmed using a molecular orbital approach.) Notice that there is no g/u symmetry indicated in this case because the molecule does not include an inversion center being a heteronuclear diatomic molecule!

✓ Example 9.5.3

What molecular terms arise for CO formed from a ground state carbon atom and a ground state oxygen atom?

Solution

The ground state of both C and O is ^3P. the following table summarizes the decomposition of the two atomic states from spherical to cylindrical symmetry.

	C (^3P)	**O (^3P)**	**Λ and S**
M_L	+1, 0, -1	+1, 0, -1	±2, ±1, ±1, 0, 0, 0
S	1	1	2, 1, 0

The resultant state are Δ, 2Π and 3Σ. Of the three Σ states, two will form a pair of Σ^+/Σ^-. The last S state must have its +/- symmetry determined by the Wigner-Witmer rule.

$$L_C + L_O + \Sigma l_C + \Sigma l_O = 1 + 1 + 2 + 4 = 8 \text{ (even)}$$

So the final Σ state is $\Sigma+$. The spin states generated are quintet, triplet and singlet. So the set of molecular states generated are

$$^5\Delta,\ ^5\Pi,\ ^5\Pi,\ ^5\Sigma^+,\ ^5\Sigma^-,\ ^5\Sigma^+$$
$$^3\Delta,\ ^3\Pi,\ ^3\Pi,\ ^3\Sigma^+,\ ^3\Sigma^-,\ ^3\Sigma^+$$
$$^1\Delta,\ ^1\Pi,\ ^1\Pi,\ ^1\Sigma^+,\ ^1\Sigma^-,\ ^1\Sigma^+$$

The ground state of CO is in fact $^1\Sigma^+$, but as always, this can only be reliably predicted using the molecular orbital method.

The number of states generated from separated atoms increases rapidly as the angular momentum in the separated atoms increases.

Molecular Orbital Method

The molecular orbital method requires the construction of a molecular orbital diagram. As was the case in the atomic term symbol problem, the molecular terms can be constructed considering only partially filled subshells. The quantum numbers will then be given by the vectoral sums of the one-electron quantum numbers. Consider the orbital diagram for the oxygen molecule.

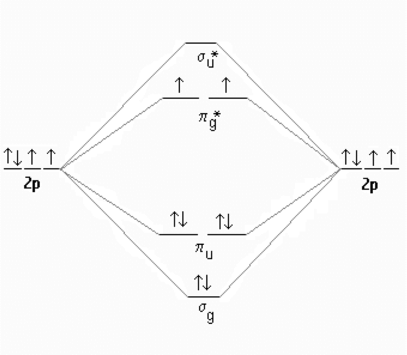

Figure 9.5.1

The only important electrons in this case are the two π_g^* electrons. (Ignore all of the ones in completely filled subshells - just as was done in the case of atoms as these always contribute $\Lambda = 0$ and $S = 0$.) The orbital angular momentum λ of one of the π_g^* electrons will cancel that of the other as one will have a value of $\lambda = -1$ and the other has $\lambda = +1$. (This is similar to the atomic case where one electron was in an orbital with $m_l = -1$ and the other in an orbital with $m_l = +1$. The sum of the two is zero.) Thus, Λ will be 0. Hence the predicted term will be a Σ state.

Since one of the π_g^* orbitals is symmetric with respect to reflection through a plane containing the nuclei and the other is antisymmetric, the predicted term will be antisymmetric with respect to this symmetry operation.

$$(sym) \times (antisym) = antisym$$

Thus, the state will be of Σ^- symmetry. In a similar manner, the gerade/ungerade symmetry can be determined by the product of the one-electron orbital symmetries.

$$(g) \times (g) = g$$

Finally, the spin multiplicity can be determined in the usual way.

$$\begin{aligned} S &= s_1 + s_2, s_1 + s_2 - 1, \ldots, s_1 - s_2 \\ S &= 1 \text{ and } 0 \end{aligned}$$

The predicted terms for this electronic configuration are ${}^3\Sigma_g^-$ and ${}^1\Sigma_g^-$. The ground state of O_2 is ${}^3\Sigma_g^-$. And since this result was generated using the molecular orbital method, the result is reliable that this is indeed the ground state of the O_2 molecule!

9.6: Herzberg Diagrams

One of the important reasons for describing the electronic structures and angular momentum coupling in diatomic molecules is to apply these descriptions to the prediction of the rotational branch structure in molecular spectra. As always, the first concern when predicting patterns in molecular spectra is the determination of selection rules. The selection rules for which the transition moment does not vanish are summarized below.

$$\Delta S = 0$$

$$\Delta \Lambda = 0, \pm 1$$

$$+ \leftrightarrow -, \; - \leftrightarrow +$$

Based on these selection rules, Herzberg diagrams can be used to predict the rotational branch structure and “first lines” in each branch based on the symmetries of upper and lower states in a given transition.

In order to discuss this very useful tool, we shall begin by discussing the description of a single state, starting with simple symmetry ($^1\Sigma^+$). In order to proceed, it is important to note the +/- symmetry of rotational wavefunctions. Basically, the rotational wavefunction is symmetric with respect to reflection through a plane containing the internuclear axis if R is even, and antisymmetric if R is odd. Thus the symmetry of the total wavefunction, given by

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

is given by the product of the symmetries of ψ_{elec}, ψ_{vib} and ψ_{rot}. In the case of a $^1\Sigma^+$ state, ψ_{elec} is +. ψ_{vib} is always + for vibration of a diatomic molecule. The rotational contribution (y_{rot}) will alternate for increasing R or J. (In the case of a $^1\Sigma^+$ state, R and J have the same value, since $\Lambda = 0$ and $S = 0$.)

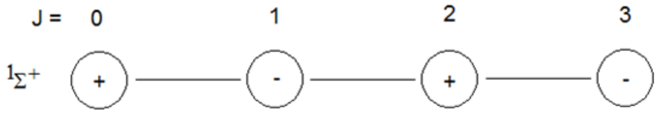

Figure 9.6.1

The above Herzberg diagram summarizes the +/- symmetry for the first few rotational levels.

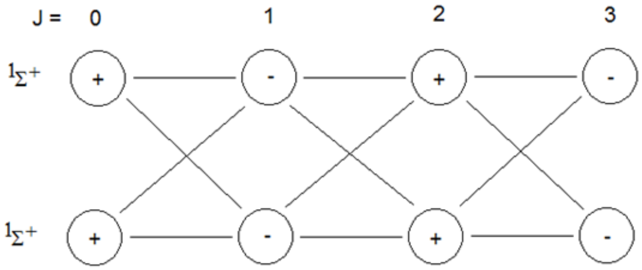

Figure 9.6.2

Based on this diagram, and the selection rule that + ↔ - and $- \leftrightarrow +$, the branch structure for a $^1\Sigma^+ \leftrightarrow ^1\Sigma^+$ transition can be predicted. Clearly, R- and P-branches are predicted in the rotational structure. This is the proper Herzberg diagram for the description of the 1-0 rotation-vibration spectrum of HCl (or other closed shell heteronuclear diatomic molecules.) Notice that $\Delta J = 0$ (Q-branch) transitions are impossible since the parity (+/- symmetry) does not change in such transitions, and hence they are forbidden.

The Herzberg diagram description of a $^1\Sigma^-$ state is not too different than that for a $^1\Sigma^+$ state. The only difference is that the +/- symmetry changes such that levels with odd J are now + and those with even J are now -.

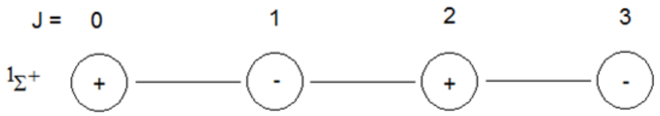

Figure 9.6.3

The description of a $^1\Pi$ state can be based on modifications to the descriptions of $^1\Sigma^+$ and $^1\Sigma^-$ states. Two important differences must be taken into account. First, since J is given by the sum of Λ and R (or Ω and R in Hund's case (a), but this will only be important if $S \neq 0$, which is not the case for a singlet state.) Second, since Π states (like Δ, Φ, etc.) have two components, both must be included in the diagram.

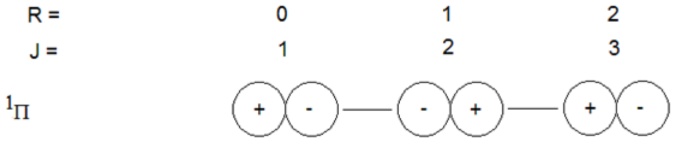

Figure 9.6.4

The description of a $^1\Pi$–$^1\Sigma^+$ transition can now be constructed. Note that P- Q- and R-branches are predicted. Also notice the "first line" in each branch. If the Π state is the upper state, the first lines in each branch are $P(2)$, $Q(1)$ and $R(0)$. (There can be no $P(1)$ line as the $J = 0$ level is missing in the upper state.) This is a pattern is a one way to recognize a $^1\Pi$–$^1\Sigma^+$ transition.

A reversal of state, such that the $^1\Sigma^+$ state is the upper state, causes the pattern to change. In the case of a $^1\Sigma^+ - {}^1\Pi$ transition, he first lines in each branch are predicted to be $P(1)$, $Q(1)$ and $R(1)$.

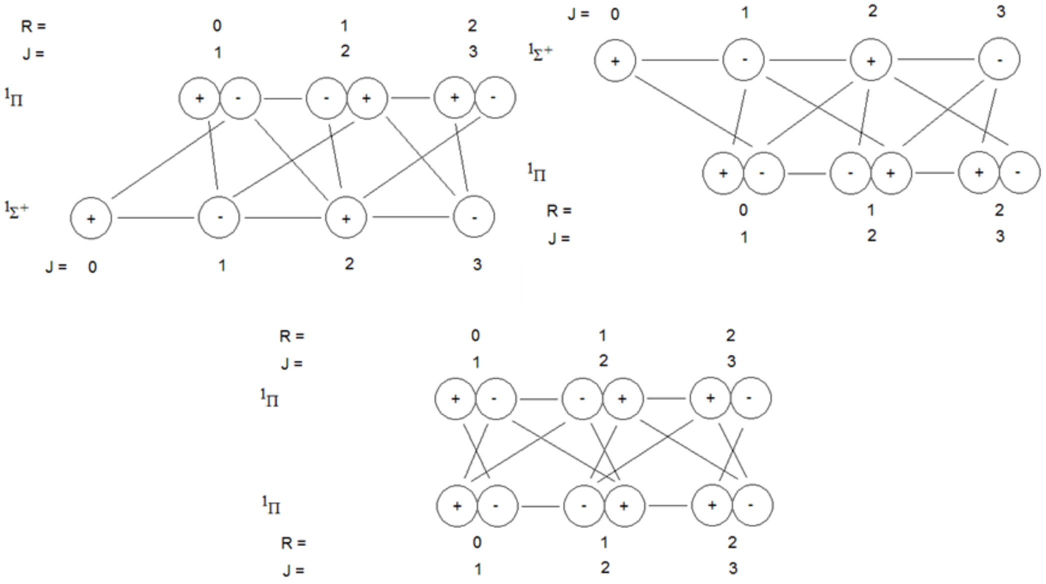

Figure 9.6.5

A $^1\Pi$–$^1\Pi$ transition becomes a little more complex as well. In this case, it can be seen that there are two Q-branches predicted! These will be resolved only if the two Λ components of at least one of the Π state are significantly different in energy. The first lines are predicted to be $P(2)$, $Q_1(1)$, $Q_2(1)$ and $R(1)$.

While the description here has been limited to singlet states of Σ and Π symmetry, these tools can be extended to describe and predict a great deal of rotational fine structure patterns in spectroscopic transitions (Herzberg, 1950). The patterns can get extremely complex for systems with high spin or orbital angular momenta. The picture can become even more complex when nuclear spin exists in the molecule which can couple to orbital, spin and/or rotational angular momenta. Entire books are dedicated to sorting out these patterns and interpreting the spectra of molecules which require these considerations (Brink, 1994) (Bunker, 2009).

9.7: Vibronic Transitions

Just as rotational motion is important in understanding vibrational spectra, vibrational (as well as rotational) motion(s) are important in understanding electronic transition is molecules. Electronic transitions in which vibrational structure is resolved are sometimes referred to a **vibronic transition**. When rotation is thrown in to the mix, the term “**rovibronic transitions**” is sometimes used.

Vibronic transitions can be discussed in terms of the transition moment. Keeping in mind that the wavefunction for a vibronic state can be expressed as a product

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

and that the transition moment is given by

$$\int \Psi^*_{tot}\vec{\mu}\,\Psi_{tot}d\tau$$

Substitution yields

$$\int (\psi_{elec}\psi_{vib})^*\vec{\mu}\,(\psi_{elec}\psi_{vib})\,d\tau$$

Since the dipole moment operator is a derivative operator, the chain rule must be employed, which yields

$$\int \psi^*_{elec}\psi_{elec}d\tau \int \psi^*_{vib}\vec{\mu}\psi_{vib}d\tau + \int \psi^*_{elec}\vec{\mu}\psi_{elec}d\tau \int \psi^*_{vib}\psi_{vib}d\tau$$

Since the electronic wavefunction must be orthogonal, the first term will vanish for transitions between two different electronic states. The second term however, does not vanish. In face, the magnitude of the $\int \psi^*_{vib}\psi_{vib}d\tau$ will be determined by the overlap of the two vibrational levels. (Note that since these represent vibrational wavefunctions in different electronic state, there is no reason for the wavefunctions to be orthogonal.)

