

Introduction to Quantum Mechanics

At the beginning of the 20th century, classical physics (CP) seemed to be capable of explaining almost every physical phenomenon. However, there were a few phenomena that posed intractable problems. In time, they pushed physics to reevaluate the fundamental laws describing matter and energy. The newly formulated laws are called quantum mechanics (QM) (or more generally quantum electrodynamics, but we needn't be concerned with that). QM is particularly necessary for describing the universe at the very small scale of molecules, atoms, and subatomic particles. As we will see, QM and CP become essentially equivalent for things of large size (**classical correspondence principle**). This is reassuring because it affirms the process of scientific observation and the formulation of theories that gave rise to CP in the first place; the only difficulty is that those observations were of things of macroscopic scale, and as it turns out the conclusions were not transferable to the submicroscopic scale.

QM is essential to chemistry because several realms of chemical phenomena are understandable only with reference to it. Examples are:

- Periodic trends in the periodic table
- Chemical bonding
- Spectroscopy: interaction of matter with electromagnetic radiation

In introductory chemistry, you were exposed to QM briefly. When you discussed atomic orbitals ($s, p, d, f \dots$), quantum numbers (n, l, m_l, m_s), hybrid orbitals and valence bond theory, molecular orbitals and molecular orbital theory, you were dealing with QM. In this course, we want to deepen your understanding of QM and to extend it to spectroscopy, which is not usually covered in introductory chemistry. We have only a brief time, and so we will concentrate on the principles. That will give you a foundation for expanding your knowledge in the future if the need arises.

These lecture notes have been prepared because we will have to cover selected topics from several chapters in the text in a short time. These notes should bring the concepts together and guide your studying.

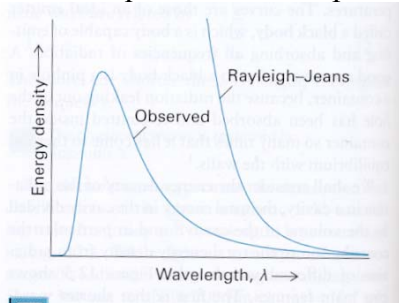
Failures of Classical Physics

The most important phenomena that CP was incapable of explaining are:

- Blackbody radiation
- Heat capacities of solids
- Photoelectric effect
- Line spectra
- Electron diffraction

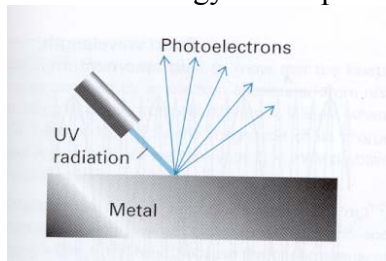
A **blackbody** is an object that emits radiation upon heating. The coil of an electric stove is an example. It is black at low temperature but emits electromagnetic radiation (EMR) and turns red when heated (and would turn blue if heated further). CP asked the question: can we predict the frequencies of EMR emitted by a blackbody when it is heated? The answer was yes, under a few assumptions: that EMR had the properties of waves, with the corollary that any amount of radiation could be emitted, from a tiny bit as tiny as you like, to a large amount, depending on the heat available to convert to EMR. CP predicted that at any particular temperature, EMR would be emitted with a whole range of frequencies. The distribution of frequencies changes with temperature.

However, the application of CP to blackbodies yielded an absurd result, called the “**ultraviolet catastrophe**”: that for any given temperature, the amount of energy given off as EMR (more precisely, the “energy density”) increases as frequency (ν) increases (or equivalently, as wavelength (λ) decreases) and keeps increasing toward infinity. (This distribution is known as the “Rayleigh-Jeans law.”) Clearly the amount of energy emitted by a blackbody in the form of EM cannot be infinite. Everyone understood it was absurd, but no one could figure out the problem with the theory. We will not be concerned with equations for this phenomenon but will note the result graphically:



We met **heat capacities** in thermodynamics, where we saw that they represent, loosely put, the amount of energy required to raise the temperature of one mole of a sample by one degree (we were careful to distinguish between C_v and C_p). Different substances have different heat capacities, and it became a challenge to predict the heat capacity of a substance on the basis of its other properties. Two French scientists, Dulong and Petit, proposed a theory that seemed to explain the heat capacities of monatomic solids quite well. It was based on assumptions about the vibrations that individual atoms and groups of atoms within the solid matrix undergo. Central to the theory was that vibrations of any frequency are allowed. The theory matched experiment quite well at moderate to high temperature, but at low temperature it predicted a heat capacity much too high. The failure was obvious, but the reason for it was not.

