

#2

**PROBLEM SET**  
SOLUTIONS

② We have:

$$\textcircled{1} \quad |\psi\rangle = \frac{1}{\sqrt{3}} |3\ 1; \frac{3}{2}\ \frac{1}{2}\rangle + \sqrt{\frac{2}{3}} |2\ 0; \frac{1}{2}\ -\frac{1}{2}\rangle$$

In the  $L^2, L_z, S^2, S_z$  basis, this becomes: (using the Clebsch-G. coefficients)

$$\textcircled{2} \quad |\psi\rangle = \frac{1}{3} |3\ 1\ 1\rangle \otimes | \frac{1}{2} - \frac{1}{2} \rangle + \frac{\sqrt{2}}{3} |3\ 1\ 0\rangle \otimes | \frac{1}{2} \frac{1}{2} \rangle + \frac{\sqrt{2}}{3} |2\ 0\ 0\rangle \otimes | \frac{1}{2} - \frac{1}{2} \rangle$$

a) The expectation value of energy is:

$$\begin{aligned} \langle E \rangle &= \left(\frac{1}{\sqrt{3}}\right)^2 \cdot \left(-\frac{13.6 \text{ eV}}{3^2}\right) + \left(\sqrt{\frac{2}{3}}\right)^2 \cdot \left(-\frac{13.6 \text{ eV}}{2^2}\right) \\ &= \frac{11}{54} \cdot (-13.6 \text{ eV}) \end{aligned}$$

b) From the formula  $\textcircled{2}$ , we see that the state is a linear combination of states with

$$L_z = \hbar \quad \text{PROBABILITY } \left(\frac{1}{3}\right)^2 = \frac{1}{9}$$

$$L_z = 0 \quad \text{PROBABILITY } \left(\frac{\sqrt{2}}{3}\right)^2 + \left(\sqrt{\frac{2}{3}}\right)^2 = \frac{8}{9}$$

c) From  $\textcircled{2}$ , we find

$$\begin{aligned} \langle S_z \rangle &= \left(\frac{1}{3}\right)^2 \cdot \left(-\frac{\hbar}{2}\right) + \left(\frac{\sqrt{2}}{3}\right)^2 \cdot \left(\frac{\hbar}{2}\right) + \left(\sqrt{\frac{2}{3}}\right)^2 \cdot \left(-\frac{\hbar}{2}\right) \\ &= -\frac{5}{18} \hbar \end{aligned}$$

$$\begin{aligned} \text{d) From } \textcircled{2}, \text{ we have } \langle J^2 \rangle &= \left(\frac{1}{\sqrt{3}}\right)^2 \cdot \hbar^2 \left(\frac{3}{2}\right)\left(\frac{5}{2}\right) + \left(\sqrt{\frac{2}{3}}\right)^2 \cdot \hbar^2 \left(\frac{1}{2}\right)\left(\frac{3}{2}\right) \\ &= \frac{7}{4} \hbar^2 \end{aligned}$$

3a)

We have for  $n=3$ ,  $l=0, 1, 2$  while for  $n=2$ , we can have  $l=0, 1$ .

Including electron spin, states with some  $l$  give states with total angular momentum  $l \pm \frac{1}{2}$  and  $l - \frac{1}{2}$ . So the possible values for  $J$  are:

$$n=3: J = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}$$

$$n=2 J = \frac{1}{2}, \frac{3}{2}$$

The energy levels after taking into account fine structure are dependent on  $n$  and  $J$  only. So we have levels at  $n=3$  and two levels at  $n=2$ . The energies are:

$$n=3 \quad \begin{array}{c} J=\frac{5}{2} \\ J=\frac{3}{2} \\ J=\frac{1}{2} \end{array}$$

$$n=2 \quad \begin{array}{c} J=\frac{3}{2} \\ J=\frac{1}{2} \end{array}$$

$$E_{n,J} = -\frac{13.6 \text{ eV}}{n^2} \left( 1 + \frac{\alpha^2}{n^2} \left( \frac{n}{J+\frac{1}{2}} - \frac{3}{4} \right) \right) *$$

The spectral lines come from transitions from one of the 3  $n=3$  states to one of the two  $n=2$  states, so we have  $\boxed{6}$  possible wavelengths (we can check that no two are the same).