Franck-Condon Factors

The intensity of a band in a vibronic transition will be governed by the magnitude of the Frank-Condon Factor for the band. The **Franck-Condon factor** (FCF) is defined by

$$FCF = \left[\int \psi'_{vib}\psi''_{vib}d\tau\right]^2$$

which is governed purely by the degree of overlap between the upper state vibrational wavefunction and that in the lower state. The overlap will be large for $\Delta v = 0$ if the potential energy functions of the upper and lower states are similar (similar ω_e, $\omega_e x_e$, r_e, etc.) and strong sequences will be observed in the spectrum. If, however, the equilibrium bond length changes significantly, the maximum Franck-Condon overlap will occur for combinations of v’ and v” for which $\Delta v \neq 0$. In these cases, strong progressions will be observed.

The Franck-Condon principle is closely associated with the Born-Oppenheimer approximation. In cases where the Born-Oppenheimer breaks down, the Franck-Condon principle is compromised as well.

9.8: Term Symbols for Polyatomic Molecules

Term symbols are used to designate electronic states of polyatomic molecules, much the same as they are used to designate electronic states for both atomic systems and diatomic molecules. These can be derived in much the same manner as we have developed for diatomic molecules, by taking combinations of atomic orbitals, whose symmetries have been decomposed from the spherical symmetry of the atoms to the lowered symmetry of the molecule.

An example would be H_3^+, which is the most common triatomic ion in the universe. (It is also an excellent example of a three-center two-electron bond in so far as it is the simplest example of a molecule possessing such a bond!) The combination of three 1s orbitals on the three atoms will yield three molecular orbitals. The decomposition of symmetry is described in the following section.

9.9: Group Theoretical Approach to Molecular Orbitals

One of the more powerfully predictive things we can do with Group Theory is predict the symmetries of molecular orbitals. Molecular orbital symmetries can have huge ramification on chemical bonding and chemical reactions.

The first thing we would like to be able to do is to predict the symmetries of the molecular orbitals that arise from the linear combinations of atomic orbitals. This is not too difficult. In fact, the process has many aspects in common with determining molecular vibration symmetries. The process can be summarized as follows:

1. Separate the molecule into groups of equivalent atoms.
2. For each set of equivalent atoms, determine the reducible representation that describe the atomic orbitals to be used in the construction of molecular orbitals. This is determined by assuming that the point group is centered on an atom containing the orbitals. Call this Γ_{ao}.
3. Determine $\Gamma_{unmoved}$ for the set of equivalent atoms.
4. Multiply $\Gamma_{ao} \otimes \Gamma_{unmoved}$ to determine $\Gamma_{reducible}$ for each set of equivalent atoms.
5. Add all of the $\Gamma_{reducible}$ that you have determined for each individual set of equivalent atoms. Call the result Γ_{MO}.
6. Γ_{MO} can then be resolved into components. These components give the symmetries of the molecular orbitals that result from the linear combinations of the atomic orbitals you have selected.

✓ Example 9.9.1

The Molecular Orbitals for a Water Molecule.

Solution

For this example, we shall consider the 1s orbitals on the H atoms, and the 2s and 2p orbitals on O. As it turns out, s orbitals are always totally symmetric in any point group, since they possess spherical symmetry. The p orbitals will transform as the x, y and z axes. So the following set of tables is used to generate Γ_{MO} for water.

First, determine Γ_H describing the H atoms.

C_{2v}	E	C_2	σ_{xz}	σ_{yz}
$\Gamma_{H(1s)}$	1	1	1	1
Γ_{unm}	2	0	0	2
Γ_H	2	0	0	2

Next, determine Γ_O describing the four orbitals on the O atom.

C_{2v}	E	C_2	σ_{xz}	σ_{yz}
$\Gamma_{O(2s)}$	1	1	1	1
$\Gamma_{O(2p)}$	3	-1	1	1
Γ_{red}	4	0	2	2
Γ_{unm}	1	1	1	1
Γ_O	4	0	2	2

Next, determine Γ_{MO} as the sum of $\Gamma_H + \Gamma_O$

C_{2v}	E	C_2	σ_{xz}	σ_{yz}
Γ_H	2	0	0	2
Γ_O	4	0	2	2
Γ_{MO}	6	0	2	4

Now, decompose Γ_{MO} under C $_{2v}$ symmetry!

C_{2v}	E	C_2	σ_{xz}	σ_{yz}
Γ_{MO}	6	0	2	4
-3 A_1	3	3	3	3
	3	-3	-1	1
-B_1	1	-1	1	-1
	2	-2	-2	2
-2 B_2	2	-2	-2	2
	0	0	0	0

So

$$\Gamma_{MO} = 3A_1 + B_1 + 2B_2$$

The molecular orbitals of water are shown below.

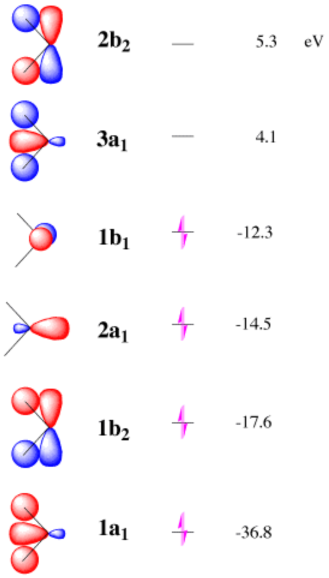

Figure 9.9.1: The above orbitals are generated based on a PM3 (semiempirical) orbital calculation of water. The numbering does not match the actual orbitals, but the symmetries are correct.

The $1a_1$ orbital was not generated in this example because it is essentially the 1s orbital on oxygen, which was not included in the basis set of functions we originally used. Also missing from our set are the $2b_2$ and $3b_2$ orbitals, which require the addition of $3p_x$ and $3d_{xz}$ orbitals on oxygen, which were not included. These orbitals are “virtual orbitals” as they are unoccupied.

The electronic configuration of H_2O is given by

$$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2$$

The overall symmetry of the electronic state is given by the product of the se symmetries, counting each one twice since each orbital contains two electrons. In fact, all closed shell molecules (all subshells filled) will have an electronic symmetry that is totally symmetric. In this case, the electronic state is $^1A_1$.

If the lowest unoccupied molecular orbital is of B_2 symmetry, then the first excited state of the molecule will be

$$(1b_1)^1(4a_1)^1$$

The total electronic symmetry is given by $B_1 \otimes A_1 = B_1$. The electronic configuration would give rise to both singlet and triplet states.

To test whether or not the transition to this state is allowed, the transition moment integral must not vanish.

$$\int \psi' \overrightarrow{\mu} \psi" \, d\tau = \int B_1 \cdot \begin{pmatrix} B_1 \\ B_2 \\ A_1 \end{pmatrix} \cdot A_1 d\tau$$

This integral clearly will not vanish by symmetry for the component along the x-axis. Hence, the transition to this excited state of water will be a perpendicular transition.

✓ Example 9.9.2

Formaldehyde

Solution

To generate the molecular orbitals in formaldehyde, consider the 1s orbitals on H, the 2s and 2p orbitals on C and O.

First, determine Γ_H describing the H atoms.

C_{2v}	E	C_2	σ_{xz}	σ_{yz}
$\Gamma_{H\,(1s)}$	1	1	1	1
Γ_{unm}	2	0	0	2
Γ_H	2	0	0	2

Next, determine Γ_C and Γ_O describing the four orbitals on the C atom and the O atom.

C_{2v}	E	C_2	σ_{xz}	σ_{yz}
$\Gamma_{C(2s)}$	1	1	1	1
$\Gamma_{C(2p)}$	3	-1	1	1
Γ_{red}	4	0	2	2
Γ_{unm}	1	1	1	1
Γ_C	4	0	2	2

C_{2v}	E	C_2	σ_{xz}	σ_{yz}
$\Gamma_{O(2s)}$	1	1	1	1
$\Gamma_{O(2p)}$	3	-1	1	1
Γ_{red}	4	0	2	2
Γ_{unm}	1	1	1	1
Γ_O	4	0	2	2

The total reducible representation to be reduced is given by $\Gamma_H + \Gamma_C + \Gamma_O$.

C_{2v}	E	C_2	σ_{xz}	σ_{yz}
Γ_H	2	0	0	2
Γ_C	4	0	2	2
Γ_O	4	0	2	2

C_{2v}	E	C_2	σ_{xz}	σ_{yz}
Γ_{MO}	10	0	4	6

Decomposition of this reducible representation shows

$$\Gamma_{MO} = 5A_1 + 2B_1 + 3B_2$$

The electronic configuration for formaldehyde is given by

$$(1a_1)^2(2a_1)^2(3a_1)^2(4a_1)^2(1b_2)^2(5a_1)^2(1b_1)^2(2b_2)^2$$

The $(1a_1)$ and $(2a_1)$ orbitals did not come from the above analysis as they are essentially the as orbitals on O and C that were not included in the basis set. The lowest energy unoccupied orbital is $(2b_1)$, so the first excited electronic state will have an electronic configuration given by

$$(5a_1)^2(1b_1)^2(2b_2)^1(2b_1)^1$$

This yield both triplet and singlet spin functions and an orbital function with symmetry given by $b_2 \otimes b_1 = a_2$. And as it turns out, the first electronic transition in formaldehyde is **orbitally forbidden** since no choice of a component of the dipole moment operator can be used to create a totally symmetric integrand for the electric dipole transition moment integral.

$$\int A_2 \cdot \begin{pmatrix} B_1 \\ B_2 \\ A_1 \end{pmatrix} \cdot A_1 d\tau$$

In order to see this transition in formaldehyde, there must be some involvement from vibrational motion that changes the symmetry of the overall wavefunction. Recall that

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

if the Born-Oppenheimer approximation holds. The symmetries for the vibrational wavefunctions (which can be derived using the method previously discussed) are given by

$$\Gamma_{vib} = 3A_1 + B_1 + 2B_2$$

So excitation of a B_1 or B_2 vibrational mode (yielding an overall symmetry for the total wavefunction of either B_2 or B_1 respectively) will cause the transition to “turn on”. This type of **vibronically allowed transition** is not uncommon (similar behavior is observed in benzene) and is characterized by a missing 0-0 band in the electronic spectrum of the molecule.

9.10: References

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9.11: Vocabulary and Concepts

antibonding orbital

bonding orbital

Born-Oppenheimer approximation

Coulomb integrals

exchange integral

Franck-Condon factor

gerade

Herzberg Diagrams

Hund’s case (a)

Hund’s case (b)

linear combinations of atomic orbitals

Molecular Orbital Method

Molecular Orbital theory

negative overlap

orbitally forbidden

overlap integral

paramagnetic

rovibronic transitions

Separated Atom Method

ungerade

United Atom Method

vibronic transition

vibronically allowed transition

Wigner-Witmer rule

9.12: Learning Objectives

After mastering the material covered in this chapter, one will be able to:

1. Describe the Born-Oppenheimer Approximation and how it is used to construct potential energy surfaces describing the vibration of a diatomic molecule.
2. Construct a molecular orbital diagram for a diatomic molecule depicting both bonding and antibonding orbitals of s and p symmetries including inversion symmetry (g/u) as appropriate for homonuclear diatomic molecules. Utilize the diagram to
    a. Predict the ground state electronic configuration of a diatomic molecule, including
        i. Magnetic properties
        ii. Bond order
3. Describe the differences between Hund's Angular Momentum Cases (a) and (b) and how these cases manifest in the resulting energy levels in real molecules.
4. Determine molecular term symbols for diatomic molecules using the
    a. United Atom Method
    b. Separated Atom Method
    c. Molecular Orbital Method
5. Construct Herzberg Diagrams and use them to
    a. Determine the band structure of a spectroscopic transition, including the "first line" in each branch.
6. Derive the formulation for the Franck-Condon factor and explain how it determines relative intensity of vibrational bands in an electron transition.
7. Utilize the tools of Group Theory to predict the symmetries of the molecular orbitals that arise from linear combinations of atomic orbitals for a polyatomic molecule.

CHAPTER OVERVIEW

10: Lasers

One of the most important tools in scientific measurement and the development of technology in general is the **laser**. The word “laser” is an acronym for Light Amplification by Stimulated Emission Radiation. What a laser does is use a spectroscopic transition to amplify the intensity of a light source by stimulating emission from the upper state of the transition. In order to do this, the system must have a population inversion.

10.1: Fractional Population of Quantum States

A molecule will exist in a quantum state with an energy determined by that quantum state. For a sample containing a large number of molecules, several quantum states will be available, and the molecules will be distributed among them. If the sample is thermalized[1], the distribution will follow the Maxwell-Boltzmann distribution law.

