Solved Homework

We are asked to find $<x>$ and $<x^2>$ for the first two harmonic oscillator wave functions, which are

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

and

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

So, for $<x>$ we have

$$\langle x \rangle_{n=0} = \langle \Psi_0(x)|x|\Psi_0(x) \rangle$$
$$\langle x \rangle_{n=1} = \langle \Psi_1(x)|x|\Psi_1(x) \rangle$$

Before we do any heavy lifting with the integrals, note that Ψ_0 is an even function, Ψ_1 is an odd function, and x is an odd function. So, we have integrals of either even x odd x even or odd x odd x odd. Either case results in an odd function, so the expectation value in both cases is zero. Remember that in our derivation x (or r) represents the *displacement* from the equilibrium bond length between the two balls. Thus, a value of zero implies the equilibrium distance (i.e., the bottom of the potential energy well). Since *all* harmonic oscillator wave functions are either even or odd, *all* of the wave functions have $<x> = 0$. That is, they are all symmetric about the equilibrium length, and the average of all of our experiments to measure bond length will be the equilibrium bond length *irrespective of what vibrational state we measure.*

As for $<x^2>$, now life is not so easy, since parity says the integrals need not be zero. Let's start with Ψ_0.

$$\langle x^2 \rangle_{n=0} = \int_{-\infty}^{\infty} \left(\frac{\sqrt{k\mu}}{\pi\hbar} \right)^{1/4} e^{-\sqrt{k\mu}x^2/2\hbar} x^2 \left(\frac{\sqrt{k\mu}}{\pi\hbar} \right)^{1/4} e^{-\sqrt{k\mu}x^2/2\hbar} dx$$

$$= \left(\frac{\sqrt{k\mu}}{\pi\hbar} \right)^{1/2} \int_{-\infty}^{\infty} x^2 e^{-\sqrt{k\mu}x^2/\hbar} dx$$

An integral table provides

$$\int_{-\infty}^{\infty} x^2 e^{-ax^2} dx = \frac{1}{2a} \left(\frac{\pi}{a} \right)^{1/2}$$

If we plug in the appropriate value of a we have

$$\langle x^2 \rangle_{n=0} = \left(\frac{\sqrt{k\mu}}{\pi\hbar} \right)^{1/2} \left(\frac{\hbar}{2\sqrt{k\mu}} \right) \left(\frac{\pi\hbar}{\sqrt{k\mu}} \right)^{1/2}$$

$$= \left(\frac{\hbar}{2\sqrt{k\mu}} \right)$$

Let's do a quick sanity check on this answer. It says that as the force constant k gets larger, the average of the squared displacement from the equilibrium bond length will get smaller. That makes sense: stiffer spring, less displacement as it vibrates. It also says that as the reduced mass goes up, the average displacement will be smaller. That too makes intuitive sense. Kinetic energy goes up with mass, so in the same vibrational period we will have to slow down (and thus go less far) to maintain the same energy if the mass increases.

Now, what about the case for Ψ_1? There we have

$$\langle x^2 \rangle_{n=1} = \int_{-\infty}^{\infty} \left(\frac{\sqrt{k\mu}}{4\pi\hbar} \right)^{1/4} \left[2 \left(\frac{\sqrt{k\mu}}{\hbar} \right)^{1/2} x \right] e^{-\sqrt{k\mu}x^2/2\hbar} x^2 \left(\frac{\sqrt{k\mu}}{4\pi\hbar} \right)^{1/4}$$

$$\times \left[2 \left(\frac{\sqrt{k\mu}}{\hbar} \right)^{1/2} x \right] e^{-\sqrt{k\mu}x^2/2\hbar} dx$$

$$= \left(\frac{\sqrt{k\mu}}{4\pi\hbar} \right)^{1/2} \left(\frac{4\sqrt{k\mu}}{\hbar} \right) \int_{-\infty}^{\infty} x^4 e^{-\sqrt{k\mu}x^2/\hbar} dx$$

