

## Problem Set 6: solutions

1. Explain why each of the following sets of quantum numbers  $(n, l, m_l, m_s)$  is not permitted for hydrogen:

$$(2, 2, -1, +\frac{1}{2})$$

$$(3, 1, +2, -\frac{1}{2})$$

$$(4, 1, +1, -\frac{3}{2})$$

$$(2, -1, +1, +\frac{1}{2})$$

**Solution:** Let's look at them one by one:

$$(2, 2, -1, +\frac{1}{2}) \tag{1}$$

From this we gather  $n=2$ , which means that  $l$  is restricted to the set  $\{0, 1\}$ . Since this set claims  $l=2$ , it is clearly invalid.

$$(3, 1, +2, -\frac{1}{2}) \tag{2}$$

Here we have  $n=3$  and  $l=1$ . This restricts  $m_l$  to the set  $\{-1, 0, 1\}$ , so the listed value of  $m_l=+2$  is invalid.

$$(4, 1, +1, -\frac{3}{2}) \tag{3}$$

We need only look at the value of  $m_s$ . The electron spin quantum number can be only  $+\frac{1}{2}$  or  $-\frac{1}{2}$ , not  $-\frac{3}{2}$ .

$$(2, -1, +1, +\frac{1}{2}) \tag{4}$$

Here we have  $n=2$ . The value of  $l$  is restricted to zero *positive* integers less than  $n$ , so the claim of  $l=-1$  makes this set invalid.

2. List the excited states (in spectroscopic notation) to which the 4p state can make downward transitions.

**Solution:** Ignoring spin, the relevant selection rule is  $\Delta l = \pm 1$ . For the 4p state,  $l = 1$ , so we can move to states that are lower in energy (such that we have a downward transition) that have  $l = \{0, 1\}$ , i.e., s and d states. Given  $n = 4$ , we are left with transitions to 3d, 3s, 2s, and 1s.

In our simplest model of the hydrogen atom, the 4s state would have the same energy as the 4p state, and no transition is possible. However, you now know that spin-orbit coupling makes the 4s state slightly lower in energy than the 4p state, so a downward transition  $4p \rightarrow 4s$  is also in principle possible. In this case we would have to worry about spin conservation and whether the transition requires a spin flip, and it becomes a bit complicated. Let's just say it is unlikely. (No points off if you missed this one, since it is a subtlety.)

**3. Splitting of Hydrogen lines.** The electron's intrinsic magnetic moment  $\vec{\mu}_s$  and intrinsic spin angular momentum  $\vec{S}$  are proportional to each other; their relationship can be written as

$$\vec{\mu}_s = -g_s \frac{e}{2m} \vec{S} = -g_s \mu_B \frac{\vec{S}}{\hbar} \quad (5)$$

with  $g_s \approx 2$ . The energy of the electron in an effective magnetic field  $\vec{B}$  is  $E = -\vec{\mu}_s \cdot \vec{B}$ .

In hydrogen, transitions occur between two spin-orbit-split 2p states and a single 1s state, leading to two emission lines. If the emission wavelength in the absence of spin-orbit coupling is 656.47 nm, and the spin-orbit splitting is 0.016 nm, estimate the strength of the effective magnetic field produced by the electron's orbital motion (i.e., the effective field due to the spin-orbit interaction) which results in this wavelength difference.

**Solution:** We can make use of the result below to relate the energy and wavelength differences, viz.:

$$|\Delta\lambda| = \left| \frac{d\lambda}{dE} \right| \Delta E = \frac{hc}{E^2} \Delta E = \frac{\lambda^2}{hc} \Delta E \quad (6)$$

Given a wavelength difference, we can find the energy difference. In a magnetic field, electrons take on two different energy states depending on whether their spins are parallel or antiparallel to the field, with their difference in energy being  $2\mu_s B$ . Given  $g_s = 2$ ,  $\mu_s = \mu_B$ , and the energy difference in a magnetic field is  $\Delta E = 2\mu_B B$ . Thus,

$$\Delta E = 2\mu_B B = \frac{hc\Delta\lambda}{\lambda^2} \quad (7)$$

Solving for B, and using the numbers given,

$$B = \frac{hc\Delta\lambda}{2\mu_B \lambda^2} \approx 0.4 \text{ T} \quad (8)$$

4. *Multiplicity of atomic magnetic moments.* Calculate the magnetic moments that are possible for the  $n=4$  level of Hydrogen, making use of the quantization of angular momentum. You may neglect the existence of spin. Compare this with the Bohr prediction for  $n=4$ .

**Solution:** If  $n=4$ , then we have possible values for  $l$  of  $l=\{0, 1, 2, 3\}$ . This gives us the magnetic moments possible:

$$\mu = -\mu_B \sqrt{l(l+1)} \quad (9)$$

$$\mu = \{0, \sqrt{2}, \sqrt{6}, 2\sqrt{3}\}\mu_B \quad (10)$$

By comparison, the Bohr model would predict for level  $n$  a magnetic moment of  $n\mu_B$ , or  $4\mu_B$  in this case.