Maxwell-Boltzmann Distribution Law

According to the **Maxwell-Botlzmann distribution** law, the fraction of the number of molecules in the sample that are in a specific quantum state will be given by

$$\frac{N_i}{N_{tot}} \propto d_i e^{-\frac{E_i}{kT}}$$

where N_i/N_{tot} is the fraction of the total number of molecules in the i^{th} quantum state which has energy E_i relative to the lowest energy the molecule can attain. If the fraction of molecules in each quantum state is added, the result must be unity.

$$\sum_i \frac{N_i}{N_{tot}} = 1$$

Partition Functions

To ensure this, a **partition function** is introduced to normalize the distribution.

$$q = \sum_i d_i e^{-\frac{E_i}{kT}}$$

And so

$$\frac{N_i}{N_{tot}} = \frac{d_i e^{-\frac{E_i}{kT}}}{q}$$

The partition function, which is a function of temperature as well as the physical properties of the molecules under consideration, can be expressed as a product of partition functions for each type of motion available in the molecule. If electronic, vibrational and rotational energy levels only are considered, the partition function can be expressed as

$$q_{tot} = q_{elec} q_{vib} q_{rot}$$

When considering each type of motion, it is important to consider both the energy levels and the degeneracies of states. As was seen in the case of rotational motion (Chapter IV), at low energies, the degeneracy part of the expression dominates, but at higher energies, the exponential part of the function takes over. If the energy $E_i$is very large (relative to kT) then there will be essentially no population in the i^{th} level. This is the case, in general, for electronic excitation; the energy level is so high in energy relative to kT that there are essentially no molecules in excited electronic state *except at extraordinarily high temperatures*. In this case, where the energy is very large relative to kT

$$\begin{aligned} q &= d_1 e^{-\frac{0}{kT}} + \sum_{i \neq 1} d_i e^{-\frac{E_i}{kT}} \\ &\approx d_1 \cdot 1 + \sum_{i \neq 1} d_i e^{-\infty} \\ &= d_1 + \sum_{i \neq 1} d_i \cdot 0 \\ &= d_1 \end{aligned}$$

Naturally, q will become larger for motions will small energy level differences (such as rotational motion) where the word “small” is always considered relative to kT.

Based on the above equations and the degeneracies and energy level expressions for the harmonic oscillator (for q_{vib}) and the rigid rotor (for d_{rot}) the following approximate expressions can be used to estimate partition functions for each type of motion.

	Expression	Approx. Exp.	Magnitude Estimate
q_{elec}	$q = \sum_i d_i e^{-\frac{E_i}{kT}}$	d_1	1
$q_{<}vib$	$q = \sum_v d_v e^{-\frac{hc\omega_e(v+1/2)}{kT}}$	$\left(1 - e^{-\frac{\omega_e hc}{kT}}\right)^{-1}$	1-10
q_{rot}	$q = \sum_J (2J+1) e^{-\frac{hcBJ(J+1)_i}{kT}}$	kT/B	100-1000

Rotational and Vibrational Temperatures

The above discussion suggests that the temperature of a system can be determined by measuring the populations of individual quantum states. This can be done using spectroscopic intensity data. A line or band in spectrum will be more intense if there are a larger number of molecules in the originating state of the transition. (This is essentially Beer’s Law that says that spectral intensity is proportional to concentration.)

Sometimes these analyses will yields results that are not consistent between different types of motion within the molecule. For example, analysis of the vibrational intensity distribution may yield a temperature that is different than the analysis of the rotational intensity distribution. For this reason, scientists often refer to the “**vibrational temperature**” or the “**rotational temperature**” of a sample. These are non-equilibrium situations and are usually dependent on the dynamics of how a molecule was formed within a sample. Some pathways may leave an excess of energy in vibrational modes whereas other may lead to rotationally hot product molecules due to an excess of energy in rotational motion. Typically after a large number of collisions which energy may be transferred from one molecule to another, these temperatures will equilibrate and the Maxwell-Boltzmann distribution law will describe all fractional populations irrespective of the type(s) of motion that dominate(s) an energy level.

Population Inversion

In the case where all available energy levels are singly degenerate, the **Maxwell-Boltzmann distribution** law suggests that fractional population should decrease with increasing energy. In some cases, the non-equilibrium distribution of molecules through the available quantum states becomes inverted. Again, this situation can be created by the specific dynamics of how a system is prepared. In the case that a population inversion can be created, a laser can be made that uses the sample of molecules with this inverted population as a gain medium to create the laser light output.

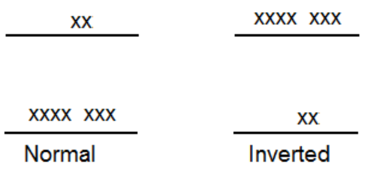

Figure 10.1.1

Theoretically, any system in which a **population inversion** can be induced can be used as a gain medium for a laser.

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1. The word “Thermalized” means that all of the molecules in the sample are in “thermal contact” with one another (typically due to a large frequency of collisions with other molecules in the sample) so that there is an equilibrium established for the exchange of energy between molecules in the sample.

10.2: Types of Lasers

There are many different types of lasers built on many different principles and techniques of creating population inversions. A population inversion can be induced in a system through the fast absorption of light, a chemical reaction that creates a non-equilibrium distribution of molecules, “zapping” a system with electrons, or many other ways. We will consider several of them in this section.

Two-level laser

The simplest type of laser is a two-level laser, although many argue that a true two-level laser cannot exist[1]. None the less, it is instructive to consider a simplified system with only two levels, in which a population inversion has been introduced. Once the population inversion has been achieved, light of a frequency that matches the resonance between the two levels is passed through the sample. This can “tickle” a molecule into dropping to the lower level by giving off a photon. If this happens, the stimulated emission will be coherent (in phase and of the same frequency) as the stimulating photon. If many molecules are stimulated to emit, the gain will be substantial and a strong beam of coherent, monochromatic light will be produced.

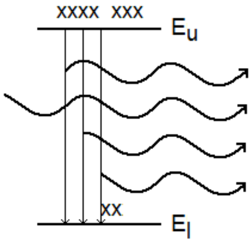

Figure 10.2.1

Naturally as laser output is achieved, the upper-level population will deplete and that of the lower level will grow. When a Maxwell-Boltzmann distribution is established, laser output will cease. So in order to keep the laser operating, the upper state must be repopulated or the lower state must be depopulated. The nature of the laser is defined by the manner in which these population/depopulation events occur. The manner in which the light is manipulated can also define the nature of the laser and how it operates.

Three-level lasers

There are several examples of three-level lasers. In these systems, a third level is introduced in order to either populate the upper level of the laser transition or depopulate the lower level. This difference defines two types of three-level laser systems.

In the case that the third level (E_1) lies above the upper level of the laser transition (E_u), the following schematic energy level diagram will result.

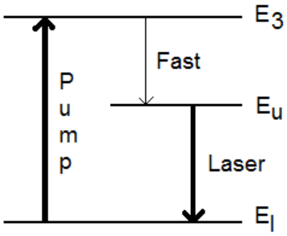

Figure 10.2.2

In this system, The level E_3 is populated by the absorption of light (which is what is depicted in the diagram above) or some other method. The transition between E_1 and E_u is much faster than the transition between E_u and the lower level of the laser transition, E_l. As such E_u will be populated quickly and a population inversion will be established. As this laser operates, E_u will be depopulated, so a fresh supply of molecules in this level must be provided by the pump source cycling molecules out of E_l and back to E_3.

An example of this type of three-level laser is the ruby laser[2], in which the gain medium is a ruby crystal. The pump exciting molecules from E_l to E_3 is provided by a flash lamp. Since the flash lamp is pulsed, this system produces pulsed laser output. The wavelength of the ruby laser output is 694.3 nm. The helium-neon (HeNe) laser (Microwave Determination of Average Electron

Energy and Density in He–Ne Discharges, 1964) is another example of this type of laser. The HeNe laser is a continuous wave laser (meaning it is not pulsed like the ruby laser) that produces red light at 632.8 nm.

A second type of three-level laser is one on which the third level (E_3) lies below the lower level (E_l) of the laser transition. In this system, the upper level of the laser transition is populated either by a chemical or electrical pump or by a chemical reaction. The lower level is depopulated by a fast transition (or a chemical reaction). Since this depopulation happens faster than the population of E_l through the laser transition, a population inversion is maintained easily.

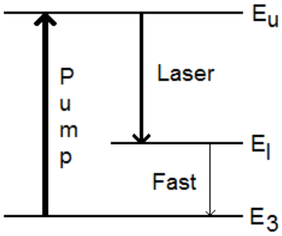

Figure 10.2.3

An example of this type of laser is the chemical laser in which the upper level of the laser transition is populated through a chemical reaction which creates vibrationally excited molecules (Spencer, Jacobs, Mirels, & Gross, 1969) (Kasper & Pimentel, 1965) (Hinchen, 1973). Such lasers typically produce output in the infrared.

Four-level lasers

A four-level laser incorporates elements of both types of three-level lasers by having an energy level above the upper level of the laser transition that rapidly populates E_u and one below the lower state of the laser transition that rapidly depopulates the lower level, E_l.

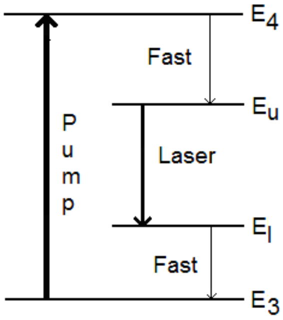

Figure 10.2.4

Briefly, a pump (usually supplied by a flash lamp) excites molecules from E_3 to E_4. A fast transition from E_4 to E_u populates the upper state of the laser transition. A fast transition from E_l to E_3 then depopulates the lower level of the laser transition, maintaining a population inversion between E_u and E_l until E_4 is no longer able to populate E_u.

The Nd:YAG (Geusic, Marcos, & Van Uitert, 1964) (neodymium YAG) laser is an example of a four level laser. In this laser, neodymium (III) ions entrained in a yttrium aluminum garnet crystal provide the four energy levels. The laser produces a polarized pulsed output at 1064 nm.

Q-switching

One of the important devices that makes a Nd:YAG laser (and many others) is a **Q-switch**. A Q-switch is a polarized filter that changes direction fo polarization when an electrical potential is applied to it. In one orientation, the switch blocks laser output light (preventing stimulated emission amplification) and in the other orientation, it allows for this light to pass.

The Q-switch is used to limit laser gain (which would deplete the upper level of the laser transition) until an optimal population inversion is achieved. The Q-switch is then “opened” and laser output is generated until the population inversion is relaxed. The timing is critical and must be tuned for each laser (and usually re-optimized several times a day while the laser is in operation, as changes in temperature can change the characteristics of the YAG crystal dramatically.

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1. Others argue that excimer lasers and dye lasers are two-level lasers. The difference depends on what is considered a “level”.

2. There are actually two levels in a ruby laser that act as E 3. For a complete description, see (Maiman, 1960)

10.3: Examples of Laser Systems

There are many types of laser commonly used in science today. The range of applications of lasers in science and technology is extremely broad, ranging from household applications (such as television remote controls) to manufacturing applications (such as laser cutting and welding, or laser lithography used in the manufacture of microelectronics), to medicine (including specific procedures such as laser eye surgery) to basic fundamental science. The specific needs of a particular job determine which laser is best for the job.

N_2 laser

A nitrogen laser is a **continuous wave** laser that provides ultraviolet output at 337 nm, but can be tuned to several wavelengths near its strongest output line. The laser gain transition is the 0-0 band in the B-X transition of N_2. The upper state is populated by subjecting the gas to an electrical discharge. Applications of theN_2 laser is pumping of dye lasers (described in section B.4.d), diagnostics of air samples and laser desorption techniques.

Excimer Lasers

An excimer laser is one in which the upper state of the transition is a **metastable state** of a molecule, and the lower state is dissociative. Because the lower state is not bound, molecules that land in that state after emitting a photon immediately dissociate, allowing for no buildup of population in the lower level of the laser transition. As such, any population in the upper state implies a population inversion.

The upper (metastable) state is populated by a pulsed electrical discharge through a gas containing the precursors of the excimer molecules. Since these precursors (usually involving HCl or HF gas) are particularly caustic (to say nothing of how reactive the soup of radicals and ions produced by the electrical discharge are!) these laser require a very high level of maintenance. However, because of the simplicity of the energy level scheme, these lasers are very easy to tune to provide strong laser output. These lasers are used in a number of applications including the pumping of dye lasers and laser eye surgery. The pulses that emanate from these laser have a time on the order of a few nanoseconds.

The output wavelength of an excimer laser is determined by the particular excimer formed in the discharge. The most commonly used excimer lasers are XeCl (308 nm) and ArF (193 nm.) The following table shows several common excimers and their output wavelengths.

Table: Common Excimers with Output Wavelengths

Excimer	Wavelength (nm)
ArF	193
KrCl	222
KrF	248
XeCl	308
XeF	351

Rare Gas Ion Lasers

Another important class of lasers is the **rare gas ion laser**. In this laser, the gain medium is provided by an ion of a noble as (such as Ar^+). The gas is ionized by means of an electrical discharge. These lasers typically have several wavelengths which can be selected for the output. These lasers are used widely as pump lasers for dye lasers and also in Laserium light shows.

