Lecture 1

We will now begin our study of **quantum mechanics**. Quantum mechanics is the branch of physics and chemistry that describes the behavior of light, matter and energy in the limits of molecular scales of size (on the order of nanometers or less), mass (between 10^{-20} kg for a large protein or nucleic acid and 10^{-31} kg for an electron) and energy (on the order of 10^{-18} J or less). Clearly these are substantially smaller scales than we deal with on an everyday basis. For example, the smallest distance that you can easily estimate with your naked eye is about 0.2 mm or 2×10^{-4} m, a factor of 100,000 larger than the distances with which quantum mechanics concerns itself.

There are **three enormous differences between the approaches taken by thermodynamics and quantum mechanics**. First, we have the one that we have just mentioned. Thermodynamics is a theory that describes the transformations of matter in bulk. Quantum mechanics describes the behavior of isolated molecules and atoms or small groups of atoms and molecules. We can describe this by saying that **thermodynamics deals with the macroscopic behavior of systems, while quantum mechanics deals with the behavior of microscopic systems**. Note that while it is possible for quantum mechanics to describe macroscopic systems (at least in theory ☺), the difficulty in directly solving quantum mechanical equations for macroscopic systems makes this untenable. In addition, it turns out that while using quantum mechanics for macroscopic systems is accurate, thanks to one of the many brilliant contributions of Neils Bohr, the correspondence principle, it is unnecessary.

The second difference is tied to the first. **Thermodynamics does not need to postulate anything about the nature of the material we are examining**. We do not need to know whether a gas is made of particles with space between them or continuous matter, as long as we can measure certain properties, such as α, κ_T, p and T. In contrast, quantum mechanics is a theory of the microscopic structure and dynamics of matter. We are concerned with the movements and energies not only of individual atoms, but of the electrons and nucleons which make up these particles. It matters whether matter is made of combinations of fundamental particles interacting through space, or a continuous smear of matter called phlogiston. So **quantum mechanics involves a substantial amount of speculation about the nature of matter**.

The third difference is that **thermodynamics is restricted to the study of matter in equilibrium**. While a great deal of the current research in quantum mechanics is on determining equilibrium properties of matter, major efforts are also being made in applying quantum mechanics to the ways that systems change, i.e., their dynamics, using time dependent versions of quantum mechanics or time-dependent perturbation theory. Therefore, **quantum mechanics can study systems both in equilibrium and disequilibrium**.

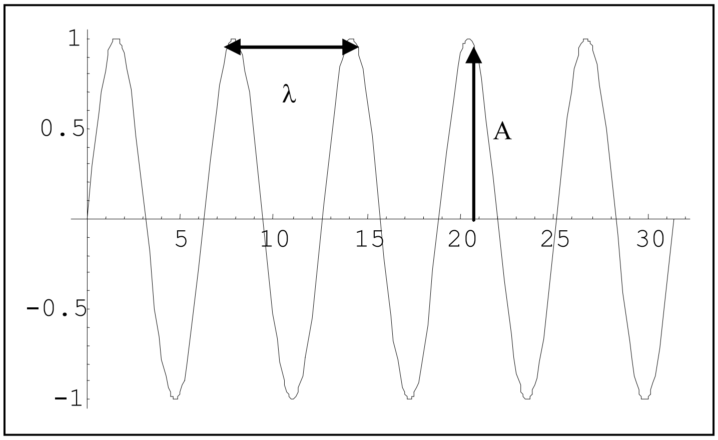
The fundamental features of quantum mechanics were developed between 1905 and 1925. Before 1890 or so, physicists thought that all known phenomena could be explained by the two magnificent achievements of classical physics, classical or Newtonian mechanics, and the electromagnetic theory of Maxwell. Notice the phrase “all known phenomena”. The downfall, of course, was new experiments concerning microscopic phenomena whose results could not be explained by the laws of classical physics.

I'd like to mention four of these phenomena, and the postulates that were put forth to explain them. The four phenomena and experiments were blackbody radiation, the photoelectric effect, atomic line spectra, and wave-matter duality. We'll begin with blackbody radiation.

Blackbody radiation is a phenomenon that I hope all of you are familiar with. Simply, if you heat an object, it gives off light. In particular, **a black body is defined as one that absorbs and emits light without favoring any particular frequencies**.

In the course of this semester we'll be talking about various objects absorbing or emitting light. An important piece of information about emission or absorption of light is the spectrum of the light that is given off or absorbed. The **spectrum is a graph of the intensity of light as a function of the frequency or wavelength of the light**. All of the terms I just used are critical in describing wave phenomena, so let's quickly review them.

All waves can be described as linear combinations of sine waves with phases between 0 and 2π radians. If we have a normal sine wave, as below, the **wavelength** is the distance between crests and has the symbol λ. The wave is also characterized by an amplitude and an intensity. The amplitude is the height of the wave, and can be either positive or negative. This amplitude A is related to the **intensity** by



