**The Harmonic Oscillator**

Consider a diatomic molecule. Such a molecule has a single degree of freedom, the bond length. If the molecule is stable, the potential energy will have a minimum at what is called the equilibrium bond length, it will rise to infinity as the atoms are pushed closer and closer together (nuclear fusion!), and it will rise to a plateau as the atoms are pulled so far from one another that they no longer interact. The level of this plateau defines the zero of energy (see figure below).
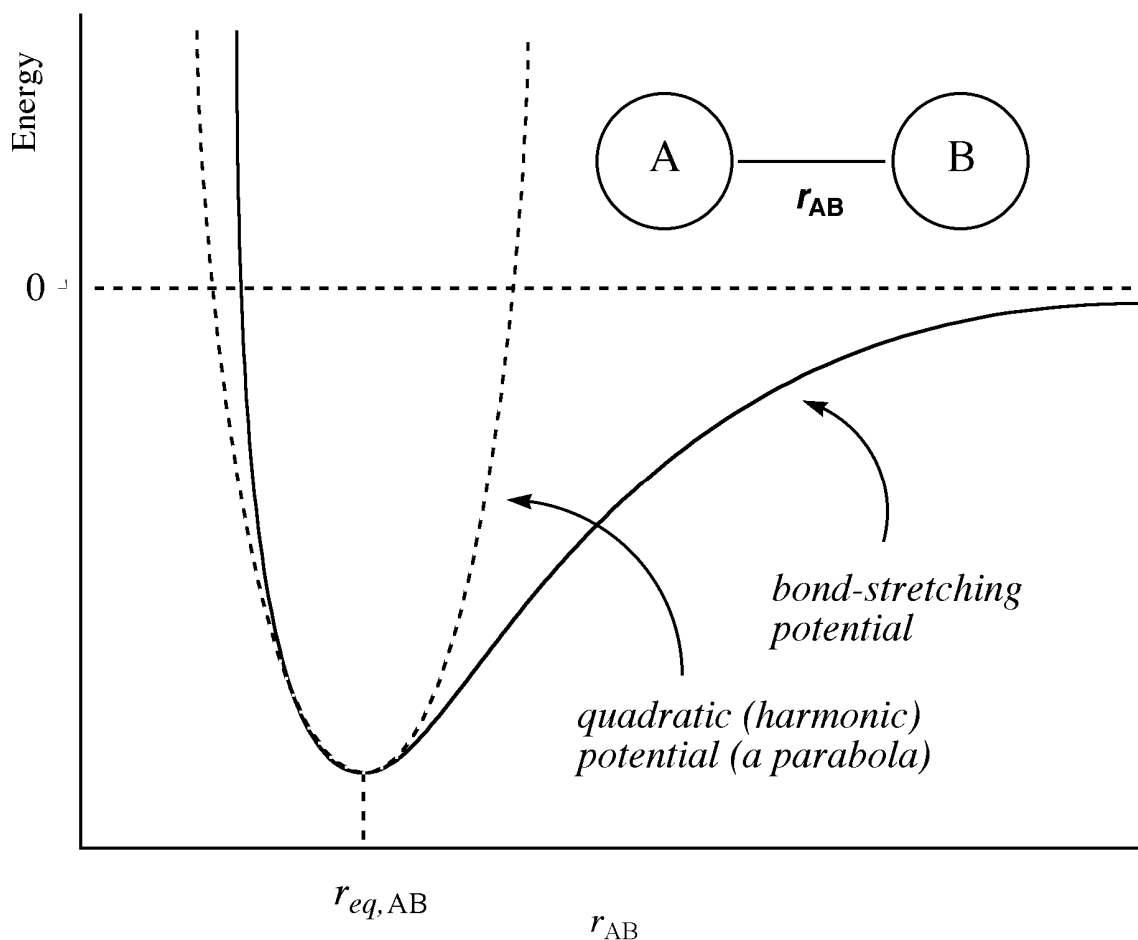
If we consider the vibrational motion of the molecule, we expect there to be solutions to the time-independent Schrödinger equation that will correspond to stationary vibrational states of the system behaving as a quantum mechanical system. That is, there will be a wave function from which the probability of finding any particular range of bond lengths can be computed. To find such stationary states, we need to solve

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + V(r) \right]\Psi(r) = E\Psi(r) \tag{9-1}$$

where μ is some sort of effective mass for the vibration (called the "reduced mass"; it's not simply the mass of atom A + atom B: that mass would be appropriate if we were thinking of the molecule AB as a free particle translating through space, but vibration is a different kind of motion, and we'll get back to μ later), the one dimension we care about is the bond length r (we could as easily use x in our notation, but r is more conventional), and the potential energy V is just the curve in the above figure.