Tunable Dye Lasers

Tunable dye lasers are a very flexible type of laser as they provide selectable output wavelengths. Many of them can be scanned through a set of wavelengths which can be very useful in a number of applications (such as laser spectroscopy.) The gain medium in a dye laser is provided by a strong fluorescent dye dissolved in a liquid solvent (such as methanol.) The range of output wavelengths is determined by the specific dye. Commercially available dyes are available that span the entire visible spectrum. Ring dye lasers are capable of very high resolution (narrow wavelength or frequency range.)

Pulse Amplification

Pulse amplification is a technique used to increase the output power of a laser. In this technique, a seed beam is passed through a dye cell and is crossed by a pulsed pump beam which excites the dye, providing another stage of gain for the seed beam. Most dye lasers have at least one stage of pulse amplification in them to achieve suitable power for the specific application.

Frequency Doubling

Another useful technique that extends the wavelength output range of laser is **frequency doubling**. In this technique, laser output is focused on a special crystal (such a beta-Barium Borate or BBO) which has nonlinear optical properties that allow it to fuse two photons of frequency ω into one photon with frequency 2ω. Frequency doubling is not a terrifically efficient process and usually comes at a significant price to output intensity. However, the benefit of frequency doubling a tunable dye laser output is that one can extend the tunable range of laser output into the ultraviolet.

Ultrafast Lasers

A fairly recent development in technology is the development of **ultrafast lasers**. This class of device delivers laser output in very short (on the order of femtoseconds) pulses of laser output. On this time scale, it is possible to take snapshots of chemical reaction intermediates since the laser pulse time is comparable to the lifetime of a chemical intermediate. These lasers, however, have very brad spectral output due to the **Heisenberg uncertainty principle** precluding simultaneously small uncertainties in time and wavelength.

10.4: Laser Spectroscopy

Typical **spectroscopy** experiments require four elements: 1) a light source, 2) a sample, 3, a monochrometer and 4) a detector. In laser methods, a laser can serve as both a light source and a monochrometer. It can also serve as just one of those two, or be used in a totally different way such that it serves as neither!

Total Fluorescence

In a **total fluorescence** experiment, the laser is used as both the light source as well as the monochrometer. The data obtained is similar to that obtained in a regular absorption spectroscopy experiment.

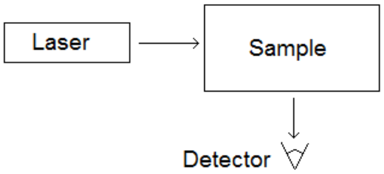

Figure 10.4.1

The laser used in this kind of experiment would typically be a tunable dye laser that will be scanned through a range of wavelengths in order to map the absorption spectrum of the sample. The detector must be placed at an angle to the incident laser beam in order to minimize direct exposure to the laser light, which will swamp the signal (and probably ruin the detector!) What is detected is actually photons produced in the fluorescence of the sample, which is increased whenever the laser frequency coincides with a resonance frequency.

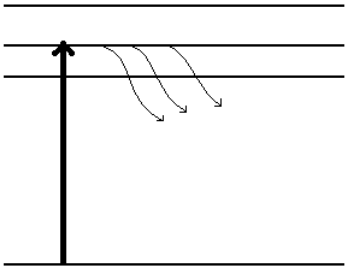

Figure 10.4.2

Monitoring fluorescence intensity as a function of excitation laser wavelength produces an absorption spectrum of the molecule. By and large, the total fluorescence method yields information about the upper state of a transition since scanning the tunable laser maps the energy levels in the upper state.

Dispersed Fluorescence

In a **dispersed fluorescence** spectrum, The wavelength of the excitation laser is fixed and the fluorescence is collected by a monochrometer and separated into its wavelength components.

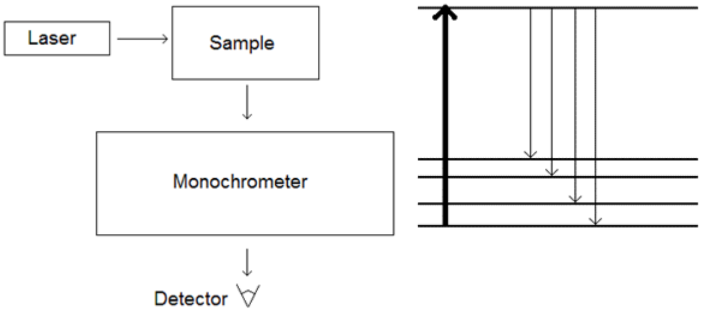

Figure 10.4.3

By separating the fluorescence into its wavelength components, the lower level energy levels are mapped. As such, this experiment is similar to an emission spectrum, but has the advantage of having only a single upper level quantum state. This type of experiment yields information about the lower level of the transition.

Molecular Beam Spectroscopy (A Sub-Doppler Method)

Laser excitation (total fluorescence) spectroscopy and dispersed fluorescence spectroscopy have resolution that is limited by the instrumentation and the natural **Doppler width** of the lines in the spectrum (caused by the motion of molecules in the gas phase, which can be parallel, antiparallel or at some angle to the direction of the laser beam propagation.) A number of techniques exist that allow for sub-Doppler resolution (resolution that is better than the **Doppler limit** would otherwise allow.

10.5: References

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10.6: Vocabulary and Concepts

continuous wave

dispersed fluorescence

Doppler limit

Doppler width

frequency doubling

Heisenberg uncertainty principle

laser

Maxwell-Boltzmann distribution

Maxwell-Botlzmann distribution

metastable state

partition function

population inversion

Pulse amplification

Q-switch

rare gas ion laser

rotational temperature

spectroscopy

total fluorescence

Tunable dye lasers

ultrafast lasers

vibrational temperature

10.7: Problems

1. A dye laser produces pulses of 15.0 mJ at a wavelength of 564 nm. How many photons are being produced per pulse?
2. In the above problem, consider the optical gain medium occupying a volume of 1.00 mL. What is the minimum concentration (in mol/L) of chromophores needed to produce pulses of 15.0 mJ at 564 nm?
3. Consider a two-level system, in which the difference in energy is 1.0 eV. If both levels are singly degenerate, calculate the fractional population of each level at 10 K, 100 K, and 1000 K.

CHAPTER OVERVIEW

11: Quantum Strangeness

Figure 11.1

In the television show “The Big Bang Theory”, Dr. Sheldon Cooper describes the best use of his time as a scientist to “*employ his rare and precious mental faculties to tear the mask off of nature and stare at the face of God.*” [1] And while the fictitious character may have an inflated view of the magnitude of his research efforts, he is not in poor company in terms of the feelings that science is a tool to be used to see the nature of God in nature itself. Albert Einstein is quoted as saying “*Science without religion is lame. Religion without science is blind.*” [2] Another quote attributed to Einstein is, “*I want to know God’s thoughts; the rest is just details.*” [3] Of course, Einstein claimed some familiarity with the intentions of the Creator when he quipped in a letter to Max Born, “*Quantum mechanics is certainly imposing. But an inner voice tells me that it is not yet the real thing. The theory says a lot, but does not really bring us any closer to the secret of the "old one." I, at any rate, am convinced that He does not throw dice.*” [4]

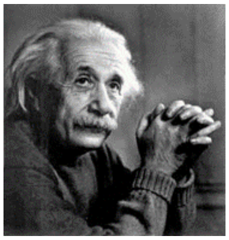

Figure 11.2

Much has been made of Einstein’s opinions of God as a craps player. Through the 1920s and 1930s, Einstein and Niels Bohr had many conversations on the ramifications of the quantum theory. In response to Einstein’s quip about a non-dice-playing deity, Bohr is said to have responded, “*Einstein, stop telling God what to do!*”[1] Of course, Bohr was very well aware of the strangeness of the quantum theory and how it shook the very roots of conventional wisdom about nature. Bohr is quoted as saying, “*Anyone who is not shocked by quantum theory has not understood it.*” [5]

Naturally, Einstein found quantum theory quite shocking indeed. One of his earliest objections was that the quantum theory required that one dismiss a deterministic view of the universe. The philosophy of **Determinism** states that if all is known about a system at one point in time, then all can be known about that system at all points in time. Bohr, on the other hand, had no difficulties in dismissing determinism in favor of a quantum theory. Eventually, the debate would focus on the indeterminacy predicted by the Heisenberg Uncertainty Principle for complimentary variables (variables for which the corresponding quantum mechanical operators do not commute, such as position and momentum.)

Figure 11.3

In fact, the spirited (but mostly amiable) debates between Einstein and Bohr did the development of quantum theory an enormous service. (not all of Bohr’s debates were amiable. Some of his discussions with Werner Heisenberg left Heisenberg reportedly in tears! Heisenberg said of these discussions, “*Since my talks with Bohr often continued till long after midnight and did not produce a satisfactory conclusion, ...both of us became utterly exhausted and rather tense.*”) [6]

By poking at the forefronts of what the theory predicts and what it can not predict, the Bohr-Einstein debates pushed quantum theory forward by enormous leaps. In this chapter, we will examine how various people have probed the “strangeness” of the quantum theory and the bizarre behavior it predicts (or in some cases, the bizarre behavior that was discovered almost by accident.) Much of the strangeness of quantum mechanics continues to be researched actively and colors such important topics as quantum communications and quantum computing.

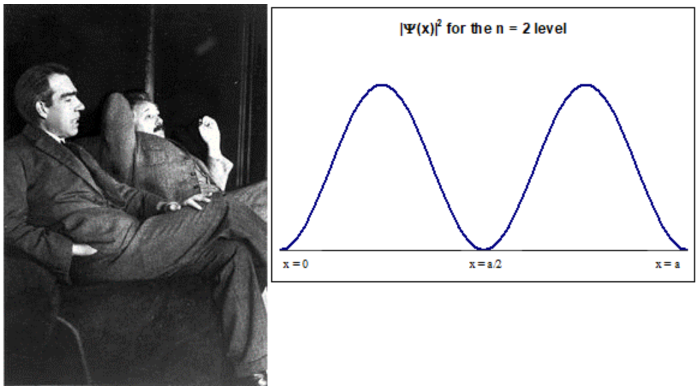

Figure 11.4

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1. The Big Bang Theory, CBS Television, 2011. W430W9405
2. A. Einstein, "Science, Philosphy, and Religion: a Symposium," 1941. W430W9405
3. E. Salaman, "A Talk with Einstein," The Listener, vol. 54, pp. 370-371, 1955. W430W9405
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11.1: Nodes and Wave Nature

One of the first introductions students of the Quantum Theory receive involves the nodes in the wavefunctions of a one-dimensional particle in a box. The probability of measuring the particle to exist at any given position in the box is given by the square of the wavefunction. For the $n=2$ level, the squared wavefunction is plotted above.

The figure shows that the probability of measuring the position of the particle at positions $x=\frac{a}{4}$ and $x=\frac{3a}{4}$ or the maxima and that there is zero probability of measuring the particle to exist at the endpoints or at $x=\frac{a}{2}$, the middle position of the box. One might wonder how the particle can travel from one side of the box to the other without ever actually being in the middle. If one models the particle as a small ball bearing traveling from end to end in an evacuated, sealed glass tube (consistent with a deterministic view in which the particle has a definite location at all times) the prediction is clearly troubling. For many, this creates a dilemma.

The reconciliation of this dilemma requires that one abandon a notion of determinism in embracing the wave-nature of the particle. Namely, if one accepts the wave description of the particle, the notion of a definite location become meaningless since the wave must be delocalized across the entire box. In fact, the wave even exists at the central node despite the value of the wavefunction being zero! This concept provides a clear challenge to the notion of determinism that is suggested by Newtonian physics. The idea of “matter waves” also lead to a proposal by Louis de Broglie that matter-wave interference should be observable.

11.2: Quantum Interference

Thomas Young showed in 1803 [7] that light traveling through a pair of parallel slits will produce an interference pattern that follows Bragg's Law for diffraction. This was a huge problem to the existing Newtonian theory of light, as place CityNewton had postulated that light is, in fact, a stream of particles. With the advent of a quantum theory, light was postulated to have a dual nature, having properties of both particles and waves. This dual nature, of course would be applicable to the description of matter as well according to Louis de Broglie. At this point, things started to get really interesting. But before we go into that, let's think about the two-slit experiment in terms of the Heisenberg Uncertainty Principle.

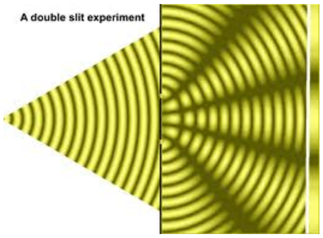

Figure 11.2.1

Recall that the Uncertainty principle states that there is a small minimum value for the product of the uncertainties of position and momentum.

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

This concept can be used to describe why a light wave is diffracted by a slit. As the photon or other wave-particle passes through the slit, the uncertainty of the position of the wave-particle is basically given by the size of the slit. The uncertainty in momentum then allows for the spreading of the wave-particle spatially. This is illustrated in the diagram. This interpretation is very useful in understanding how Einstein used this experiment as a criticism of the Uncertainty Principle and of the Quantum Theory itself.