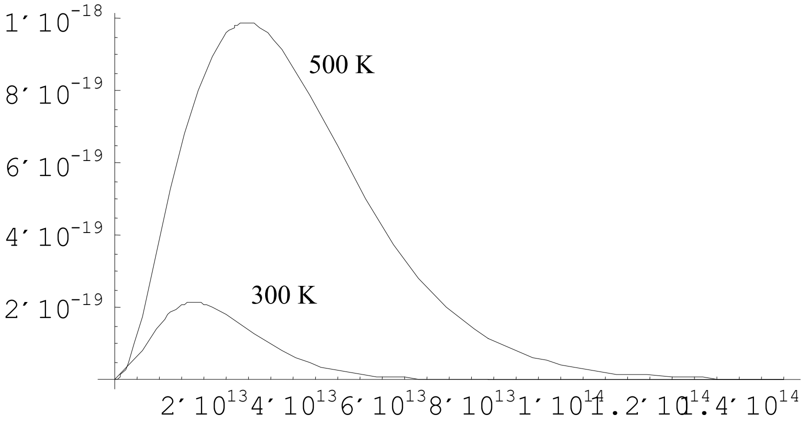
$$I = A^2.$$

This **amplitude is dependent both on position and time**, i.e., $A = A(x,t)$. This means that if at a given time we move along the wave, the amplitude changes, but also that if we stay in one place the amplitude at that position will change with time, since the wave is moving. The **frequency** has the symbol ν, and is the number of crests of the wave that pass a given point in a second. For **light, the frequency and wavelength are related by the equation**

$$\boldsymbol{\lambda\nu = c},$$

where c is the speed of light, 3.00 x 10^8 m/s.

Having defined these terms let's examine the **spectrum of a black body**. At very low frequencies, the black body emits very small amounts of light, i.e., there is a low emission intensity. In addition, the emittance at high frequencies is low as well, with a maximum in the middle. **Blackbody emittance always shows this type of distorted bell-shaped curve**. This is conventionally shown by plotting the energy density vs. the frequency. The **energy density, ρ(ν,T) dν is the energy per unit volume emitted between frequencies ν and ν + dν**. (The reason that we have to divide by the volume is that the amount of light emitted depends on the size of the blackbody – a larger blackbody can emit more light than a smaller one.) A typical plot of energy density at two different temperatures for a black body is shown here.



As this plot shows, another important feature of blackbody radiation is that the **distribution of frequencies and intensities (the spectrum) changes with temperature**.

As temperature increases, the overall intensity increases, i.e., a black body source is brighter at high temperature than at low temperatures. In addition, the peak frequency, the frequency with the highest intensity, shifts to higher and higher frequency as the temperature increases. This is expressed quantitatively as the Wien displacement law,

$$\nu_{\max} = T\ x\ 1.035x10^{11} K^{-1} s^{-1},$$

where T is the temperature in K.

The problem that this phenomenon presented to classical physicists is that no one could come up with an expression to match either the experimental frequency dependence or the temperature dependence. The best attempt was the Rayleigh-Jeans law (derived by ….wait for it… Rayleigh and Jeans),

$$\rho(\nu, T) = \frac{8\pi \nu^2 kT}{c^3}$$

where k is Boltzmann's constant, $R/N_o = 1.381 \times 10^{-23}$ J K^{-1}, *T* is the temperature in Kelvin and *c* is the speed of light in a vacuum, 3.00×10^8 m/s. The problem with this equation is that while it reproduces the experimental energy density pretty well at low frequencies, once it reaches the maximum, it just keeps going up. Since this failure occurs at frequencies that in many cases correspond to ultraviolet radiation, this shortcoming of classical physics was called the **ultraviolet catastrophe**.

Enter Max Planck in 1900. He derived an equation that fit black body experiments,

$$\rho(\nu, T) = \frac{8\pi h(\nu / c)^3}{e^{h\nu/kT} - 1},$$

where h is a constant now called Planck's constant, with $h = 6.6262 \times 10^{-34}$ J s. However, in order to do so he had to assume that **the energy given off or absorbed by the solid came in discreet, discontinuous units called quanta, where the energy of a quantum**

is given by $E = h\nu$, and where ν is the frequency of vibration of the crystal. This was a total break with classical ideas which assumed that the energy emitted could take on any value. In other words, classical physics said that no matter how small the amount of energy that was emitted, it could be divided into smaller units (this is what is meant by any continuous distribution). Planck said that there was some tiny energy unit that could no longer be subdivided. This meant that in order to explain blackbody radiation, a new characteristic of crystalline vibration, quantization, or discontinuity in the energy spectrum, had to be called in. However, while this concept was incompatible with classical electromagnetism, it did not have an immediate impact on physics. Most physicists simply felt that quantization was a meaningless mathematical construct, rather than a physical reality, and that in time a better theory would come along, that would discard this "unphysical" postulate, and return blackbody radiation to the fold of classical physics. However, the phenomenon of the photoelectric effect, and Einstein's explanation of it, soon added a second blow to the bastion of classical physics.

Lecture 2

The second phenomenon that led to the development of quantum mechanics was the **photoelectric effect**. In this experiment, light of a given frequency and intensity is shined on a metal surface and electrons are ejected. The frequency and intensity are then changed and the rate of electron emission and the kinetic energy of the electrons are monitored. Two features observed in experiments on the photoelectron effect disagree with classical theories. First, the experiments show that **the kinetic energy of the ejected electrons is independent of the intensity of the incident light**. How did this differ from the predictions of classical physics? According to classical physics, light consists of perpendicular electric and magnetic fields oscillating perpendicular to their direction of travel. The classical theory of the photoelectron effect essentially says that when light shines on a metal surface, the electrons in that metal oscillate in unison with the electric field of the light wave. The bigger the intensity of the light wave, the bigger the oscillation of the electron. If the intensity is big enough, the electron breaks free. Now here's the first key point. In classical physics, the energy of a light wave is proportional to the intensity. Therefore, the kinetic energy of the ejected electron should increase as the intensity of the light increases. Unfortunately, this was not observed. When the intensity of the source increased, the kinetic energy stayed the same. The only thing that happened when the intensity of the light increased was that the number of electrons emitted increased.