An integral table provides

$$\int_{-\infty}^{\infty} x^4 e^{-ax^2} dx = \frac{3}{4a^2} \left(\frac{\pi}{a} \right)^{1/2}$$

If we plug in the appropriate value of a we have

$$\left\langle x^2 \right\rangle_{n=1} = \left(\frac{\sqrt{k\mu}}{4\pi\hbar} \right)^{1/2} \left(\frac{4\sqrt{k\mu}}{\hbar} \right) \left(\frac{3\hbar^2}{4k\mu} \right) \left(\frac{\pi\hbar}{\sqrt{k\mu}} \right)^{1/2}$$

$$= \left(\frac{3\hbar}{2\sqrt{k\mu}} \right)$$

So, the average of the squared displacement is three times larger for $n = 1$ than for $n = 0$. We will look more closely at the wave functions themselves below, and this result will be consistent with the appearance of the probability densities.

Based on the above two results, you might be tempted to predict, in general, that for eigenstate n

$$\left\langle x^2 \right\rangle_n = \left[\frac{(2n+1)\hbar}{2\sqrt{k\mu}} \right]$$

And, you would be correct! Note that the average of the square displacement increases linearly with increasing n.

Analysis of The Harmonic Oscillator Wave Functions

The QM harmonic oscillator wave functions are shown on the next page, as are their square moduli, which represent their probability distributions. There are several important things to note. We'll discuss some of these in more detail below, but for now, let's just list them (there is some overlap with the list from last lecture).

1) The zeroth level wave function is not at the zero of energy. It's height above the zero of energy (the bottom of the potential well) is called the zero-point energy, and is equal to $(1/2)h\nu$.

2) The zeroth level wave function has no nodes, and each higher level wave function has one more node than the one below it.

3) For all of the wave functions, the expectation value of the kinetic energy is exactly equal to the expectation value of the potential energy (this is not obvious from inspection, but is the subject of tomorrow's homework).