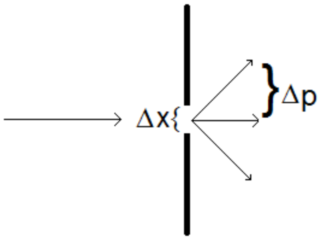

Figure 11.2.2

In 1924 [8] [9], Louis de Broglie proposed a wave description of all matter by proposing his famous wavelength relationship

$$\lambda = h/p$$

His predictions that matter-wave interference could be observed was confirmed in 1927 in independent experiments by George Thomson, who observed diffraction patterns in electron beams passing through thin metal films [10] and by Clinton Davison and Lester Germer, who observed electron diffraction on an electron beam focused on a crystalline nickel metal surface. [11] Thomson and Davisson shared the Nobel Prize in Physics in 1937 for these discoveries.

While the observation of interference of matter waves gave a great deal of credibility to the emerging quantum theory, Einstein was still troubled. In a series of interactions with Bohr, Einstein would propose thought experiments which he believed would uncover an inconsistency in the quantum theory by violating the Heisenberg Uncertainty Principle. Bohr would then consider the experiment and, in particular, the apparatus that would be used to make the measurements Einstein had proposed. Then, in presenting the "apparatus" to Einstein, Bohr would explain the flaw in Einstein's reasoning and how such a measurement could not violate the predictions of quantum mechanics.

One such exchange occurred over the concept of the "two-slit" experiment. In this experiment, a beam of electrons travels through a screen before arriving at a detector. In the screen, there are two slits through which the beam may pass. Each of these slits will diffract the beam, and lead to an interference pattern as the beam hits a detector screen. The diffraction is confirmed by the interference pattern observed on the detector.

To make matters even more interesting, if one slit is blocked, the result is the disappearance of the interference pattern. Instead, the recorded signal is consistent with the electrons traveling through the single unblocked slit.

For light waves, this phenomenon was well understood, thanks to the experiments of Young. But for matter waves, the picture becomes someone bizarre. There is not much of a problem if one considers what happens when the beam is turned on continuously. In this case, there are plenty of electrons making the transit and it is easy to imagine each as having a wave nature which can interfere with all of the other electrons making the transit.

The real excitement happens when the electron source is slowed down so that only one electron is making the transit at a time. If the resulting signals generated when the electrons reach the detector are integrated, over time an identical interference pattern emerges! “How can that be?” I hear you cry. And the question would indeed be very profound.

One explanation is that each electron traverses the distance from the gun through the slits by taking both possible pathways. This explanation is equivalent to saying that the electron becomes delocalized as soon as it leaves the source, takes all possible pathways to the detector and then becomes localized once again when it interacts with the detector, revealing its final position. Such an explanation would be very problematic to a person clinging to the philosophy of Determinism.

Einstein’s description of the phenomenon provided an important piece of the puzzle in terms of probing the limitations of quantum theory. Einstein argued that a particle passing through a slit would only have its path altered if it imparted some momentum to the screen containing the slit through a collision. That collision would have to cause the screen to move a tiny amount (due to conservation of momentum.) And if that movement could be detected, then one would then simultaneously know both the position of the particle (as it passed through the slit) and its momentum (due to the momentum imparted to the slit itself.) And this would create a violation of the Heisenberg Uncertainty principle.

Bohr’s response was quick and decisive. He pointed to the fact that Einstein had only attempted to apply the Uncertainty Principle to the wave-particle that passed through the slit and not to the slit itself. In fact, the uncertainty in the momentum of the slit will be the same as the uncertainty in the momentum of the wave-particle (since similar methods are used to measure them.)

$$\Delta p_{slit} = \Delta p_{wp}$$

Further, the uncertainty of the position of the wave-particle is equal to the uncertainty of the position of the of the slit.

$$\Delta x_{slit} = \Delta x_{wp}$$

Additionally, the slit itself must satisfy the Uncertainty Principle in that

$$\Delta x_{slit} \Delta p_{slit} \geq \hbar/2$$

simple substitution shows that if the slit is governed by the Uncertainty Principle, then the wave-particle must be as well.

$$\Delta x_{wp} \Delta p_{wp} \geq \hbar/2$$

This argument does not prove that quantum mechanics is correct, but it does show that it is self-consistent.

Very recently, scientists have used a modified approach to the double-slit experiment to reopen the question. [12] In this experiment, laser light shines on a screen with two pinholes. A clever detection system is used that detects only those photons that pass through one of the pinholes (a particle-like behavior.) But at the same time, detecting wires are placed in the positions of the destructive interference fringes (where no light should fall), confirming that no light is detected in these dark fringes (which is a consequence of the wave nature of light.) As such, the experiments demonstrate that light can show both the wave and particle nature simultaneously – something that Bohr had predicted to be impossible based on the idea of complementarity. Clearly, the debate continues and forms the subject of current research.

Bohr and Einstein would have several of these types of debates over the course of the late 1920s. Each time, Einstein would propose a thought experiment which he believed would violate the Uncertainty Principle, and each time Bohr would counter with a demonstration that, in fact, there was no violation at all. It seemed that Einstein was defeated. However, that was far from the case!

However, before exploring Einstein’s next move, let’s consider another experiment that shows the strangeness of quantum mechanics. It will be useful in framing a discussion of Einstein’s next move.

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11.3: The Stern-Gerlach Experiment

One of the very interesting aspects of many small particles, including electrons, is that of spin. (The original Stern-Gerlach experiment [13] was performed on a beam of silver atoms, but the result apply to electrons as well.) The property of spin creates a magnetic moment for these particles. For electrons, which have $s = \frac{1}{2}$, the component of angular momentum along an external axis can take two possible values, $m_s = \pm\frac{1}{2}$. That means that an electron traveling through an inhomogeneous magnetic field can align its magnetic moment either with or against the external field. The ramifications are very interesting.

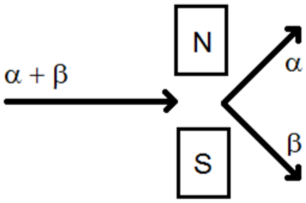

Figure 11.3.1

A beam of electrons that passes through an inhomogeneous magnetic field will be split into two beams. Those electrons whose magnetic moment aligned with the field will be deflected in one direction, and those with a magnetic field aligned against the external field will be deflected in the other. Each beam can then be considered as containing only electrons that are either “spin up” ($\alpha, m_s = +\frac{1}{2}$) or “spin down” ($\beta, m_s = -\frac{1}{2}$). As such, if one of the beams passes through another magnetic field that it oriented parallel to the first, no further splitting occurs since all of the electrons in that sub-beam have their spins aligned.

However, things get very interesting when the second magnetic field is oriented at 90° to the first. Since the magnetic moments of the electrons are aligned perpendicular to the external magnetic field, there should be no effect. What actually happens is that the beam again splits into two sub-beams, just as the original beam did!

If the second magnetic field is placed at some other angle, the beam will still split into two components, but the intensities will be determined by the magnitude of the projection of the electron magnetic moment along the external axis. That magnitude is easily calculable if one thinks of the spin wavefunction as a linear combination of two spin functions in the rotated axis system.

$$\Psi_{spin} = \frac{1}{\sqrt{2}} cos(\theta) \cdot \alpha + \frac{1}{\sqrt{2}} sin(\theta) \cdot \beta$$

where θ is the angle between the two magnetic fields. The factors of $\frac{1}{\sqrt{2}}$ are to normalize the wavefunction. The probabilities then of measuring the spin as either an α or β state is given by the squares of the corresponding Fourier coefficients.

$$P(\alpha) = \frac{1}{2}\cos^2(\theta)$$

$$P(\beta) = \frac{1}{2}\sin^2(\theta)$$

This conclusion will be useful in interpreting later results.

One very important question that the Stern-Gerlach result raises deals directly with Determinacy. The question is whether or not an individual electron “knows” that it is α or β before interacting with the detector. The results (particularly for the experiments where a beam of selected spin particles is resplit) suggests that it is the interaction with the detector that forces the particle into one state or the other.

In this manner, the Stern-Gerlach result shows is that making a measurement on a system will, in fact, alter that system. The interaction of the electrons with the external field causes an alignment of the individual magnetic moments (either with or against the external field.)

The types of experiments (and specifically spin detectors) used in the Stern-Gerlach experiment can be used to help to frame the next step in the Einstein-Bohr debates on the completeness of quantum mechanics.

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13. W. Gerlach and O. Stern, "Das magnetische Moment des Silberatoms," Zeitschrift für Physik, vol. 9, p. 353–355, 1922. W430W9405

11.4: Spooky Action at a Distance

In 1935, Einstein raised the stakes in the quantum debate significantly. Along with his postdoctoral co-authors, Boris Podolsky and Nathan Rosen, published one of the most famous papers in the history of the quantum theory debates. The EPR paper [14] (so called based on the initials of the authors) would create a veritable firestorm within the community that championed the Copenhagen interpretation of Quantum Mechanics.

The EPR paradox

The EPR paper proposed a paradox in the form of a thought experiment, much as the several thought experiments proposed by Einstein to Bohr at the various Solvay Conferences. In the paradox, Einstein used the concepts of a conserved center of mass and conserved momentum in a fragmenting particle to show that either a measurement on one fragment must affect the properties of the other, or that the quantum theory had to be incomplete.

The thought experiment involved the fragmentation of a particle into two fragment particles. The fragment particles would be linked through a single wavefunction describing the entire system. After some time of traveling apart, it was assumed that the two fragment particles could no longer interact as they were physically separated by a distance.

At some point following the fragmentation, the position is measure for one of the fragment particles. This, thought the conservation of the center of mass, would determine the position of the other particle. Then, by measuring the momentum of the counter fragment, the momentum of the first fragment would be determined through the conservation of momentum. As such, there would be simultaneous knowledge of both position and momentum for both particles, in violation of the Uncertainty Principle.

Figure 11.4.1

The argument in the EPR paper was that since a measurement on one fragment determined the properties of the counter fragment, and that the two fragments were separated in space, that the properties of the counter fragment must have been determined all along, irrespective of having been measured. (Einstein referred to the phenomenon of measurement on one fragment affecting properties on the counter fragment as “Spooky action at a distance.) In other words, Indeterminacy as suggested by the Heisenberg Uncertainty Principle must be a fallacy. The only other explanation possible was that the Quantum Theory had to be incomplete. With this argument, people had to take very seriously the possibility that a theory of “local reality” in which properties exist with definite values, as opposed to only coming to being through the interaction with a detector of some sort, as a distinct possibility.

Bohr responded within months. He attacked a specific assumption of the set up of the EPR paradox, namely that a measurement of the properties of one particle would not “disturb the system in any way.”

Hidden Variables

The EPR paradox was both eloquent and succinct. It touched off quite a storm within the community as well as it shock the very foundations of the quantum theory. But perhaps even more interestingly, it spurned a whole new avenue of research into understanding the ramifications. Specifically troubling was the idea that the wavefunction describing a system did not, in fact, provide a complete description of that system.

Scientists began to wonder if there might be some “hidden variables” in a system that allowed properties to be both hidden under the vagueness of a wavefunction and also determined by the definite values of the variables, irrespective of whether or not the system was observed or measured.

In 1951, David Bohm published a textbook [15] on quantum theory that included a good deal of discussion on the EPR paradox. In it, he suggested measuring the nuclear spins of hydrogen atoms that result from the dissociation of a singlet-state hydrogen molecule. The spins would be correlated through the conservation of angular momentum and could thus take the place of the measurements of position and momentum in the EPR version.

In Bohm’s version of the EPR experiment (sometimes called the EPRB experiment) the spin states of the hydrogen atoms would be correlated as the atoms would be “entangled”. And since angular momentum had to be conserved, measurement of the spin of one atom along the laboratory fixed z-axis would determine the value along the z-axis for the other atom. But what if the measurement was made along the x- or y-axes? If the EPR definition of reality is to be believed, these values must also be determined (or real.)

Of course quantum mechanics only allows for the measurement of one of the components, as the operators for the three components do not commute. Thus, if the EPR definition of reality is correct, then the wavefunction by necessity must be incomplete. There would need to be hidden variables.

Even more significantly, Bohm's proposed experiments could be carried out in a laboratory, rather than being limited to the realms of thought.

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14. B. P. Albert Einstein and N. Rosen, "Can Quantum-Mechanical Description of Physical Reality Be Considered Complete?," Physical Review, vol. 47, pp. 777-780, 1935. W430W9405
15. D. Bohm, Quantum Theory, New York: Prentice-Hall, 1951. W430W9405

11.5: Bell's Inequality

Bohm's work on the EPR paradox reawakened an interest in the topic. One physicist who took a particular interest in the topic was John S. Bell. Bell proposed a mathematical model that could in fact distinguish between local hidden variable theories and quantum theory [16].

Consider a set of things U which can be subdivided into three overlapping subsets, A, B and C. Bell's theorem states: the number of members of A that are not a member of B plus all members of B that are not a member of C must be greater than or equal to the number of members in the subset of A that are not also in subset B.