The **photoelectric effect** was particularly perplexing. When a metal is irradiated with ultraviolet (UV) radiation, electrons (called photoelectrons in this context) are ejected. Escaping the surface of the metal requires that an electron have at least a certain minimum energy whose value depends on the metal, much as a rocket must have a certain minimum energy to escape the Earth’s gravitational field.



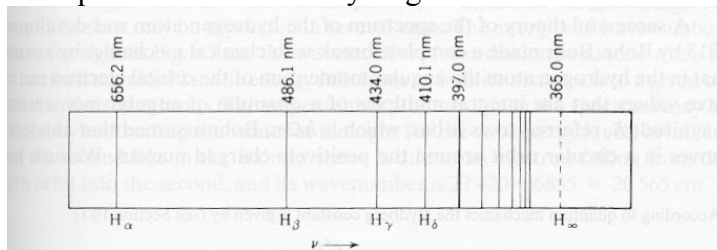
The experimental observations of the photoelectric effect are listed below, together with what CP would have expected. Note that the CP expectation is based on the idea that EMR is purely a wave phenomenon.

- No electrons are ejected, no matter how long the period of irradiation, unless the frequency of EMR is greater than a certain minimum value. *CP expectation: any frequency should lead to ejection of an electron, although larger frequencies would require greater time because they carry less energy per unit time.*

- The kinetic energy of the electrons varies linearly with the frequency of EMR but is independent of the intensity. *CP expectation: unclear. If electrons are emitted as soon as they acquire sufficient energy, all should have the same small kinetic energy. In any case, kinetic energy should depend on the frequency and intensity of EMR in the same way.*
- Even at low intensity, some electrons are ejected immediately if the frequency is above the threshold value. *CP expectation: electrons should never be emitted immediately, because the EMR wave must “wash over” the electron until enough has been absorbed to allow ejection.*

Clearly, there was a problem with the CP picture.

It is found that when gases are heated, they emit EMR of particular frequencies (or, equivalently, wavelengths). The spectra of emitted EMR are therefore called **line spectra** (each emitted frequency corresponds to a spectral line). From the standpoint of CP, this is a perplexing phenomenon. When EMR is emitted, a molecule itself must lose energy so that total energy is conserved. This can correspond to a decrease in the energy of internal vibrational, rotational, or electronic energy. But why should only particular frequencies of radiation be allowed? There are no obvious restrictions on the amount of internal vibrational, rotational, or electronic energy a molecule can possess...from the point of view of CP. (Later, we will see that QM imposes definite restrictions.) A sample line spectrum for atomic hydrogen is shown below.



The final experiment we will mention is the **diffraction of electrons**. Diffraction, like refraction, had been understood as a property of waves. Diffraction is caused by the interference between waves caused by an object placed in their path, and it results in a pattern of light and dark fringes. It was found that an electron beam pointed at a metal surface gave rise to a diffraction pattern (Davisson-Germer experiment). Could it be that electrons, thought in CP to be particles, have some properties characteristic of waves?

Wave-particle duality and formulation of concepts undergirding QM.

Until these perplexing phenomena were recognized, scientists had sharply distinguished two kinds of physical phenomena: particles and waves. A sampling of properties of each and the laws they obey (according to CP) are listed below:

<u>Particle</u>	<u>Wave</u>
mass	wavelength
momentum	frequency
velocity	velocity
$F = ma$	$\frac{d^2\Psi}{dt^2} = v^2 \frac{d^2\Psi}{dx^2}$

The failures of CP described above suggested that at times, EMR exhibits properties formerly thought to belong exclusively to particles, while electrons exhibit properties formerly thought to belong exclusively to waves. Thus the distinction between waves

and particles became blurred, and we speak now of the wave-particle duality. The ideas extend beyond electrons and EMR to all small entities. In general, we find that as an entity's mass increases, its particle nature becomes more important and its wave nature becomes less important. We will now discuss a few of the concepts that led to the formulation of mature QM theory.

Einstein, on the basis of a related idea put forward by Planck, proposed that EMR is emitted and absorbed in small packets called **photons**, and the energy of an individual photon is related to its frequency by

$$E = h\nu$$

Thus EMR has both a particle nature and a wave nature. This quantization of EMR was able to solve the conundrums of blackbody radiation, heat capacities of solids, and the photoelectric effect.