The second problem with the classical physics predictions for the photoelectric effect is that, as can be seen from our discussion, one of the predictions of the classical theory is that any wavelength can cause a photon to be emitted as long as the intensity is high enough. Unfortunately, this was not observed either. If a plot is made of electron kinetic energy vs. frequency, we find that as we increase our frequency from 0, that there is a range of frequencies in which no electrons are emitted. When we reach a threshold frequency ν_0, photons are emitted with zero kinetic energy. As the frequency increases from this threshold frequency, the kinetic energy of the ejected electrons increases linearly.

To explain these results, Einstein, in a 1905 paper, postulated that **light exists in little packets (or particles) of energy**, which G.N. Lewis labeled photons, and **which had energy equal to hν**, where ν is the frequency of the photon and h once again is Planck's constant. In other words, Einstein postulated that the energy was proportional to the frequency and NOT the intensity as classical physics predicted. From this point, Einstein just turned to our old friend from thermodynamics, the law of conservation of energy. He argued that the photon energy equaled the energy necessary to eject the electron, which he labeled the work function, Φ, plus the kinetic energy of the electron, i.e.,

$$h\nu = \Phi + 1/2\ mv^2.$$

This simple equation can explain both of our observations. First, to eject an electron with zero kinetic energy requires a photon with frequency Φ/h. Any photon with lower frequency won't have enough energy to eject the electron. This explains the existence of a threshold frequency. In addition, if we write our equation to solve for kinetic energy, we get

$$1/2mv^2 = h\nu - \Phi.$$

Since Φ is a constant for each metal, this equation tells us that the kinetic energy of the ejected electrons will increase linearly with frequency.

The postulate that light exists in particle form, i.e., as packets of energy, also explains the effect of increasing the intensity of the incident radiation. Since intensity is energy/unit area, and since each of these photons has energy equal to hν, the only way to increase the intensity is to increase the number of photons. Since a single photon can eject a single electron at most, increasing the intensity increases the number of incident photons and therefore the number of ejected electrons. This explanation of the photoelectric effect, along with his classic paper on Brownian Motion, earned Einstein the Nobel Prize in 1921.

Note that Einstein's explanation represents an extension of Planck's ideas. Where Planck had only said that the energy emitted or absorbed by a black body had to be quantized, Einstein said that light energy itself had to be quantized, where quantized is taken to mean that the energy comes in discrete units, or quanta. The photoelectric effect also suggested that light had characteristics both of particles and of waves, a completely new idea called wave-particle duality.

Einstein's result was important not just because it extended Planck's ideas but also because it involved the same fundamental constant required in Planck's work. When the constant h appeared in Planck's theory of blackbody radiation, it was not considered significant, but simply was thought to be an arbitrary number adjusted to fit the data to the blackbody curves. However, when the same constant appeared in Einstein's explanation of an independent phenomenon, and in an equation for the energy of light, it began to appear that this constant was not arbitrary but had some fundamental significance.

Einstein’s conclusion that light has some particle characteristics led to an interesting corollary. Einstein concluded that as a particle, light must have a well-defined momentum. However, Einstein carried this idea even farther when he calculated the **momentum of a photon**. Remember that until then, momentum had been considered a property of particles, so when Einstein was able to demonstrate that photons had momentum, it strengthened the growing belief that light had both particle and wave properties. Einstein's equation for the momentum of a photon was $p = h/\lambda$, where p is the momentum, h is Planck's constant, and λ is the wavelength of the photon. Einstein's momentum calculation has been confirmed both qualitatively and quantitatively by experiments many times over.

The next phenomena that caused trouble for classical physics were the spectra of atoms. Remember that according to classical physics, energies should be continuous. In general, classical physics was most comfortable with continuous phenomena, and this included the frequencies of light absorbed and emitted by matter. For example, the radiation emitted by a black body varies continuously with wavelength. Remember, in the theory of blackbody radiation, it was not the emitted light itself which violated classical understanding, but the hypothesis that the motion of the solids which emitted the light was quantized.

The emission and absorption spectra of atoms were quite another problem. These spectra rather than being continuous take the form of lines. The emission spectra show groups of lines with spaces in between in which no light is emitted, while the absorption spectra show absorption lines with no absorption in between. They are intrinsically discontinuous. Classical physics could produce no theory that could account for these discontinuities.

The discontinuities are particularly regular in the spectrum of hydrogen. Hydrogen has three groups of emission lines between the ultraviolet and the near infrared regions of the electromagnetic spectrum. The **Lyman** series, in the ultraviolet, begins at 121.6 nm and ends at 91.2 nm, the **Balmer** series, in the visible, begins at 656.3 nm and ends at 264.7

nm, while in the infrared, the **Paschen** series begins at 1876.0 nm and ends at 820.6 nm. We can talk of the ends of these series because in each series the lines get closer and closer together until they converge to the final value and therefore the final value of such a series is called the **convergence limit**.

Rydberg showed that the frequencies of all of these series could be accounted for by a single simple formula. This formula is often expressed using a unit called wavenumbers to report the positions of the lines. The **wavenumber**, $\overline{\nu}$, which has the units cm^{-1}, is defined by

$$\overline{\nu} = \frac{1}{\lambda} = \frac{\nu}{c},$$

where the wavelength is in units of cm, and the speed of light is in units of cm/s. These units were introduced just to keep the numbers that spectroscopists have to work with reasonably small, yet still have a unit like frequency that is directly proportional to energy. Since

$$E = h\nu$$

and

$$\nu = \overline{\nu}c,$$

where c is the speed of light in cm/s, energy and wavenumbers are related by

$$E = hc\overline{\nu}.$$

The **Rydberg formula** in these units is

$$\frac{1}{\lambda} = \overline{\nu} = R(\frac{1}{n_1^2} - \frac{1}{n_2^2})$$

where n_2 and n_1 are integers such that $n_2 > n_1$ and R is the Rydberg constant, 109,677.5856 cm^{-1}. For example, the first line in the Lyman spectrum corresponds to $n_1 = 1$ and $n_2 = 2$, and has the wavenumber $\bar{\nu}$ = R(1-.25) = 82, 258 cm^{-1}. Since $\lambda = 1/\bar{\nu}$, this is equal to 121.6 nm, the same wavelength that we observe experimentally. The fact that integers are an integral part of the Rydberg equation is the mathematical way of saying that the spectra are discontinuous. Once again, classical physics could not account for the discontinuities.

