

Solutions Midterm Quiz: Atomic and Molecular Physics 475
March 9, 2011

Use of text book (Foot) permitted. Total 44 points. Individual values follow each question. Try and resist the temptation to look up all of the answers or you will run out of time. The written answers don't need to be long; they need to convince me that you know and understand the answer.

1. Give some evidence for the atomic theory of matter with names of prominent scientists. (Doesn't need to be complete but I would like 2 concrete pieces of evidence/contributions and show the relation to atomic theory.) (6)

Answer:

- (a) Faraday did electrolysis experiments to show that forces in matter were electromagnetic in nature, different elements had different valences, there was a light, charged, fundamental constituent to atoms (electrons). He also found the Faraday constant which gives the charge of one mole of electrons.
 - (b) Rutherford scattering by using alpha particles showed that there were very small, very dense, highly positively charged parts to matter, what we now call the atomic nucleus.
 - (c) Balmer, Rydberg, and Ritz measured and modelled the spectral lines of one-electron atoms. The spectral lines could uniquely identify different elements.
 - (d) Zeeman measured the splitting of spectral lines due to a magnetic field. This effect could be predicted by oscillations of particles with a particular e/m inside of atoms.
 - (e) Thomson's measurement of e/m of cathode rays and the verification that the e/m was the same for all cathode materials and trace gases in the tube verified that "electrons" were a fundamental constituent of matter (a bit harder to link to atomic theory except that electrons were identified as part of atomic structure).
 - (f) Einstein and Perrin made predictions and measurements of Brownian motion in matter that was caused by impacts with individual molecules. This was one of the first definitive measurements of Avogadro's number.
 - (g) Bohr's theory explained the Rydberg formula. It was based on quantization but it was also based on a planetary model of individual atoms. It also predicted that atoms would be roughly 1 Å in size.
2. What is the Zeeman effect? By explicit calculation give a scale for the frequency splitting between optical modes with $B = 1$ T. What are the 3 modes of oscillation when a magnetic field is applied to an oscillating electron (eigenvectors and eigenfrequencies) and how are they named? How are these modes related to the selection rules for m for electric dipole transitions in hydrogen? (10)

Answer: The Zeeman effect is the splitting of spectral lines when atoms are placed in a DC magnetic field. For the normal Zeeman effect the splitting is given by the Larmor frequency, Ω_L . Converting from radial frequency to cyclic frequency

$$\delta f = \frac{\Omega_L}{2\pi} = \frac{eB}{4\pi m_e} \quad (1)$$

(Note the fundamental role played by e/m .) Substituting $B = 1$ T this gives $\Omega_L = 8.8 \times 10^{10} \text{ s}^{-1}$ and $\delta f = 14$ GHz. If you compare to a typical optical frequency of $c/(500 \text{ nm}) = 6 \times 10^{14} \text{ Hz}$ then $\delta f/f \approx 2 \times 10^{-5} \approx 20$ ppm.

The three modes of oscillation are σ^+ , σ^- and π with radial frequencies of $\omega_0 + \Omega_L$, $\omega_0 - \Omega_L$ and ω_0 respectively. If the direction of the magnetic field is the z -direction then the 3 respective position eigenvectors are

$$\begin{pmatrix} \cos(\omega_0 + \Omega_L)t \\ \sin(\omega_0 + \Omega_L)t \\ 0 \end{pmatrix}, \begin{pmatrix} \cos(\omega_0 - \Omega_L)t \\ -\sin(\omega_0 - \Omega_L)t \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 0 \\ \cos \omega_0 t \end{pmatrix} \quad (2)$$

The radiation has a very particular polarization depending on the mode; σ^+ is left-circularly polarized, σ^- is right-circularly polarized, and π is linear polarized. It is through this polarization that the relationship is made to the δm selection rules. By using complex numbers it is possible to express the polarization vector of any monochromatic wave in terms of these components (see equation 2.33). The different A components correspond to radiation emitted or absorbed from each of the three different values for δm .

3. Express y/r in terms of spherical harmonics and explicitly demonstrate the equality. (4)

I essentially covered this in the tutorial and it pretty much written in equation 2.31.

$$\frac{y}{r} = \sin \theta \sin \phi = i\sqrt{\frac{2\pi}{3}}(Y_{1,-1} + Y_{1,1}) \quad (3)$$

Using the definitions of spherical harmonics in Table 2.1

$$i\sqrt{\frac{2\pi}{3}}(Y_{1,-1} + Y_{1,1}) = i\sqrt{\frac{2\pi}{3}} \left(\sqrt{\frac{3}{8\pi}} \sin \theta e^{-i\phi} - \sqrt{\frac{3}{8\pi}} \sin \theta e^{i\phi} \right) \quad (4)$$

$$= i\sqrt{\left(\frac{2\pi}{3}\right) \left(\frac{3}{8\pi}\right)} \sin \theta (-2i) \left(\frac{e^{i\phi} - e^{-i\phi}}{2i} \right) \quad (5)$$

$$= -2i^2 \frac{1}{2} \sin \theta \sin \phi = \frac{y}{r} \quad (6)$$

4. Give an example of a metastable state in hydrogen. Why is it metastable? Label this state as appropriate for LS coupling (4)

Answer: The 2s electron configuration of hydrogen is metastable. It is metastable because it is not the ground state (or lowest energy state) 1s and given time it will decay to the ground state but at a rate much slower than say 2p. The reason for this is that the selection rules for electric dipole radiation state that $\Delta \ell = \pm 1$. The transition from the $\ell = 0$ 2s state to the $\ell = 0$ 1s state would have $\Delta \ell = 0$ so it cannot decay by electric dipole radiation.

