3 The Harmonic Oscillator

What we have been doing over the last few weeks has been somewhat abstract and at times seemed far removed from chemistry, although as you will see throughout the year, it will be quite relevant.

Today I would like to begin a discussion of a problem in quantum mechanics that has clear and important practical implications in chemistry: *the harmonic oscillator.*

Its importance is derived from the fact that to a good approximation, vibrational motions of molecules can be modeled as harmonic oscillators. As we will see more clearly later in the course, transitions between vibrational energy levels of molecules (*i.e*., the eigenstates of the Hamiltonian for vibrational motion) lead to absorption of light in the infrared region of the spectrum. The manner in which a molecule absorbs infrared light is a fingerprint of that molecule and hence a valuable tool for molecular identification. Moreover, properties such as heat capacities and chemical reaction rates are strongly linked to a molecules vibrational motion. Thus, a good place to begin to understand molecular vibrations is the harmonic oscillator problem.

The energy levels of a diatomic molecule are very closely predicted by solving the quantum mechanics of a harmonic oscillator, and while those of polyatomic molecules may seem quite a bit more complicated, to first order they can be considered as a superposition of harmonic oscillator energy levels. So the principles we will learn here will be applicable not only to diatomics but to polyatomics as well.

Brief outline of what we will do:

1. After defining what we mean by a harmonic oscillator, we will treat the problem using classical mechanics.

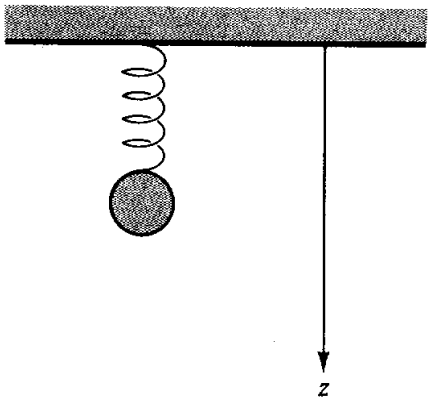
2. We will then introduce the solutions of the time-independent Schrödinger equation for a harmonic oscillator and look at the nature and properties of the eigenvalues and eigenfunctions. Here we will introduce a few new concepts that I did not mention in our previous simple models.

3. We will then go back and work through the mathematics required to arrive at the solution. The form of the Schrödinger equation is more difficult than those we have already solved, and we will have to introduce some new mathematical approaches to solve it.

3.1 Classical Harmonic Oscillator

Let us begin by defining what we mean by a harmonic oscillator.

As depicted below, consider a mass connected to a wall by a spring. The only force on the mass is from the spring.



As you would expect, the force on the mass will be some function of the displacement of the spring from its equilibrium value.

Let the displacement of the spring from its equilibrium value be denoted by x so that $x = z - l_0$. The *harmonic approximation* states that the force on the mass is simply proportional to the displacement from the equilibrium position, that is

$$F = -k(z - l_0) = -kx$$

This is a statement that the spring obeys *Hooke's Law*.

The negative sign indicates that the force acts to restore the mass to its equilibrium position. If we define positive z as the downward direction, then when z is greater than l_0, the force is negative; that is, it acts in the upward direction restoring the mass to its equilibrium position. If $z<l_0$, the force is positive and pushes the mass down.

The proportionality constant k represents the stiffness of the spring. A very high value of k would represent a stiff spring, which would require a large force to compress or extend, and a low value of k represents a loose, floppy spring, which is easy to compress or extend.

To solve the classical problem, we start with Newton's second law, $F = ma$.

$$F = ma = m\frac{d^2z(t)}{dt^2} = -k\left(z(t) - l_0\right)$$

We have simply set the mass times the acceleration equal to the Hooke's Law force.

Using $x(t) = z(t) - l_0$

We find that $\frac{d^2z(t)}{dt^2} = \frac{d^2x(t)}{dt^2}$

so $m\frac{d^2x(t)}{dt^2} = -kx(t)$

$$\frac{d^2x(t)}{dt^2} + \frac{k}{m}x(t) = 0$$

This is a linear second order differential equation with constant coefficients.

Let us guess a solution of the form:

$$x(t) = e^{\alpha t}$$

Substituting this into the differential equation:

$$\alpha^2 e^{\alpha t} + \frac{k}{m}e^{\alpha t} = 0$$

$$\alpha^2 + \frac{k}{m} = 0$$

$$\alpha^2 = -\frac{k}{m} \quad \Rightarrow \quad \alpha = \pm i\sqrt{\frac{k}{m}}$$

Let's set

$$\omega = \sqrt{\frac{k}{m}} \qquad \text{so} \qquad x(t) = ce^{\pm i\omega t}$$

The most general solution is

$$x = c_1 e^{+i\omega t} + c_2 e^{-i\omega t}$$

Remember we showed earlier in the course that using Euler's formula we could write this

$$x(t) = A\cos(\omega t) + B\sin(\omega t)$$

where A and B are just combinations of c_1 and c_2.

We can evaluate the constants A and B by considering the initial conditions (*i.e.* the conditions at t=0). Suppose we stretch the spring to a length z_0 so that its initial displacement is $x_0 = z_0 - l_0$ and then let it go.

$$x(t=0) = x_0 = A\cos(0) + B\sin(0) \qquad \Rightarrow \qquad A = x_0$$

Thus

$$x(t) = x_0\cos(\omega t) + B\sin(\omega t)$$

The initial velocity is zero since we start at rest. The velocity is just given by

$$\mathrm{v}(t) = \frac{dx(t)}{dt} = -x_0\omega\sin(\omega t) + B\omega\cos(\omega t)$$

so

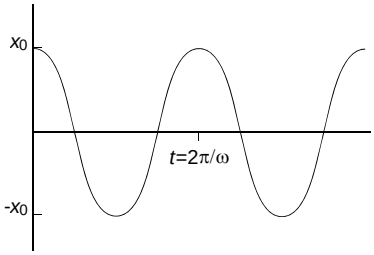
$$\mathrm{v}(t=0) = 0 = -x_0\omega\sin(0) + B\omega\cos(0) \qquad \Rightarrow \qquad B = 0$$

Thus

$$x(t) = x_0\cos(\omega t)$$

where $\omega = \sqrt{\frac{k}{m}}$ from the boundary conditions given above.

If we plot the displacement from equilibrium $x(t)$ versus t it looks like the following:



The displacement of the mass oscillates between x_0 and $-x_0$ with a frequency of ω radians/sec or $\omega/2\pi$ cycles/sec.

Let us look at the potential, kinetic, and total energy of the harmonic oscillator.

Remember the force is given by:

$$F = -kx$$

From classical mechanics, we know that a force can be expressed as a derivative of the potential energy

$$F(x) = -\frac{dU(x)}{dx}$$

where $U(x)$ is the potential.

We can therefore express $U(x)$ as:

$$U(x) = -\int F(x)dx$$

$$= \int kx\,dx$$

$$= \frac{1}{2}kx^2 + c$$

The integration constant here is arbitrary and can be used to fix the absolute zero of energy. This is usually taken to be zero when $x = 0$.

Therefore the potential energy of a harmonic oscillator is

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

or, as a function of time:

$$U(t) = \frac{k}{2}x_0^2\cos^2(\omega t)$$

The kinetic energy can be given by

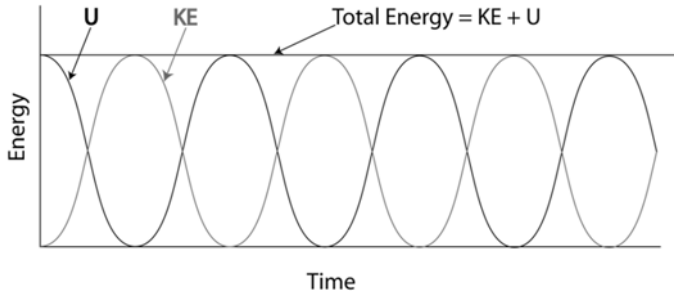
$$K(t) = \frac{1}{2}m\left(\frac{dz(t)}{dt}\right)^2 = \frac{1}{2}m\left(\frac{dx(t)}{dt}\right)^2$$

Using $x(t) = x_0\cos(\omega t)$

gives $\frac{dx}{dt} = -\omega x_0\sin(\omega t)$

So we get $K(t) = \frac{1}{2}m\omega^2 x_0^2\sin^2(\omega t)$

We can plot both the potential energy and kinetic energy:



The fact that the system starts with all potential energy and no kinetic energy comes from our choice of initial conditions (we said that we would stretch the string holding it still and then let go.)