4) From (3), it follows that the average potential and kinetic energies each increase by $(1/2)h\nu$ as we go from one level to the next. It seems obvious that the potential energy increases, since the wave function samples more distant regions of the potential, and we will look at the kinetic energy below.
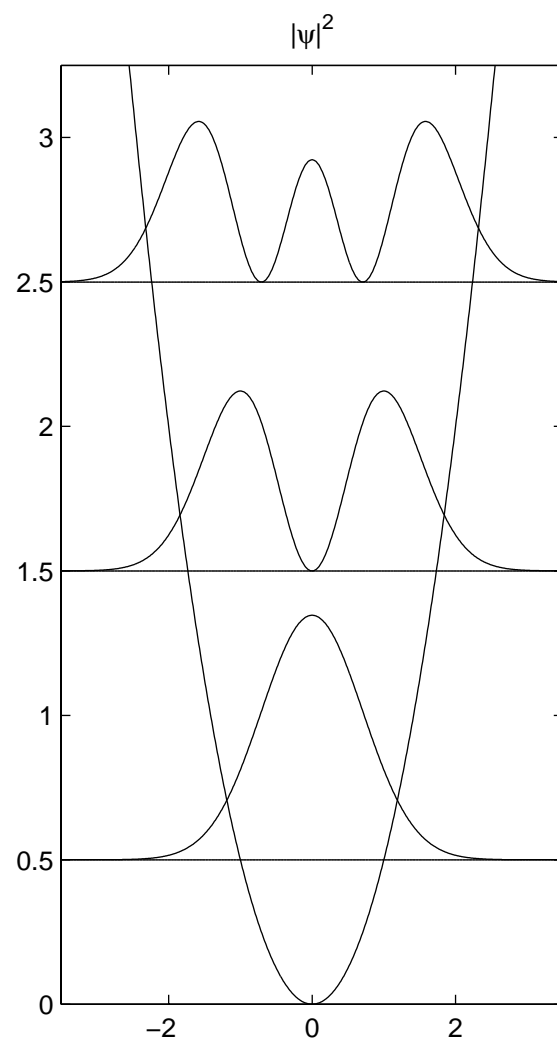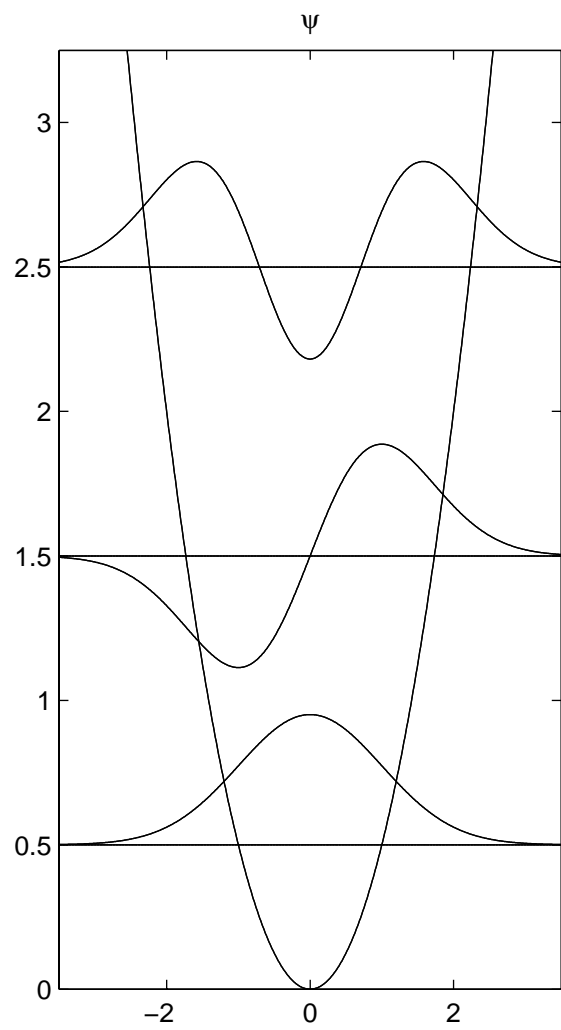
5)   The probability distributions of the wave functions penetrate the potential barrier. This is very much like what we saw with tunneling. It is possible to find bond lengths that correspond to the system having negative kinetic energy. [Note that this seems like a paradox only if you permit yourself to imagine that you can know the kinetic energy without measuring it. If you measure it, it *will* be positive, but then you won't have been able to measure the bond length to an accuracy beyond that permitted by the uncertainty principle...]

6)   Although all of the energy levels have $<x> = 0$, only the probability amplitude of the ground state is *peaked* at $x = 0$ (indeed, there is a *node* there for all the levels with odd n!) For higher and higher levels, the maximum probabilities shift to the "walls" of the potential. The points $-x$ and x where the potential is equal to the total energy are called the "classical turning points".

7)   Spectroscopic transitions between harmonic oscillator energy levels are permitted only for changes to the level immediately above or immediately below, i.e., $n \rightarrow n \pm 1$. The energy of the photon required for this transition is $E = h\nu$ where the frequency of the photon is exactly the same frequency as that of the harmonic oscillator (since the separation in energy levels of the harmonic oscillator is also $h\nu$). We'll look at spectroscopy more below.

Zero-Point Energy

An interesting aspect of zero point energy is that, for the same potential energy function (which is to say the same force constant), it depends on the reduced mass μ. Recall that the zero-point vibrational energy is