De Broglie proposed that a wavelength could be assigned to particles, and that the wavelength is related to the momentum by

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

where h is a constant ($h = \text{Planck's constant} = 6.626 \times 10^{-34} \text{ Js}$). In this context, λ is called the **de Broglie wavelength**. Note the inverse relation between λ and p .

De Broglie's reasoning is suggested by the following: for matter, $E = mc^2$ while for EMR, $E = h\nu = \frac{hc}{\lambda}$. Equating the two relationships, substituting the general velocity v for the speed of light c , and recognizing $mv^2 = \frac{(mv)^2}{m} = \frac{p^2}{m}$ yields $\frac{p^2}{m} = \frac{h\nu}{\lambda}$ or, upon multiplying by m , $p^2 = \frac{hmv}{\lambda} = \frac{hp}{\lambda}$. This simplifies to the de Broglie relationship.

Recognizing that electrons possess the property of wavelength explains why they exhibit diffraction.

Heisenberg proposed a famous relationship which has since been called the **Heisenberg uncertainty principle**:

$$\Delta x \cdot \Delta p \geq \frac{\hbar}{2} \quad \left(\hbar \equiv \frac{h}{2\pi} \right)$$

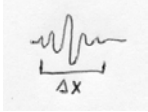
where Δx is interpreted as uncertainty in position and Δp as uncertainty in momentum. This comes from combining a property of waves with the de Broglie relationship. Waves obey the relationship:

$$\Delta x \cdot \Delta \left(\frac{1}{\lambda} \right) \geq \frac{1}{4\pi}$$

Substituting for λ in the above equation leads to Heisenberg's equation. But what does the above equation mean? Consider a sinusoidal wave having a particular wavelength:



This wave continues infinitely in both directions. Consequently we would say that it is unconfined in position ($\Delta x = \infty$), but the wavelength (and consequently its reciprocal) has one precise value ($\Delta\left(\frac{1}{\lambda}\right) = 0$).

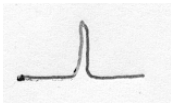


This waveform is somewhat localized in space (Δx as shown as is clearly not infinite). This wave is not a simple sinusoidal wave, but it can be formed by summing several sinusoidal waves having different wavelengths:



Therefore one cannot speak of the waveform as possessing one particular wavelength. One can, though, describe the range of wavelengths (or their reciprocals) one needs to

sum to get the waveform: $\Delta\left(\frac{1}{\lambda}\right) = \frac{1}{1} - \frac{1}{1.2} = 0.17$



This waveform is completely localized in space ($\Delta x = 0$). To create this waveform from simple sinusoidal waves, one would need to sum an infinite number having different wavelengths, and one would find $\Delta\left(\frac{1}{\lambda}\right) = \infty$.

If one continues this analysis and makes it mathematically precise, one obtains the relationship between Δx and $\Delta\left(\frac{1}{\lambda}\right)$ given above. For waves, Δx and $\Delta\left(\frac{1}{\lambda}\right)$ are

interpreted as a **localization** in terms of space and reciprocal wavelength, respectively. The Heisenberg uncertainty principle, though, is interpreted as **uncertainty** in position and momentum. One can measure position precisely, but then one has no idea about momentum. Or one can measure momentum precisely, but then one has no idea about position. Or one can measure both to moderate precision. This relationship seems paradoxical, but it has been confirmed many times. The properties of position and momentum are called **conjugate**. There are other pairs of conjugate properties, and they also exhibit an uncertainty relation. An example is energy and time:

$$\Delta E \cdot \Delta t \geq \frac{\hbar}{2}$$

Proposal of Schrödinger equation

In the 1920s, Erwin Schrödinger proposed a new equation, similar to the wave equation but different in an important way, that describes the behavior of material objects. This equation is called the **Schrödinger equation**, and it is given below together with the wave equation for comparison:

Wave equation

Schrödinger equation

$$\frac{d^2\Psi}{dt^2} = v^2 \frac{d^2\Psi}{dx^2} \qquad -\frac{\hbar}{i} \frac{d\Psi}{dt} = -\frac{\hbar^2}{2m} \frac{d^2\Psi}{dx^2} + V\Psi$$

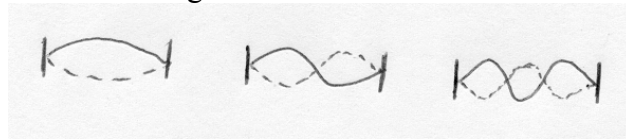
where v is velocity, t is time, x is position (in one dimension), i is the square root of negative one, and V is potential energy. The symbol Ψ is a function describing the wave itself. An example solution is a sine function, which you can verify satisfies the equation by substitution.

$$\Psi = A \sin\left(\frac{2\pi}{\lambda} x - \frac{2\pi}{\lambda} vt\right)$$

Here A is the amplitude of the wave, and λ is the wavelength. A cosine function would also satisfy the equation (try it). Note that Ψ depends on both x and t .

