PH 253 Exam II Solutions

1. The state of a free particle is described by the following wave function

$$\psi(\mathbf{x}) = \begin{cases} 0 & \mathbf{x} < -\mathbf{b} \\ \mathbf{A} & -\mathbf{b} \leqslant \mathbf{x} \leqslant 2\mathbf{b} \\ 0 & \mathbf{x} > 2\mathbf{b} \end{cases}$$
(1)

(a) Determine the normalization constant A.

(b) What is the probability of finding the particle in the interval [0, b]?

(c) Determine $\langle x \rangle$ and $\langle x^2 \rangle$ for this state.

(d) Find the uncertainty in position $\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$.

As above, we can normalize the wavefunction by integrating its square over all space. Conveniently, the wavefunction is zero except over the interval [-b, 2b]

$$\int |\psi(\mathbf{x})|^2 \, \mathrm{d}\mathbf{x} = \int_{-b}^{2b} \mathbf{A}^2 \, \mathrm{d}\mathbf{x} = 3b\mathbf{A}^2 = 1 \qquad \Longrightarrow \qquad \mathbf{A} = \frac{1}{\sqrt{3b}} \tag{2}$$

The probability of finding the particle in [0, b] means integrating the probability density, $|\psi|^2$ over that interval:

$$P(x \in [0, b]) = \int_{0}^{b} A^{2} dx = \int_{0}^{b} \frac{1}{3b} dx = \frac{1}{3}$$
(3)

Finding $\langle x \rangle$ proceeds as above, though now we integrate over all space. As with the normalization integral above, we need only integrate over the interval where ψ is nonzero:

$$\langle \mathbf{x} \rangle = \int_{-b}^{2b} \frac{\mathbf{x}}{3b} \, \mathrm{d}\mathbf{x} = \frac{1}{3b} \left[\frac{1}{2} \mathbf{x}^2 \right]_{-b}^{2b} = \frac{1}{6b} \left(4b^2 - b^2 \right) = \frac{b}{2} \tag{4}$$

Similarly,

$$\langle \mathbf{x}^2 \rangle = \int_{-\mathbf{b}}^{2\mathbf{b}} \frac{\mathbf{x}^2}{3\mathbf{b}} \, d\mathbf{x} = \frac{1}{3\mathbf{b}} \left[\frac{1}{3} \mathbf{x}^3 \right]_{-\mathbf{b}}^{2\mathbf{b}} = \frac{1}{9\mathbf{b}} \left[8\mathbf{b}^3 + \mathbf{b}^3 \right] = \mathbf{b}^2 \tag{5}$$

Thus,

$$\Delta \mathbf{x} = \sqrt{\langle \mathbf{x}^2 \rangle - \langle \mathbf{x} \rangle^2} = \sqrt{\mathbf{b}^2 - \frac{\mathbf{b}^2}{4}} = \pm \frac{\mathbf{b}\sqrt{3}}{2} \tag{6}$$

2. The Schrödinger equation for a simple harmonic oscillator of mass m can be written

$$-a^4 \frac{d^2 \psi}{dx^2} + x^2 \psi = \frac{2E}{C} \psi \tag{7}$$

where $a^4 = \hbar^2/mC$, C is the force constant, and E the energy. ⁱ

(a) Below are the wave functions for the first two states; find their energies in terms of $\hbar \omega_0$.