$$E_{ZPVE} = \frac{1}{2}h\nu$$

$$= \frac{h}{4\pi}\sqrt{\frac{k}{\mu}} \qquad (10\text{-}1)$$

$$= \frac{h\sqrt{k}}{4\pi}\sqrt{\frac{m_A + m_B}{m_A m_B}}$$

where A and B are the two atoms involved in the bond. So, let us consider the case of different isotopes. That is, atomic nuclei having the same number of protons (so they are the same elements) but a different number of neutrons (so they are different masses). Since the elements do not change, we do not really expect k to change as a function of isotope. It is the electrical force that holds a bond together, and that electrical force has no dependence on neutral neutrons in the atomic nuclei. However, the reduced mass will change. Consider, for example, A is a carbon atom (C, mass 12 amu) and B is either a hydrogen atom (H, mass 1 amu) or a deuterium atom (D, mass 2 amu). The reduced masses of the C–H and C–D systems are (12/13) and (24/14) respectively, i.e., they differ by about a factor of 2, with the C–D value being larger than the C–H value. Since ZPVE

depends inversely on the square root of the reduced mass, we expect it to be smaller for the C–D bond than for the C–H bond.

Bond length
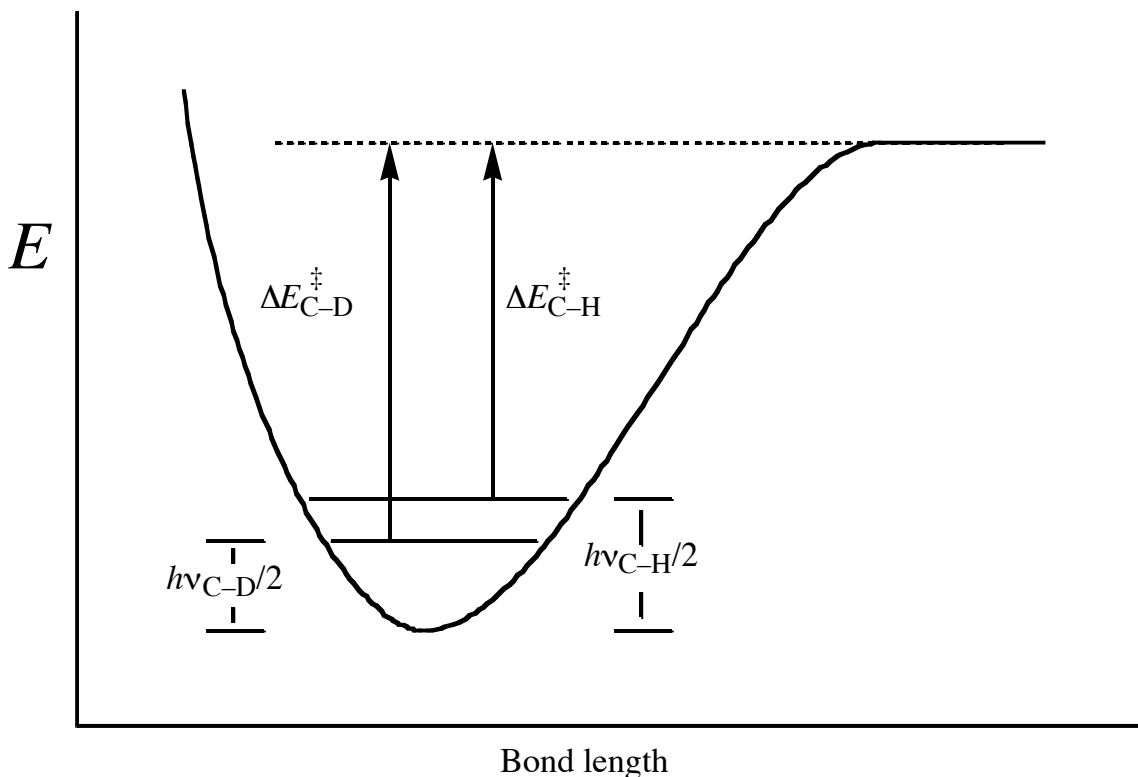
      Is there a chemical consequence to this difference? Indeed there is! Recall that we used a harmonic potential to *approximate* the *real* bonding potential. The real potential has a dissociation limit at large r that corresponds to breaking the bond. At that limit, we have two atoms as isolated particles—no bond between them, no oscillator, no zero-point energy (free particles can have zero energy). So, the energy required to break the bond is the difference in energy between the zeroth vibrational level and the dissociation energy. Since the zeroth level is $(1/2)h\nu$ above the common well bottom, the C–D ground vibrational state is at lower energy than the C–H ground vibrational state, and it will require more energy to break the C–D bond than the C–H bond. This situation is exactly what one observes experimentally. At room temperature, a C–H bond is about 7 times more likely to be broken than an otherwise equivalent C–D bond challenged by the same abstracting reagent.