I just made a claim that classical physics could not come up with a theory to account for the line spectra of atoms, yet I also just taught you about the Rydberg formula. CAN ANYONE TELL ME WHY, WHEN THE RYDBERG FORMULA EXISTS, I CLAIMED THAT THERE WAS NO THEORY TO EXPLAIN THE LINE SPECTRA OF HYDROGEN? [The Rydberg equation fails to explain why the line spectra are discontinuous – it simply summarizes the results of several experiments and expresses them in the form of a succinct equation. Equations or principles that summarize experiments are called laws. A theory must contain an explanation for the observed behavior.]

Neils Bohr was able to explain the spectrum of hydrogen and the Rydberg equation with his model of the hydrogen atom. The key concept of his model has to do with a property called **angular momentum**. Let’s quickly review this concept since it is important in many chemical phenomena, including NMR spectroscopy.

Remember that **linear momentum has the definition p = mv**. The momentum is a constant of motion for linear motion. Now consider a particle rotating in a plane around some fixed central point at a distance r from the center. The momentum is no longer a constant of motion, because as the particle rotates, the direction of the velocity vector is continually changing. This suggests that new variables which are constant for angular motion are desirable.

We start by defining the frequency of rotation, which is the number of times the particle passes an angular position on the plane in a second. If the frequency of rotation is ν_{rot}, then the magnitude of the velocity of the particle is

$$v = 2\pi r\nu_{rot}.$$

We can also define a new type of velocity called **angular velocity** as

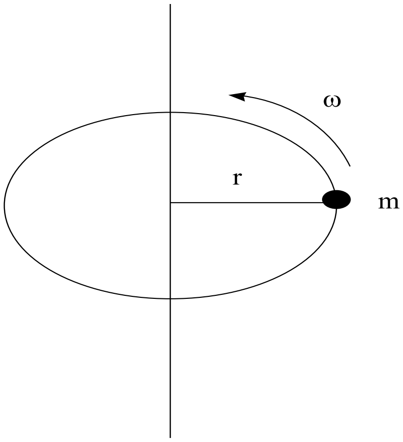
$$\omega = 2\pi\nu.$$

This angular velocity is the rate at which the revolving particle sweeps through the angles of the circle in radians, $\frac{d\theta}{dt}$ and is related to the magnitude of our linear velocity by

$$v = r\omega.$$

The **kinetic energy, T,** of our particle is equal to

$$T = 1/2\ mv^2 = 1/2\ mr^2\omega^2.$$



It is convenient at this point to define another new variable for circular motion called the **moment of inertia**,

$$I \equiv mr^2.$$

Just as mass represents the resistance to linear acceleration, the moment of inertia represents the resistance to angular acceleration. Introduction of the moment of inertia allows us to write the kinetic energy of the rotating particle as

$$T = 1/2I\omega^2.$$

Our equations of motion for linear motion and angular motion are analogous. We see that in our two equations for kinetic energy that m is analogous to I, while v corresponds to ω. What this suggests is that there should be a quantity for rotating systems that is analogous to the momentum mv. Such a quantity exists and is called the angular momentum,

$$\ell \equiv I\,\omega = mvr.$$

It turns out that just as m, v, and p are convenient parameters to describe the dynamics of linear motion, I, ω, and ℓ are much more convenient when describing the dynamics of circular motion.

Lecture 3

Bohr's theory of the atom, first proposed in 1913, was built from the following three hypotheses.

1) Electrons in atoms have stationary orbits. I.E., the radii of the orbits are fixed. (Of all of Bohr's hypotheses, this is the least intuitive, since in classical mechanics all macroscopic objects have orbits that decay, unless energy is continuously provided to keep the orbit stable. Think of satellites and the first space station.)

2) The angular momentum of the electrons in these orbits is quantized according to $\ell = mvr = n\hbar$, where $\hbar$ is $h/2\pi$. Again, quantization means that the angular momentum cannot vary continuously, but must change in discrete steps (quanta). In this formula, the quantization lies in the presence of the integers n, which Bohr labeled quantum numbers. If the range of angular momenta were continuous, the integer n would have to be replaced by a positive real number.

3) The spectrum of hydrogen arises when an electron in one orbit moves to a different orbit, and the energy difference between the two is emitted or absorbed as a photon of energy $h\nu$. The photon is emitted if the electron moves from an orbit of high energy to one of low energy, and the photon is absorbed if the electron moves from an orbit of low energy to one of high energy.

The first implication of Bohr's model of the hydrogen atom is that the electron in the hydrogen atom can only occupy orbits with certain fixed radii. By combining his hypotheses with results from classical physics, Bohr was able to come up with a formula for the radii of these orbits,

$$r = \frac{4\pi\varepsilon_0\hbar^2 n^2}{\mu e^2},$$

where ε_o is a constant called the permittivity of free space, 8.854 x 10^{-12} $C^2N^{-1}m^{-2}$, n is an integer greater than zero called the principle quantum number, e is the charge of an electron, 1.602 x 10^{-19} C, and μ is a quantity called the reduced mass.