You can see that the potential and kinetic energy are 180° out of phase. The energy transfers back and forth between being all kinetic energy and no potential and then all potential energy and no kinetic. Where the energy starts is determined by the initial conditions.

Note that when the energy is all potential, the spring is at one of its turning points: the mass is turning around and going the other way. When the energy is all kinetic is when the mass passes through its equilibrium configuration.

You can see that because of the phase difference, the total energy remains constant, that is *total energy is conserved*. The system is called a *conservative system*. This will be the case whenever the force can be written as a derivative of the potential. (Cases that *do not* fall into this category are those that have forces like frictional or viscous forces.)

To show quantitatively that the energy of a classical harmonic oscillator remains constant, we need only sum our expressions for U and K.

$$E(t) = U(t) + K(t) = \frac{k}{2} x_0^2 \cos^2(\omega t) + \frac{1}{2} m\omega^2 x_0^2 \sin^2(\omega t)$$

Remembering that

$$\omega = \sqrt{\frac{k}{m}}$$

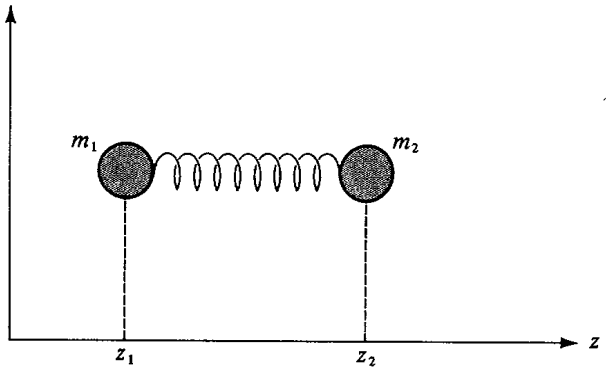
we can write

$$E(t) = \frac{kx_0^2}{2}\left[\cos^2(\omega t) + \sin^2(\omega t)\right]$$

$$= \frac{kx_0^2}{2}$$

So the total energy is a constant and is equal to the potential energy at its turning point.

We now want to make the Harmonic Oscillator problem look more like a diatomic molecule; not just a mass attached to a wall.



Consider two masses connected by a spring. We now get two equations of motion, one for each mass.

$$m_1 \frac{d^2 z_1(t)}{dt^2} = k\left(z_2(t) - z_1(t) - l_0\right)$$

$$m_2 \frac{d^2 z_2(t)}{dt^2} = -k\left(z_2(t) - z_1(t) - l_0\right)$$

Notice the sign convention:

$z_2(t) - z_1(t) > l_0$ the spring is stretched

$z_2(t) - z_1(t) < l_0$ the spring is compressed

Note that the force on each mass is in the direction to restore it to the equilibrium position. Notice also that the force on mass 1 is equal and opposite from the force on mass 2. This must be so (Newton's third law)

This means that

$$m_1 \frac{d^2 z_1(t)}{dt^2} + m_2 \frac{d^2 z_2(t)}{dt^2} = 0$$

Or

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

Let us introduce what is called the *center-of mass-coordinate.*

$$Z(t) = \frac{m_1 z_1(t) + m_2 z_2(t)}{M}$$

where $M = m_1 + m_2$

We can then write the equation above as:

$$M \frac{d^2 Z(t)}{dt^2} = 0$$

This means that the acceleration of the particle as a whole equals zero. (Remember we said that the force was due only to the spring). Thus, the whole system moves through space at constant velocity (no acceleration).

The motion of the two mass system *must* depend only on the relative separation of the two masses, *z*, where

$$z(t) = z_2(t) - z_1(t)$$

We can take our original differential equations, divide them by their relative masses, and subtract them

$$\frac{d^2 z_2(t)}{dt^2} - \frac{d^2 z_1(t)}{dt^2} = -\frac{k}{m_2}\left(z_2(t) - z_1(t) - l_0\right) - \frac{k}{m_1}\left(z_2(t) - z_1(t) - l_0\right)$$

$$\frac{d^2}{dt^2}\left(z_2(t) - z_1(t)\right) = -k\left(\frac{1}{m_1} + \frac{1}{m_2}\right)\left(z_2(t) - z_1(t) - l_0\right)$$

Using the definition of a reduced mass,

$$\frac{1}{m_1}+\frac{1}{m_2}=\frac{m_1+m_2}{m_1 m_2}=\frac{1}{\mu}$$

we can write this as

$$\frac{d^2 z(t)}{dt^2}=-\frac{k}{\mu}\left(z(t)-l_0\right)$$

If we now let

$$x(t)=z(t)-l_0$$

we finally arrive at:

$$\mu\frac{d^2 x(t)}{dt^2}+kx(t)=0$$

This is an important result. This result is the same as the mass attached to a wall, but the mass is replaced by the reduced mass μ. You can see that if m_1 or $m_2 \to \infty$ then $\mu \to m_2$ or m_1 and the equation would be the same as before.

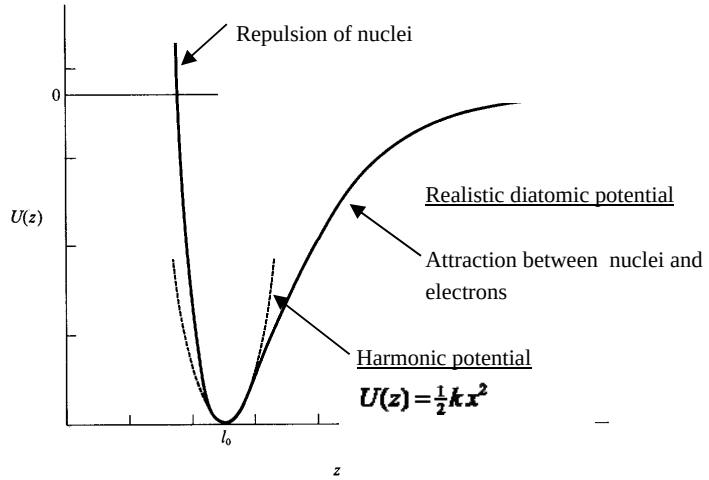
The fact that $m \to \mu$ means that the frequency will now be

$$\omega=\sqrt{\frac{k}{\mu}}$$

In general, if the potential only depends upon relative coordinates, then we can separate off the center of mass motion and reduce the two-body problem to a one body problem with mass equal to μ. We will therefore use μ in the rest of our discussion.

Before we go on to discuss the quantum mechanical harmonic oscillator problem, it is important to consider how good such a harmonic oscillator ball and spring model is for a vibrating diatomic molecule. Below is a typical internuclear potential for a diatomic molecule. At small internuclear separation, the potential rises sharply. This is due to the repulsion of the positively charged nuclei. The well is due to the balance between the nuclear repulsion and the attraction between nuclei and electrons. The flattened out part at large internuclear distance z indicates that as a bond is stretched, the restoring force is no longer linear because the chemical bond begins to break. The asymptotic energy is the bond dissociation energy.

We can superimpose a harmonic potential on this typical internuclear potential curve:



You can see that in some sense it is rather unrealistic to model this potential by a harmonic oscillator in that it takes an infinite amount of energy to break the bond (*i.e*. go to an infinite internuclear separation). However, the shape of the well near the bottom does a very good job of fitting the real potential, and as we will see when we solve the quantum mechanics of this problem, most of the energy levels that one observes experimentally are in the part of the well which is fit well by a harmonic potential.

So the harmonic oscillator approximation is good for small amplitude vibrations where Hooke's Law holds (*i.e*., those near the bottom of the well).

To put this into more mathematical terms, we could write our real potential function as a Taylor series in z about the equilibrium position, l_0.

$$U(z) = U(l_0) + \left(\frac{dU(z)}{dz}\right)_{z=l_0}(z-l_0) + \frac{1}{2!}\left(\frac{d^2U(z)}{dz^2}\right)_{z=l_0}(z-l_0)^2 + + \frac{1}{3!}\left(\frac{d^3U(z)}{dz^3}\right)_{z=l_0}(z-l_0)^3 + \ldots$$

The first term determines the absolute energy at the bottom of the well. This is not very important since we usually look at the difference in energy between two levels. We will therefore set it to zero.

The second term is the slope of the curve (first derivative), and by definition, this must vanish near the bottom of the well.