In the LS coupling scheme this state would be labelled 2s $^2S_{1/2}$.

5. What is *fine structure*? Physically (not just the formula) why is the degree of fine structure splitting so much bigger in lead than in hydrogen? Referring to Fig. 1.3 where is fine structure evident? How big is it in this case? (6)

Answer: Fine structure arises from an extension of the Hamiltonian to include relativistic effects. A proper solution would involve the Dirac equation but it possible to class them as the relativistic mass correction, spin-orbit interaction, and Darwin term (for $\ell = 0$ states). (Note: the Lamb shift is not predicted by the Dirac equation; you need to quantize the electric and magnetic fields as well to calculate it).

Our studies of relativity have told us that the first order relativistic corrections are on the order of $\frac{v^2}{c^2}$ (consider the γ factor of special relativity). The inner electrons in lead move much faster than they do in hydrogen so we expect larger corrections. We also expect relativistic corrections to break the degeneracy with respect to ℓ (recall our discussion of Sommerfeld's elliptical orbits). That is exactly what we see in Fig. 1.3. The innermost or K shell with $n = 1$ only permits $\ell = 0$. The $n = 2$ or L shell can have $\ell = 0$ or $\ell = 1$ and the degeneracy is broken. The overall splitting is between 3 and 4 keV. (I believe that the 3 levels correspond to a Lamb shifted $2 S_{1/2}$, $2 P_{1/2}$, and $2 P_{3/2}$. Remember they are flipped upside down on this diagram.)

6. In our discussion of excited states of helium we used degenerate perturbation theory. Why? Give the expressions for the energy shifts and the names that go with them in the early part of Foot Chapter 3. What modification is made to the perturbing Hamiltonian later in Chapter 3 and how is that modification related to the energy levels shown in Foot Fig. 3.4? (8)

Answer: There are two electrons in helium and the Hamiltonian, which involves the Coulomb potential of the nucleus and the perturbation (electrostatic repulsion between the electrons), predicts that the excited states are degenerate with respect to exchange of the electrons (so for example being a bit loose with the notation the state $1s1p$ has the same energy as $1p1s$). However because we are dealing with identical fermions the state itself must be antisymmetric (in both spin and spatial coordinates) under particle exchange. The spin and spatial coordinates are distinct so in order to have overall antisymmetry one of them must change sign under exchange and the other must not. Consider the spatial coordinates: $\psi_{1s1p} \neq \pm\psi_{1p1s}$ so the eigenstates under particle exchange must be a linear combination of these degenerate states. These linear combinations have different energies because of the K exchange term and the same energy under the J or direct integral term.

Later in the chapter we change the “perturbation” so that we treat the “inner” electron as though it sees a $2e$ nucleus and the outer electron as though it sees a shielded nucleus with a charge $1e$. You might also consider that setting the zero of energy to singly ionized He a modification. (Of course there is no such thing as inner and outer in QM since you still need to be able to switch the electrons and get the same state but it is very convenient to use this language.). Now J and K are different and both become smaller as the outer electron moves farther away, so the higher energy states approach the H energy levels. The new J is represents a downward shift for both singlet and triplet states and the $2K$ is still the splitting between the states.

7. Don't calculate it but include the correct expressions for the R functions in equation 3.31 to give a closed expression for J_{1s2p} for helium (Be careful with the Z -values.) (6)

Answer: From Table 2.2

$$R_{1,0}(Z = 2) = \left(\frac{2}{a_0}\right)^{\frac{3}{2}} 2 \exp\left(-\frac{2r}{a_0}\right) \quad (7)$$

$$R_{2,1}(Z = 1) = \left(\frac{1}{2a_0}\right)^{\frac{3}{2}} \frac{2}{\sqrt{3}} \frac{r}{2a_0} \exp\left(-\frac{r}{2a_0}\right) \quad (8)$$

and then subbing into (3.31) and combining some terms

$$J_{1s2p} = \frac{e^2}{4\pi\epsilon_0} \int_0^\infty \left\{ \int_{r_2}^\infty \left(\frac{1}{r_1} - \frac{1}{r_2}\right) \left(\frac{2}{a_0}\right)^3 4 \exp\left(-\frac{4r_1}{a_0}\right) r_1^2 dr_1 \right\} \frac{r_2^4}{24a_0^5} \exp\left(-\frac{r_2}{a_0}\right) dr_2 \quad (9)$$

Then if you wanted to actually evaluate it make sure that a_0 matches all of the length dimensions.

$$J_{1s2p} = \frac{e^2}{3\pi\epsilon_0 a_0} \int_0^\infty \left\{ \int_{r_2}^\infty \left(\frac{a_0}{r_1} - \frac{a_0}{r_2} \right) \left(\frac{r_1}{a_0} \right)^2 \exp\left(-\frac{4r_1}{a_0}\right) d\left(\frac{r_1}{a_0}\right) \right\} \left(\frac{r_2}{a_0} \right)^4 \exp\left(-\frac{r_2}{a_0}\right) d\left(\frac{r_2}{a_0}\right) \quad (10)$$