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 $2 \times 10^{-4}$ m, a factor of 100,000 larger than the distances with which quantum mechanics concerns itself.

There are **three huge 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**.

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 $\alpha$, $\kappa_T$, $p$ 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. So quantum mechanics involves
a substantial amount of speculation about the microscopic nature of matter.

The third difference is that thermodynamics is restricted to 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.
Therefore, quantum mechanics can study systems in both equilibrium and
disequilibrium.

Quantum mechanics was 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
photoelectron 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.

If we have a normal sine wave, as below, the wavelength is the distance between crests and has the symbol λ. It 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 we move along the wave, the amplitude changes, but also that if we stay in one place the amplitude at that position will change too, 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

\[ \lambda \nu = c, \]

where c is the speed of light, \( 3.00 \times 10^8 \) m/s.

Having defined these terms let’s examine the spectrum of a black body. At very low frequency, we have a low intensity emitted. In addition, the emittance at high frequencies is low as well, with a maximum in the middle. Blackbody emittance always shows this type of bell shaped curve. This is conventionally shown by plotting the
energy density vs. the frequency. The energy density, $\rho(\nu, T) \, d\nu$ is the energy per unit volume emitted between frequencies $\nu$ and $\nu + d\nu$. A typical plot of energy density vs. temperature for a black body is shown here. Another important feature of blackbody radiation is that this distribution of frequencies and intensities 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,

$$\nu_{\text{max}} = \frac{T}{0.035 \times 10^{11}} \, K^{-1} \text{Hz},$$

where T is the temperature in K, and Hz = s$^{-1}$, the SI unit of frequency.

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 temperature dependence. The best attempt was the Rayleigh-Jeans law,

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

where k is Boltzmann's constant, $R/N_o = 1.381 \times 10^{-23}$ J K$^{-1}$. 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 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,

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

where \( h \) is a constant 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, and where the energy of a quantum is given by \( E = \hbar \nu \), where \( \nu \) is the frequency of vibration of the crystal. This was a total break with classical ideas that assumed that the energy emitted could take on any value.
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 emitted. The frequency and intensity are then changed and the rate of electron emission and the kinetic energy of the electrons are monitored. Two features of the photoelectron effect disagree with classical theories. First, the experiments show that the kinetic energy of the emitted 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 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. The only thing that happened when the intensity of the light increased was that the number of electrons emitted increased.

I said at the beginning of this discussion that there were two problems with the classical theory of the photoelectric effect. The second is that, as can be seen from our discussion, one of the predictions of the 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 energy vs. frequency, we find that as we increase our frequency from 0, that there is a range in which no electrons are emitted. When we reach a threshold frequency $\nu_0$, photons are emitted with no kinetic energy. As the frequency increases from this threshold frequency, the kinetic energy of the emitted photons increases linearly.

To explain these results, Einstein postulated that light exists in little packets of energy, which G.N. Lewis labeled photons, and which had energy equal to $hv$, where $\nu$ is the frequency of the photon and $h$ once again is Planck's constant. 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, $\Phi$, plus the kinetic energy of the electron, i.e.,

$$hv = \Phi + \frac{1}{2}mv^2.$$ 

This simple equation can explain both of our observations. First, to eject an electron with zero kinetic energy requires a photon with frequency $\Phi/h$. 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

$$\frac{1}{2}mv^2 = hv - \Phi.$$ 

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

The postulate that light exists in packets of energy, i.e., in particle form, 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 $h\nu$, 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.

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 itself had to be quantized. Quantized is taken to mean that the energy comes in discrete units, or quanta. The photoelectron effect also suggests that light had characteristics of particles, a completely new idea.

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 though to be an arbitrary number obtained 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.

The next phenomena that caused trouble for classical physics were the spectra of atoms, in particular the spectrum of the hydrogen atom. 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 light itself which violated classical understanding, but the hypothesis that the motion of the electrons which emitted the light was quantized.

The emission and absorption spectra of atoms was 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 clear in the spectrum of hydrogen. Hydrogen has three main groups of emission lines. 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 8206 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 uses a unit called wavenumbers to report the positions of the lines. The wavenumber, $\bar{\nu}$, which has the units cm$^{-1}$, is defined by

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

where the wavelength is in units of cm. 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. The Rydberg formula in these units is
\[
\frac{1}{\lambda} = \nu = R\left(\frac{1}{n_2} - \frac{1}{n_1}\right)
\]

where \(n_2\) and \(n_1\) are integers such that \(n_2 > n_1\) and \(R\) is the Rydberg constant, \(109,677.5856\ \text{cm}^{-1}\). For example, the first line in the Lyman spectrum corresponds to \(n_1 = 1\) and \(n_2 = 2\), and has the wavenumber \(\nu = R(1-.25) = 82,258\ \text{cm}^{-1}\). Since \(\lambda = 1/\nu\), 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.]