(b) Suggest a general formula for energy the nth state. How does it differ from Planck's hypothesis for the energy of his oscillators?

$$\psi_0 = \left(\frac{1}{a\sqrt{\pi}}\right)^{1/2} e^{-x^2/2a^2}$$
$$\psi_1 = \left(\frac{1}{2a\sqrt{\pi}}\right)^{1/2} 2\left(\frac{x}{a}\right) e^{-x^2/2a^2}$$

To save you some time, we note $\frac{d}{dx}(e^{-x^2/2a^2}) = -\frac{x}{a^2}e^{-x^2/2a^2}$ and $\frac{d^2}{dx^2}(e^{-x^2/2a^2}) = \frac{x^2-a^2}{a^4}e^{-x^2/2a^2}$

First, the ground state. Note that we can write the second derivative of the wavefunction in terms of the original wavefunction, which will save us a considerable amount of time:

$$\frac{d^2\psi_0}{dx^2} = \frac{d^2}{dx^2} \left(\frac{1}{a\sqrt{\pi}}\right)^{1/2} e^{-x^2/2a^2} = \left(\frac{1}{a\sqrt{\pi}}\right)^{1/2} \left(\frac{x^2 - a^2}{a^4}\right) e^{-x^2/2a^2} = \left(\frac{x^2 - a^2}{a^4}\right)\psi_0 \qquad (8)$$

This is the start of one big trick we've used again and again: manipulate the differential equation to get a simpler equation in terms of the original function ... but we'll get to that. Plugging this in our Scrödinger equation, we have:

$$-a^{4}\frac{d^{2}\psi_{0}}{dx^{2}} + x^{2}\psi_{0} = \frac{2E}{C}\psi_{0}$$
(9)

$$-a^4 \left(\frac{x^2 - a^2}{a^4}\right) \psi_0 + x^2 \psi_0 = \frac{2E}{C} \psi_0 \tag{10}$$

Keep in mind that what we are trying to do here is find the conditions under which this equation has a general solution for all x, we are *not* trying to solve for x! Now, if this equation is to have a general solution, it must be true for any old value of x. For that to be true, the coefficients of the x^2 terms must be equal, and the constant terms must be equal. Picking out the coefficients, we come up with two equations:

$$-x^2 + x^2 = 0 (11)$$

$$a^2 = \frac{2E}{C} \tag{12}$$

ⁱNote $\omega_{o} = 2\pi f_{o} = \sqrt{C/m}, a = (\hbar/\sqrt{mC})^{1/2} = \sqrt{\hbar/m\omega_{o}}.$

The first is of limited utility. The second yields the energy in terms of the force constant:

$$\mathsf{E} = \frac{1}{2}\mathsf{C}\mathfrak{a}^2 = \frac{1}{2}\mathsf{C}\frac{\hbar}{\sqrt{\mathsf{m}\mathsf{C}}} = \frac{1}{2}\hbar\sqrt{\frac{\mathsf{C}}{\mathsf{m}}} = \frac{1}{2}\hbar\omega \tag{13}$$

For the first excited state, we proceed similarly, though it is substantially more tedious ... to save a little clutter, we will define $A_1 = \left(\frac{1}{2\alpha\sqrt{\pi}}\right)^{1/2}$. The derivative calculation proceeds:

$$\psi_1 = 2\mathsf{A}_1\left(\frac{\mathsf{x}}{\mathsf{a}}\right)\mathsf{e}^{-\mathsf{x}^2/2\mathsf{a}^2} \tag{14}$$

$$\frac{d\psi_1}{dx} = A_1 \frac{2}{a} e^{-x^2/2a^2} + A_1 \frac{2x}{a} \left(-\frac{x}{a^2}\right) e^{-x^2/2a^2} = A_1 e^{-x^2/2a^2} \left(\frac{2}{a} - \frac{2x^2}{a^3}\right)$$
(15)

$$\frac{d^2\psi_1}{dx^2} = A_1\left(-\frac{x}{a^2}\right)e^{-x^2/2a^2}\left(\frac{2}{a} - \frac{2x^2}{a^3}\right) + A_1e^{-x^2/2a^2}\left(-\frac{4x}{a^3}\right)$$
(16)

$$= 2A_1 e^{-x^2/2a^2} \left(\frac{x^3}{a^5} - \frac{3x}{a^3}\right) = \left(\frac{x^2}{a^4} - \frac{3}{a^2}\right) 2A_1 \left(\frac{x}{a}\right) e^{-x^2/2a^2}$$
(17)

$$= \left(\frac{x^2}{a^4} - \frac{3}{a^2}\right)\psi_1\tag{18}$$

Again, we have the second derivative in terms of the original wavefunction. Substituting into our Schrödinger equation,

$$-a^4 \left(\frac{x^2}{a^4} - \frac{3}{a^2}\right)\psi_1 + x^2\psi_1 = \frac{2\mathsf{E}}{\mathsf{C}}\psi_1 \tag{19}$$