The **reduced mass** has the formula $\mu = \frac{m_1 m_2}{m_1 + m_2}$. It is used to simplify the treatment of a class of problems involving two particles bound together by a central force. A **central force is one that can be represented as acting along a straight line between two particles**. One example of a central force is the bond between two atoms. Another example of a central force is the coulomb attraction between the proton and electron in our hydrogen atom. For the hydrogen atom the reduced mass is given by

$$\mu = \frac{m_e m_p}{m_e + m_p} = \frac{9.100x10^{-31}kg\,x\,1.673\,x10^{-27}kg}{9.100x10^{-31}kg + 1.673\,x10^{-27}kg} = 9.095x10^{-31}kg$$

Notice that the reduced mass of the hydrogen atom is slightly smaller than the mass of the lighter of our two particles, the electron. You will find that **the upper bound of the reduced mass will be the mass of the lighter of the two particles, while the lower bound is 1/2 of the mass of the lighter particle.** This is because the reduced mass is the effective resistance to acceleration for the two particle system, and two particles coupled by a central force accelerate more easily than the lighter particle alone.

The second implication of Bohr's hypothesis is that **the energies that an electron can have will also be limited to certain values that will be discontinuous, i.e. the electron energies in a Bohr hydrogen atom are quantized**. Bohr used his hypotheses and the laws of classical physics to come up with a formula for these energies,

$$E_n = \frac{-\mu e^4}{8\varepsilon_0{}^2 h^2 n^2}$$

The significance of the negative sign here is to indicate that the hydrogen atom is more stable than the electron and proton when they are separated. In this convention, if there is no interaction, the energy is set to zero. A negative energy means that the system is more stable than the separated particles and a positive energy means that the system is less stable.

The third implication of Bohr's model is that we will observe spectra that follow Rydberg's formula. To see this, remember that Bohr said that emission of light from H atoms occurs when an electron in one orbit drops to another orbit with lower energy, and that the difference in energy appears as a photon. Therefore the difference in energy of the two hydrogen atom states must equal the energy of the photon. In equation form this becomes

$$E_{n2} - E_{n1} = \Delta E = h\nu.$$

If we substitute Bohr's formula for the energy of an electron in an orbit with quantum number n we get

$$h\nu = \frac{\mu e^4}{8\varepsilon_0{}^2 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

If we remember that $\nu = c\bar{\nu}$, then we can rewrite this in terms of wavenumbers to get

$$\bar{\nu} = \frac{\mu e^4}{8\varepsilon_0^2 h^3 c}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Notice that this equation bears a marked resemblance to the Rydberg formula. In fact, comparison of the two equations shows that if Bohr's model is correct that the Rydberg constant is given by

$$R = \frac{\mu e^4}{8\varepsilon_0^2 h^3 c}$$

When we plug in the values of the constants in this equation, we find that the theoretical value of the Rydberg constant is 109,681 cm^{-1}, a number which compares favorably with the best experimental value of 109,678 cm^{-1}. Note that while the difference in the values of R is small, it is still significant. Successive improvements in quantum theory have resulted in theoretical calculations of R which are closer and closer to the best experimental measurements.

Bohr's model was very successful for hydrogen, but it has its limitations. One of these is that it can't predict how bright a given line in the hydrogen spectrum will be, i.e., it can't predict the intensity of the line. The second is that it fails absolutely in describing the behavior of any atom with two electrons or more. The failure of Bohr's model lay primarily in too great a dependence on classical ideas. There were a few more key ideas that needed to fall into place before a new mechanics could be developed which could accurately describe atoms, molecules and elementary particles.

The next piece of the puzzle was provided in 1924 by **de Broglie**, a French aristocrat turned physicist. After the Einstein photoelectric effect paper, de Broglie proposed that not just photons, but all matter, would show wave particle duality. De Broglie went through a thought process something like this. ‘Einstein showed that light, which everyone thought was a wave, had particle characteristics and momentum. Perhaps matter, which we thought consisted of particles, acts like a wave. This means that it must have a wavelength.’ To find the wavelength of a particle, de Broglie turned the Einstein formula around to get

$$\lambda = h/p = h/mv,$$

where m is the mass of the particle, and v is its velocity, **the de Broglie formula**. De Broglie's formula was counterintuitive, since most of us have seen no evidence that macroscopic particles (golf balls, baseballs, basketballs), and very macroscopic particles like physical chemistry textbooks have any wavelike behavior. However, only three years later, De Broglie's hypothesis and his formula were both proven correct by an experiment done at Bell Laboratories in Murray Hill, New Jersey by two American physicists, Davisson and Germer.

The Davisson-Germer experiment showed that **electrons accelerated near the speed of light and passed through a crystalline material form interference patterns**. This was a particularly astonishing result, because interference is a phenomenon that is exhibited solely by waves, and electrons were definitely matter, particles.

Because interference is a basic property of waves, and because it will be important in our understanding of chemical bonding, this is another basic concept I'd like to review. **Interference** is most clearly demonstrated by the double slit experiment. You have a light source and a screen. In between the light source and the screen there is a board with two slits in it. Cover up one slit, and you get a smooth distribution of light with a single intensity maximum. Cover this one and open up the other and you get the same thing. But open up both slits at the same time and you get an undulating intensity pattern, with alternating bright and dim spots, or in other words, alternating intensity minima and maxima.