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** \(p = mv\). Now consider a particle rotating in a plane around some fixed central point at a distance \(r\) from the center.
The frequency of rotation is the number of times the particle passes an angular position on the plane in a second. If the frequency of rotation is \( v_{\text{rot}} \), then the velocity of the particle is

\[
v = 2\pi v_{\text{rot}}.
\]

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

\[
\omega = 2\pi v
\]

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

\[
v = r\omega.
\]

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

\[
K = \frac{1}{2} mv^2 = \frac{1}{2} mr^2 \omega^2.
\]

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

\[
K = \frac{1}{2}I\omega^2.
\]
We see that in our two equations for kinetic energy that \( m \) corresponds to \( I \), while \( v \) corresponds to \( \omega \). What this suggests is that there should be a quantity for rotating systems that corresponds 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, \( I \), \( \omega \), and \( \ell \) are much more convenient when describing the dynamics of circular motion.
Bohr's contribution lay in the following three hypotheses.

1) Electrons in atoms have stationary orbits. I.e., the radii of the orbits are fixed.

2) The angular momentum of the electrons in these orbits is quantized according to \( \omega = mvr = n\hbar \), where \( \hbar = h/2\pi \).

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 \( \varepsilon_0 \) is a constant called the permittivity of free space, \( 8.854 \times 10^{-12} \text{ C}^2\text{N}^{-1}\text{m}^{-2} \), \( n \) is an integer greater than zero called the principle quantum number, \( e \) is the charge of an electron, \( 1.602 \times 10^{-19} \text{ C} \), and \( \mu \) 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 acts 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

\[ \mu = \frac{m_e m_p}{m_e + m_p} = \frac{9.100 \times 10^{-31} \text{kg} \times 1.673 \times 10^{-27} \text{kg}}{9.100 \times 10^{-31} \text{kg} + 1.673 \times 10^{-27} \text{kg}} = 9.095 \times 10^{-31} \text{kg} \]

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.

The second implication of Bohr's hypothesis is that the energies that an electron may 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,

\[ E_n = -\frac{\mu e^4}{8\varepsilon_0 \hbar^2 n^2} \]

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. In equation form this becomes

\[ E_{a2} - E_{a1} = \Delta E = hv. \]
If we substitute Bohr's formula for the energy of an electron in an orbit with quantum number $n$ we get

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

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

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

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

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

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$^{-1}$.

**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 key step was an experiment by **Davisson and Germer** at AT&T Bell Labs. In this experiment, they showed that **electrons accelerated near the speed of**
light and passed through a crystalline material showed interference patterns. This was a particularly astonishing experiment, 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. 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 and recombining it, 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**.

Now remember that one of the conclusions we drew from the photoelectron effect was that light had some particle characteristics. 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 \( p = \frac{h}{\lambda} \), where \( p \) is the momentum, \( h \) is Planck's constant, and \( \lambda \) is the wavelength of the photon.

After the Davisson and Germer experiment, **Louis de Broglie**, a French aristocrat turned physicist, went through a thought process something like this. Einstein showed
that light, which everyone thought was a wave, had particle characteristics, and momentum. We now know that 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

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

the de Broglie formula. De Broglie’s formula has been proven correct many times. One way that it has been confirmed is that electrons with de Broglie wavelengths in the X-ray region show the same interference patterns as X-rays of the same wavelength.

The final result that preceded the development of the 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. It is simply

$$\delta p \delta x \geq \frac{h}{2}.$$

It means that the uncertainty in the position of a particle x the uncertainty in the momentum of a particle has to be greater than or equal to Planck’s constant divided by $4\pi$. 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 is such a small number. However,
in the limit of quantum energies and quantum dimensions, the degree of uncertainty becomes significant.

Heisenberg's reasoning can be approximated as follows. 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 $\lambda$ 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 $h/2$.

The implications of this principle are far reaching. It is the death of the concept of the trajectory, which is so central to classical mechanics. A trajectory is the 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. When we talk about Bohr orbits, we are saying that the electrons in a hydrogen atom move in circular trajectories. The key point here is that in order to have well defined trajectories, you 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 electrons in solids and in atoms are limited to discrete 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 and Heisenberg’s quantum mechanics 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, 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 *The Second Creation*, by Crease and Mann, which is 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, we use the Dirac equation, 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 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 it’s 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. The wavefunctions that are obtained 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 $a \pm i b$, is called a complex number.

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

$$e^{2i\theta} = \cos \theta \pm i \sin \theta$$

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. 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 \textit{eigenfunctions} and the energies that are associated with these eigenfunctions are called \textit{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 \( \psi \), 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 - 7i, its complex conjugate is 5 + 7i. 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 $|\psi^2(x)|$.

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 **normalized function**. **All wavefunctions must either be normalized, or 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.,

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

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$^22\pi x$ 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 \( \sin^2 2\pi x \, dx \)? 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 \( z = 2\pi x \). This makes our integral

\[
B^2 \int \sin^2 z \, dz = 1
\]

We need to do two more things. First we need to match the differential with the variable \( z \). This is easy. Since \( z = 2\pi x \), \( dz = 2\pi \, dx \) which implies that \( dx = dz/2\pi \). 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 \( z = 2\pi x \), when \( x = -1/2 \), \( z = -\pi \) and when \( x = 1/2 \), \( z = \pi \). 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 \(-\pi\) to 0 as from 0 to \(\pi\), 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

\[
\frac{B^2}{\pi} = 1 \quad \text{or} \quad B = \sqrt{2}
\]

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, \( \psi(x) \) must be \textbf{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, \( \psi(x) \) must be a \textbf{continuous function}. 