And, again, for a general solution for all x, we must have the coefficients of the x^2 terms equal to one another, and the constant terms must also be equal. The coefficients of the quadratic terms leads to nothing new, as before, but equating the constant terms we have again a condition on energy:

$$3a^2 = \frac{2E}{C}$$
(20)

$$\mathsf{E} = \frac{3}{2}\mathsf{C}\mathfrak{a}^2 = \frac{3}{2}\hbar\omega \tag{21}$$

Consistent with Planck's hypothesis, the energy *difference* between the ground and first excited states is $\hbar\omega$, but the energies themselves come in half-integral amounts rather than integral amounts. As we have discussed, the energy of the nth state of the harmonic oscillator is $E_n = (n + \frac{1}{2}) \hbar\omega$, whereas the Planck' theory predicts $E_n = n\hbar\omega$. The existence of the "zero point" energy, a finite energy of $\frac{1}{2}\hbar\omega$ even in the n = 0 state, was first noted by Einstein and Stern in 1913 in their explanation of the specific heat of hydrogen gas at low temperatures. This residual zero point energy persists even as one approaches absolute zero, and implies that a quantum harmonic oscillator will always be in motion.

3. A phenomenological expression for the potential energy of a bond as a function of spacing is given by

$$U(\mathbf{r}) = \frac{A}{r^{n}} - \frac{B}{r^{m}}$$
(22)

For a stable bond, m < n. Show that the molecule will break up when the atoms are pulled apart to a distance

$$\mathbf{r}_{\mathbf{b}} = \left(\frac{\mathbf{n}+1}{\mathbf{m}+1}\right)^{1/(\mathbf{n}-\mathbf{m})} \mathbf{r}_{\mathbf{o}} \tag{23}$$

where r_0 is the equilibrium spacing between the atoms. Be sure to note your criteria for breaking used to derive the above result.

The condition defining equilibrium is that the force vanishes, or equivalently that the potential energy is a minimum. If the equilibrium spacing is r_0 , then

$$F(r_{o}) = -\frac{dU}{dr}\Big|_{r_{o}} = \frac{nA}{r_{o}^{n+1}} - \frac{mB}{r_{o}^{m+1}}$$
(24)

$$\frac{nA}{mB} = \frac{r_o^{n+1}}{r_o^{m+1}} = \frac{r \cdot r_o^n}{r \cdot r_o^m} = r_o^{n-m}$$
(25)

$$\implies r_{o} = \left(\frac{nA}{mB}\right)^{\frac{1}{n-m}}$$
(26)

Is this really a minimum? We can check with the second derivative test: if $d^2U/dr^2 = -dF/dr > 0$ at r_o , have a maximum. We will need dF/dr shortly anyway. You didn't really need to do this on the test, since you were given that the stability condition m < n, but it is instructive:

$$-\frac{dF}{dr} = \frac{d^2 U}{dr^2} = \frac{n(n+1)A}{r^{n+2}} - \frac{m(m+1)B}{r^{m+2}}$$
(27)

$$\frac{d^{2}U}{dr^{2}}\Big|_{r_{o}} = n(n+1)A\left(\frac{mB}{nA}\right)^{\frac{n+2}{n-m}} - m(m+1)B\left(\frac{mB}{nA}\right)^{\frac{m+2}{n-m}}$$
(28)