      For tritium (T, mass 3 amu, a radioactive isotope of hydrogen), the difference in reduced mass with hydrogen is even larger, and the strength of the bond is quite large. It has been estimated that if all the hydrogen atoms in your body were to be replaced by tritium, you would die more quickly from your enzymes being unable to make and break bonds to T than from the massive radiation poisoning you would instantly begin to suffer!

Nodes and Kinetic Energy

Although the homework for today deals with QMHO kinetic energies, let us examine a completely general rule: for substantially similar wave functions, the more nodes, the greater the average kinetic energy. A proof of this point is disarmingly simple. Consider for an arbitrary wave function Ψ

$$\langle T \rangle = \int_{-\infty}^{\infty} \Psi^*(x) \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right] \Psi(x) \, dx$$

$$= -\frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \Psi^*(x) \left[\frac{d^2 \Psi(x)}{dx^2} \right] dx \qquad (10\text{-}2)$$

(we are working in one dimension, x, for simplicity in notation, but the proof is completely general). How shall we evaluate the integral we are left with? One approach is to integrate by parts. Let us take

$$u = \Psi^*(x) \quad \text{and} \quad dv = \frac{d^2 \Psi(x)}{dx^2} dx$$

$$du = \frac{d\Psi^*(x)}{dx} dx \quad \text{and} \quad v = \frac{d\Psi(x)}{dx} \qquad (10\text{-}3)$$

in which case we have

$$\int_{-\infty}^{\infty} \Psi^*(x) \left[\frac{d^2 \Psi(x)}{dx^2} \right] dx = \left(\Psi^*(x) \frac{d\Psi(x)}{dx} \right) \Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \frac{d\Psi^*(x)}{dx} \left[\frac{d\Psi(x)}{dx} \right] dx$$

$$= 0 - 0 - \int_{-\infty}^{\infty} \left| \frac{d\Psi(x)}{dx} \right|^2 dx \qquad (10\text{-}4)$$

$$= -\int_{-\infty}^{\infty} \left| \frac{d\Psi(x)}{dx} \right|^2 dx$$

If we plug this into eq. 10-2 we have

$$\langle T \rangle = \frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \left| \frac{d\Psi(x)}{dx} \right|^2 dx \qquad (10\text{-}5)$$

So, what is the meaning of the integral of the square modulus of the derivative of the wave function? Well, let us remember what the derivative means. If the wave function is changing rapidly with x, the derivative will be large in magnitude. If it is changing slowly with x, the derivative will be small in magnitude. As we are working

with the square modulus, it does not matter here what the *sign* of the derivative is, or whether it is real or complex, all that matters is the magnitude.

It should be clear that as a wave function develops more nodes, its derivative will have larger amplitude over more space than for a wave function that has fewer nodes. It is perhaps simplest to see this by taking the absurd case. Imagine the wave function were to have nodes infinitely close to one another (a *lot* of nodes...). In that case, the function is dashing almost straight up and down crossing the axis at every position. Its slope (i.e., its first derivative) must be effectively infinite at every position, so it will have maximal kinetic energy. It should be simple to see that as the spacing between nodes increases because there are fewer of them, the integrated square modulus of the slope will decrease, and thus the kinetic energy decreases.

Note that this result is completely general. Everyone learns in freshman chemistry that, for a given principle quantum number, s orbitals are lower in energy than p orbitals which are lower than d orbitals, etc. This is actually not quite true, as we will see later, but what *is* true is that the *first* s orbital is lower in energy than the *first* p orbital is lower in energy than the *first* d orbital in part because s orbitals have no planar nodes, p orbitals have one planar node, d orbitals have two planar nodes, etc., and the kinetic energies of electrons in the orbitals with more nodes are higher (more positive, less favorable). We'll get to a more rigorous discussion of atomic orbitals later in the class, but this is the quick and intuitive explanation.