Later in the class, we will get to how one might use quantum mechanics to *predict* the bonding potential, but for now let's just accept that it is a nice physical observable that can be measured. However, to plug it into our eq. 9-1, we need some convenient mathematical representation of that curve. We could somehow develop a spline fit or other elegant form, but that might make the solution of the differential equation quite difficult. For the moment, let's keep things really simple. One way to represent *any* function is from knowledge of that function's value, and the value of its derivatives, at a single point. We may then use a so-called Taylor expansion to compute the function's value at any other point. If we choose as our function our bond potential V, our coordinate as r, and our known point as the equilibrium bond distance, we have

$$V(r) = V\left(r_{eq}\right) + \left.\frac{dV}{dr}\right|_{r=r_{eq}}\left(r - r_{eq}\right) + \frac{1}{2!}\left.\frac{d^2V}{dr^2}\right|_{r=r_{eq}}\left(r - r_{eq}\right)^2 + \frac{1}{3!}\left.\frac{d^3V}{dr^3}\right|_{r=r_{eq}}\left(r - r_{eq}\right)^3 + \cdots \tag{9-2}$$

For the sake of simplicity, we now do several things. First, define the zero of energy to be $V(r_{eq})$. That makes term 1 on the r.h.s. equal to zero. Next, notice that r_{eq} defines the local minimum on the bond potential curve. Since it is a critical point on the curve, we know that the first derivative of V must be zero at that point. So, now the second term on the r.h.s. is zero. The next term, the quadratic term, is not zero. So, let's throw away all the other terms in the series; that is, we truncate our Taylor expansion at the quadratic term. If we do that, our generator for V is limited to a single term that defines a parabola the "steepness" of which is a function of the second derivative of V. That parabola is shown as a dashed curve in the above figure. Note that it is too "loose" on the compressed side of the bond, and too "tight" on the stretched side (not to mention that it never turns over to become a constant), but it's not a bad representation of V near the bottom of the well.

Quadratic potential functions are also known as harmonic functions. Notice that the force, which is the negative first derivative of the potential, is

$$F(r) = -\frac{d}{dr}\left[\frac{1}{2!}\frac{d^2V}{dr^2}\bigg|_{r=r_{eq}}\left(r - r_{eq}\right)^2\right]$$

$$= -k\left(r - r_{eq}\right)$$

(9-3)

where we use k to represent the second derivative of V at r_{eq} (remember that's just a number, since we're evaluating it at a particular point, so it is independent of r for purposes of taking the derivative). Systems where the force is linear in the displacement are well known in classical physics. A good example of such a system is a ball connected to a fixed position by a spring, and one refers to k as the spring "force constant". Stiff springs have large force constants and it takes a lot of energy to stretch/compress them and vice versa for loose springs.

Remember that we defined r_{eq} to be zero, so if we replace V in eq. 9-1 with our truncated Taylor expansion for V we have

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + \frac{1}{2}kr^2\right]\Psi(r) = E\Psi(r)$$

(9-4)

For notational convenience, we now introduce two new variables defined as

$$\alpha = \frac{2\mu E}{\hbar^2} \quad \text{and} \quad \beta^2 = \frac{\mu k}{\hbar^2}$$

(9-5)

In that case, the Schrödinger equation becomes

$$\left[\frac{d^2}{dr^2} + \left(\alpha - \beta^2 r^2\right)\right]\Psi(r) = 0$$

(9-6)

and we need to solve that differential equation.

Such a solution is *not* trivial. We will do it here in slow and painful detail, not primarily because solving differential equations is good for the soul, but more because carrying out the solution is informative in illustrating how *quantization* comes into play.