$$= \left(\frac{mB}{nA}\right)^{2} \left[n\left(n+1\right)A\left(\frac{mB}{nA}\right)^{\frac{n}{n-m}} - m\left(m+1\right)B\left(\frac{mB}{nA}\right)^{\frac{m}{n-m}}\right]$$
(29)

$$= \left(\frac{\mathrm{mB}}{\mathrm{nA}}\right)^{2} \left(\frac{\mathrm{mB}}{\mathrm{nA}}\right)^{\frac{\mathrm{m}}{\mathrm{n}-\mathrm{m}}} \left[\mathrm{n}\left(\mathrm{n}+1\right)\mathrm{A} - \mathrm{m}\left(\mathrm{m}+1\right)\mathrm{B}\left(\frac{\mathrm{mB}}{\mathrm{nA}}\right)^{\frac{\mathrm{m}-\mathrm{n}}{\mathrm{n}-\mathrm{m}}}\right]$$
(30)

$$= \left(\frac{\mathrm{mB}}{\mathrm{nA}}\right)^{2} \left(\frac{\mathrm{mB}}{\mathrm{nA}}\right)^{\frac{\mathrm{n}}{\mathrm{n}-\mathrm{m}}} \left[\mathrm{n}\left(\mathrm{n}+1\right)\mathrm{A} - \mathrm{m}\left(\mathrm{m}+1\right)\mathrm{B}\left(\frac{\mathrm{nA}}{\mathrm{mB}}\right)\right]$$
(31)

$$= \left(\frac{\mathbf{m}B}{\mathbf{n}A}\right)^{\frac{\mathbf{n}-\mathbf{m}}{\mathbf{n}-\mathbf{m}}} \left[\mathbf{n}\left(\mathbf{n}+1\right)A - \mathbf{n}\left(\mathbf{m}+1\right)A\right]$$
(32)

$$= nA\left(\frac{mB}{nA}\right)^{\frac{m+2}{n-m}} \left[n-m\right] > 0 \tag{33}$$

Clearly, the only way this expression will be positive is if n > m, as previously stated. This means that the repulsive force has a higher index than the attractive force, and it is of shorter range.

What about breaking the molecule? For distances smaller than r_0 , the force is repulsive, while for dis-

tances greater than r_0 it is attractive – in either case, it serves to try and restore the equilibrium position. However, the competition between the shorter-range repulsive force and longer-range attractive force means that there is a critical distortion of the molecule for $r > r_0$ at which the force is maximum, and any stronger force (or larger displacement) will separate the constituents to an arbitrarily large distance – the molecule will be broken.

We have the force between the molecular constituents above:

$$F(r) = \frac{nA}{r^{n+1}} - \frac{mB}{r^{m+1}}$$
(34)

so we can readily calculate the maximum force with which the bond may try to restore its equilibrium. The force above is the force with which the molecule will respond if we push or pull on it.ⁱⁱ The maximum force will occur when dF/dr=0, at a radius r_b

$$\frac{dF}{dr} = -\frac{n(n+1)A}{r_b^{n+2}} + \frac{m(m+1)B}{r_b^{m+2}} = 0$$
(35)

$$\frac{n(n+1)A}{m(m+1)B} = \frac{r_b^{n+2}}{r_b^{m+2}} = r_b^{n-m}$$
(36)

$$\implies r_{b} = \left(\frac{nA}{mB}\right)^{\frac{1}{n-m}} \left(\frac{n+1}{m+1}\right)^{\frac{1}{n-m}} = r_{o} \left(\frac{n+1}{m+1}\right)^{\frac{1}{n-m}}$$
(37)