Note that whereas the wave equation takes a **second derivative with respect to time**, the Schrödinger equation takes a **first derivative**. One cannot derive the Schrödinger equation from the wave equation by using the de Broglie relationship or some other equivalence. The Schrödinger equation was a brand new hypothesis.

Have you ever plucked a metal guitar string and seen the string vibrate, but the vibrations seem to stand in place? The phenomenon is known as a **standing wave**, and it results when an incoming wave is reflected at a clamped endpoint. The interference pattern of the incoming and reflected waves results in a waveform that does not seem to move. The amplitude changes from positive to negative, but otherwise the wave doesn't seem to change. The pictures below represent standing waves of different wavelength "trapped" between two clamped endpoints. The solid curves represent the amplitude at one time, and the dashed curves represent the amplitude a short interval later; after yet another interval, the wave would again look like the solid curves.



As we will see, an electron in an atom (or molecule) is much like a standing wave. In fact, an atomic orbital is the electron's equivalent of a standing wave. The nucleus "traps" the electron much as the end-clamps "trap" the waves pictured above. Often, we are not concerned about the time behavior of the standing wave or electron, but we care very much about time-independent properties of the waveform (for example, the points at which the amplitude is always zero, which are called **nodes**). From the wave equation and the Schrödinger equation above, it is possible to derive simpler equations that describe eliminate the time behavior and describe the standing wave. (The transformation involves a technique called separation of variables, but that is for another course.) The resulting time-independent equations are:

Time-independent forms of the equations

Wave equation

$$-\frac{d^2\psi}{dx^2} = \left(\frac{2\pi}{\lambda}\right)^2 \psi$$

Schrödinger equation

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

where E represents total energy (kinetic plus potential).

Notice, incidentally, that the time-independent Schrödinger equation can be rearranged to

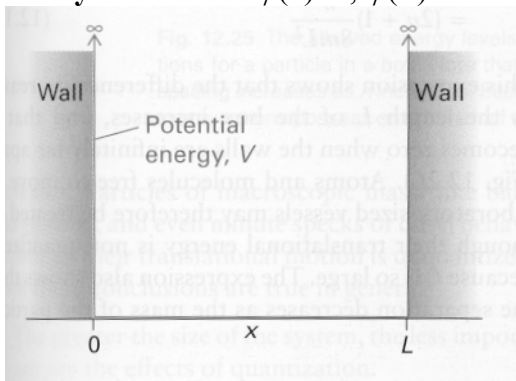
$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = (E - V)\psi = \frac{p^2}{2m} \psi$$

where we have recognized that $E-V=K=p^2/2m$ where E is total energy, V is potential energy, and K is kinetic energy. This equation can be rearranged to give the wave equation, if you use the de Broglie relationship between λ and p (try it)! However, do not be misled into believing Schrödinger's insight was this simple. The time-dependent form of the Schrödinger equation, which is the more general one, cannot be derived from the time-dependent wave equation. Remember, one has a first derivative with respect to time, while the other has a second derivative. Schrödinger's idea was a daring, new hypothesis—which has stood up to every test since it was proposed.

Simple examples of problems using Schrödinger

It is very fortunate for us that solutions to the Schrödinger equation (SE) for simple problems are often closely related to solutions to more complicated problems of great interest. We will begin by looking at three one-dimensional problems in detail. We will see that there are two things to pay attention to: the **potential energy** and the **boundary conditions**.

The first is often described as the **particle-in-a-box** problem. We envision a particle confined to a particular region. We accomplish this by letting the potential energy be huge (infinite) everywhere except in the region where the particle is allowed; there the potential energy is zero. This essentially constructs very high “walls” so that the particle cannot escape. As a consequence, the wave function must be zero everywhere except inside the “box,” which means that the value of ψ is zero at both ends of the box. Defining the ends of the box as $x=0$ and $x=L$ yields the following conditions, called **boundary conditions**: $\psi(0)=0$, $\psi(L)=0$.