This phenomenon is called interference. It is a result of two things. The first is the fact that waves vary periodically. Light of one pure color, called monochromatic light, can be represented as a simple sine wave. If the wave has an amplitude A, its maximum value is A and its minimum will be -A. If we overlay two of these waves we can do it in a number of ways. One is to overlay them so that all the positive peaks line up. In this case when we sum the waves, the resulting amplitudes are twice as high as either of the original waves. This is called **constructive interference**. Now consider the case where the positive peaks line up with the negative peaks. When we add the waves the amplitudes cancel, and there is no resultant intensity. Since adding the waves destroys them this is called **destructive interference**. So you see that depending on how the peaks of the waves line up, we can have either reinforcement of the intensity or canceling of the intensity. (If this doesn't seem real to you, think of waves in the ocean. Positive amplitude would correspond to the peaks of waves (which are higher than a calm ocean surface), and negative amplitude would correspond to troughs of waves (which are lower than a calm ocean surface). If the trough from one ocean wave and the peak from another ocean wave met at the same place, they would cancel and the result would appear to be the calm ocean surface.) The variable that describes the way that the peaks line up is called the **phase**. We say that **if waves have opposite phases then we will observe destructive interference**, and **if waves have the same phase we will have constructive interference**. Interference patterns can be produced by splitting a light source into two parts that travel different distances and recombining them, or by shining light on a grating. Typically, a crystalline solid is used as a grating for light in the x-ray region of the spectrum. Practical applications of these interference concepts are FTIR's, which use interference patterns to determine IR spectra, and lasers, whose incredible brightness comes from many repetitions of constructive interference.

We can see that interference is a phenomenon closely tied to waves. Thus when Davisson and Germer observed interference patterns for electrons it was quite a shock because it led to only one conclusion - **electrons - and, by extension, other particles - have wavelike characteristics**. This provided qualitative proof of the DeBroglie hypothesis. However, Davisson and Germer also provided quantitative proof of the DeBroglie equation. By calculating the wavelength of the electrons that hit their crystal using the DeBroglie formula, they were able to demonstrate that the observed diffraction pattern was the same that would have been observed for X-rays of the same wavelength passing through the crystal.

The final result that preceded the development of quantum mechanics was the Heisenberg Uncertainty principle, Heisenberg's most famous, and third most important contribution to modern physics. [What were the first two? Second, the simultaneous development of a second form of quantum mechanics at the same time as Schrödinger. First, failing to develop an atomic bomb for the Nazis.] The Heisenberg uncertainty principle is innocent looking enough. In its most common form, it is simply

$$\delta p \, \delta x \geq \hbar/2.$$

In this equation, δ means the uncertainty in the measured value of a quantity, and $\hbar$ is simply ${}^{h}\!/_{2\pi}$. Therefore this equation means that the uncertainty in the position of a particle times the uncertainty in the momentum of a particle has to be greater than or equal to Planck's constant divided by 4π. In other words, if you know where the particle is with infinite precision you can't know where it's going, and if you know where it's going with infinite precision, you can't know where it is.

This principle has little effect on classical physics in its normal domain, i.e., large particles, and high energies, because Planck's constant, 6.6262×10^{-34}, is such a small number that the uncertainties for macroscopic systems will be unmeasurably small. However, in the limit of quantum energies and quantum dimensions, the degree of uncertainty becomes significant.

We can use the following thought experiment to demonstrate the reasonableness of Heisenberg's principle, although the exact derivation is somewhat subtler. Suppose you have an electron with an exactly known momentum that you want to locate. The only way to locate such a small particle is to scatter a photon off of it. The uncertainty in the location of an electron located this way is approximately equal to the wavelength of the photon, since we can use the wavelength of a photon as a measure of its size. This means that we can write $\delta x \approx \lambda$. The shorter the wavelength of the photon, the smaller the uncertainty in the position of the electron is. Now when two particles collide, some fraction of the momentum of one particle is transferred to the other. You've all seen this when a cue ball in pool strikes another ball and starts it moving. A photon with wavelength λ has momentum $p = h/\lambda$. When it strikes the electron some or all of its momentum may be transferred to the electron. We don't know how much. Thus the uncertainty in the momentum induced by the photon striking the electron is $\delta p \approx h/\lambda$. Now if we take the product of the two uncertainties we get $\delta x \, \delta p \approx h$. This matches the requirement of the Heisenberg principle that the uncertainty be greater than or equal to $\hbar/2$.

The implications of this principle are far reaching. It is the death of the concept of the trajectory (at least on the quantum scale), which is so central to classical mechanics. A trajectory is the exact knowledge of how the position and momentum of an object change over time. We are all intuitively familiar with this concept. For example if I throw this eraser to _____________ (s)he will be able to make at least a valiant attempt at catching it because (s)he can predict the position and momentum as it approaches her (him) from its previous behavior. Quantitatively, knowing a trajectory of a particle means knowing both its position and its momentum (in what direction the position will change, and how quickly it will change) simultaneously with infinite precision.

When we talk about electrons in Bohr orbits, we are saying that the electrons in a hydrogen atom move in circular trajectories. The key point here is that since the orbits are circular trajectories, we have to know both the position and the momentum of the particle exactly and at the same time. Heisenberg says that we can't. So we can't have electrons moving in well-defined orbits. We can only talk about where we can find electrons OR where they are going. Therefore, from now on we have to find a way to describe the behavior and dynamics of matter without trajectories, and therefore without causality.

Lecture 4

Let me summarize our results about the behavior of matter on the scale of molecules. The energies of solids and electrons in solids and atoms are limited to discrete discontinuous units called quanta. The energies of photons are also quantized. Quantization of photon energy also implies that light occupies a discrete space, or in other words, has particle characteristics. Matter, in turn, has wave characteristics, in particular a wavelength. Finally, there are certain pairs of observables, like energy and time, or position and momentum, for which we cannot simultaneously measure values with infinite precision. For position and momentum, this implies that we cannot speak of trajectories for particles that are sufficiently small.