Now, how do we know this is the *maximum* force, and not a minimum force? We grind through another derivative ... we must have $d^2F/dr^2 > 0$ for a maximum:

$$\begin{aligned} \frac{d^{2}F}{dr^{2}} &= \frac{n\left(n+1\right)\left(n+2\right)A}{r^{n+3}} - \frac{m\left(m+1\right)\left(m+2\right)B}{r^{m+3}} = r^{n+3} \left[n\left(n+1\right)\left(n+2\right)A - \frac{m\left(m+1\right)\left(m+2\right)B}{r^{m-n}}\right] \\ \frac{d^{2}F}{dr^{2}}\Big|_{r_{b}} &= r_{o}^{n+3}\left(\frac{n+1}{m+1}\right)^{\frac{n+3}{n-m}} \left[n\left(n+1\right)\left(n+2\right)A - m\left(m+1\right)\left(m+2\right)Br_{o}^{n-m}\left(\frac{n+1}{m+1}\right)^{\frac{n-m}{n-m}}\right] \\ &= r_{o}^{n+3}\left(\frac{n+1}{m+1}\right)^{\frac{n+3}{n-m}} \left[n\left(n+1\right)\left(n+2\right)A - m\left(n+1\right)\left(m+2\right)Br_{o}^{n-m}\right] \end{aligned}$$
(38)

$$=r_{o}^{n+3}\left(\frac{n+1}{m+1}\right)^{\frac{n+3}{n-m}}\left[n\left(n+1\right)\left(n+2\right)A-m\left(n+1\right)\left(m+2\right)B\left(\frac{nA}{mB}\right)\right]$$
(39)

$$= r_{o}^{n+3} \left(\frac{n+1}{m+1}\right)^{\frac{n+3}{n-m}} \left[n\left(n+1\right)\left(n+2\right)A - n\left(n+1\right)\left(m+2\right)A \right]$$
(40)

$$=\operatorname{An}\left(n+1\right)r_{o}^{n+3}\left(\frac{n+1}{m+1}\right)^{\frac{n+m}{n-m}}\left[n-m\right]>0$$
(41)

For the second to last line, we noted that $r_o^{n-m} = nA/mB$. Once again, if n > m, the second derivative is positive, and thus the force is maximum at r_b . Applying a force sufficiently strong to stretch the bond

ⁱⁱSee HW9, problem 5.

to a separation r_b will serve to break it. Incidentally, the maximum force required is

$$\begin{split} \mathsf{F}(\mathsf{r}_{\mathsf{b}}) &= \frac{\mathsf{n}\mathsf{A}}{\mathsf{r}_{\mathsf{o}}^{\mathsf{n}+1}} \left(\frac{\mathsf{n}+1}{\mathsf{m}+1}\right)^{\frac{\mathsf{n}+1}{\mathsf{m}-\mathsf{n}}} - \frac{\mathsf{m}\mathsf{B}}{\mathsf{r}_{\mathsf{o}}^{\mathsf{m}+1}} \left(\frac{\mathsf{n}+1}{\mathsf{m}+1}\right)^{\frac{\mathsf{m}+1}{\mathsf{m}-\mathsf{n}}} = \left(\frac{\mathsf{n}+1}{\mathsf{m}+1}\right)^{\frac{\mathsf{n}+1}{\mathsf{m}-\mathsf{n}}} \left[\frac{\mathsf{n}\mathsf{A}}{\mathsf{r}_{\mathsf{o}}^{\mathsf{n}+1}} - \frac{\mathsf{m}\mathsf{B}}{\mathsf{r}_{\mathsf{o}}^{\mathsf{m}+1}} \left(\frac{\mathsf{n}+1}{\mathsf{m}+1}\right)\right] \\ &= \left(\frac{\mathsf{n}+1}{\mathsf{m}+1}\right)^{\frac{\mathsf{n}+1}{\mathsf{m}-\mathsf{n}}} \left[\mathsf{n}\mathsf{A}\left(\frac{\mathsf{n}\mathsf{A}}{\mathsf{m}\mathsf{B}}\right)^{\frac{\mathsf{n}+1}{\mathsf{m}-\mathsf{n}}} - \mathsf{m}\mathsf{B}\left(\frac{\mathsf{n}\mathsf{A}}{\mathsf{m}\mathsf{B}}\right)^{\frac{\mathsf{m}+1}{\mathsf{m}-\mathsf{n}}} \left(\frac{\mathsf{n}+1}{\mathsf{m}+1}\right)\right] \end{split}$$
(42)