To show this, let's first settle on some notation. We'll call the number of items that are in subset A, but not in subset B by the symbol $N(A_+B_-)$ and the number of items in subset B but not in subset C by $N(B_+C_-)$. Etcetera. This notation coupled with the use of some Venn diagrams, the concept of the inequality should become clear.

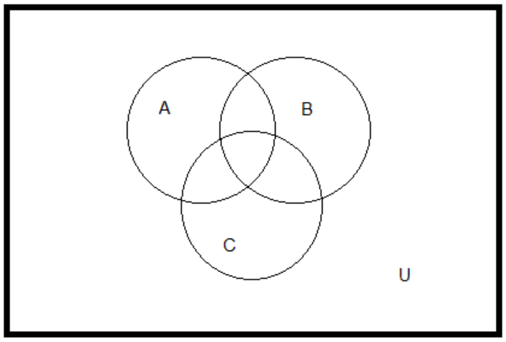

Figure 11.5.1

It should be clear that $N(A_+B_-)$ can be easily shown to be given by the number of items in subset A, not in subset B and in subset C, plus the number in A, not in B and not in C.

$$N(A_+B_-) = N(A_+B_-C_+) + N(A_+B_-C_-)$$

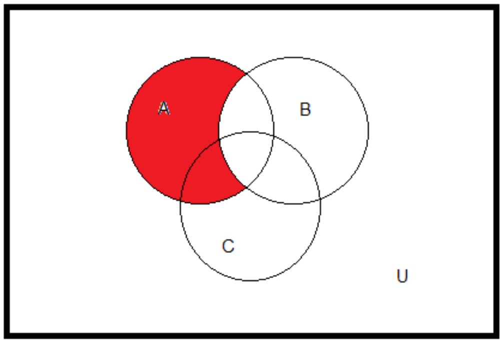

Figure 11.5.2

Similar sums can be derived for $N(B_+C_-)$ and $N(A_+C_-)$

$$N(B_+C_-) = N(A_+B_+C_-) + N(A_-B_+C_-)$$

$$N(A_+C_-) = N(A_+B_+C_-) + N(A_+B_-C_-)$$

Shown below is the sum for $N(B_+C_-)$.

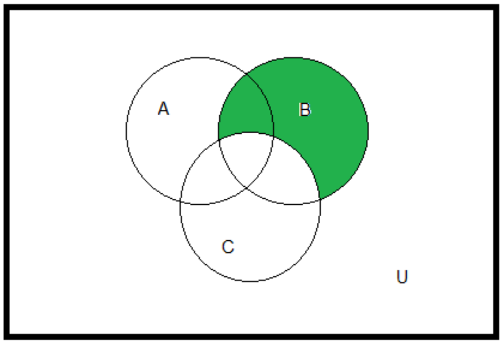

Figure 11.5.3

Adding the terms for $N(A_+B_-)$ and $N(B_+C_-)$ gives

$$N(A_+B_-)+N(B_+C_-)=N(A_+B_-C_+)+N(A_+B_-C_-)+N(A_+B_+C_-)+N(A_-B_+C_-)$$

This can be simplified by grouping the terms for $N(A_+B_+C_-)$ and $N(A_+B_-C_-)$ and recognizing that their sum gives $N(A_+C_-)$.

$$N(A_+B_-)+N(B_+C_-)=N(A_+B_-C_+)+N(A_-B_+C_-)+N(A_+C_-)$$

So long as neither $N(A_+B_-C_+)$ nor $N(A_-B_+C_-)$ are negative (which they can not be) then we arrive at CityplaceBell’s inequality:

$$N(A_+B_-)+N(B_+C_-)\geq N(A_+C_-)$$

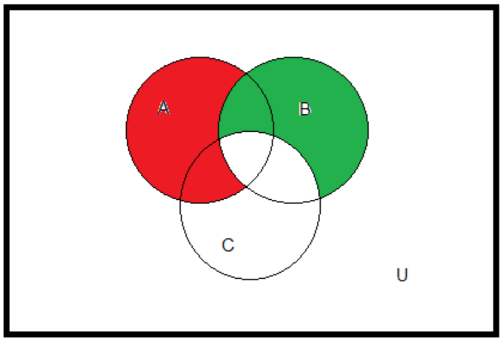

Figure 11.5.4

Employing the Stern-Gerlach results to Test Bell’s Inequality

On the face of it, place CityBell’s result does not seem that extraordinary. In fact, it almost seems trivial. However, it is only trivial when the results of tests that would place an object into group A, B or C are not correlated. When the results are correlated, the result becomes a bit perplexing.

Consider the dissociation of a pion (also called a π meson), which is a subatomic particle with zero spin and zero charge. It can decompose into a positron and an electron (to conserve charge), each traveling in opposite directions (such that momentum is conserved.) The spins will also be entangled in such a way as to conserve angular momentum.

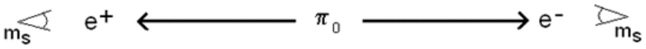

Figure 11.5.5

In fact, the spin state of the electron/positron pair will be given by the familiar singlet spin function:

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

This suggests that if the positron (subscript +) is detected in the α spin state, the electron (subscript -) will necessarily be forced into the β spin state. The wavefunction allows for equal probability that the positron will be detected in the α spin state or the β spin state, but detection in either state forces an immediate collapse of the wavefunction for the electron. This is the “spooky action at a distance" that Einstein so vehemently rejected in the EPR paper [14]. Einstein also insisted that the spin state of the positron was a "real" property that existed with a definite value for the entire transit of the positron from the decay event to the detector. And quantum mechanics, in Einstein's view, was incomplete in that it could not predict the "realness" of that spin state. If Einstein's view was correct, then correlated measurements of the two spin states would have to satisfy CityplaceBell's inequality.

With the results of the Stern-Gerlach experiments, we can actually determine exactly what quantum mechanics will predict. To do this, we will set up our detectors to detect the spin to the dissociated fragments, but we will rotate the detectors relative to one another. In a laboratory-fixed coordinate system, we will set detector A at 0° rotation, B at 30° and C and 60°. What we want to know is the probability that if one detector measures its particle to be in spin state α that the other will measure its particle to be in spin state β. That probability will be related to the angle of rotation of the second detector relative to the first. According to the Stern-Gerlach result, the probability is given by $\frac{1}{2}\sin(\theta_2-\theta_1)$, where θ_2 and θ_1 are the angles of the second and first detectors in the pair respectively.

So if we define $P(A_+B_-)$ as the probability that detector A detects an $\alpha spin$ and detector B fails to detect a β spin, we can construct the following table based on three specific experimental configurations:

Experiment	θ_1	θ_2	Case	$\theta_1-\theta_2$	$\frac{1}{2}sin^2(\Delta\theta)$
1	0°	30°	$P(A_+B_-)$	30°	0.125
2	30°	60°	$P(B_+C_-)$	30°	0.125
3	0°	60°	$P(A_+C_-)$	60°	0.375

After collecting data from a very large set of measurements using these configurations, we will have can compare the experimental distribution of outcomes to what is predicted by quantum mechanics, and thus conclude if it is possible to have a locality variable that predetermines our outcomes, or if the measurements are purely probabilistic. If the locality variable exists, then Bell's Inequality must hold [17].

$$P(A_+B_-)+P(B_+C_-)\geq P(A_+C_-)$$

However, if Quantum Mechanics allows for a locality variable to redetermine the measured outcomes of the three experiments, then the following must be true:

$$0.125+0.125\geq 0.375$$

Except that it simply isn't true. (In fact, it isn't even true for extremely large values of the sum 0.125 + 0.125.) The above set of experiments was proposed by Alain Aspect in 1976 [17], and results published in 1982 [18]. And while the results were criticized due to the "detection loophole", results of similar experiments being conducted up to 2015 [20] confirmed Aspect's results. Alain Aspect shared the 2022 Nobel Prize in Physics with John Clauser and Anton Zeillinger "for experiments with entangled photons, establishing the violation of Bell inequalities and pioneering quantum information science". [21]

Since Aspect's result was derived completely independent of any theory of hidden variables, it should be clear that the result is incompatible with any such theory. In fact, the result shows that one must divorce oneself from any ideas of local realism for quantum mechanical particles. One simply must conclude that it is the observation that creates the reality and that no reality for observable properties on quantum mechanical system can exist independent of their observation. (Of course, Sheldon Cooper would also point out that one can be beaten up simply for referring to oneself as "one.") [19]

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1. This quote, while very clever, is disputed, as a very similar quote is also attributed to Enrico Fermi.↩

CHAPTER OVERVIEW

12: Appendices

12.1: Appendix I

Some Useful Mathematical Identities

$$\sin(\alpha \pm \beta) = \sin(\alpha)\cos(\beta) \pm \cos(\alpha)\sin(\beta)$$

$$\cos(\alpha \pm \beta) = \cos(\alpha)\cos(\beta) \mp \sin(\alpha)\sin(\beta)$$

$$\sin(x) = x - \frac{x^3}{3!} + \frac{x^5}{5!} - \cdots + (-1)^{n+1}\frac{x^{2n-1}}{(2n-1)!}$$

$$\cos(x) = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \cdots + (-1)^n\frac{x^{2n}}{(2n)!}$$

$$e^{\pm i\theta} = \cos(\theta) \pm i\sin(\theta) \qquad \cos(\theta) = \frac{e^{i\theta} + e^{-i\theta}}{2} \qquad \sin(\theta) = \frac{e^{i\theta} - e - i\theta}{2}$$

Some Useful Integrals

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

$$\int \sin^2(\alpha x)dx = \frac{x}{2} - \frac{\sin(2\alpha x)}{4\alpha} \qquad \int \sin^3(\alpha x)\ dx = \frac{\cos(3\alpha x) - 9\cos(\alpha x)}{12\alpha}$$

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

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

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

$$\int \cos^2(\alpha x)dx = \frac{x}{2} + \frac{1}{4\alpha}\sin(2\alpha x) \qquad \int x\ \cos^2(\alpha x)dx = \frac{x^2}{4} + \frac{x\sin(2\alpha x)}{4\alpha} + \frac{\cos(2\alpha x)}{8\alpha^2}$$

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

$$\int_0^\infty x^n e^{-\alpha x}dx = \frac{n!}{\alpha^{n+1}} \ \text{(n a positive integer)} \qquad \int_0^\infty e^{-\alpha x^2}dx = \sqrt{\frac{\pi}{4\alpha}}$$

$$\int_0^\infty x^{2n}e^{-\alpha x^2}dx = \frac{1\cdot 3\cdot 5\cdots(2n-1)}{2^{n+1}\alpha^n}\sqrt{\frac{\pi}{\alpha}} \qquad \int_0^\infty x^{2n+1}e^{-\alpha x^2}dx = \frac{n!}{2\alpha^{n+1}}$$

Some Useful Coordinate Transformations

Plane Polar Coordinates: $0 \leq r \leq \infty\,;\,0 \leq \theta \leq 2\pi$

$$x = r\cos\theta \qquad y = r\sin\theta \qquad \theta = \arctan\left(\frac{y}{x}\right) \qquad r = \sqrt{x^2+y^2}$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2}{\partial\theta^2}$$

Spherical Polar Coordinates: $0 \leq r \leq \infty\ ;\ 0 \leq \theta \leq \pi\,;\,0 \leq \phi \leq 2\pi$

$$x = r\sin\theta\cos\phi \qquad y = r\sin\theta\sin\phi \qquad z = r\cos\theta$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

$$dx\ dy\ dz = r^2 \sin\theta\ dr\ d\theta\ d\phi$$

12.2: Appendix II – Selected Character Tables

Nonaxial Groups

C_1	E
A	1

C_s	E	σ		
A’	1	1	x, y, R_z	x^2, y^2, z^2, xy
A”	1	-1	z, R_x, R_y	xz, yz

C_i	E	i		
A_g	1	1	R_x, R_y, R_z	$x^2, y^2, z^2, xy, xz, yz$
A_u	1	-1	x, y, z	

C_n groups

C_2	E	C_2		
A	1	1	z, R_z	x^2, y^2, z^2, xy
B	1	-1	x, y, R_x, R_y	xz, yz

C_3	E	C_3	C_3^2		
A	1	1	1	z, R_z	x^2+y^2, z^2
E	1	ε	ε^*	$x+iy\,;R_x+iR_y$	(x^2-y^2, xy)
	1	ε^*	ε	$x-iy\,;R_x-iR_y$	(xz, yz)

C_4	E	C_4	C_2	C_4^3		
A	1	1	1	1	z, R_z	$x^2+y^2,\ z^2$
B	1	-1	1	-1		x^2-y^2, xy
E	1	i	-1	$-i$	$x+iy\,;R_x+iR_y$	(xz, yz)
	1	$-i$	-1	i	$x-iy\,;R_x-iR_y$	

C_5	E	C_5	C_5^2	C_5^3	C_5^4		
A	1	1	1	1	1	z, R_z	x^2+y^2, z^2
E_1	1	ε	ε^2	ε^{2*}	ε^*	$x+iy, R_x+iR_y$	(xz, yz)
	1	ε^*	ε^{2*}	ε^2	ε	$x-iy, R_x-iR_y$	
E_2	1	ε^2	ε^*	ε	ε^{2*}		(x^2-y^2, xy)
	1	ε^{2*}	ε	ε^*	ε^2		