Within $x=0$ to $x=L$, the Schrödinger equation is

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

Two solutions for this equation are

$$\psi = \sin\left(\frac{\sqrt{2mE}}{\hbar}x\right) \text{ and } \psi = \cos\left(\frac{\sqrt{2mE}}{\hbar}x\right)$$

(Plug each of these functions in to the SE to satisfy yourself that they are solutions.) A more general solution is

$$\psi = N \sin\left(\frac{\sqrt{2mE}}{\hbar} x\right) + M \cos\left(\frac{\sqrt{2mE}}{\hbar} x\right)$$

where N and M are constants (plug in again to satisfy yourself). However, if we apply the boundary conditions, we find that M must be zero, and only particular values of E are allowed, so that the acceptable solutions can be written:

$$\psi_n = N \sin\left(\frac{n\pi x}{L}\right) \quad \text{where } n = 1, 2, 3, \dots$$

We put a subscript n on ψ to emphasize that there are many solutions, each corresponding to a particular value for n . Notice that n must be a positive integer. Also notice that, since a sine wave of wavelength λ has the form $\sin(2\pi/\lambda)$, the allowed wavelengths are:

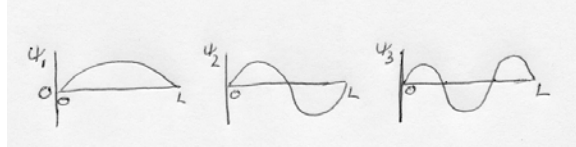
$$\lambda = \frac{2L}{n} \quad n = 1, 2, 3 \dots$$

The corresponding values of E turn out to be:

$$E_n = \left(\frac{n^2 \hbar^2}{8mL^2}\right)$$

Thus we find that there are many solutions to the SE, but only particular wavelengths and particular energies are allowed. We describe this situation by saying that the energy is **quantized**, and we therefore we call n a **quantum number**. Note that n can only take on particular, integral values. We will find that quantum numbers turn up frequently in quantum mechanics.

The first few acceptable wave functions look like this:



Suppose that we performed an experiment to find out where the particle was at a particular time. Each time we performed the experiment, we would get one particular value. If we performed the experiment many times, we would get a distribution of values. We might ask how this distribution is related to ψ . In other words, is the probability of finding the particle at a particular region of the box is related to the wave function? The answer is that there is a relationship, and the probability is proportional to $|\psi|^2$ (we use the absolute values because, for general problems, ψ can be a complex number). More precisely, we write

$$P \delta\tau = |\psi|^2 \delta\tau$$

where $P \delta\tau$ is the probability of finding the particle within a small region of space $\delta\tau$ (P itself is called the probability density.) This interpretation of $|\psi|^2$ is called the **Born interpretation**. Notice for that according to the Born interpretation, the probability of finding the particle is not the same everywhere in the box. In fact, at the nodes there is zero probability of finding the particle! More generally, it turns out that all properties of a system can be determined from the wave function. Therefore we often call ψ_n the **state of the system** (each value of n corresponds to a different state).

There are a few properties of the energy to pay close attention to. (1) Only particular values of the energy are allowed (energy is quantized). (2) The smallest allowed value of the energy is not zero; it is $\frac{h^2}{mL^2}$. This is called the **zero-point energy**. (3) As the energy increases, so does the number of nodes

Thus we have already seen several peculiar properties of quantum mechanical systems on the basis of this one simple problem: only particular states of the system are allowed, the energy may be quantized, the zero-point energy may not be zero, and the probability of finding the particle in particular regions of space may not be what we would expect intuitively.

The second simple problem is a **particle confined to move on a circular ring** of radius r . (This is an example of one-dimensional rotational motion.) The potential energy is defined as zero everywhere. Consequently the Schrödinger equation is once again

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

We won't worry about a functional form for ψ , but we will think about the allowed wavelengths. This time the boundary condition is given by the fact that $\psi(2\pi r)$ must be the same as $\psi(0)$, since otherwise ψ would not be single-valued! This means that an integral number of wavelengths must fit into one circumference of the ring, i.e.

$$\lambda = \frac{2\pi r}{m_l} \quad \text{where } m_l = 0, 1, 2, \dots$$

where we have this time given the quantum number the symbol m_l (because it will turn out to be analogous to the quantum number m_l for an electron in an atom). Once again, we see that only particular wavelengths are allowed. What about the energy? Since the potential energy is zero everywhere, the energy is entire kinetic, so

$$E_{m_l} = \frac{p^2}{2m} = \frac{(h/\lambda)^2}{2m} = \frac{(m_l h / 2\pi r)^2}{2m} = \frac{m_l^2 \hbar^2}{2mr^2} = \frac{m_l^2 \hbar^2}{2I}$$

where I is the moment of inertia, defined as $I \equiv mr^2$. Rotational motion (one-dimensional).