$$= \left(\frac{n+1}{m+1}\right)^{\frac{n+1}{m-n}} \left(\frac{nA}{mB}\right)^{\frac{n+1}{m-n}} \left[nA - nA\left(\frac{n+1}{m+1}\right)\right]$$
(43)

$$= nA\left(\frac{n+1}{m+1}\right)^{\frac{n+1}{m-n}} \left(\frac{nA}{mB}\right)^{\frac{n+1}{m-n}} \left(\frac{m-n}{m+1}\right) = \frac{nA}{r_b^{n+1}} \left(\frac{m-n}{m+1}\right)$$
(44)

4. (a) Using the Bohr model, what wavelength of photon is emitted when an electron in a hydrogen atom makes a transition from the 4f to 3d state?

(b) Show that in the presence of a magnetic field, the $4f \rightarrow 3d$ transition in hydrogen appears as three spectral lines. You may ignore spin, and assume only dipole transitions will occur (see formula sheet).

In the Bohr model, energy is independent of the angular momentum state, so we really just want the energy to go from the n=4 to the n=3 state. Given $E_n = -13.6 \text{ eV}/n^2$, the energy difference between the two states is

$$\mathsf{E}_{34} = -13.6 \,\mathrm{eV}\left(\frac{1}{4^2} - \frac{1}{3^2}\right) = 0.661 \,\mathrm{eV} \tag{45}$$

The corresponding photon wavelength is $\lambda = hc/E_{34} \approx 1876$ nm, in the infrared.

In a magnetic field B, the energy levels for a given l state will split according to their value of m_l . If the original energy of the level is E_l , then the original level will be split symmetrically into 2l + 1 sub-levels, with adjacent levels shifted by $\mu_B B$:

$$\mathsf{E}_{\mathsf{l},\mathsf{m}_{\mathsf{l}}} = \mathsf{E}_{\mathsf{l}} + \mathsf{m}_{\mathsf{l}} \mu_{\mathsf{B}} \mathsf{B} \tag{46}$$

This is shown schematically below for 4f (l = 3) and 3d (l = 2) levels. The l = 3 level has possible m_l values of $m_l = \{-3, -2, -1, 0, 1, 2, 3\}$, and thus in a magnetic field B what was a single level is now 7 individual levels. For l = 2, we have m_l values of only $m_l = \{-2, -1, 0, 1, 2\}$, and the original level becomes 5 levels upon applying a magnetic field.

Before calculating anything, we can apply the dipole selection rules, which states that m_l can change by only $0, \pm 1$. This means that, for example, from the l = 3, $m_l = 1$ level an electron may "jump" to the any of the l=2, $m_l = \{2, 1, 0\}$ levels. On the other hand, from l=3, $m_l = 3$ level an electron may only jump to the l=2, $m_l=2$ level. Following these rules, we see from the figure above that there are only 15 possible transitions allowed. Further, noting that the levels are equally spaced, by $\mu_B B$, we have in fact

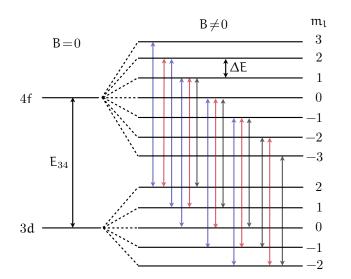


Figure 1: Allowed transitions from l = 3 to l = 2 with a magnetic field applied. Red transitions have an energy difference E_{34} , blue an energy $E_{34} + \Delta E$, and black $E_{34} - \Delta E$.

only three different transition energies.