3b)

From \*, we want to take:

$$\frac{E_{n=2, \frac{3}{2}} - E_{n=2, J=\frac{1}{2}}}{-\frac{13.6}{4} \text{ eV} + 13.6 \text{ eV}} \approx 4.44 \times 10^{-6}$$

using  $\alpha = \frac{1}{136}$

④ To take into account the electric field  $\vec{E} = E \hat{z}$ , we need to add a term to the Hamiltonian. The associated potential is  $V = -Ez$  (chosen so  $-\nabla V = \vec{E}$ ). We have chosen the potential to be 0 at the proton location, so the only contribution to the potential energy is from the electron. We get  $U = V \cdot q = -eV = eEz$ . Thus, we add a term:

$$H_z = eEz$$

as a perturbation to the Hamiltonian.

We want to know how this affects the  $|n\ell m\rangle = |100\rangle$  state. To first order in perturbation theory, we have:

$$\begin{aligned}\Delta E &= eE \langle 100 | z | 100 \rangle \\ &= eE \int dx dy dz \psi_{100}^*(r) z \psi_{100}(r)\end{aligned}$$

This vanishes because  $\psi_{100}$  is symmetric under  $z \rightarrow -z$  while  $z$  is antisymmetric.

For second order in perturbation theory, we have:

$$\Delta E = \sum_{\substack{n>1 \\ \ell,m}} \frac{|\langle n\ell m | z | 100 \rangle|^2}{E_1 - E_n} \cdot e^2 E^2$$

We need to figure out which of these are non-zero. We have:

$$\langle n\ell m | z | 100 \rangle = \int dr \cdot r^2 \cdot \sin\theta d\theta d\phi \psi_{n\ell m}^*(r, \theta, \phi) r \cos\theta \psi_{100}(r, \theta, \phi)$$

We can split the wavefunctions into an angular part and a radial part:

$$\psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r) \cdot Y_\ell^m(\theta, \phi)$$

We have:  $Y_0^0(\theta, \phi) = \left(\frac{1}{4\pi}\right)^{\frac{1}{2}}$ , so the angular integral is:

$$\int d\theta d\phi \sin\theta Y_\ell^m(\theta, \phi) \cdot \left(\frac{1}{4\pi}\right)^{\frac{1}{2}} \cdot \cos\theta$$

Now we can use that  $\cos\theta = \sqrt{\frac{4\pi}{3}} \cdot Y_1^0(\theta, \phi)$ , so the angular integral is:

$$\frac{1}{\sqrt{3}} \int d\theta d\phi \sin\theta Y_\ell^{m*}(\theta, \phi) Y_1^0(\theta, \phi) = \delta_{\ell,1} \delta_{m,0}$$

using the orthogonality relation for spherical harmonics.

So the non-zero matrix elements are:

$$\langle n10 | H | 1100 \rangle = \frac{1}{\sqrt{3}} \int_0^\infty dr \cdot r^3 \cdot R_{n1}(r) \cdot r \cdot R_{10}(r)$$

Calling this  $\frac{1}{\sqrt{3}} I_n$ , the answer for the energy shift is

$$\boxed{\Delta E^{(2)} = \frac{1}{3} \frac{e^2 E^2}{(-13 \text{ eV})} \sum_{n>1} \frac{|I_n|^2}{1 - \frac{1}{n^2}}}$$

For the extra part, we need to calculate  $I_n = \int_0^\infty dr \cdot r^3 R_{n1}(r) \cdot R_{10}(r)$ .

The radial wavefunctions take the form  $R_{n\ell}(r) = \frac{1}{a^{\frac{n+1}{2}}} \cdot F_{n\ell}(\frac{r}{a})$  where  $F_{n\ell}(x)$  is just a dimensionless function. So, changing variables to  $x = \frac{r}{a}$ ,

$$I_n = a \cdot \int_0^\infty dx x^3 \cdot R_{n1}^{a=1}(x) R_{10}^{a=1}(x).$$

The remaining numerical integral can be done using the definition of  $R_{n\ell}(x)$  in Griffiths in terms of the Laguerre polynomials.

We have an infinite sum of terms, but we expect that it converges, so we can approximate it by evaluating the terms up to some finite  $n$ . Using Maple, I find

$$\sum_{n>2} \frac{|I_n|_{a=1}^2}{1 - \frac{1}{n^2}} \approx 2.747$$

so the result for the second order shift is

$$\Delta E^{(2)} = -0.9151 \cdot \frac{e^2 E^2 a^2}{E_{n=1}}$$

$\nwarrow$  electric field  
 $\nwarrow$  -13.6 eV