We have one final note about the particle on the ring. It concerns a property called the angular momentum. More specifically, we are referring to the angular momentum about a particular axis, in this case one through the center of the ring and perpendicular to it. We will let this be the z axis, and label the corresponding angular momentum J_z . It is given by:

$$J_z = pr$$

Substituting for p gives:

$$J_z = \left(\frac{h}{\lambda}\right)r = \frac{m_l \hbar}{2\pi r} r = m_l \hbar \quad \text{where } m_l = 0, 1, 2, \dots$$

Thus the angular momentum, like the energy, is quantized. Angular momentum will turn out to be important for understanding the quantum mechanical behavior of atoms and molecules.

The last simple system we will look at is the harmonic oscillator. It will later be important for understanding infrared spectroscopy of molecules. Picture two particles connected by a spring (much as two atoms can be connected by a chemical bond). The spring has a force constant, k , and an equilibrium length, r_0 . If the string is stretched or compressed, it experiences a restoring force proportional to the distortion from the equilibrium geometry:

$$F = -kx \quad \text{where } x \equiv r - r_0$$

where k is a force constant characteristic of the spring. The negative sign ensures that the direction of the force is toward the equilibrium spring length (neither stretched nor compressed), which corresponds to $x=0$.

To apply the Schrödinger equation, we need a potential energy function, V . This can be obtained from F by recognizing that F and V are related by

$$F = -\frac{dV}{dx} \quad \text{or, inverting} \quad V(x) = -\frac{1}{2} \int_0^x F dx = \frac{1}{2} kx^2$$

The Schrödinger equation corresponding to this V can be solved exactly. We will not be concerned with the mathematical form of the solutions. We will, however, compare a graph of this harmonic potential function V with the V for a particle in a box. Both are “wells” (low energy is at the bottom of the well), but the slopes of the sides are different: vertical for a particle-in-a-box; parabolic for a harmonic oscillator.

[pictures of V(PIB) vs V(HO)]

As you might have guessed, there are infinitely many solutions to the harmonic oscillator, but they correspond to discrete energies. That is, once again, the energy is quantized. The first several wave functions look like this:

[picture of first several HO wave functions]

If you compare the lowest-energy harmonic oscillator wave function with the lowest energy particle-in-a-box wave function, you see similarities. Both have a single maximum. But the harmonic oscillator is not a sine function; it decays to zero less more slowly. That is because the potential energy function is not infinite at any finite value of x , and as a consequence, the harmonic oscillator wave function is not forced to be precisely zero at any finite value for x . To be sure, the probability for finding the system with a particular value of x becomes very small as $|x|$ gets large (that is, the spring is unlikely to be stretched or compressed by a large amount).

The energies of the harmonic oscillator wave functions are

$$E_v = (v + \frac{1}{2})h\nu \quad \text{where } v = 0, 1, 2, \dots$$

where we use the symbol v for the quantum number, h is Planck’s constant, and ν is a constant related to the force constant and the mass by:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

(we won’t derive this expression here). Note that the energy levels are equally spaced; the difference between successive levels is $h\nu$. Also note that the zero-point energy (lowest energy, corresponding to $v=0$) is $\frac{1}{2}h\nu$. Once again, the system can never have an energy of zero, and consequently, we cannot picture the system is ever completely at rest!