If we let

$$\left(\frac{d^2U(z)}{dz^2}\right)_{z=l_0} = k \qquad \text{and} \qquad \left(\frac{d^3U(z)}{dz^3}\right)_{z=l_0} = \gamma$$

we can write

$$U(z) = \frac{1}{2}k(z-l_0)^2 + \frac{1}{6}\gamma(z-l_0)^3 + \ldots$$

or

$$U(x) = \frac{1}{2}kx^2 + \frac{1}{6}\gamma x^3 + \ldots$$

where $x = z - l_0$.

If the displacement from equilibrium is small, x is small and we can neglect the x^3 term.

We are then left with

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

which is the potential for the Harmonic Oscillator.

This shows that the Harmonic Oscillator should be a good approximation for small amplitude vibrations. One can make corrections to account for "anharmonic" terms later.

It is important to realize what the meaning of k in this expression is, *i.e*. it is related to the curvature of the potential well at the minimum.

3.2 Quantum Mechanical Harmonic Oscillator Problem

Remember I said that I would introduce the solutions to the problem first and look at their physical significance. In doing so, I will introduce a few new concepts that we have not seen before. After having looked at the

solutions, we will go back and work through the mathematics required to arrive at the solution. The form of the Schrödinger equation is more difficult, and we will need some new mathematical tools to solve it.

Even though we will not solve the problem right now, let us write down the Schrödinger equation.

$$\hat{H}\psi(x) = E\psi(x)$$

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi(x)}{dx^2} + U(x)\psi(x) = E\psi(x)$$

Recall that μ is the reduced mass and using it allows us to reduce a two-body problem to that of single body of mass μ.

We can put in

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

and rearrange to get

$$\frac{d^2\psi(x)}{dx^2} + \frac{2\mu}{\hbar^2}\left(E - \frac{1}{2}kx^2\right)\psi(x) = 0$$

This differential equation is more difficult to solve than those we have done previously in that it does not have constant coefficients. There is no "simple" way to solve it. We will present the results first and then go back and solve this differential equation.

It turns out that you only get well-behaved finite solutions if the energy is quantized. We will see shortly that this quantization of energy occurs when applying the **boundary conditions.**

The result for the energy is:

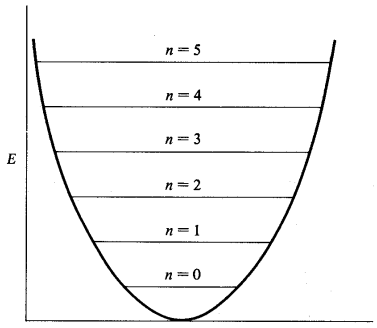
$$E_n = \hbar\sqrt{\frac{k}{\mu}}(n + \tfrac{1}{2})$$

$$= \hbar\omega(n + \tfrac{1}{2}) = h\nu(n + \tfrac{1}{2}) \qquad n = 0,1,2,3,\ldots$$

where $\omega = \sqrt{\frac{k}{\mu}}$ and $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$

Note that ν (or ω) is the *classical* expression for the frequency of the harmonic oscillator.

I will superimpose these energy levels on the potential energy curve:



There are several important things to note about the harmonic oscillator energy levels:

1) The energy levels are equally spaced, in integral units of the classical frequency.

Think about what this means. The classical frequency is related to the force constant *k*

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

Remember that *k* is related to the width of the potential (which is a parabola).

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

Larger *k* means stiffer spring (*i.e.* the energy rises faster with *x* the higher *k* is). So a stiffer spring (narrower parabola) means that the energy levels are spaced more widely. Conversely, a smaller *k* means a floppier spring (wider parabola) and more closely space energy levels.

The harmonic oscillator potential occupies a unique position among simple one-dimensional potentials in that the energy levels are spaced evenly. Any potential that has more curvature than the harmonic oscillator potential will have levels which increase in spacing as you go higher in energy. A good example is the particle in a box whose levels increase as n^2. Any potential which has less curvature than the harmonic oscillator potential will have more closely spaced levels. As we will see, the hydrogen atom potential has negative curvature and hence has energy levels that get closer together as you go up in energy.

2) The second point to notice is that even when the quantum number n=0, there is still energy in the amount of $\frac{1}{2}h\nu$.

This is called *zero point energy*. Its existence is highly *NON-CLASSICAL*. It implies that if you were to cool a system down to absolute zero and every molecule were in its lowest energy state, there would still be some energy in the oscillator.

If there were not zero point energy, the system would violate the Heisenberg Uncertainty Principle. If the energy were identically zero then the kinetic energy would be zero and hence the momentum would be zero, $p_x = 0$. The particle would be at the bottom of the well with no motion, so *x* = 0. This violates the Heisenberg uncertainty principle, since you would know both p_x and *x* precisely.

Another way to look at it is that the total energy of the oscillator can be written:

$$E = \frac{p_x^2}{2m} + \frac{1}{2}kx^2$$

To have zero energy requires both p_x and *x* to be zero (or their expectation values to be zero). This would violate the Heisenberg Uncertainty Principle.

We have looked at the eigenvalues of the Harmonic Oscillator Hamiltonian (*i.e.* the energies of the stationary states). Now let us look at the eigenfunctions. The eigenfunctions corresponding to the eigenvalues E_n are non-degenerate and are given by

$$\psi_n(x) = N_n H_n(\alpha^{\frac{1}{2}}x)e^{-\frac{1}{2}\alpha x^2}$$

where

$$\alpha = \sqrt{\frac{k\mu}{\hbar^2}}$$

The normalization constant N_n is

$$N_n = \frac{1}{\sqrt{2^n n!}}\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}$$

and the $H_n(\alpha^{\frac{1}{2}}x)$ are polynomials called ***Hermite polynomials***

These polynomials are defined by the following equation or generating function:

$$H_n(\xi) = (-1)^n e^{\xi^2}\frac{d^n}{d\xi^n}e^{-\xi^2}$$

where $\xi = \alpha^{\frac{1}{2}}x$

You can verify for yourselves that the first few Hermite polynomials are

$$H_0(\xi) = 1$$

$$H_1(\xi) = 2\xi$$

$$H_2(\xi) = 4\xi^2 - 2$$

$$H_3(\xi) = 8\xi^3 - 12\xi$$

$$H_4(\xi) = 16\xi^4 - 48\xi^2 + 12$$

Although we have not solved the Schrödinger equation for the Harmonic Oscillator yet, we can show that they are solutions to the differential equation.

Recall that the Schrödinger equation is:

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

Let us show that ψ_0 satisfies this equation:

$$\psi_0(x) = N_0 H_0(\alpha^{\frac{1}{2}}x)e^{-\frac{1}{2}\alpha x^2} = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{-\frac{1}{2}\alpha x^2}$$

We need to differentiate it an plug it back into the differential equation.

$$\frac{d\psi_0(x)}{dx} = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}\left(-\alpha x e^{-\frac{1}{2}\alpha x^2}\right)$$

$$\frac{d^2\psi_0(x)}{dx^2} = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}\left(\alpha^2 x^2 e^{-\frac{1}{2}\alpha x^2} - \alpha e^{-\frac{1}{2}\alpha x^2}\right)$$

Substituting ψ_0 and its second derivative back into the differential equation we get

$$-\frac{\hbar^2}{2\mu}\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}\left(\alpha^2x^2e^{-\frac{1}{2}\alpha x^2}-\alpha e^{-\frac{1}{2}\alpha x^2}\right)+\frac{1}{2}kx^2\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}e^{-\frac{1}{2}\alpha x^2}=E_0\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}e^{-\frac{1}{2}\alpha x^2}$$

Realizing that

$$\alpha=\sqrt{\frac{k\mu}{\hbar^2}}$$

this gives:

$$-\frac{\hbar^2}{2\mu}\frac{k\mu}{\hbar^2}x^2\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}e^{-\frac{1}{2}\alpha x^2}+\frac{\hbar^2}{2\mu}\sqrt{\frac{k\mu}{\hbar^2}}\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}e^{-\frac{1}{2}\alpha x^2}+\frac{1}{2}kx^2\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}e^{-\frac{1}{2}\alpha x^2}=E_0\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}e^{-\frac{1}{2}\alpha x^2}$$

Rearing gives:

$$\frac{\hbar}{2}\sqrt{\frac{k}{\mu}}\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}e^{-\frac{1}{2}\alpha x^2}=E_0\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}e^{-\frac{1}{2}\alpha x^2}$$