C_6	E	C_6	C_6^2	C_6^3	C_6^4	C_6^5		
A	1	1	1	1	1	1	z, R_z	x^2+y^2, z^2
B	1	-1	1	-1	1	-1		

C_6	E	C_6	C_6^2	C_6^3	C_6^4	C_6^5		
E_1	1	ε	$-\varepsilon^*$	-1	$-\varepsilon$	ε^*	$x+iy$, R_x+iR_y $x-iy$, R_x-iR_y	(xz, yz)
	1	ε^*	ε	-1	$-\varepsilon^*$	ε		
E_2	1	$-\varepsilon^*$	$-\varepsilon$	1	$-\varepsilon^*$	$-\varepsilon$		$(x^2-y^2,\ xy)$
	1	$-\varepsilon$	$-\varepsilon^*$	1	$-\varepsilon$	$-\varepsilon^*$		

D_n groups

D_2	E	$C_2(z)$	$C_2(y)$	$C_2(x)$		
A_1	1	1	1	1		x^2, y^2, z^2
B_1	1	1	-1	-1	$z,\ R_z$	xy
B_2	1	-1	1	-1	$y,\ R_y$	xz
B_3	1	-1	-1	1	$x,\ R_x$	yz

D_3	E	2 C_2	$3C_2'$		
A_1	1	1	1		x^2+y^2, z^2
A_2	1	1	-1	z, R_z	
E	2	-1	0	(x, y) (R_x, R_y)	$(x^2-y^2,\ xy)$ (xz, yz)

D_4	E	2 C_4	C_2	2 C_2'	2 C_2”		
A_1	1	1	1	1	1		x^2+y^2, z^2
A_2	1	1	1	-1	-1	z, R_z	
B_1	1	-1	1	1	-1		x^2-y^2
B_2	1	-1	1	-1	1		xy
E	2	0	-2	0	0	(x, y) $(R_x,\ R_y)$	(xz, yz)

D_5	E	2 C_5	2 C_5'	5 C_2		
A_1	1	1	1	1		$x^2+y^2,\ z^2$
A_2	1	1	1	-1	$z,\ R_z$	
E_1	2	$\mathbf{2\cos(72°)}$	$\mathbf{2\cos(144°)}$	0	(x, y) $(R_x,\ R_y)$	(xz, yz)
E_2	2	$\mathbf{2\cos(144°)}$	$\mathbf{2\cos(72°)}$	0		$(x^2-y^2,\ xy)$

D_6	E	2 C_6	2 C_3	C_2	3 C_2'	3 C_2”		
$\mathbf{A_1}$	1	1	1	1	1	1		x^2+y^2 , z^2
$\mathbf{A_2}$	1	1	1	1	-1	-1	z, R_z	
$\mathbf{B_1}$	1	-1	1	-1	1	-1		
$\mathbf{B_2}$	1	-1	1	-1	-1	1		

D_6	E	2 C_6	2 C_3	C_2	3 C_2’	3 C_2”		
$\boldsymbol{E_1}$	2	-1	1	-2	0	0	(x, y) $(R_x,\ R_y)$	(xz, yz)
$\boldsymbol{E_2}$	2	-1	-1	2	0	0		$(x^2-y^2,\ xy)$

C_{nv} groups

C_{2v}	E	C_2	σ_v	σ_v’			
A_1	1	1	1	1	z		x^2, y^2, z^2
A_2	1	1	-1	-1		R_z	xy
B_1	1	-1	1	-1	x	R_y	xz
B_2	1	-1	-1	1	y	R_x	yz

C_{3v}	E	2 C_2	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	$(x, y)\ (R_x,\ R_y)$	x^2-y^2, $xy)(xz, yz)$

C_{4v}	E	2 C_4	C_2	2 σ_v	2 σ_d		
A_1	1	1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	1	-1	-1	R_z	
B_1	1	-1	1	1	-1		x^2-y^2
B_2	1	-1	1	-1	1		xy
E	2	0	-2	0	0	(x, y) (R_x, R_y)	(xz, yz)

C_{5v}	E	2 C_5	C_5^2	5 $\boldsymbol{\sigma_v}$		
A_1	1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	1	-1	R_z	
E_1	2	$\mathbf{2\cos(72^\circ)}$	$\mathbf{2\cos(144^\circ)}$	0		(xz, yz)
E_2	2	$\mathbf{2\cos(144^\circ)}$	$\mathbf{2\cos(72^\circ)}$	0	$(x, y)\ (R_x,\ R_y)$	(x^2-y^2, xy)

C_{6v}	E	2 C_6	2 C_3	C_2	$3\sigma_v$	$3\sigma_d$		
$\boldsymbol{A_1}$	1	1	1	1	1	1	z	x^2+y^2, z^2
$\boldsymbol{A_2}$	1	1	1	1	-1	-1	$\boldsymbol{R_z}$	
$\boldsymbol{B_1}$	1	-1	1	-1	1	-1		
$\boldsymbol{B_2}$	1	-1	1	-1	-1	1		
$\boldsymbol{E_1}$	2	1	-1	-2	0	0	(x, y) $(R_x,\ R_y)$	(xz, yz)
$\boldsymbol{E_2}$	2	-1	-1	2	0	0		$(x^2-y^2,\ xy)$

C_{nh} Groups

C_{2h}	E	C_2	i	σ_h		
A_g	1	1	1	1	R_z	x^2, y^2,z^2
A_u	1	1	-1	-1	z	
B_g	1	-1	1	-1	R_x, R_y	xz, xy, yz
B_u	1	-1	-1	1	x, y	

C_{3h}	E	C_3	C_3^2	σ_h	S_3	S_s^2		
A'	1	1	1	1	1	1	R_z	x^2+y^2 , z^2
E'	1	ε	ε^*	1	ε	ε^*	$x+iy$ $x-iy$	$(x^2-y^2,\ xy)$
	1	ε^*	ε	1	ε^*	ε		
A"	1	1	1	-1	-1	-1	z	
E"	1	ε	ε^*	-1	$-\varepsilon$	$-\varepsilon^*$	R_x+iR_y R_x-iR_y	(xz, yz)
	1	ε^*	ε	-1	$-\varepsilon^*$	$-\varepsilon$		

$\boldsymbol{C_{4h}}$	E	$\boldsymbol{C_4}$	C_2	$\boldsymbol{C_4^3}$	i	$\boldsymbol{S_4^3}$	σ_h	S_4		
A_g	1	1	1	1	1	1	1	1	R_z	x^2+y^2 , z^2
B_g	1	-1	1	-1	1	-1	1	-1		x^2-y^2 , xy
E_g	1	i	-1	$-i$	1	i	-1	$-i$	R_x+iR_y	(xz, yz)
	1	$-i$	-1	i	1	$-i$	-1	i	R_x-iR_y	
A_u	1	1	1	1	-1	-1	-1	-1	z	
B_u	1	-1	1	-1	-1	1	-1	1		
E_u	1	i	-1	$-i$	-1	i	1	$-i$	$x+iy$	
	1	$-i$	-1	i	-1	$-i$	1	i	$x-iy$	

C_{5h}	E	C_5	C_5^2	C_5^3	C_5^4	σ_h	S_5	S_5^2	S_5^3	S_5^4		
$\boldsymbol{A}$'	1	1	1	1	1	1	1	1	1	1	R_z	x^2+y^2 ,z^2
E_1’	1	ε	$\boldsymbol{\varepsilon^2}$	ε^{2*}	$\boldsymbol{\varepsilon^*}$	1	ε	ε^2	ε^{2*}	ε^*	$x+iy$ $x-iy$	
	1	ε^*	ε^{2*}	ε^2	ε	1	ε^*	ε^{2*}	ε^2	ε		
E_2'	1	ε^2	$\boldsymbol{\varepsilon^*}$	ε	ε^{2*}	1	ε^2	ε^*	ε	ε^{2*}		(x^2-y^2, xy)
	1	ε^{2*}	ε	$\boldsymbol{\varepsilon^*}$	ε^2	1	ε^{2*}	ε	ε^*	ε^2		
$\boldsymbol{A}$"	1	1	1	1	1	-1	-1	-1	-1	-1	z	
E_1"	-1	ε	$\boldsymbol{\varepsilon^2}$	ε^{2*}	$\boldsymbol{\varepsilon^*}$	-1	-ε	-ε^2	-ε^{2*}	-ε^*	R_x+iR_y R_x-iR_y	(xz, yz)
	-1	ε^*	ε^{2*}	ε^2	ε	-1	-ε^*	-ε^{2*}	-ε^2	-ε		
E_2"	-1	ε	$\boldsymbol{\varepsilon^2}$	ε^{2*}	$\boldsymbol{\varepsilon^*}$	-1	-ε^2	-ε^*	-ε	-ε^{2*}		

C_{5h}	E	C_5	C_5^2	C_5^3	C_5^4	σ_h	S_5	S_5^2	S_5^3	S_5^4		
	-1	ε^*	ε^{2*}	ε^2	ε	-1	-ε^{2*}	-ε	-ε^*	-ε^2		

D_{nh} Groups

D_{2h}	E	C_2(z)	C_2(y)	C_2(x)	i	σ_{xy}	σ_{xz}	σ_{yz}		
A_g	1	1	1	1	1	1	1	1		x^2, y^2 ,z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x	yz
A_u	1	1	1	1	-1	-1	-1	-1		
B_{1u}	1	1	-1	-1	-1	-1	1	1	z	
B_{2u}	1	-1	1	-1	-1	1	-1	1	y	
B_{3u}	1	-1	-1	1	-1	1	1	-1	x	

D_{3h}	E	2 C_3	3C_2’	$\boldsymbol{\sigma_h}$	2 $\boldsymbol{S_3}$	3 $\boldsymbol{\sigma_v}$		
$\boldsymbol{A_1}$’	1	1	1	1	1	1		x^2+y^2 ,z^2
$\boldsymbol{A_2}$’	1	1	-1	1	1	-1	$\boldsymbol{R_z}$	
E’	2	-1	0	2	-1	0	(R_x, R_y)	x^2-y^2 , $xy)$
$\boldsymbol{A_1}$”	1	1	1	-1	-1	-1		
$\boldsymbol{A_2}$”	1	1	-1	-1	-1	1	z	
E”	2	-1	0	-2	1	0	(x, y)	(xz, yz)

D_{4h}	E	2 C_4	C_2	2 C_2’	2 C_2”	$\boldsymbol{i}$	2 S_4	σ_h	2 σ_v	2 σ_d		
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2 , $\boldsymbol{z^2}$
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		x^2-y^2
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	

D_{6h}	E	2 C_6	2 C_3	C_2	3 C_2’	3 C_2”	i	2 S_3	2 S_6	σ_h	3 σ_v	3 σ_d		
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1		x^2+y^2 ,$\boldsymbol{z^2}$

D_{6h}	E	2 C_6	2 C_3	C_2	3 C_2'	3 C_2"	i	2 S_3	2 S_6	σ_h	3 σ_v	3 σ_d		
A_{2g}	1	1	1	1	-1	-1	1	1	1	1	-1	-1	$\boldsymbol{R_z}$	
B_{1g}	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1		
B_{2g}	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1		
E_{1g}	2	-1	1	-2	0	0	2	-1	1	-2	0	0	(R_x, R_y)	(xz, yz)
E_{2g}	2	-1	-1	2	0	0	2	-1	-1	2	0	0		$(x^2-y^2,$
A_{1u}	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1		
B_{2u}	1	-1	1	-1	-1	1	-1	1	-1	1	1	-1		
E_{1u}	2	-1	1	-2	0	0	-2	-1	1	2	0	0	(x, y)	
E_{2u}	2	-1	-1	2	0	0	-2	1	1	-2	0	0		

D_{nd} Groups

D_{2d}	E	2 S_4	C_2	2 C_2'	2 σ_d		
A_1	1	1	1	1	1		x^2+y^2, z^2
A_2	1	1	1	-1	-1	R_z	
B_1	1	-1	1	1	-1		x^2-y^2
B_2	1	-1	1	-1	1	z	xy
E	2	0	-2	0	0	(x, y) (R_x, R_y)	(xz, yz)

D_{3d}	E	2 C_3	3C_2'	i	2 $\boldsymbol{S_6}$	3 $\boldsymbol{\sigma_d}$		
A_{1g}	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	-1	1	1	-1	$\boldsymbol{R_z}$	
$\boldsymbol{E_g}$	2	-1	0	2	-1	0	(R_x, R_y)	x^2-y^2, $xy)$, (xz, yz)
A_{1u}	1	1	1	-1	-1	-1		
A_{2u}	1	1	-1	-1	-1	1	z	
$\boldsymbol{E_u}$	2	-1	0	-2	1	0	(x, y)	

D_{4d}	E	2 S_8	2 C_4	2 $S_8{}^3$	C_2	4 C_2'	4 σ_d		
A_1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_2	1	1	1	1	1	-1	-1	R_z	
B_1	1	-1	1	-1	1	1	-1		
B_2	1	-1	1	-1	1	-1	1	z	
E_1	2	$\sqrt{\mathbf{2}}$	0	-$\sqrt{\mathbf{2}}$	-2	0	0	(x, y)	

D_{4d}	E	2 S_8	2 C_4	2 $S_8{}^3$	C_2	4 C_2’	4 σ_d		
E_2	2	0	-2	0	2	0	0		x^2-y^2, $xy)$
E_3	2	-$\sqrt{\mathbf{2}}$	0	$\sqrt{\mathbf{2}}$	-2	0	0	(R_x, R_y)	(xz, yz)

S_n Groups

Cubic Groups

T_d	E	8 C_3	3 C_2	6 S_4	6 σ_d		
A_1	1	1	1	1	1		x^2+y^2+z_2
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		(2z_2-x^2-y^2, $x^2-y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy,xz,yz)

O_h	E	8C_3	6C_2	6C_4	3C_2	$\boldsymbol{i}$	6S_4	8S_6	3σ_h	6σ_d		
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2+ z_2
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	-2	0		(2z_2- x^2-y^2, $x^2-y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	$(R_x$, R_y, $R_z)$	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		$(xy,xz,$ $yz)$
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		

Icosahedral Group

Linear Groups

Index

Glossary

angular node | An angular node will occur where the angular part of the electronic wavefunction equals zero.

ansatz | An educated guess or an additional assumption made to help solve a problem, and which is later verified to be part of the solution by its results.

atomic orbitals | Atomic orbital is a mathematical function describing the location and wave-like behavior of a single electron in an atom. This function can be used to calculate the probability of finding any electron of an atom in any specific region around the atom's nucleus.