We encounter another odd feature of quantum mechanics if we consider the kinetic energy of the harmonic oscillator. Consider the lowest-energy state of the system, for

which the total energy is the zero-point energy $E_0 = \frac{1}{2}h\nu$. When the “spring” is stretched just enough, the potential energy will equal the total energy. This will occur for the following values of x :

$$V = \frac{1}{2}x^2 = \frac{1}{2}h\nu \Rightarrow x = \pm\sqrt{h\nu}$$

The positive value corresponds to stretching; the negative value corresponds to compression. For these values of x , the kinetic energy, which is the difference between the total energy and the potential energy, is zero. Now the wave function has nonzero values for larger (or smaller) values of x than these. This implies that the particle can penetrate into these regions, and that there the kinetic energy is negative! Clearly this has no classical analogy; classically, a negative kinetic energy makes no sense. However, this prediction of quantum mechanics, that there is a finite probability that a particle may be found in a region corresponding to negative kinetic energy, has been validated many times. We often use the term “tunneling” to describe the penetration of a quantum mechanical particle into a region where the total energy is less than the potential energy (i.e., kinetic energy is negative). The most common scenario is of a particle approaching a potential energy barrier with less energy than the height of the barrier. Classically, the particle will be always be reflected; quantum mechanically, there is a small but nonzero probability of passing through the barrier.

It turns out that the probability of tunneling decreases rapidly as the mass of a system increases and is rarely important in chemistry for the motion of heavy atoms. However, it can be important for hydrogen. In fact, it is the source of the deuterium isotope effect that is so useful for studying reaction mechanisms. Deuterium (^2H) and protium (^1H) are nearly identical chemically, but protium is a much better “tunneler.” Consequently, if a hydrogen (or proton) transfer is the rate-limiting step in a reaction, substitution of deuterium for protium will alter the rate constant.

Let us summarize what we have seen for these few simple systems:

(1) To solve the Schrödinger equation, we need to know the shape of the potential energy function, V (that is, we need to know V as a function of x).

(2) There may be infinitely many solutions for the Schrödinger equation for a given physical system.

(3) Often, only particular values of the total energy, E , are allowed. Then energy is quantized.

(4) Quantum numbers (such as n , l , m_l , and m_s) are a mathematical consequence of the Schrödinger equation. The dimensionality of the system and the form of the potential energy function dictate how many quantum numbers there are and how they are related to the physical system.

(5) The lowest energy a quantum mechanical system is permitted to have is called the zero-point energy. Often the zero-point energy is greater than zero; in such a case, the system can never be completely at rest. The zero-point energy has many important consequences. For example, it can make it difficult to construct physical experiments in which the temperature approaches absolutely zero closely.

(5) Often, the wave function is nonzero (though generally small) in regions where the potential energy exceeds the total energy, i.e. the kinetic energy is negative. This is called tunneling. Tunneling is important in chemistry mainly for electrons and hydrogen,

which have small masses. One example of the importance of tunneling for chemistry is the deuterium isotope effect.

We will now explore three applications of quantum mechanics to chemistry. (1) The energies and wave functions of electrons in atoms (and, by extension, in molecules). (2) The absorption of EMR in the microwave region of the spectrum by diatomic molecules, which can be understood with the particle-on-a-ring model above. (3) The absorption of EMR in the infrared region of the spectrum by diatomic molecules, which can be understood with the harmonic oscillator model above.

Consider an atom or ion that contains a single electron (e.g. H, He⁺, Li²⁺ etc.). The electron will be attracted to the nucleus because the charges are opposite. To analyze the system, we need the potential energy. The force is inversely proportional the square of the distance (Coulomb's law); the corresponding potential energy is therefore inversely proportional to the first power of the distance:

$$V = \frac{-Ze^2}{4\pi\epsilon_0 r}$$

Here e is the magnitude of the charge on an electron, and Z is the number of charge units on the nucleus (1 for H, 2 for He etc.). The negative sign signifies that the electron and nucleus have opposite charges. You main thing to notice in the denominator is r , but for completeness we note that ϵ_0 is the permittivity of a vacuum (a constant). A graph of V vs r is shown below, and the allowed energy levels are marked. Because the force between the electron and nucleus is attractive, the potential energy is a well that traps any electron with less than the ionization energy. Of course, since the walls of the potential energy well are not vertical, there is a nonzero though small probability of finding the electron even a fairly large distance from the nucleus.

[graph of V vs r for H atom]

We will not derive solutions to the Schrödinger equation for a single-electron atom or ion, but we will observe pictures of them. They are just the s , p , d , ... orbitals you met in inductory chemistry:

[pictures of orbitals]

The wave functions depend on four quantum numbers: n , l , m_l , and m_s . Three coordinates are required to specify the location of the electron with respect to the nucleus (x , y , z ; or r , θ , ϕ), and there are three corresponding quantum numbers (n , l , m_l). The last quantum number, m_s , arises because electrons have a property called spin. The quantum number n , the principal quantum number, describes how large the orbital is, that is, whether electrons in it tend to be close to or far from the nucleus. The quantum numbers l and m_l , called the secondary and the magnetic quantum number, respectively, describe the shape or the orbital. Notice that orbitals can have nodes, and the number of nodes for orbitals with a given value of l increases with n . We will not discuss these quantum numbers further, as you met them in introductory chemistry.