Taking the definition of

$$\omega=\sqrt{\frac{k}{\mu}}$$

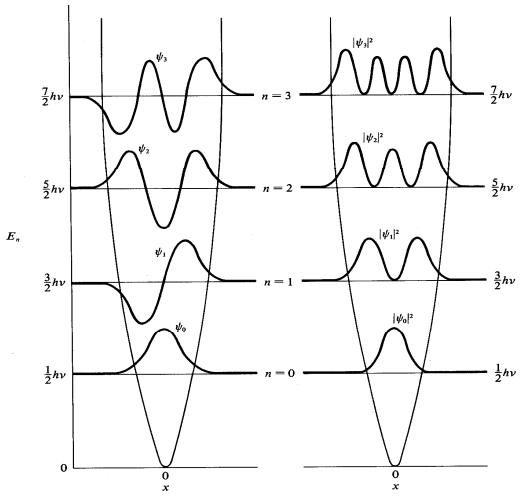
one finds:

$$\frac{1}{2}\hbar\omega\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}e^{-\frac{1}{2}\alpha x^2}=E_0\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}e^{-\frac{1}{2}\alpha x^2}$$

Hence we have shown that $\psi_0(x)$ is an eigenfunction of the Hamiltonian and that the corresponding eigenvalue is:

$$E_0=\frac{1}{2}\hbar\omega$$

The solutions to the Schrödinger equation give the following picture for a vibrating diatomic molecule. Note that *x* is the displacement from equilibrium.



There are several important things to notice about these eigenfunctions and related probability distributions:

1. They are qualitatively similar to the particle in the box.

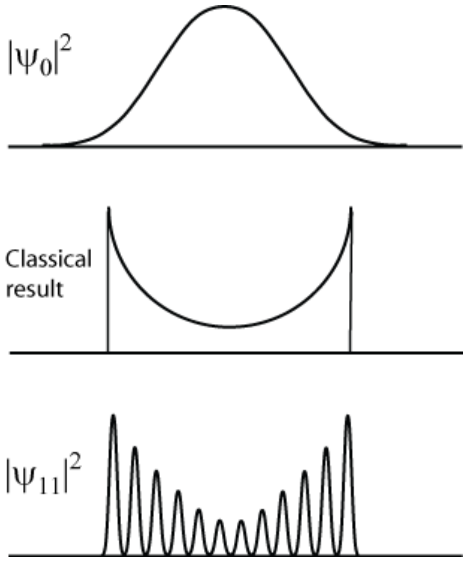
   - Simple oscillatory functions. The number of nodes increases with energy.
   - Note that it will always be true that the lowest energy wavefunction will have no nodes, the next wavefunction will have one, etc.
   - Also note that here the lowest wavefunction is ψ_0 and not ψ_1 like in the particle in a box. This results from the different boundary conditions.
   - In the particle-in-a-box wavefunctions there are *n*-1 nodes. Here there are *n* nodes.

2. The even numbered wave functions are even functions about *x*=0 and the odd numbered functions are odd about *x*=0.

   even function: $f(-x) = f(x)$
   odd function: $f(-x) = -f(x)$

3. There exists a finite probability for the quantum mechanical oscillator to exist outside the classical boundary. Recall that the particle-in-a-box wave functions went identically to zero at the boundary, but this was because the potential went to infinity. This penetration into the classically forbidden region is called tunneling and we will elaborate on it in just a moment.

   The probability distribution for ψ_0 of the harmonic oscillator is in stark contrast to the classical result. Classically the oscillator spends most of its time at the turning points. However, as *n* gets higher, the probability distribution begins to build up at the turning point and approaches the classical result. This is an example of the *Bohr Correspondence Principle*, that in the limit of high quantum number, the quantum mechanical result approaches the classical result.



I would like to digress briefly and discuss **even and odd functions.**

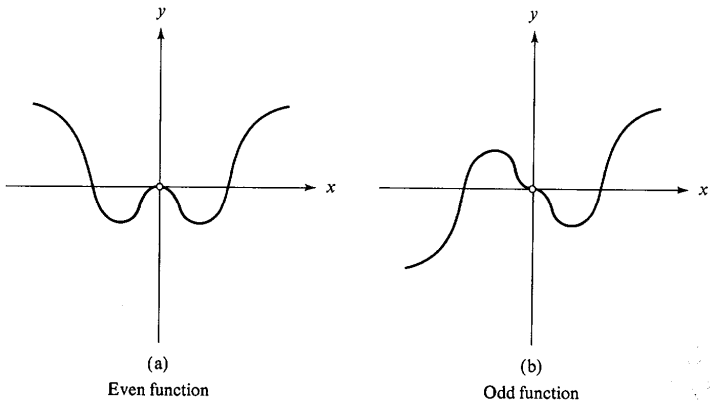
An even function is one in which $f(-x) = f(x)$ and therefore for an even function:

$$\int_{-\infty}^{\infty} f(x)dx = 2\int_{0}^{\infty} f(x)dx$$

An odd function is one in which $f(-x) = -f(x)$ and therefore for an odd function:

$$\int_{-\infty}^{\infty} f(x)dx = 0$$

Since the positive contribution to the area at $x>0$ exactly cancels the negative contribution at $x<0$, see the figure below.



(a) Even function (b) Odd function

Examples of even and odd functions:

$f(x) = \cos(x)$	Even
$f(x) = \sin(x)$	Odd
$f(x) = x$	Odd
$f(x) = e^{-x^2}$	Even
$f(x) = e^{-x}$	Neither

Not all functions are even or odd. Many have no symmetry about $x=0$.

Note:	(even) (even)	$\rightarrow$	even function
	(odd) (odd)	$\rightarrow$	even function
	(even) (odd)	$\rightarrow$	odd function

Example:	$x\sin(x)$	$\rightarrow$	even function
	(odd) (odd)		

proof: $f(x) = x\sin(x)$

$$f(-x) = (-x)\sin(-x) = -x(-\sin(x)) = x\sin(x) = f(x)$$

The Hermite polynomials are even and odd functions, and this greatly simplifies doing integrations.

Note that the exponential part of the wavefunction, $e^{-\frac{1}{2}\alpha x^2}$ is even, so the harmonic oscillator wavefunctions reflect the evenness or oddness of the Hermite polynomial. As we noted before, the Hermite polynomials are either even or odd functions.

$H_0(\xi) = 1$ Even

$H_1(\xi) = 2\xi$ Odd

$H_2(\xi) = 4\xi^2 - 2$ Even

$H_3(\xi) = 8\xi^3 - 12\xi$ Odd

In general: n = even $\rightarrow$ H_n is even
n = odd $\rightarrow$ H_n is odd

This property will help us greatly in evaluating integrals. For example, integrals of the type

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi_n^*(x) x \psi_n(x) dx = 0$$

We do not need to explicitly do the integral in this case because if ψ_n is even or odd, the integrand will be odd and the integral equals zero.

The even/odd behavior of the harmonic oscillator wavefunctions can help us to verify that they are orthogonal to one another.

Example: Prove that ψ_0 and ψ_1 are orthogonal to one another.

$$\psi_0(x) = N_0 e^{-\frac{1}{2}\alpha x^2} \qquad \psi_1(x) = N_1 (2\alpha^{\frac{1}{2}} x) e^{-\frac{1}{2}\alpha x^2}$$

$$\int_{-\infty}^{\infty} \psi_0(x)\psi_1(x) dx = N_0 N_1 \int_{-\infty}^{\infty} e^{-\frac{1}{2}\alpha x^2} (2\alpha^{\frac{1}{2}} x) e^{-\frac{1}{2}\alpha x^2} dx$$

$$= 2N_0 N_1 \alpha^{\frac{1}{2}} \int_{-\infty}^{\infty} x e^{-\alpha x^2} dx = 0$$

since the integrand is odd.

Note: this general rule cannot be used to evaluate integrals of the type

$$\int_{-\infty}^{\infty} \psi_{n1}(x)\psi_{n2}(x) dx = N_{n1} N_{n2} \int_{-\infty}^{\infty} H_{n1}(x) H_{n2}(x) e^{-\alpha x^2} dx$$

where H_{n1} and H_{n2} are both even. One must calculate the integral in this case.

3.3 Tunneling Effects

I would now like to make a brief digression into an aspect of the harmonic oscillator wave functions that I mentioned earlier. Recall that when we looked at the Harmonic oscillator wavefunctions we observed that there was a finite amplitude outside the classical potential, that is in a classically forbidden region. This corresponds to the particle having a finite probability of being in a classically forbidden region. This phenomenon is called tunneling.