Beer's Law | The Beer-Lambert law relates the optical attenuation of a physical material containing a single attenuating species of uniform concentration to the optical path length through the sample and absorptivity of the species.

Bohr magneton | A physical constant and the natural unit for expressing the magnetic moment of an electron caused by either its orbital or spin angular momentum. $(\mu_{B\,=}\,e\hbar/2m_e)$

Bosons | Bosons are particles with integer spin (s = 0, 1, 2, ...).

Bound state | A state is called bound state if its position probability density at infinite tends to zero for all the time. Roughly speaking, we can expect to find the particle(s) in a finite size region with certain probability.

Bra–ket notation | The bra–ket notation is a way to represent the states and operators of a system by angle brackets and vertical bars, for example, |α> and |α><β|.

Collapse | "Collapse" means the sudden process which the state of the system will "suddenly" change to an eigenstate of the observable during measurement.

commutator | The commutator of two operators elements **a** and **b** is defined by **[a,b]=ab-ba**. The commutator is zero if and only if **a** and **b** commute.

commute | The commutator of two operators elements **a** and **b** is defined by **[a,b]=ab-ba**. The commutator is zero if and only if **a** and **b** commute.

Correspondence principle | For every observable property of a system there is a corresponding quantum mechanical operator.

cyclic boundary condition | A boundary condition associated with regularly repeating intervals. For quantum rigid rotors, this implied the wavefunction must equal itself upon a full rotation, i.e., ψ(0º)=ψ(360º).

Degeneracy | If the energy of different states (wavefunctions that are not scalar multiple of each other) are the same, the states are called **degenerate**.

Degenerate energy level | If the energy of different state (wave functions which are not scalar multiple of each other) is the same, the energy level is called degenerate. There is no degeneracy in 1D system.

Density matrix | Physically, the density matrix is a way to represent pure states and mixed states. The density matrix of pure state whose ket is |α> is |α><α|.

Density operator | Physically, the density matrix is a way to represent pure states and mixed states. The density matrix of pure state whose ket is |α> is |α><α|.

dipole moment | The electric dipole moment is a measure of the separation of positive and negative electrical charges within a system and is a measure of the system's overall polarity.

Dirac notation | The bra–ket notation is a way to represent the states and operators of a system by angle brackets and vertical bars, for example, |α> and |α><β|.

Eigenstates | An eigenstate of an operator A is a vector satisfied the eigenvalue equation: A | a > = λ | a >, where λ is a scalar (the eigenvalue).

eigenvalue | Any value of λ that is is a solution to the eigenvalue problem (A·v=λ·v) is known as an eigenvalue of the matrix A.

eigenvalue equation | An eigenvalue problem is A·v=λ·v, where A is an n-by-n matrix, v is a non-zero n-by-1 vector and λ is a scalar (that can be real or complex).

eigenvector | Any value of v that is is a solution to the eigenvalue problem (A·v=λ·v) is known as an eigenvevctor of the matrix A.

Energy spectrum | The energy spectrum refers to the possible energy of a system.
For bound system (bound states), the energy spectrum is discrete; for unbound system (scattering states), the energy spectrum is continuous.

even function | A function is even if f(x)=f(-x)

Expectation value | The expectation value is the probabilistic expected value of the result (measurement) of an experiment. It can be thought of as an average of all the possible outcomes of a measurement as weighted by their likelihood, and as such it is not the most probable value of a measurement; indeed the expectation value may have zero probability of occurring

Fermions | Fermions are particles with half-integer spin (s = 1/2, 3/2, 5/2, ...).

Fine Structure Constant | 1/137 . The fine structure constant is a mathematical constant that is given as the ratio of the classical and quantum electromagnetic constants. It is also known as **Sommerfeld's constant.**

forbidden transition | A eigentstate to eigenstate transition with zero probability of being observed. This is determined by the relevant transition moment integral

g-factor | A dimensionless quantity that characterizes the magnetic moment and angular momentum of an atom, a particle or the nucleus. It is essentially a proportionality constant that relates the observed magnetic moment μ of a particle to its angular momentum quantum number and a unit of magnetic moment. (also known as spin gyromagnetic ratio)

gyromagnetic ratio | The ratio of its magnetic moment to its angular momentum, and it is often denoted by the symbol γ, gamma (also known as magnetogyric ratio)

Hamiltonian | The operator represents the total energy of the system.

Hermite polynomials | A family of orthogonal polynomials. In quantum mechanics, they results from solving the harmonic oscillator model.

Hermitian | A Hermitian matrix is a complex square matrix that is equal to its own conjugate transpose—that is, the element in the i-th row and j-th column is equal to the complex conjugate of the element in the j-th row and i-th column, for all indices i and j. aij=aji* . Hermitian matrices always have real eigenvalues. Operators connected to physical observable are Hermitian since observables must be real.

Hermitian operator | An operator satisfying $A = A^{\dagger}$.

Hilbert space | Given a system, the possible pure state can be represented as a vector in a Hilbert space. Each ray (vectors differ by phase and magnitude only) in the corresponding Hilbert space represent a state.

Identity operator | Operator that does not change the elements it operates on.

Indistinguishable particles | If a system shows measurable differences when one of its particles is replaced by another particle, these two particles are called distinguishable.

Ket | A wave function expressed in the form $|a\rangle$ is called a ket.

Lambshift | Relativistic correction of the difference in energy levels of the $^2S_{1/2}$ and $^2P_{1/2}$ hydrogen atom not predicted by the Dirac equation

Laplacian | The Laplacian is a differential operator that is given by the divergence of the gradient.

LCAO | This is is a simple method of quantum chemistry that yields a qualitative picture of the molecular orbitals in a molecule.

Legendre polynomials | A family of complete and orthogonal polynomials with numerous applications. In quantum mechanics, they results from solving the rigid rotor model.

Linear combination of atomic orbitals | This is is a simple method of quantum chemistry that yields a qualitative picture of the molecular orbitals in a molecule.

Maclaurin series | The Maclaurin series is an expansion of a function in an infinite sum of polynomial terms that are expressed in terms of the function's derivatives at **zero**.

magnetogyric ratio | The ratio of its magnetic moment to its angular momentum, and it is often denoted by the symbol γ, gamma (also known as magnetogyric ratio

Mixed state | A mixed state is a statistical ensemble of pure state.

molecular orbitals | A molecular orbital is a mathematical function describing the location and wave-like behavior of a single electron in a molecule. This function can be used to calculate chemical and physical properties such as the probability of finding an electron in any specific region. The LCAO approximation is often used to approximate molecular orbitals as a series of atomic orbitals

node | Location where the quantum mechanical wavefunction is zero and therefore, with no probability amplitude.

Normalized wave function | A wave function |a > is said to be normalized if < a | a> = 1.

Observable | Mathematically, it is represented by a Hermitian operator.

observer effect | When an observed system is disturbed by the act of observation. This is often the result of instruments that, by necessity, alter the state of what they measure in some manner.

odd function | A function is odd if -f(x)=f(-x)

operator | A mathematical entity that transforms one function into another [Richard Fitzpatrick]

orbital angular momentum | The classical definition of angular momentum is L = r **✕** p. The quantum-mechanical counterparts of these objects share the same relationship where r is the quantum position operator, p is the quantum momentum operator, × is cross product, and L is the orbital angular momentum operator. L (just like p and r) is a vector operator whose components operators are L_x, L_y, L_z, which are the projection of L on the x, y, and z axis, respectively

overtone | A band that occurs in a vibrational spectrum of molecule that is associated with the transition from the ground state (v=0) to the second excited state (v=2).

Pauli exclusion principle | The principle that two or more identical fermions (e.g., electrons) cannot occupy the same quantum state within the same quantum system simultaneously. An alternative formulation is that no two fermions can have the same set of quantum numbers in a system

Pure state | A state which can be represented as a wave function / ket in Hilbert space / solution of Schrödinger equation is called pure state. See "mixed state".

Quantum numbers | A way of representing a state by several numbers

Radial distribution function | The square of the radial distribution function describes the probability of finding an a electron a given distance from the nucleus. This is related to the radial probability density by adding a factor of $4\pi r^2$ (the volumen element of a sphere). The radial distribution functions depend on both n and l.

radial node | A radial node will occur where the radial part of the electronic wavefunction equals zero.

radial probability density | The probability density for the electron to be at a point located the distance r from the nucleus. The radial radial probability density depend on both n and l.

reduced mass | The "effective" inertial mass appearing in the two-body problems. It is a quantity which allows two-body problems to be solved as if they were one-body problems.

rotational constant | A constant commonly used to describe molecular free rotation that depends on the distribution of mass within the molecule (i.e, moment of inertia, I) and other constants: $B=h/(8\pi^2cI)$

selection rule | Selection rules describes when the probability of transitioning from one level to another cannot be zero. They explicitly come from evaluating the relevant transition moment integral

selection rules | Selection rules describes when the probability of transitioning from one level to another cannot be zero. They explicitly come from evaluating the relevant transition moment integral

spherical harmonics | Spherical harmonics are functions of the spherical polar angles θ and φ and appear as eigenfunctions of (squared) orbital angular momentum. They form an orthogonal and complete set. Any harmonic is a function that satisfies Laplace's differential equation.

spin | Spin is a quantized property of all particles, both matter and force, in the Universe. Matter particles have half-integer spin (1/2, 3/2,…) and force particles integer spin (0, 1, 2,…). Spin is intrinsic angular momentum possessed by the particles. The spin of a particle is sort of analogous to that of a spinning top, except that the particle can only spin at one speed, can't stop or even slow down, and is infinitesimally small. It is important to note that in no way are the particles actually spinning. [CC-BY-SA]

spin gyromagnetic ratio | A dimensionless quantity that characterizes the magnetic moment and angular momentum of an atom, a particle or the nucleus. It is essentially a proportionality constant that relates the observed magnetic moment μ of a particle to its angular momentum quantum number and a unit of magnetic moment. (also known as g-factor)

square-integrable | A square-integrable function is a real- or complex-valued measurable function for which the integral of the **square** of the absolute value is finite.

State vector | synonymous to "wave function".

Stationary state | A stationary state of a bound system is an eigenstate of Hamiltonian operator. Classically, it corresponds to standing wave.

stationary states | This is a quantum state with all observables independent of time. It is an eigenvector of the Hamiltonian.

Taylor series | The Taylor series is an expansion of a function in an infinite sum of polynomial terms that are expressed in terms of the function's derivatives at a single point.

Time-Independent Schrödinger Equation | A modification of the Time-Dependent Schrödinger equation as an eigenvalue problem. The solutions are energy eigenstate of the system.

transition moment integral | The integral representing the probability for a transition between an initial eigenstate and a final eignestate by the absorption or emission of photon(s)

uncertainty principle | The uncertainty principle (put forward by Werner Heisenberg) states that there will always be an intrinsic uncertainty in determining both a particle's position and momentum (i.e., you cannot know both exactly at the same time). This has nothing to do with science's ability to detect the properties of momentum and position. [CC-BY-SA]

wavenumber | The wavenumber is a unit of frequency that is equal to the frequency (in Hertz) divided by the speed of light. This is typically in unit of cm^{-1}. Since wavenumbers are proportional to frequency, and to photon energy (by E=hv), it is also a unit of energy.

zero point motion | Fluctuation in the position of an object necessitated by having zero point energy. This is a consequence of the Heisenberg uncertainty principle.

Zero-point energy | Zero-point energy (ZPE) is the lowest possible energy that a quantum mechanical system may have.

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