Answers to Homework Set 3

From lecture 9: (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?

(a) Eq. 9-6 can be rewritten as

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

which is in standard form where the eigenvalue is negative α.

(b) To show that e^{-ar^2} is an eigenfunction with proper choice of *a* we require

$$\left[\frac{d^2}{dr^2} - qr^2 \right] e^{-ar^2} = z e^{-ar^2}$$

Evaluating the l.h.s. we have

$$\left[\frac{d^2}{dr^2} - qr^2 \right] e^{-ar^2} = -2ae^{-ar^2} + 4a^2 r^2 e^{-ar^2} - qr^2 e^{-ar^2}$$

$$= -\left[2a + \left(q - 4a^2 \right) r^2 \right] e^{-ar^2}$$

and for the prefactor on the r.h.s. to be a constant (so as to satisfy the eigenvalue condition) it must be true that a is $\sqrt{q}/2$ in which case the eigenvalue will be $-2a$, which is simply $-\sqrt{q}$.

(c) Given that eq. 9-6 was rewritten as above, it is clear that q corresponds to β^2 and the eigenvalue a will then simply be $-\beta$. From eq. 9-5 we know β and thus we have

$$a = -\frac{\sqrt{\mu k}}{\hbar}$$

but a is also $-\alpha$ based on our rewriting of eq. 9-6 above. So, noting from eq. 9-5 what α is defined to be, we now have

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

if we now solve for E we have

$$E = \frac{\hbar}{2}\sqrt{\frac{k}{\mu}}$$

which by comparison to eq. 9-22 is indeed the correct result for $n = 0$ (remember that $\hbar$ is $h/2\pi$).

(d) The trial function we have been examining is a gaussian function without nodes (i.e., it is nonnegative everywhere) so it must be the ground state wave function. Note that this process above could be repeated to get energies for the various excited states by including powers of r (that would introduce nodes) and enforcing orthogonality, but it would get to be rather painful rather quickly…

From lecture 10: 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 = ^{3}H)? (e) In units of s^{-1}, what is the vibrational frequency of HBr in the state with quantum number n = 5?

(a) In the ground state, a QMHO has zero-point vibrational energy equal to $h\nu/2$ where ν is the vibrational frequency. The vibrational frequency is equal to the frequency of the photon that is absorbed in order to induce a transition between levels. So, HBr has more zero-point vibrational energy than DBr. Moreover, we showed in the in-class homework that for the QMHO the average kinetic energy is exactly equal to the average potential energy both of which are one-half of the total energy. Since HBr has more total energy than DBr, perforce it will have more average kinetic energy than DBr.

(b) In atomic mass units, the reduced mass of DBr is 158/81. The conversion from amu to kg is approximately 1.67×10^{-27} kg amu^{-1}. Thus, the reduced mass of DBr is about 3.26×10^{-27} kg.

(c) It is a quick matter to verify that the HBr and DBr frequencies differ by the square root of the ratio of their reduced masses (see part (d) for example of TBr) so the two must indeed have the same force constant. As we know the vibrational frequency (in units of wavenumbers, which must be multiplied by the speed of light to convert to units of s^{-1}; see part (e) for example) and the reduced mass for DBr (from above), we can compute k by rearrangement of

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

to

$$k = 4\pi^2 \mu \nu^2$$

which gives a value of about 354 N m^{-1}.

(d)   Since the force constant is the same irrespective of isotope, we only need the reduced-mass ratio to make the requested prediction. In atomic mass units, HBr has a reduced mass of 79/80 and TBr has a reduced mass of 237/82. So, the vibrational frequency of TBr (and hence the frequency at which it absorbs radiation) should be the frequency of HBr times the square root of the ratio of the reduced masses [(79 x 82) / (80 x 237)] which gives a value of about 1426 cm^{-1}.

(e) The vibrational frequency of the harmonic oscillator is the same for *all* quanum levels, and it is equal to the frequency of radiation absorbed to induce a transition between levels. For HBr that frequency is 2439 cm^{-1}. To convert to units of s^{-1} we need to multiply by the speed of light, $c = 3 \times 10^{10}$ cm s^{-1} which gives a frequency of 7.3×10^{13} s^{-1}.

From lecture 11: All of the angular momentum operators that we have discussed thus far are Hermitian. For an arbitrary function Φ

having finite total angular momentum, what is required for it to be true that

$$\langle \Phi | L_+ L_- | \Phi \rangle = \langle \Phi | L_- L_+ | \Phi \rangle$$

where $L_+ L_-$ is the operator defined by sequential application of the lowering operator and then the raising operator, and vice versa? Note that an "arbitrary" function means that it need *not* be an eigenfunction of L^2. If you don't know where to start on this problem, which is certainly not trivial, take another look at eqs. 6-7 and 6-8 and their surrounding discussion and think about how you might be able to apply analogous reasoning to this problem.

An arbitary function can be expressed as a linear combination of the eigenfunctions of L_z since, as eigenfunctions of a Hermitian operator, they are orthonormal and span all space. Since the expectation value of L^2 for the arbitrary function is finite, there will be a maximum and a minimum value for m_l, i.e., the linear expansion will involve a finite number of terms. So, for our arbitrary function Φ, we have

$$\Phi = c_{-m_l} \Psi_{-m_l} + c_{-m_l+1} \Psi_{-m_l+1} + \ldots + c_{m_l-1} \Psi_{m_l-1} + c_{m_l} \Psi_{m_l}$$

where the various values c are coefficients multiplying the eigenfunctions of L_z that are indexed by their respective eigenvalues.