The spacing between two adjacent levels ΔE is the Zeeman energy given above, $\Delta E = \mu_B B$. From our schematic above, it is clear that the only possible transition energies in a magnetic field are the original transition energy E_{34} (no change in m_1), or the original transition energy plus or minus ΔE (m_1 changes by ± 1). Thus, the new transition energies must be

$$E_{34} \longmapsto \{E_{34} - \Delta E, E_{34}, E_{34} + \Delta E\} = \{E_{34} - \mu_B B, E_{34}, E_{34} + \mu_B B\}$$
(47)

That is, the original transition energy plus two new ones.

5. By considering the visible spectrum of hydrogen and He⁺, show how you could determine spectroscopically if a sample of hydrogen was contaminated with helium. (Hint: look for differences in the visible emission lines, $\lambda \approx 390 \sim 750$ nm. A difference of 10 nm is easily measured.)

We know the energies in a hydrogen atom are just $E_n = -13.6 \text{ eV}/n^2$ for a given level n. For the He⁺ ion, the only real difference is the extra positive charge in the nucleus. If we have Z positive charges in the nucleus, the energies become $E_n = -13.6 \text{ eV}Z^2/n^2$. For Z = 2, we just end up multiplying all the energies by a factor 4. The questions are: does this lead to any new radiative transitions, are they in the visible range, and are they well-separated enough? We can just list the energy levels for the two systems and see what we come up with.

We already know that the visible transitions in Hydrogen occur when excited states relax to the n = 2 level, and that for large n the transitions will probably have an energy too high to be in the visible range. Thus, we can probably find a new transition for He⁺ by just considering the first several levels alone. We see a couple of things already. The n=2 state for He⁺ happens to accidentally have the same energy

	H	He ⁺	
n	E _n (eV)	E _n (eV)	
I	-13.6	$-13.6\cdot 4$	
2	$-13.6 \cdot \frac{1}{4}$	-13.6	
3	$-13.6 \cdot \frac{1}{9} \\ -13.6 \cdot \frac{1}{16} \\ -13.6 \cdot \frac{1}{25}$	$-13.6 \cdot \frac{4}{9}$	
4	$-13.6 \cdot \frac{1}{16}$	$-13.6 \cdot \frac{1}{4}$	
5	$-13.6 \cdot \frac{1}{25}$	$-13.6 \cdot \frac{4}{25}$	

as the n = 1 state for H, likewise for the n = 4 state for He⁺ and the n = 2 state for H. That means that we can't just pick transitions at random, some of them will accidentally have the same energy.

However, the n = 3 state for He⁺ has the curious fraction 4/9 in it, which can't possibly occur for H. Transitions into the n = 3 state should yield unique energies. Let's compute the visible transitions in hydrogen H, since there are only a few, and see if some He⁺ transitions stick out in the in-between wavelengths:

H transition	$\lambda_H (nm)$	He ⁺ transition	λ_{He^+} (nm)
$3 \rightarrow 2$	656	$4 \rightarrow 3$	469
$4 \rightarrow 2$	486	$3 \rightarrow 2$	164
$5 \rightarrow 2$	434		
$6 \rightarrow 2$	410		

Already with just the $4 \rightarrow 3$ transition in He⁺, we have an expected emission (or absorption) at 469 nm, a full 17 nm from the nearest H line, and well in the visible range to boot (a nice pretty blue). Should be easy to pick out!

6. Find the most probable radius and the expected value of the radial position $\langle r \rangle$ of an electron in the 2s state.

$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_o}\right)^{3/2} \left(2 - \frac{r}{a_o}\right) e^{-r/2a_o} \tag{48}$$

where a_0 is the Bohr radius, $a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 0.529 \times 10^{-10}$ m. Make use of the integrals given on the formula sheet.