It arises from the fact that a quantum mechanical particle is a wave and does not respond like a particle to a potential barrier. I would like to make a brief digression to consider tunneling a little further.

Recall the Schrödinger equation for the particle-in-a-box:

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

$$\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + E\psi(x) = 0$$

$$\frac{d^2\psi(x)}{dx^2} + \frac{2mE}{\hbar^2}\psi(x) = 0$$

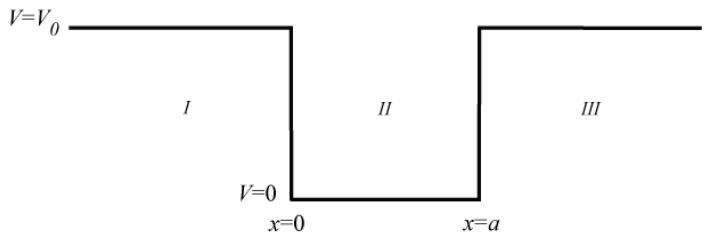
The solution to this is a function which when differentiated twice must be multiplied by a negative constant to fulfill this equation. Recall that the general solutions are complex exponentials, *i.e.*

$$\psi(x) = e^{\pm i\alpha x} \qquad \text{where} \qquad \alpha = \sqrt{\frac{2mE}{\hbar^2}} \qquad \text{(note that } \alpha \text{ is real)}$$

We then converted the complex exponentials to sines and cosines using Euler's formula.

Then we applied the boundary conditions that $\psi(0) = 0$ and $\psi(a) = 0$ since the potential was infinite in the region outside the box. Remember it was in applying the boundary conditions that the energy quantization was required.

Consider now the following potential:



In any one-dimensional potential like this where the potential abruptly changes from one region to another, one simply solves the Schrödinger equation separately in each region since the potential (and hence the Hamiltonian) is different in each region. One then has to require that the wavefunction from each region matches up smoothly at the boundaries and that there are no kinks in the wave function (*i.e.* the slopes match up as well)

Let us look at the wave function in region I when the energy is less than V_0.

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V_0\psi(x) = E\psi(x)$$

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m(E - V_0)}{\hbar^2}\psi(x) = 0$$

Since $E<V_0$, the second term will always be negative. The solution to this equation is therefore

$$\psi(x) = e^{\pm kx} \qquad \text{where} \qquad k = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}} \quad (k \text{ will always be real})$$

Recall that before we got complex exponentials which are sines and cosines. Now we get real exponentials. Let us match up the wave functions inside the box and outside in the case where the walls are finite.

We will specify the region number as a subscript of the k in the exponent, realizing that in a region where $E<V_0$

$$k_I = k_{III} = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$$

whereas in region II where $V = 0$ we have $\psi(x) = e^{\pm ik_{II}x}$

$$k_{II} = \sqrt{\frac{2mE}{\hbar^2}}$$

In all cases, k is real.

So in regions I - III the solutions are

$$\psi_I(x) = c_1 e^{-k_I x} + c_2 e^{+k_I x}$$

$$\psi_{II}(x) = c_3 e^{-ik_{II}x} + c_4 e^{+ik_{II}x}$$

$$\psi_{III}(x) = c_5 e^{-k_{III}x} + c_6 e^{+k_{III}x}$$

Consider region I for a moment. As $x \to -\infty$, for this function to remain finite, c_1=0.

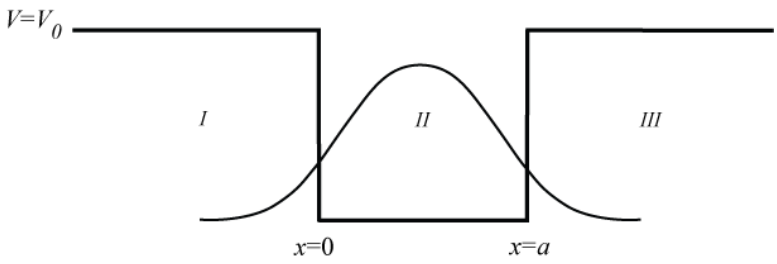
Thus $\psi_I(x) = c_2 e^{k_I x}$

Similarly in region III, to keep the wavefunction finite as $x \to \infty$, $c_6 = 0$.

Thus,

$$\psi_{III}(x) = c_5 e^{-k_{III}x}$$

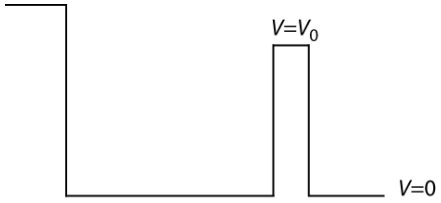
Let us then qualitatively look at the total wavefunction and see how it matches up at the boundaries.



Classically, a particle in such a well would simply undergo elastic collisions with the wall. If the energy is less that the barrier V_0, there is zero probability of finding the particle outside the well.

Quantum mechanically, however, one way to view the situation is that the particle penetrates into the wall somewhat (although it is not precise to talk about trajectories of quantum mechanical particles.)

Consider now the following potential.



Consider a particle with energy less than V_0. In the right hand region, the solutions are sines and cosines. In the well, they are sines and cosines. In the classically forbidden regions, the wavefunction will be real exponentials.

A wave function for a particle initially trapped in this potential well will decay exponentially into the barrier but still be finite when it comes out the other side. So although the particle does not have enough energy to get over the barrier, it can *tunnel* through the barrier and the probability can leak out.

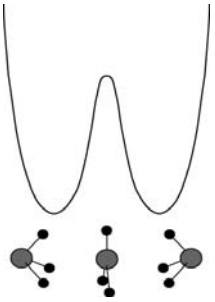
To make this a bit closer to our experience, if tunneling were to occur on a macroscopic scale, one would see the following. If you roll a ball up a hill but do not give it enough energy to reach the crest of the hill and go down the other side, tunneling would correspond to the ball suddenly disappearing from the side you rolled it up and reappearing on the other side of the crest, even though it did not have enough energy to get over the crest.

The probability of tunneling depends on the mass of the particle and the height and shape of the barrier, thus one does not observe it for macroscopic objects. (Although the probability is finite, for all practical purposes it is zero)

It turns out that tunneling phenomena are prevalent in many areas of physics, chemistry and biology. In biological molecules, since electrons are so light, electron transfer among proteins or photosynthetically related compounds involves electron tunneling.

A relatively recent experimental technique is called a tunneling electron microscope. It relies upon electron tunneling to map out the wave functions of atoms on a surface.

A famous example in chemistry is that of the ammonia molecule. Ammonia can undergo an inversion process illustrated in the figure below. At energies below the barrier, it can transform from one side to the other by tunneling.



Tunneling is strictly a consequence of the wave nature of the particle.

We assumed that the potential of a diatomic molecule can be approximated by an harmonic oscillator. This implies that the deviation from the equilibrium distance has to be small. In contrast to the classical case, the quantum mechanical Harmonic oscillator does not have a well-defined vibrational amplitude because of tunneling (the wave function decays exponentially) making it difficult to validate the approximation.

However, one can use the variance or better the standard deviation as a measure. Remember that $\langle x \rangle = 0$ due to symmetry, so we only have to calculate $\langle x^2 \rangle$. We therefore have:

$$x_{rms} = \sqrt{\langle x^2 \rangle}$$

Let us calculate $\langle x^2 \rangle$ for ψ_0

We have $$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{-\frac{1}{2}\alpha x^2}$$

in which case

$$\langle x^2 \rangle = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx$$

From integral tables:

$$\int_0^{\infty} x^2 e^{-\alpha x^2} dx = \frac{1}{4\alpha}\left(\frac{\pi}{\alpha}\right)^{\frac{1}{2}}$$

Thus

$$\langle x^2 \rangle = 2\left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} \int_0^{\infty} x^2 e^{-\alpha x^2} dx = \frac{1}{2\alpha}$$

Consequently,

$$x_{rms} = \sqrt{\langle x^2 \rangle} = \frac{1}{\sqrt{2\alpha}}$$

It turns out that this root mean square displacement is small compared to the equilibrium bond length. It is typically on the order of 5% of the bond length.

3.4 Molecular Absorption of Infrared Radiation

For a harmonic oscillator potential I had stated earlier that

$$E_n = \hbar\sqrt{\frac{k}{\mu}}\left(n + \frac{1}{2}\right) = h\nu\left(n + \frac{1}{2}\right) \qquad n = 0,1,2,3,\ldots$$

In absorbing a photon to make a transition from one harmonic oscillator energy level to another, one can show that there is a selection rule in that $\Delta n = \pm 1$.