To begin, we consider the asymptotic behavior of eq. 9-6. When r becomes very large, the equation becomes effectively

$$\left[\frac{d^2}{dr^2} - \beta^2 r^2\right]\Psi(r) = 0 \tag{9-7}$$

A tried and true way to solve differential equations is simply to guess (honest!). Here, we've seen a similar looking differential equation for the wavefunction of a tunneling particle in the barrier region, and it seems like a good guess might be

$$\Psi(r) = e^{\pm\beta r^2/2}$$

$$\frac{d}{dr}\Psi(r) = \pm\beta r e^{\pm\beta r^2/2} \tag{9-8}$$

$$\frac{d^2}{dr^2}\Psi(r) = \pm\beta e^{\pm\beta r^2/2} + \beta^2 r^2 e^{\pm\beta r^2/2} \approx \beta^2 r^2 e^{\pm\beta r^2/2}$$

Notice that the second derivative is exactly equal to the potential term we want to cancel, provided we remember that we are working in the large r regime, so the term involving only β as a prefactor will become negligible compared to the one involving $\beta^2 r^2$. Another issue is whether we should use the positive or negative argument of the exponential in Ψ. This is easy, however. If we were to use the positive argument, Ψ would go to infinity as r goes to infinity, but we require our wave function to go to zero at infinity in order to ensure normalization. So, it is apparent that a good solution to Ψ will be

$$\Psi(r) = f(r)e^{-\beta r^2/2} \tag{9-9}$$

where we are taking β to be the positive square root of β^2, defined in eq. 9-5 and f is a function of r that fails to dominate at large r, but leads to eq. 9-6 being satisfied at smaller values of r.

In order to learn more about f, let's plug it into eq. 9-6. If we do, we have

$$0 = \left[\frac{d^2}{dr^2} + \left(\alpha - \beta^2 r^2\right)\right]f(r)e^{-\beta r^2/2} \tag{9-10}$$

The second derivative we need is determined from

$$\frac{d^2}{dr^2}\left[f(r)e^{-\beta r^2/2}\right] = \frac{d}{dr}\left\{\frac{d}{dr}\left[f(r)e^{-\beta r^2/2}\right]\right\}$$

$$= \frac{d}{dr}\left[\frac{df(r)}{dr}e^{-\beta r^2/2} - \beta r f(r)e^{-\beta r^2/2}\right]$$

$$= \frac{d^2 f(r)}{dr^2}e^{-\beta r^2/2} - \frac{df(r)}{dr}\beta r e^{-\beta r^2/2} - \beta f(r)e^{-\beta r^2/2}$$

$$- \frac{df(r)}{dr}\beta r e^{-\beta r^2/2} + \beta^2 r^2 f(r)e^{-\beta r^2/2}$$

(9-11)

If we insert this second derivative into eq. 9-10 and collect terms we have

$$0 = e^{-\beta r^2/2}\left[\frac{d^2 f(r)}{dr^2} - 2\beta r\frac{df(r)}{dr} + (\alpha - \beta)f(r)\right]$$

(9-12)

Notice that eq. 9-12 can only be true in general if the term in *brackets* is zero. This is a new differential equation for *f* that we must solve! Again, some simplification can be obtained by introducing a new variable

$$y = \sqrt{\beta}r \quad \Rightarrow \quad r = \frac{y}{\sqrt{\beta}}$$

$$\Rightarrow \quad \frac{d}{dr} = \sqrt{\beta}\frac{d}{dy}$$

(9-13)

If we introduce this substitution into the differential equation in brackets in eq. 9-12 we have

$$0 = \beta\frac{d^2 f(y)}{dy^2} - 2\beta y\frac{df(y)}{dy} + (\alpha - \beta)f(y)$$

$$= \frac{d^2 f(y)}{dy^2} - 2y\frac{df(y)}{dy} + \left(\frac{\alpha}{\beta} - 1\right)f(y)$$

(9-14)

The typical approach to solve a differential equation of the form of eq. 9-14 is to assume

$$f(y) = \sum_{n=0}^{\infty}c_n y^n$$

(9-15)

since any continuous, smooth, single-valued function of *y* can be represented by such a power series. Solution of eq. 9-14 then comes down determining the coefficients c_n that satisfy eq. 9-14.