The most likely distance corresponds to the distance at which the probability of finding the electron is maximum. This is distinct from the expected value of the radius $\langle r \rangle$. The probability of finding an electron at a distance r in the interval [r, r + dr], in spherical coordinates, is the squared magnitude of the wavefunction times the volume of a spherical shell of thickness dr and radius r:

$$P(\mathbf{r}) d\mathbf{r} = |\psi|^2 \cdot 4\pi \mathbf{r}^2 d\mathbf{r} \qquad \text{or} \qquad P(\mathbf{r}) = |\psi|^2 \cdot 4\pi \mathbf{r}^2 \tag{49}$$

Given ψ_2 s above, we have

$$P(\mathbf{r}) = \left| \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_o} \right)^{3/2} \left(2 - \frac{\mathbf{r}}{a_o} \right) e^{-\mathbf{r}/2a_o} \right|^2 \cdot 4\pi \mathbf{r}^2 = \frac{1}{8a_o^3} \left(4\mathbf{r}^2 - \frac{4\mathbf{r}^3}{a_o} + \frac{\mathbf{r}^4}{a_o^2} \right) e^{-\mathbf{r}/a_o}$$
(50)

The most probable radius occurs when

$$\frac{dP}{dr} = 0 = \left(\frac{1}{8a_o^3}\right) \left(8r - \frac{12r^2}{a_o} + \frac{4r^3}{a_o^2}\right) e^{-r/a_o} - \left(\frac{1}{8a_o^4}\right) \left(4r^2 - \frac{4r^3}{a_o} + \frac{r^4}{a_o^2}\right) e^{-r/a_o}$$
(51)

$$0 = \left(\frac{re^{-r/a_o}}{8a_o^3}\right) \left(8 - 12\frac{r}{a_o} + 4\frac{r^2}{a_o^2} - 4\frac{r}{a_o} + 4\frac{r^2}{a_o^2} - \frac{r^3}{a_o^3}\right)$$
(52)

At this point, we can already see the trivial solutions r = 0 and $r = \infty$, which just like last time are uninteresting minima of the probability distribution. The interesting solutions are more easily found if we make a variable substitution $x = r/a_0$:

$$0 = 8 - 16x + 8x^2 - x^3 \tag{53}$$

One can factor this thing by synthetic division and find the roots to be $\{2, 3 \pm \sqrt{5}\}$, but it is just as easily done on your average graphic calculator if you just want the numbers ...

$$\mathbf{x} = \frac{\mathbf{r}}{\mathbf{a}_{o}} = \left\{ 0, 3 \pm \sqrt{5} \right\} \approx \{0.764, 2.00, 5.24\}$$
(54)

Direct substitution, or a quick plot of P(r) verifies that $r = 0.764a_o$ is a local maximum, $r = 2.00a_o$ is a local minimum (zero, actually), and $r = 5.24a_o$ is the global maximum we seek.

The expected radius is found by integrating $x\psi^2$ over all space, as in problem 1, excepting that we are now in three dimensions:

$$\langle \mathbf{r} \rangle = \int_{0}^{\infty} \mathbf{r} \mathbf{P}(\mathbf{r}) \, d\mathbf{r} = \int_{0}^{\infty} \frac{\mathbf{r}}{8a_{o}^{3}} \left(4\mathbf{r}^{2} - \frac{4\mathbf{r}^{3}}{a_{o}} + \frac{\mathbf{r}^{4}}{a_{o}^{2}} \right) e^{-\mathbf{r}/a_{o}} \tag{55}$$

$$=\frac{1}{8a_{o}^{3}}\int_{0}^{\infty}4r^{3}e^{-r/a_{o}}-\frac{4}{a_{o}}r^{4}e^{-r/a_{o}}+\frac{1}{a_{o}^{2}}r^{5}e^{-r/a_{o}}\,dr$$
(56)

Integrating by terms, and using our handy table of integrals provided,

$$\langle \mathbf{r} \rangle = \frac{1}{8a_o^3} \left(4\frac{3!}{a_o^{-4}} - \frac{4}{a_o}\frac{4!}{a_o^{-5}} + \frac{1}{a_o^2}\frac{5!}{a_o^{-6}} \right) = \frac{a_o}{8} \left(24 - 96 + 120 \right) = 6a_o \tag{57}$$