It was necessary to find a new version of mechanics that included all of these features. In the 20's, Schrödinger and Heisenberg both came up with theories that accounted for these results. While neither theory was complete, both provided foundations upon which more and more accurate versions of quantum mechanics were based. To give a brief history, Schrödinger's quantum mechanics, based on differential equations, and Heisenberg's quantum mechanics, based on linear algebra, yielded accurate results for many experimental observations, but did not yield electron spin. Dirac, by treating the mass of the electron relativisitically, came up with an equation whose solution yielded the electron spin and predicted the existence of the positron. Subsequent modifications by Feynman, Schwinger, Tomonaga, Gell-Mann, Weinberg, Abdus Salam and Glashow have resulted in a quantum mechanics which can account for all electromagnetic phenomena, the weak force, which controls the decay of fundamental particles, and some aspects of the strong force, which holds nuclei together, overcoming the coulomb repulsion between the protons. Anyone interested in reading more of the fascinating history of quantum mechanics should read either The Second Creation, by Crease and Mann, or The Making of the Atomic Bomb by Richard Rhodes, both of which are in our library.

In chemistry, we usually limit our attention to the Schrödinger and Heisenberg models of quantum mechanics, adding the electron spin in an ad hoc manner. Sometimes, for heavy atoms, such as bromine, mercury or iodine, where the core electrons are moving at relativistic speeds, the Schrodinger equation predicts incorrect bond lengths and bond energies, so we use the Dirac equation (or other methods to include relativistic effects), but that is outside of the sphere of our course.

Schrödinger postulated an equation for the behavior of a particle that was analogous to the classical mechanical equation for the dynamics of a wave. The most general form of this equation depends both on time and position. We will spend most of our time on a special case called the **time independent Schrödinger equation**, which is sufficient for many problems in chemistry.

For a single particle that is constrained to move only along the x-axis, the time independent Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}+V(x)\psi(x)=E\psi(x),$$

where m is the mass of the particle, V(x) is the **potential energy** in which the particle moves, E is the total energy (kinetic plus potential) of the particle, and $\psi(x)$ is called the **wavefunction** of the particle and is a function of the position only. We will talk about the solution of this equation and the interpretation of the results in some detail, but in brief, the way that this equation is solved is by finding a function $\psi(x)$, that meets the requirement that when its second derivative is taken and multiplied by $-\frac{\hbar^2}{2m}$ and added to the product of the function with the potential V(x) yields the original function times a constant, which we will call E. While this sounds like a daunting procedure, it is a procedure that is well established for many problems, and we will learn how to solve for the wavefunction one problem at a time. Some of these problems will be too advanced for this course, so in those cases, it will be enough for you to take the wavefunctions I provide for you, and to demonstrate that they are solutions of the Schrödinger equation. To reiterate – our tasks will be 1) to learn how to write the Schrödinger equation for a given problem. 2) Given the Schrödinger equation for a given problem learn either how to solve for the wavefunction ψ or to demonstrate that a given wavefunction ψ is a solution of the Schrödinger equation. 3) Learn how to extract measurable predictions about our problem from the wavefunctions.

The wavefunctions that are obtained by solving the Schrödinger equation can be either real functions or complex functions. Remember that the concept of **complex numbers** arises from the square roots of negative numbers. There is no real number that can be squared to yield a negative number. However, if we introduce a new number *i*, where *i* is defined as the square root of -1, it is now possible to write down square roots of negative numbers. For example, the square root of -a is given by

$$\sqrt{-a} = i\sqrt{a} \ ,$$

where a is a positive number. Any number that is a real number times *i* is called an **imaginary number**. Any number that has both real and imaginary parts, i.e., any number of the form a ± *i* b, where a and b are real numbers, is called a complex number.

It is possible for complex numbers to be the arguments of functions. Complex numbers take on particular importance in quantum mechanics because of the **Euler relation**,

$$e^{\pm i\theta} = \cos\theta \pm i\sin\theta$$

The Euler relation connects exponentials of complex numbers to sine and cosine functions, which are the functions that describe wave behavior. The Euler relation also leads to a really wonderful equation,

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

This equation, rather unexpectedly, connects the three most important transcendental numbers in an extremely simple relation.

Let's return to the Schrödinger equation,

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + V(x)\psi(x) = E\psi(x)$$

This equation is a second order differential equation, because it contains a second derivative ($\frac{\partial^2\psi(x)}{\partial x^2}$). When we set up an equation like this, our only knowns are the mass of the particle and the potential energy function in which it moves. Our goal in solving an equation like this is to find those wavefunctions $\psi(x)$ that are solutions of this equation and the energies that are associated with these wavefunctions. The wavefunctions that solve the Schrödinger equation have the special name **eigenfunctions** and the energies that are associated with these eigenfunctions are called **eigenvalues**. In general, there will not be a single solution to the equation, but rather a set of solutions. We will indicate this by labeling an individual eigenfunction $\psi_i(x)$, and the associated energy E_i.

It is fairly simple to find the solution to this equation for the simplest cases, and we will do this shortly. However, in general, solving the Schrödinger equation is quite involved, so for most cases, I will merely show you how to set up the equation and what the results are. Even though I won't be expecting you to solve the Schrödinger equation, I will expect you to be able to confirm that what I claim is a solution actually is one. In principle, the procedure for this is trivial - you merely take the solution and plug it in to the equation and see if it yields a constant times itself. In practice, the math can be quite involved. We will demonstrate this for the simplest couple of cases. The more complicated cases will be left to you as homework.