Consequently, the transition will occur at a photon energy given by

$$\Delta E = E_{n+1} - E_n = \hbar\sqrt{\frac{k}{\mu}} = \hbar\omega = h\nu \qquad \text{for all } n.$$

Please note that infrared absorption occurs when the light is "on resonance" with the classical oscillator frequency.

Because the levels are equally spaced, transitions between any pair of levels will coincide. In general at room temperature one observes only one vibrational transition, Δn=+1 originating in n=0 because most molecules are in n=0.

Thus if we make a measurement of the absorption frequency we can find k and hence the potential curve since we know how to calculate μ from the masses of the atoms. In this way we are able to learn something about the binding between the two atoms in the molecule.

3.5 Solution to the Schrödinger Equation for the Harmonic Oscillator

Recall that the potential energy of the harmonic oscillator is

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

The Schrödinger Equation is then

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

Let us multiply through by $-\frac{2\mu}{\hbar^2}$ and rearrange to get

$$\frac{d^2\psi(x)}{dx^2} + \left(\frac{2\mu E}{\hbar^2} - \frac{\mu k}{\hbar^2}x^2\right)\psi(x) = 0$$

Let us now make the following substitutions:

$$\lambda = \frac{2\mu E}{\hbar^2} \qquad \text{and} \qquad \alpha^2 = \frac{k\mu}{\hbar^2}$$

We are left with

$$\frac{d^2\psi(x)}{dx^2} + \left(\lambda - \alpha^2 x^2\right)\psi(x) = 0$$

Let's make one more substitution:

$$\xi = \alpha^{\frac{1}{2}}x$$

And hence

$$\frac{d}{d\xi} = \frac{1}{\sqrt{\alpha}}\frac{d}{dx} \qquad \text{or} \qquad \frac{d}{dx} = \sqrt{\alpha}\frac{d}{d\xi}$$

And thus

$$\frac{d^2}{dx^2} = \alpha\frac{d^2}{d\xi^2}$$

We now have

$$\frac{d^2\psi(\xi)}{d\xi^2} + \left(\frac{\lambda}{\alpha} - \xi^2\right)\psi(\xi) = 0 \qquad \text{Eqn. I}$$

This equation still does not have constant coefficients. One way to simplify this equation somewhat is to consider the behavior of the differential equation as $\xi \to \infty$. This will give us the restrictions on ψ when ξ is large.

For large ξ, $\xi^2 >> \lambda/\alpha$ thus

$$\frac{d^2\psi(\xi)}{d\xi^2} - \xi^2\psi(\xi) = 0 \qquad \text{Eqn. II}$$

We want our solutions $\psi(\xi)$ to approach the solutions of this equation at large values of ξ. The solution to Eqn. II is not simple either, since the coefficient of ψ is not constant. If we were to try a solution to Eqn. II of the form $\psi(\xi) = e^{\beta\xi^2}$ one can show that in the limit of large ξ, $\beta = \pm 1/2$ gives a function that has the correct limiting behavior.

We can show this by substituting $\psi(\xi) = e^{\beta\xi^2}$ into Eqn. II to get

$$2\beta e^{\beta\xi^2} + 4\beta^2\xi^2 e^{\beta\xi^2} - \xi^2 e^{\beta\xi^2} = 0$$

or

$$\left[\xi^2\left(4\beta^2 - 1\right) + 2\beta\right]e^{\beta\xi^2} = 0$$

Because ξ is large we can ignore the second term in the brackets and see that $\beta = \pm 1/2$ does give us a solution to Eqn. II. It is therefore a valid solution to Eqn. 1 *in the limit of large* ξ You could easily verify this.

However, note that for β = +1/2, $\psi(\xi)$ blows up, and this is unacceptable for a wave function. Thus, we will look for solutions to the original equation (Eqn. 1), with limiting behavior $\psi(\xi) \to e^{-\frac{1}{2}\xi^2}$ as $\xi \to \infty$. This is a type of boundary condition in a sense, and as we will soon see, application of the boundary condition leads to quantization of the energy.

We will therefore try a solution to the Schrödinger Equation (Eqn. I) of the form

$$\psi(\xi) = H(\xi)e^{-\frac{1}{2}\xi^2}$$

where $H(\xi)$ is a function to be determined. We must impose the requirement on $H(\xi)$ that it falls off quickly enough at large ξ so that the exponential term dominates at large ξ and thus gives ψ the right limiting behavior. We must take the second derivative of $\psi(\xi)$ substitute it back into the differential equation and get an equation for the functions $H(\xi)$.

For the first derivative we have

$$\frac{d\psi(\xi)}{d\xi} = -\xi H(\xi)e^{-\frac{1}{2}\xi^2} + \frac{dH(\xi)}{d\xi}e^{-\frac{1}{2}\xi^2}$$

For the second:

$$\frac{d^2\psi(\xi)}{d\xi^2} = -H(\xi)e^{-\frac{1}{2}\xi^2} - \xi\frac{dH(\xi)}{d\xi}e^{-\frac{1}{2}\xi^2} + \xi^2 H(\xi)e^{-\frac{1}{2}\xi^2} + \frac{d^2H(\xi)}{d\xi^2}e^{-\frac{1}{2}\xi^2} - \xi\frac{dH(\xi)}{d\xi}e^{-\frac{1}{2}\xi^2}$$

$$= \left(\frac{d^2H(\xi)}{d\xi^2} - 2\xi\frac{dH(\xi)}{d\xi} + \left[\xi^2 - 1\right]H(\xi)\right)e^{-\frac{1}{2}\xi^2}$$

Putting this into our differential equation

$$\frac{d^2\psi(\xi)}{d\xi^2}+\left(\frac{\lambda}{\alpha}-\xi^2\right)\psi(\xi)=0$$

gives

$$\left(\frac{d^2H(\xi)}{d\xi^2}-2\xi\frac{dH(\xi)}{d\xi}+\left[\xi^2-1\right]H(\xi)\right)e^{-\frac{1}{2}\xi^2}+\left(\frac{\lambda}{\alpha}-\xi^2\right)H(\xi)e^{-\frac{1}{2}\xi^2}=0$$

$$\left(\frac{d^2H(\xi)}{d\xi^2}-2\xi\frac{dH(\xi)}{d\xi}+\left[\frac{\lambda}{\alpha}-1\right]H(\xi)\right)e^{-\frac{1}{2}\xi^2}=0$$

The exponential term does not equal zero, thus

$$\frac{d^2H(\xi)}{d\xi^2}-2\xi\frac{dH(\xi)}{d\xi}+\left[\frac{\lambda}{\alpha}-1\right]H(\xi)=0$$

Solving this differential equation is then equivalent to solving the original equation since we can find $\psi(x)$ from $H(\xi)$. There are no approximations here.

This equation still does not have constant coefficients; however this differential equation has been studied in detail long before the development of quantum mechanics and is known as Hermite's differential equation. It arises in problems of scattering light of various types of geometrical surfaces.

The standard technique for solving this equation is the so-called ***series method*** or ***power series solution***.

In the series method, we assume $H(\xi)$ can be written as a power series

$$H(\xi)=a_0+a_1\xi+a_2\xi^2+a_3\xi^3+a_4\xi^4+\ldots$$

$$\frac{dH(\xi)}{d\xi}=a_1+2a_2\xi+3a_3\xi^2+4a_4\xi^3+\ldots$$

$$\frac{d^2H(\xi)}{d\xi^2}=1\cdot 2a_2+2\cdot 3a_3\xi+3\cdot 4a_4\xi^2+\ldots$$

We now substitute the series for $H(\xi)$ and its derivatives back into the differential equation and collect terms with like powers of ξ:

$$\left[1\cdot 2a_2+\left(\frac{\lambda}{\alpha}-1\right)a_0\right]+\left[2\cdot 3a_3+\left(\frac{\lambda}{\alpha}-1-2\cdot 1\right)a_1\right]\xi+\left[3\cdot 4a_4+\left(\frac{\lambda}{\alpha}-1-2\cdot 2\right)a_2\right]\xi^2+\left[4\cdot 5a_5+\left(\frac{\lambda}{\alpha}-1-2\cdot 3\right)a_3\right]\xi^3+\ldots=0$$

For this series to vanish for all values of ξ, each of the coefficients must vanish separately

$$1\cdot 2a_2+\left(\frac{\lambda}{\alpha}-1\right)a_0=0$$

$$2\cdot 3a_3+\left(\frac{\lambda}{\alpha}-1-2\cdot 1\right)a_1=0$$

$$3\cdot 4a_4+\left(\frac{\lambda}{\alpha}-1-2\cdot 2\right)a_2=0$$

$$4\cdot 5a_5+\left(\frac{\lambda}{\alpha}-1-2\cdot 3\right)a_3=0$$

or in general

$$(n+2)(n+1)a_{n+2}+\left(\frac{\lambda}{\alpha}-1-2n\right)a_n=0 \qquad n=0,1,2,3,\ldots$$

We can rearrange this to get

$$a_{n+2}=-\frac{\left(\frac{\lambda}{\alpha}-1-2n\right)}{(n+1)(n+2)}a_n$$

This type of formula is called a ***recursion*** formula. It gives one coefficient in the series expansion of $H(\xi)$ in terms of a previous coefficient. This is a two-term recursion formula in that it skips by 2.