Spectroscopy of the QM Harmonic Oscillator—Infrared Spectroscopy

As a general rule for most bonds at room temperature, the separation between vibrational energy levels is such that a Boltzmann population of vibrational states (i.e., a thermal equilibrium of vibrational states) consists almost entirely of the zeroth vibrational level.

As noted above, the selection rule for allowed transitions in the QMHO is to allow only $n \rightarrow n \pm 1$. Thus, essentially the only allowed transition at room temperature is that from the ground state to the first excited state level. (We will not prove the selection rule; suffice it to say that it derives from some interesting mathematical properties of the Hermite polynomials.)

Typical chemical bonds, to the extent that they can be approximated as harmonic potentials, have force constants of a magnitude such that the frequency of light that is equal to the QMHO frequency (remember that absorption requires $h\nu_{light} = \Delta E_{0 \rightarrow 1} = h\nu_{QMHO}$) is in the infrared region of the spectrum.

Infrared frequencies usually are not expressed in units of s^{-1}, but rather in "wavenumbers", which are abbreviated as cm^{-1}. The relationship between the two is $\omega = \nu/c$ where ω is the frequency in wavenumbers, ν is the frequency in s^{-1}, and c is the

speed of light in cm s^{-1} (3.0 x 10^{10}). In wavenumbers, the IR region of the spectrum runs from about 4000 to 400 cm^{-1}.

Because different bonds have different force constants and different reduced masses, individual absorptions corresponding to vibrational excitations tend to be well dispersed in the IR range, and IR spectroscopy can be a very useful tool for assigning molecular functionality (as most students of organic chemistry have already learned).

Here, we will simply note that IR spectra are also useful in identifying isotopic substitution. As already pointed out above for the ZPVE, ν_{QMHO} is different for different isotopes in the same bond, and so ν_{light} must also be different. The relationship predicted from quantum mechanics is exactly the one that is observed experimentally. For example, C–H bonds typically absorb IR radiation at about 3000 cm^{-1}. Given that the reduced mass of the C–D bond is roughly half that of the C–H bond, we would expect the frequencies of absorption to differ by a factor of roughly 1.4 (the square root of two) with the C–D value being smaller, i.e., about 2150 cm^{-1}. This is exactly where such absorptions are indeed seen.

When heavier atoms are involved, changes in isotopic mass have a much smaller effect on the reduced mass, but the resolution of a good IR spectrometer is usually on the order of 1 cm^{-1}, so it is usually quite straightforward to identify isotope shifts in frequencies. These can be very useful in assigning structure when one can use synthesis to introduce isotopes into particular positions.

Homework

To be solved in class:

Evaluate the average kinetic energy for the 0th harmonic oscillator wave function (the ground state). Noting that the average potential energy is $<kx^2/2> = (k/2)<x^2>$, and that we just computed $<x^2>$ at the beginning of this lecture, show that for this state (and indeed, it turns out true for any state) the average kinetic energy is exactly equal to the average potential energy.

To be turned in for possible grading Feb. 17:

HBr and DBr (H = ^{1}H, D = ^{2}H, and Br = ^{79}Br) are observed to absorb infrared radiation at 2439 and 1750 cm^{-1}, respectively. Answer the following questions:

(a) In the ground vibrational state, which has more average kinetic energy, HBr or DBr?

(b) In units of kg, what is the reduced mass of DBr?

(c) In units of N m^{-1}, what is the force constant for the HBr bond? Is it the same for the DBr bond?

(d) At what frequency would TBr be expected to absorb radiation $(T = {}^3H)$?

(e) In units of s^{-1}, what is the vibrational frequency of HBr in the state with quantum number $n = 5$?