If we add a second electron to an atom or ion, the potential energy function becomes more complicated. There is a second attractive Coulombic term for the interaction or the second electron with the nucleus, and there is a repulsive Coulombic term describing the interaction of the electrons with each other:

$$V = \frac{-Ze^2}{4\pi\epsilon_0 r_1} + \frac{-Ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

where r_1 and r_2 label the distances of electrons 1 and 2 from the nucleus, and r_{12} is the distance between the two electrons. If the repulsive term were neglected, the wave function would just be two orbitals of the type we met above, one for electron 1 and one for electron 2 (there are issues associated with the indistinguishability of electrons, but we will suppress those for now). The presence of the repulsive term alters the orbitals somewhat, but their shapes remain roughly the same. Therefore we can continue to speak of s , p , d , etc. orbitals. There is an important qualitative difference in the energies, though. Without the repulsive term, the energy depends only on the principal quantum number, n . When the repulsive term is included, the energy also depends on l . Therefore, for example, the 2s and 2p orbitals have identical energies for H (or He^+ or C^{5+}), but different energies for He (or C or ...).

What about an electron in a molecule? We will confine our discussion to the simplest possible case: H^{2+} , which is an ion with two nuclei but only one electron. The potential energy function is now:

$$V = \frac{-Z_a e^2}{4\pi\epsilon_0 r_a} + \frac{-Z_b e^2}{4\pi\epsilon_0 r_b} + \frac{Z_a Z_b}{4\pi\epsilon_0 r_{ab}}$$

where Z_a and Z_b are the charges on nuclei a and b (both 1 for H^{2+}), r_a and r_b are the distances of the electron from nucleus a and b , and r_{ab} is the distance between the nuclei. One can often predict the shape of the wave function from the form of the potential energy function. The interesting thing about this ion is that the orbitals, which of course correspond to wave functions, are now spread out in space around both nuclei. This is because the electron is attracted to both nuclei and spends some time in the vicinity of each. We often refer to such orbitals as molecular orbitals (MOs), as opposed to the atomic orbitals (AOs) discussed above.

[picture of MOs of H_2^+]

The orbital on the left is called a bonding orbital because the electron spends much time between the nuclei, which corresponds to a chemical bond. The orbital on the right is called antibonding, because the electron is not found between the nuclei often.

The solutions to the SE for a hydrogenic atom are the atomic orbitals 1s, 2s, 2p, etc.

If an atom has more than one electron, the electron-electron repulsion distorts the orbitals a little and increases their energies.

The solution to the SE for a complicated problem is often similar to the solution to the SE for a related, simpler problem.

Aufbau principle.

Wave functions can be expressed as linear combinations of basis functions.

Cartesian space: three basis functions needed

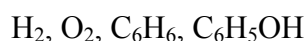
Function (Hilbert) space: infinite number of basis functions needed

Solutions to the SE for a simple problem often form a set of basis functions for constructing the solution to the SE for a more complicated problem.

Molecules have molecular orbitals (MOs) because each electron feels attractive force of all the nuclei (and repulsive force of all the other electrons).

The wave function for the molecular ion H_2^+ can be constructed from solutions to the SE for neutral atom H.

Inner MOs look very much like AOs, but outer MOs are often delocalized over several nuclei.



Reactions generally involve outer MOs, so delocalization is important for understanding reactivity.

Diels-Alder reaction

MO theory successful for explaining:

Reactivity

Spectra

However, MO theory does not give a good description of chemical bonds.

Valence bond (VB) theory concentrates on chemical bonds.

Total wave function can be constructed directly from atom-centered functions instead of from MOs. The atom-centered functions are the hybridized orbitals you are familiar with (sp^2 , sp^3 etc.)

We don't have time to talk much about VB theory. Both MO and VB theories are valid, both are useful, they are complementary, they bring different insights, both are usually used in an approximate form, and both can be made as exact as you want by doing a lot of work.

Historically, VB was developed first, later MO theory was much preferred and VB theory fell into disfavor, but today VB has experienced a renaissance.