Thus, if one chooses two arbitrary constants, a_0 and a_1 then the recursion formula gives two independent sets of coefficients

$$H_{even}=a_0+a_2\xi^2+a_4\xi^4+\ldots$$

$$H_{odd}=a_1\xi+a_3\xi^3+a_5\xi^5+\ldots$$

Recall that the Harmonic oscillator solutions are either odd functions or even functions. This is where this property arises in this system.

We can use the recursion relation to solve for all the even a's in terms of a_0 and all the odd a's in terms of a_1. Thus there are two unknown constants (as you would expect for a second order differential equation). The first few of these relations are (for the even terms):

$$a_2=-\frac{1}{1\cdot 2}\left(\frac{\lambda}{\alpha}-1\right)a_0$$

$$a_4=-\frac{1}{3\cdot 4}\left(\frac{\lambda}{\alpha}-1-2\cdot 2\right)a_2=\frac{1}{4!}\left(\frac{\lambda}{\alpha}-1\right)\left(\frac{\lambda}{\alpha}-1-2\cdot 2\right)a_0$$

and for the odd terms:

$$a_3=-\frac{1}{2\cdot 3}\left(\frac{\lambda}{\alpha}-1-2\cdot 1\right)a_1$$

$$a_5=-\frac{1}{4\cdot 5}\left(\frac{\lambda}{\alpha}-1-2\cdot 3\right)a_3=\frac{1}{5!}\left(\frac{\lambda}{\alpha}-1-2\cdot 1\right)\left(\frac{\lambda}{\alpha}-1-2\cdot 3\right)a_1$$

Now, as I mentioned before, we need to require $H(\xi)$ to converge at large ξ sufficiently rapidly that the exponential part of the wave function, $e^{-\frac{1}{2}\xi^2}$, will dominate. We must make the power series fit the boundary condition $\psi(\xi)\to 0$ as $\xi\to\infty$.

To do this, we need to look at the relative size of successive coefficients, a_n at large n.

From the recursion relation:

$$\lim_{n\to\infty}\frac{a_{n+2}}{a_n}=\frac{2n}{n^2}=\frac{2}{n}$$

For large n, $a_{n+2} << a_n$. This better be true if the series is to converge. But, does this converge fast enough to satisfy the boundary conditions?

To determine this, let us look at a function that we know blows up at large ξ. We can compare the rate of convergence with our power series.

$$e^{\xi^2} = 1 + \xi^2 + \ldots + \frac{\xi^n}{\frac{n}{2}!} + \frac{\xi^{n+2}}{\left(\frac{n}{2}+1\right)!} + \ldots$$

$$= 1 + \xi^2 + \ldots + b_n \xi^n + b_{n+2} \xi^{n+2} + \ldots$$

For large *n* we find

$$\lim_{n\to\infty} \frac{b_{n+2}}{b_n} = \frac{\frac{n}{2}!}{\left(\frac{n}{2}+1\right)!} = \frac{1}{\left(\frac{n}{2}+1\right)} = \frac{2}{n}$$

So you can see that our power series in ξ has the same asymptotic behavior as e^{ξ^2}

If $\lim_{\xi\to\infty} H(\xi) = e^{\xi^2}$ then $\lim_{\xi\to\infty} H(\xi) e^{-\frac{1}{2}\xi^2} = e^{\frac{1}{2}\xi^2}$

This will not satisfy the boundary condition. We therefore must terminate the series after a certain number of terms so that we have a polynomial of finite length as a solution rather than a power series.

Recall that our recursion relation is

$$a_{n+2} = -\frac{\left(\frac{\lambda}{\alpha} - 1 - 2n\right)}{(n+1)(n+2)} a_n$$

You can see that if we let

$$\left(\frac{\lambda}{\alpha} - 1 - 2n\right) = 0$$

And thus

$$\frac{\lambda}{\alpha} = 2n + 1$$

This will make a_{n+2} be the first zero term and hence all the subsequent *a*'s will be zero. It breaks off the series after *n* terms. Thus, we will get an entire set of polynomials that have an increasing number of terms as the integer *n* increases. This will insure that the function $H(\xi)$ converges rapidly enough to satisfy the boundary conditions.

Remember that λ is related to the energy. Thus, to make the solution satisfy the boundary conditions, we have quantized the energy levels. We have seen this same principle in solving the Schrödinger equation for other simple 1-dimensional potentials. Here, the quantization comes in making the series converge.

Note that if *n* is even, the odd terms will not go to zero. However, since we have only even or odd solutions, this is ok.

Let us now look at the energy levels:

$$\frac{\lambda}{\alpha} = \frac{\frac{2\mu E}{\hbar^2}}{\sqrt{\frac{\mu k}{\hbar^2}}} = 2n + 1$$

This yields

$$E_n = \hbar\sqrt{\frac{k}{\mu}}\left(n+\frac{1}{2}\right)$$

$$= h\nu_{classical}\left(n+\frac{1}{2}\right)$$

where $$\nu_{classical} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

The wavefunctions can be given by:

$$\psi_n(\xi) = N_n H_n(\xi) e^{-\frac{1}{2}\xi^2}$$

In making the function $H(\xi)$ have the right behavior at large ξ we got quantization of the energy.

We forced the power series for $H(\xi)$ to be finite by causing one of the coefficients to go to zero at a particular *n*. All the higher terms will also go to zero. We therefore obtained a set of solutions $H(\xi)$ that terminate after different number of terms. You can see that this is what gives us different number of nodes in our wavefunctions as we go to high quantum numbers.

If you look back at the expressions we obtained when we first set the coefficients of each power of ξ equals zero, and let (λ/α) - 1 = 2*n*, we get

$$a_2 = -\frac{1}{1\cdot 2}\left(\frac{\lambda}{\alpha}-1\right)a_0 = \frac{2n}{1\cdot 2}a_0$$

$$a_4 = \frac{1}{4!}\left(\frac{\lambda}{\alpha}-1\right)\left(\frac{\lambda}{\alpha}-1-2\cdot 2\right)a_0 = \frac{2n(2n-4)}{4!}a_0$$

One can show that in general

$$H_n(\xi) = a_0\left[1-\frac{2n}{2!}\xi^2+\frac{2^2 n(n-2)}{4!}\xi^4-\frac{2^3 n(n-2)(n-4)}{6!}\xi^6+\ldots\right] \qquad n = \text{even}$$

$$H_n(\xi) = a_1\left[\xi-\frac{2(n-1)}{3!}\xi^3+\frac{2^2(n-1)(n-3)}{5!}\xi^5-\ldots\right] \qquad n = \text{odd}$$

You can see how each of these truncates after a finite number of terms, which depends on the quantum number *n*.

The values of a_0 and a_1 are arbitrary (since the overall wave function has a normalization constant). By convention, a_0 and a_1 are chosen so that the coefficient of the highest power of ξ, that is ξ^n is 2^n.

This gives

$$a_0 = (-1)^{\frac{n}{2}}\frac{n!}{\frac{n}{2}!}$$

and

$$a_1 = (-1)^{\frac{n-1}{2}} \frac{2n!}{\frac{n-1}{2}!}$$

Remember that I had given you another form for the Hermite polynomials a few lectures ago

$$H_n(\xi) = (-1)^n e^{\xi^2} \frac{d^n}{d\xi^n} e^{-\xi^2}$$

This is more compact and easier to work with.