Let's consider the derivatives of f for eq. 9-15. They are

$$f(y) = c_0 + c_1 y + c_2 y^2 + c_3 y^3 + \cdots$$

$$\frac{df(y)}{dy} = c_1 + 2c_2 y + 3c_3 y^2 + 4c_4 y^3 + \cdots \qquad (9\text{-}16)$$

$$\frac{d^2 f(y)}{dy^2} = 2c_2 + 6c_3 y + 12c_4 y^2 + 20c_5 y^3 + \cdots$$

If we plug these series into eq. 9-14 and collect terms of equivalent powers in y, we have

$$0 = \left[2c_2 + c_0 \left(\frac{\alpha}{\beta} - 1 \right) \right]$$

$$+ \left[6c_3 + c_1 \left(\frac{\alpha}{\beta} - 3 \right) \right] y$$

$$+ \left[12c_4 + c_2 \left(\frac{\alpha}{\beta} - 5 \right) \right] y^2 \qquad (9\text{-}17)$$

$$+ \left[20c_5 + c_3 \left(\frac{\alpha}{\beta} - 7 \right) \right] y^3$$

$$+ \cdots$$

The only way that eq. 9-17 can be satisfied for *all* values of y is if every term in brackets is *individually* equal to zero. Thus, for the first term, we would have the requirement

$$c_2 = - \frac{c_0 \left(\dfrac{\alpha}{\beta} - 1 \right)}{2} \qquad (9\text{-}18)$$

and for the second

$$c_3 = - \frac{c_1 \left(\dfrac{\alpha}{\beta} - 3 \right)}{6} \qquad (9\text{-}19)$$

Notice that c_4 depends on c_2, which itself depended on c_0, and similarly the series of c_n for n odd is completely determined by c_1. The relation between the various values of c is called a "recursion relation". If you look carefully, you will see that in general we have

$$c_{m+2} = -\frac{\left(\dfrac{\alpha}{\beta} - 2m - 1\right)}{(m+1)(m+2)} c_m \qquad (9\text{-}20)$$

where $m \geq 0$. Interestingly, the odd and even coefficients are independent of one another. Note that the even coefficients multiply even powers of y, and a linear combination of even functions of y has even parity. The odd coefficients multiply odd powers of y, and a linear combination of odd functions of y has odd parity. If we want our wave functions to be eigenfunctions of the parity operator (as they should be, since the parity operator commutes with the Hamiltonian of eq. 9-4) we will require either c_0 or c_1 to be zero in any wave function (and, by the recursion relation of eq. 9-20, all other even or odd coefficients, respectively, will also be zero).

Now, note that if we allow the power series expansion of eq. 9-15 to go on infinitely, our wave function would diverge for large values of y, and we cannot permit this for a well behaved wave function. Thus, we require there to be a value of c_j that is zero for a finite value of j. Once that term is zero, the recursion relation ensures that all further terms are also zero. *This is the point at which quantization enters!* Since there is a smallest value of j for which c_j vanishes—let's call it $n + 2$—eq. 9-20 makes it clear that the only way to make $c_{n+2} = 0$ (since $c_n \neq 0$) is for

$$\left(\frac{\alpha}{\beta} - 2n - 1\right) = 0 \qquad (9\text{-}21)$$

If we plug in our original definitions for α and β (eq. 9-5), we have, after rearrangement,

$$\begin{aligned} E &= \left(n + \frac{1}{2}\right) h\left(\frac{1}{2\pi}\sqrt{\frac{k}{\mu}}\right) \\ &= \left(n + \frac{1}{2}\right) h\nu \end{aligned} \qquad (9\text{-}22)$$

where we have replaced the last term in parentheses by ν, the "frequency". That is because the term in parentheses is the classical oscillation frequency for a spring having force constant k and mass μ (for springs, as for pendula, the oscillation frequency is independent of initial displacement).

Before finishing our work on our differential equations, let us consider eq. 9-22. It says several very important things. In particular, it indicates that

1) For each value of n there is a unique energy for the quantum mechanical harmonic oscillator (QMHO). Thus, *there are no degenerate levels.*

2) The separation between *any* two adjacent levels is $h\nu$.

3) For $n = 0$, the energy is *not* zero, it is $1/2(hv)$. This is the "zero-point" energy. This is again a manifestation of the Heisenberg uncertainty principle. If the oscillator had zero energy, it would be at the bottom of the well. That would be an exact position (there is only one minimum) and an exact momentum (zero), and since those operators don't commute for this system, that is not permitted.