5. *Transitions in a magnetic field.* Transitions occur in an atom between  $l=2$  and  $l=1$  states in a magnetic field of 2.0 T, obeying the selection rules  $\Delta m_l = 0, \pm 1$ . If the wavelength before the field was turned on was 680.0 nm, determine the wavelengths that are observed. You may find the following relationship useful:

$$|\Delta\lambda| = \left| \frac{d\lambda}{dE} \right| \Delta E = \frac{hc}{E^2} \Delta E = \frac{\lambda^2}{hc} \Delta E \quad (11)$$

Recall that the Zeeman effect changes the energy of a single-electron atom in a magnetic field by

$$\Delta E = m_l \left( \frac{e\hbar}{2m_e} \right) B \quad \text{with} \quad m_l = -l, -(l-1), \dots, 0, \dots, l-1, l \quad (12)$$

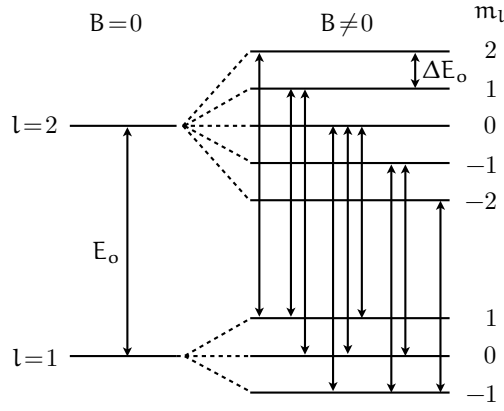
For convenience, note that  $e\hbar/2m_e = \mu_B \approx 57.9 \mu\text{eV/T}$ , and neglect the existence of spin.

**Solution:** 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  $\mu_B B$ :

$$E_{l,m_l} = E_l + m_l \mu_B B \quad (13)$$

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

Before calculating anything, we can apply the dipole selection rules, which states that  $m_l$  can



**Figure 1:** Allowed transitions from  $l=2$  to  $l=1$  with a magnetic field applied.

change by only  $0, \pm 1$ . This means that, for example, from the  $l=2, m_l=1$  level an electron may “jump” to the any of the  $l=1, m_l=\{2, 1, 0\}$  levels. On the other hand, from  $l=2, m_l=2$  level an electron may only jump to the  $l=1, m_l=1$  level. Following these rules, we see from the figure above that there are only 9 possible transitions allowed. Further, noting that the levels are equally spaced, we have in fact only three different transition energies.

The spacing between the levels  $\Delta E_o$  is the Zeeman energy given above,  $\Delta E_o = \mu_B B$ . From our schematic above, it is clear that the only possible transition energies in a magnetic field are the original transition energy (no change in  $m_l$ ), or the original transition energy plus or minus  $\Delta E_o$  ( $m_l$  changes by  $\pm 1$ ). The original transition energy  $E_o$  is readily found from the given wavelength  $\lambda=500$  nm:

$$E_o = \frac{hc}{\lambda} \approx 1.82 \text{ eV} \quad (14)$$

Thus, the new transition energies must be

$$E_o \mapsto \{E_o - \Delta E_o, E_o, E_o + \Delta E_o\} = \{E_o - \mu_B B, E_o, E_o + \mu_B B\} \quad (15)$$

That is, the original transition energy plus two new ones. We can easily convert these two new energies into two new wavelengths by the energy-wavelength relationship  $E=hc/\lambda$ . However, this does require some numerical precision (i.e., carrying at least 7-8 digits in your calculations, and knowing the requisite constants to commensurate precision), and it is somewhat easier to simply calculate the change in energy by itself. Since we know the energy changes by  $\pm \Delta E_o$ , using the formula given we have

$$|\Delta\lambda| = \frac{\lambda^2 \Delta E_o}{hc} = \frac{\lambda^2 \mu_B B}{hc} \approx 0.043 \text{ nm} \quad (16)$$

The shift in energy of  $\Delta E_o$  implies a shift in wavelength of  $\Delta\lambda \approx 0.043$  nm, meaning the new transitions must be at the original wavelength  $\lambda$  plus or minus  $\Delta\lambda$ :

$$\lambda \mapsto \{\lambda - \Delta\lambda, \lambda, \lambda + \Delta\lambda\} = \{679.957, 680.000, 680.043\} \text{ nm} \quad (17)$$

**6.** By considering the visible spectrum of hydrogen and  $\text{He}^+$ , 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.)

**Solution:** 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  $\text{He}^+$  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. Thus, we can probably find a new transition for  $\text{He}^+$  by just considering the first few higher levels above  $n=2$ . We only need one new spectral line to be able to find  $\text{He}^+$ , so we may as well just consider a few transitions at first and see if we get lucky.

	H	$\text{He}^+$
n	E <sub>n</sub> (eV)	E <sub>n</sub> (eV)
1	-13.6	$-13.6 \cdot 4$
2	$-13.6 \cdot \frac{1}{4}$	-13.6
3	$-13.6 \cdot \frac{1}{9}$	$-13.6 \cdot \frac{4}{9}$
4	$-13.6 \cdot \frac{1}{16}$	$-13.6 \cdot \frac{4}{4}$
5	$-13.6 \cdot \frac{1}{25}$	$-13.6 \cdot \frac{4}{25}$

We see a couple of things already. The  $n=2$  state for  $\text{He}^+$  happens to accidentally have the same energy as the  $n=1$  state for H, likewise for the  $n=4$  state for  $\text{He}^+$  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. In particular, the even numbers will always match up with an existing H transition.

However, the  $n=3$  state for  $\text{He}^+$  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  $\text{He}^+$  transitions stick out in the in-between wavelengths:

Already with just the  $4 \rightarrow 3$  transition in  $\text{He}^+$ , 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

H transition	$\lambda_{\text{H}}$ (nm)	He <sup>+</sup> transition	$\lambda_{\text{He}^+}$ (nm)
3 → 2	656	4 → 3	469
4 → 2	486	3 → 2	164
5 → 2	434		
6 → 2	410		

blue). Should be easy to pick out!