If we consider applying the lowering operator to Φ, recall that it will annihilate the eigenfunction having the most negative eigenvalue, and transform every other eigenfunction to the one having the next lower eigenvalue, i.e.,

$$L_- \Phi = \mathbf{0} + c_{-m_l+1} \Psi_{-m_l} + \ldots + c_{m_l-1} \Psi_{m_l-2} + c_{m_l} \Psi_{m_l-1}$$

If we then apply the raising operator, it has no effect on the null wave function (remember, the null wave function is not the eigenfunction of L_z having eigenvalue zero, it is the absence of any wave function at all) and it takes every other eigenfunction up to the one having the next higher quantum number. Thus

$$L_+ L_- \Phi = \mathbf{0} + c_{-m_l+1} \Psi_{-m_l+1} + \ldots + c_{m_l-1} \Psi_{m_l-1} + c_{m_l} \Psi_{m_l}$$

Now obtaining the expectation value just involves left multiplying by Φ, integrating over all space, and normalizing. That is

$$\frac{\langle\Phi|L_+L_-|\Phi\rangle}{\langle\Phi|\Phi\rangle} = \frac{\left\langle \begin{array}{c} c_{-m_l}\Psi_{-m_l} + c_{-m_l+1}\Psi_{-m_l+1} + \ldots + c_{m_l-1}\Psi_{m_l-1} + c_{m_l}\Psi_{m_l} \\ \bigg| \mathbf{0} + c_{-m_l+1}\Psi_{-m_l+1} + \ldots + c_{m_l-1}\Psi_{m_l-1} + c_{m_l}\Psi_{m_l} \end{array} \right\rangle}{\left\langle \begin{array}{c} c_{-m_l}\Psi_{-m_l} + c_{-m_l+1}\Psi_{-m_l+1} + \ldots + c_{m_l-1}\Psi_{m_l-1} + c_{m_l}\Psi_{m_l} \\ \bigg| c_{-m_l}\Psi_{-m_l} + c_{-m_l+1}\Psi_{-m_l+1} + \ldots + c_{m_l-1}\Psi_{m_l-1} + c_{m_l}\Psi_{m_l} \end{array} \right\rangle}$$

$$= \frac{\left|c_{-m_l+1}\right|^2 + \ldots \left|c_{m_l-1}\right|^2 + \left|c_{m_l}\right|^2}{\left|c_{-m_l}\right|^2 + \left|c_{-m_l+1}\right|^2 + \ldots \left|c_{m_l-1}\right|^2 + \left|c_{m_l}\right|^2}$$

where the second line follows from the first because of the orthonormality of the eigenfunctions Ψ.

A completely analogous analysis for the alternative operator gives

$$\frac{\langle\Phi|L_-L_+|\Phi\rangle}{\langle\Phi|\Phi\rangle} = \frac{\left\langle \begin{array}{c} c_{-m_l}\Psi_{-m_l} + c_{-m_l+1}\Psi_{-m_l+1} + \ldots + c_{m_l-1}\Psi_{m_l-1} + c_{m_l}\Psi_{m_l} \\ \bigg| c_{-m_l}\Psi_{-m_l} + c_{-m_l+1}\Psi_{-m_l+1} + \ldots + c_{m_l-1}\Psi_{m_l-1} + \mathbf{0} \end{array} \right\rangle}{\left\langle \begin{array}{c} c_{-m_l}\Psi_{-m_l} + c_{-m_l+1}\Psi_{-m_l+1} + \ldots + c_{m_l-1}\Psi_{m_l-1} + c_{m_l}\Psi_{m_l} \\ \bigg| c_{-m_l}\Psi_{-m_l} + c_{-m_l+1}\Psi_{-m_l+1} + \ldots + c_{m_l-1}\Psi_{m_l-1} + c_{m_l}\Psi_{m_l} \end{array} \right\rangle}$$

$$= \frac{\left|c_{-m_l}\right|^2 + \left|c_{-m_l+1}\right|^2 + \ldots \left|c_{m_l-1}\right|^2}{\left|c_{-m_l}\right|^2 + \left|c_{-m_l+1}\right|^2 + \ldots \left|c_{m_l-1}\right|^2 + \left|c_{m_l}\right|^2}$$

The only way these two can be equal is if the numerators are equal (the denominators already are). For that to be the case, it must be true that

$$\left|c_{-m_l}\right|^2 = \left|c_{m_l}\right|^2$$

That is, the square modulus of the coefficient for the angular momentum basis function having the most negative possible angular momentum in the z direction must be equal to that for the angular momentum basis function having the most positive possible angular momentum in the z direction. One possibility would be, for instance, that both coefficients be zero, in which case the sequential application of the raising and lowering operators would always return unchanged the starting wave function.

As a final note for the *true* rigor jockey, the above proof is ever so slightly sloppy. To be rigorous, we would have had to acknowledge that the arbitrary function Φ must actually be expressed as a linear combination of a finite number of eigenfunctions of L^2 each one of which consists of a degenerate, finite set of eigenfunctions of L_z. This makes the notation a bit messier, but the proof would otherwise be exactly the same.