4) The separation between energy levels goes up for larger force constants (tighter bonds).

5) The separation between energy levels goes up for smaller reduced masses (we will see later that this implies lighter atoms).

6) Since the energy between levels is hv, the frequency of a photon that would induce a change *between* adjacent levels (assuming that's an allowed process, which we haven't established yet) is *also* v.

Wrapping Up the Wave Functions

Let us consider now the various prefunctions $f(r)$ appearing in the wave functions of eq. 9-9. It should be clear from eqs. 9-20 and 9-21 that we will generate different wave functions by allowing successive values of c_n to be non-zero, where any individual f will involve only even or odd values of n. So, our first wave function will have only c_0 non-zero. That is, we will have

$$\Psi_0(r) = c_0 e^{-\sqrt{k u}\, r^2 / 2\hbar}$$

(9-22)

In this case, the value of c_0 is determined by requiring the wave function to be normalized. It is a simple matter of looking up the relevant integral for the square modulus of the Gaussian function (recall that an exponential function of the negative of an argument squared is called a Gaussian function) and taking c_0 to be the inverse square root. In that case, we find

$$\Psi_0(r) = \left(\frac{\sqrt{k\mu}}{\pi\hbar}\right)^{1/4} e^{-\sqrt{k\mu}\, r^2 / 2\hbar}$$

(9-23)

Our next wave function will take even coefficients to be zero, and allow only c_1 to be non-zero. That gives

$$\Psi_1(r) = c_1 \left(\sqrt{\frac{\sqrt{k\mu}}{\hbar}}\, r\right) e^{-\sqrt{k u}\, r^2 / 2\hbar}$$

(9-24)

where we now have y represented to the first power (but expressed in terms of r using eqs. 9-5 and 9-13). Again, normalization determines the value of the unknown coefficient, and we find

$$\Psi_1(r) = \left(\frac{\sqrt{k\mu}}{4\pi\hbar}\right)^{1/4} \left[2\left(\frac{\sqrt{k\mu}}{\hbar}\right)^{1/2} r\right] e^{-\sqrt{k\mu} r^2/2\hbar} \qquad (9\text{-}25)$$

where the notation looks a bit odd with the factor of 2 appearing in the brackets, but this reflects historical aspects of the Hermite polynomials and need not concern us here.

If we continued down this road, we would have additional powers of r appearing in each expression. The recursion relation between c values would guarantee only a single unknown (either c_0 or c_1) which will always be determined from imposing normalization. The polynomials generated by making these truncated series expansions are known as the Hermite polynomials. They were well known to classical physicists as they appear in the solution to certain problems of reflectance from curved surfaces. We will not dwell on their properties further here. Instead, we will simply note that the Hermite polynomials involving even values of n are even (since they include only even powers of r) and those involving odd values of n are odd.

Finally, to conclude with these wave functions, we need to specify exactly what μ is. The reduced mass for the oscillator involving balls A and B is defined to be

$$\mu = \frac{m_A m_B}{m_A + m_B} \qquad (9\text{-}26)$$

where m is the mass of an individual ball. We will not derive this expression. Note, however, that it has the right limit when one mass becomes very much larger than the other. In that case, we expect the heavy mass to move almost not at all (it is like a wall) so the reduced mass becomes the mass of the lighter object, which is exactly the mass used for a single ball attached by a spring to a wall. Note also that if the two masses are identical, the reduced mass is one-half the mass of either one.

Homework

To be solved in class:

(a) Evaluate <r> and <r²> for the QMHO ground and first excited states (i.e., quantum numbers $n = 0$ and 1).

(b) What is the latter quantity related to physically?

To be turned in for possible grading Feb. 17:

(a) Rewrite eq. 9-6 in the standard form of an eigenvalue equation.

(b) Show that by proper choice of a, the function e^{-ar^2} is an eigenfunction of the operator

$$\left(\frac{d^2}{dr^2} - qr^2 \right)$$

where q is a constant.

(c) Show how you can use the results from parts (a) and (b) to determine the energy of the ground state of the QMHO.

(d) How do you know that the eigenfunction corresponds to the ground state?