When Schrödinger first solved his equation, it was a big success, yielding the correct energies for a number of phenomena. In addition to these energies, he also got this wavefunction ψ, which was a bit of a problem, because he didn't know what it meant. The current **interpretation of the wavefunction** was first suggested by **Max Born**. It says that the wavefunction allows us to determine the probability that we will find a particle in a given region in space. More precisely, he suggested that **the wavefunction gives a probability amplitude for the particle at a given point in space**. [Analogy to waves] The actual **probability that a particle will be found in the infinitesimal region between x and x + dx** is given by

$$Prob\{x, x+dx\} = \psi^*(x)\psi(x)\,dx$$

$\psi^*(x)$ is called the complex conjugate of $\psi(x)$. You form a **complex conjugate** of a complex number by reversing the signs of all the *i*' 's in that number. For example, if we have a complex number 5 - 7*i*, its complex conjugate is 5 + 7*i*. You can also take the complex conjugate of a function by reversing the signs of each *i* in the function. For example if $\psi(x) = e^{ix} + e^{-2ix}$, the complex conjugate $\psi^*(x) = e^{-ix} + e^{2ix}$. The quantity $\psi^*\psi$, called the **probability density**, is always real and positive, because all products of a complex function and its complex conjugate are real and positive. For example, if a complex number $z = 5 + 7i$, then

$$zz^* = (5+7i)(5-7i) = 25 - 49i^2 = 25 + 49 = 74,$$

while if $f(x) = e^{ix}$, then

$$f(x)\,f(x)^* = e^{ix}e^{-ix} = e^{(ix-ix)} = e^0 = 1$$

Because of our interpretation of $\psi^*\psi$ as a probability density, it makes sense that it is always real and positive, since negative or imaginary probabilities make no sense. The probability density, $\psi^*(x)\psi(x)$, is often abbreviated as $\left|\psi^2(x)\right|$.

If we want to find the **probability that our particle is between two positions on the x axis**, we have to integrate our previous probability expression,

$$Prob\{a,b\} = \int_a^b \psi^*(x)\psi(x)dx$$

Since for a one dimensional problem the particle must be *somewhere* on the x axis,

$$Prob\{-\infty,\infty\} = \int_{-\infty}^{\infty} \psi^*\psi\, dx = 1$$

When the integral of the square of a wavefunction over all space is equal to 1, the wavefunction is called a **square normalized function**. **All wavefunctions must either be square normalized, or square normalizable**.

Let's do an example of normalizing a function. Suppose that we want to normalize $\psi(x) = \sin 2\pi x$, where the particle is restricted to lie between -1/2 and 1/2. This means that we are looking for a constant B so that $B\psi = \psi'$ is a normalized function, i.e.,

$$\int_{-1/2}^{1/2} B^* \psi^*(x) B\psi(x)dx = B^2 \int_{-1/2}^{1/2} \psi^*(x)\psi(x)dx = 1$$

For our case this becomes

$$B^2 \int_{-1/2}^{1/2} \sin^2 2\pi x\, dx = 1$$

HOW MANY OF YOU KNOW WHAT THE INTEGRAL OF SIN^{2}2πX DX IS? HOW MANY OF YOU REMEMBER HOW TO CALCULATE IT? The good news is that you really don't have to know how to. The reason is that in the CRC handbook and in various math and physics handbooks you can find **tables of integrals**, and look up the answers to integrals far more complicated than this. I've photocopied a couple of pages from one table of integrals. CAN ANYBODY FIND THE INTEGRAL OF SIN^{2}2πX DX? WHAT'S THE CLOSEST INTEGRAL YOU CAN FIND? What we need to do is put our integral in a form so that it looks exactly like the one in the table. To do this we use **substitution of variables**. We need our integral to look like sin^{2}x, so we'll create a new variable z = 2πx. This makes our integral

$$B^2 \int \sin^2 z\, dx = 1$$

We need to do two more things. First we need to match the differential with the variable z. This is easy. Since z = 2πx, we just take the differential of both sides to get dz = 2πdx which implies that dx = dz/2π. Substituting this gives

$$\frac{B^2}{2\pi} \int \sin^2 z\, dz = 1$$

Now we need to turn to the **limits of integration**. Our original limits of integration were from x = -1/2 to x = 1/2. Since we're integrating over z now, we have to find the equivalent values of z. This is also easy. Since z = 2πx, when x = -1/2, z = -π and when x = 1/2, z = π. So our integral is now

$$\frac{B^2}{2\pi}\int_{-\pi}^{\pi}\sin^2 z\,dz = 1$$

DOES THIS MATCH ONE OF THE INTEGRALS IN THE BOOK? Close but no cigar! The integral in the book is

$$\int_0^{\pi}\sin^2 x\,dx = \frac{\pi}{2}$$

Notice that the function is the same from -π to 0 as from 0 to π, so that all we need to do is recognize that

$$\int_{-\pi}^{\pi}\sin^2 zdz = 2\int_0^{\pi}\sin^2 zdz = \pi$$

Our condition for normalization now becomes

$$\frac{B^2}{\pi}\pi = 2 \quad or \quad B = \sqrt{2}$$

So our normalized wavefunction is $\psi(x) = 2^{1/2}\sin 2\pi x$.

Besides normalization, the interpretation of wavefunctions as probability amplitudes requires that our wavefunctions have two other characteristics. First, ψ(x) must be **single valued**. [Draw a single valued and a doubled valued function.] This should make sense since we can't have two different probabilities of finding the particle at a given place and time. Second, ψ(x) must be a **continuous function**.