It is important not to forget that the full solution to the Schrödinger equation is

$$\psi_n(\xi) = N_n H_n(\xi) e^{-\frac{1}{2}\xi^2} \qquad \text{where} \qquad \xi = \alpha^{\frac{1}{2}} x$$

3.6 Raising and Lowering Operators

If we want to calculate certain properties of the system, we will often encounter integrals of the type:

$$\int_{-\infty}^{\infty} \psi_n^*(x) \hat{A} \psi_m(x) dx$$

We already saw that if we want to determine the average value of the position we have to evaluate:

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi_n^*(x) x \psi_n(x) dx$$

Based upon the symmetry of the harmonic oscillator eigenfunctions it could be shown that this integral equals zero. However if we are interested in the mean deviation or variance of the position we have to evaluate

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} \psi_n^*(x) x^2 \psi_n(x) dx$$

We solved this integral for the ground state eigenfunction. Although not difficult, it is a non-trivial calculation. This is even more true if one were to evaluate this integral using the eigenfunction of higher vibrational levels.

When discussing the absorption spectrum I mentioned that there exists a selection rule $\Delta n = \pm 1$. As you will see in the spectroscopy course of next semester this selection rule follows from the evaluation of the following integral:

$$\int_{-\infty}^{\infty} \psi_n^*(x) x \psi_m(x) dx$$

Although one can calculate all these integrals explicitly, it would be worthwhile to have a way to evaluate them more easily. This can be done by making use of the so-called lowering and raising operators.

Let us start with the Hamiltonian for the harmonic oscillator:

$$\hat{H} = \frac{\hat{p}_x^2}{2\mu} + \frac{1}{2} k \hat{x}^2$$

which can also be written as:

$$\hat{H} = \frac{\hat{p}_x^2}{2\mu} + \frac{1}{2}\mu\omega^2\hat{x}^2$$

with $$\omega = \sqrt{\frac{k}{\mu}}$$

We see that the Hamiltonian contains only the operators $\hat{p}_x^2$ and $\hat{x}^2$. Since the operators $\hat{p}_x$ and $\hat{x}$ are Hermitian and thus have real eigenvalues it follows that the eigenvalues of the Hamiltonian are non-negative.

Let us at this point introduce the new operators:

$$\hat{a} = \sqrt{\frac{\mu\omega}{2}}\hat{x} + i\frac{\hat{p}_x}{\sqrt{2\mu\omega}}$$

and

$$\hat{a}^\dagger = \sqrt{\frac{\mu\omega}{2}}\hat{x} - i\frac{\hat{p}_x}{\sqrt{2\mu\omega}}:$$

Realizing that these new operators do not commute, *i.e.*

$$\left[\hat{a}, \hat{a}^\dagger\right] = \hbar$$

we can write the Hamiltonian as:

$$\hat{H} = \omega\hat{a}^\dagger\hat{a} + \tfrac{1}{2}\hbar\omega$$

One can show that the following commutation relations hold between the newly defined operators and the Hamiltonian:

$$\left[\hat{H}, \hat{a}\right] = -h\omega\hat{a}$$

$$\left[\hat{H}, \hat{a}^\dagger\right] = h\omega\hat{a}^\dagger$$

Let us now write down the eigenvalue equation, which reads:

$$\hat{H}u_E = Eu_E$$

In the past, whenever we wrote down such an equation the implication was that $\hat{H}$ contained some operators and that the eigenfunction u_E was a function of *x.* In general, this does not have to be the case as we will see later in the course when we will speak about spin.

If we have the commutator $\left[\hat{H}, \hat{a}\right]$ acting on this eigenfunction, u_E we find:

$$\left[\hat{H}, \hat{a}\right]u_E = -\hbar\omega\hat{a}u_E$$

$$\hat{H}\hat{a}u_E - \hat{a}\hat{H}u_E = -\hbar\omega\hat{a}u_E$$

With the help of the eigenvalue equation, we can rewrite this as:

$$\hat{H}\hat{a}u_E = (E - \hbar\omega)\hat{a}u_E$$

This equation states that if u_E is an eigenfunction of the Hamiltonian with eigenvalue E then $\hat{a}u_E$ is also an eigenfunction of $\hat{H}$ but with eigenvalue $E - \hbar\omega$, that is , with energy lowered by one unit of

$$\varepsilon = \hbar\omega$$

This implies that when operator $\hat{a}$ is applied to u_E it generates an eigenfunction of the Hamiltonian corresponding to the energy $E - \hbar\omega$.

We can therefore write

$$\hat{a}u_E = C(E)u_{E-\varepsilon}$$

We need the constant $C(E)$ here since even if u_E is normalized, $\hat{a}u_E$ need not to be.
If we now apply the same operators to the state $u_{E-\varepsilon}$ we find, in exactly the same way that $\hat{a}u_{E-\varepsilon}$ or, equivalently, $\hat{a}^2 u_{E-\varepsilon}$ gives a state of energy $E - 2\hbar\omega$. Thus by repeated application of operator a to any eigenfunction of the Hamiltonian, u_E , we can generate states of lower and lower energy. Appropriately, $\hat{a}$ is called a *lowering operator*. There is a limit to how many times operator $\hat{a}$ can be applied since the eigenvalues of the Hamiltonian has to be non-negative, as we saw before. Thus, the lowering procedure must end at some point. Consequently, there exists a ground state, which we will denote by u_0 , beyond which the lowering ends. So we have:

$$\hat{a}u_0 = 0$$

Analogous to the lowering operator $\hat{a}$, one can show that the operator $\hat{a}^\dagger$ when applied upon u_E increases the energy to $E + \hbar\omega$. One can thus write:

$$\hat{a}^\dagger u_E = C'(E)u_{E+\varepsilon}$$

The operator $\hat{a}^\dagger$ is appropriately called a *raising operator.*

We saw before that the Hamiltonian expressed in lower and raising operators takes on the form:

$$\hat{H} = \omega\hat{a}^\dagger\hat{a} + \tfrac{1}{2}\hbar\omega$$

If we apply the Hamiltonian onto the ground state eigenfunction u_0 we find the energy of the ground state.

$$\hat{H}u_0 = E_0 u_0$$

Putting in our definition of the Hamiltonian we find:

$$\hat{H}u_0 = \left(\omega\hat{a}^\dagger\hat{a} + \tfrac{1}{2}\hbar\omega\right)u_0$$

$$= \omega\hat{a}^\dagger\hat{a}u_0 + \tfrac{1}{2}\hbar\omega u_0$$

$$= \tfrac{1}{2}\hbar\omega u_0 = E_0 u_0$$

We will now change our notation a little, namely, we will label the state by the number of energy units $\varepsilon = \hbar\omega$ it has over the ground state energy, $E_0 = \frac{1}{2}\hbar\omega$. Thus, we can write:

$$\hat{a}u_n = C u_{n-1}$$

$$\hat{a}^\dagger u_n = C' u_{n+1}$$

where C and C' are n-dependent constants that can be determined by forcing the wavefunctions to be orthonormal. Doing this (I will not show this here) one finds:

$$\hat{a}u_n = \sqrt{n\hbar}\, u_{n-1}$$

$$\hat{a}^\dagger u_n = \sqrt{(n+1)\hbar}\, u_{n+1}$$

One should note here that $\hat{a}$ and $\hat{a}^\dagger$ move up and down the same "ladder". Hence, these operators are sometimes also referred to as ladder operators.

We can now readily calculate the energy of a given state n. We have:

$$\begin{aligned}
\hat{H}u_n &= \left(\omega\hat{a}^\dagger\hat{a} + \tfrac{1}{2}\hbar\omega\right)u_n \\
&= \omega\hat{a}^\dagger\hat{a}u_n + \tfrac{1}{2}\hbar\omega u_n \\
&= \omega\hat{a}^\dagger\sqrt{n\hbar}\,u_{n-1} + \tfrac{1}{2}\hbar\omega u_n \\
&= \omega\sqrt{(n-1+1)\hbar}\sqrt{n\hbar}\,u_n + \tfrac{1}{2}\hbar\omega u_n \\
&= \omega n\hbar u_n + \tfrac{1}{2}\hbar\omega u_n \\
&= \hbar\omega(n+\tfrac{1}{2})u_n = E_n u_n
\end{aligned}$$

This is exactly the same result we found before when we solved the differential equation, except that now we have not solved any complicated mathematical equations. This way of solving a quantum mechanical problem is closely related to the method proposed by Heisenberg.

With this at hand, one can now simply solve the integral given at the beginning of this section, something you will do in the exercises.