

Answers to the Problems in Chapter 5

Problem 5.1.

According to Box 5.1 the wave number in cm^{-1} of a line in the H-atom spectrum is given by the equation

$$\tilde{\nu} = R \left\{ \frac{1}{r^2} - \frac{1}{s^2} \right\}$$

where r and s are the principal quantum numbers of the lower and upper states respectively and R is the Rydberg constant $= me^4/8ch^3\epsilon_0$. Therefore, setting $r = 4$ and $s = 5, 6, 7, \dots$ will give the predicted wave numbers for the Paschen series.

Problem 5.2.

The above formula for $\tilde{\nu}$, with $r = 2$ and $s = 3$, and the appropriate values of R and Z from Table 5.3 (p. 105) gives

For deuterium $\tilde{\nu} = 1 \times 109707.42 \times 0.13889 \text{ cm}^{-1} \Rightarrow \lambda = 100/\tilde{\nu} = 656.28 \text{ nm}$

For Be^{3+} $\tilde{\nu} = 16 \times 109730.62 \times 0.13889 \text{ cm}^{-1} \Rightarrow \lambda = 100/\tilde{\nu} = 41.009 \text{ nm}$

Problem 5.3.

If we form the configuration l^p by adding the p electrons one at a time, the first can be placed in any one of $2l+1$ atomic orbitals and with a spin of $+\frac{1}{2}$ or $-\frac{1}{2}$. Thus, we have $2(2l+1)$ possibilities for the first electron. Since no two electrons can have the same combination of quantum numbers we have $2(2l+1) - 1$ possibilities for the second electron, $2(2l+1) - 2$ for the third, ... and $2(2l+1) - (p-1)$ for the p^{th} . But electrons are indistinguishable and the first electron we placed could have been any one of p , the second any one of $p-1$, and so on. Therefore, the total number of ways of placing the electrons, which is the total number of states, N_{states} , is:

$$N_{\text{states}} = \frac{[2(2l+1)] \times [2(2l+1)-1] \times \dots \times [2(2l+1)-p+1]}{p \times (p-1) \times (p-2) \times \dots \times 1} = \frac{[2(2l+1)]!}{[2(2l+1)-p]! \times p!}$$

[Unfortunately, there is an error in the formula for N_{states} in the book, l should be replaced by $2l+1$].

For the configuration f^4 we have $l = 3$ and $2l + 1 = 7$ so that:

$N_{\text{states}} = 14!/(10! \times 4!) = 14 \times 13 \times 12 \times 11 / (4 \times 3 \times 2) = 1001$.

Problem 5.4.

The table should look like this.

		M_S			
		+1	0	-1	
M_L	+2	(+2+½;0+½)	(+2+½;0-½)	(+2-½;0+½)	(+2-½;0-½)
	+1	(+1+½;0+½)	(+1+½;0-½)	(+1-½;0+½)	(+1-½;0-½)
	0	(+0+½;0+½)	(+0+½;0-½)	(+0-½;0+½)	(+0-½;0-½)
	-1	(-1+½;0+½)	(-1+½;0-½)	(-1-½;0+½)	(-1-½;0-½)
	-2	(-2+½;0+½)	(-2+½;0-½)	(-2-½;0+½)	(-2-½;0-½)

The microstate (+2+½;0+½) must be a component of a ³D state and we therefore cross off one entry from each M_L row and each M_S column; 15 entries in total. The highest M_S and M_L entry remaining is at the top of the $M_S = 0$ column which indicates the presence of a ¹D state. We therefore cross off one state in each M_L row of that column. No microstates remain. Thus, the states of the configuration s¹d¹ are ¹D and ³D.

Problem 5.5.

The j values for a single s electron are +½ and -½. The j values for a single d electron are (Clebsch-Gordan) 2+½ = 5/2 and 2-½ = 3/2. The possible combinations of the s-electron and d-electron m_j values are:

		$d_{5/2}$					$d_{3/2}$				
		+5/2	+3/2	+1/2	-1/2	-3/2	-5/2	+3/2	+1/2	-1/2	-3/2
$s_{1/2}$	+1/2	+3	+2	+1	0	-1	-2	+2	+1	0	-1
	-1/2	+2	+1	0	-1	-2	-3	+1	0	-1	-2

In this case, unlike the example of p² discussed in Section 5.9.2, all the possibilities above are valid because the two electrons are quite distinct. A check on this statement is the fact that we have 10 possible combinations of m_l and m_s for the d electron and two for the s giving a total of 2×10 = 20 states. Starting with the largest value of M_J in the top left hand corner of the table we find J values of 3 ($d_{5/2}$ - $s_{1/2}$ rectangle), 2 (twice, $d_{5/2}$ - $s_{1/2}$ and $d_{3/2}$ - $s_{1/2}$) and 1 ($d_{3/2}$ - $s_{1/2}$).

Problem 5.6

As an example, I evaluate the potential energy of the $R_{30}(r)$ radial function.

$$R_{30}(r) = (Z/a_0)^{3/2} (1/9\sqrt{3}) (6 - 6\rho + \rho^2) \exp(-\rho/2)$$

where $\rho = 2Zr/na_0 = \alpha r$ where $\alpha = 2Z/na_0$

[There is an error of sign in Appendix 5]

$$\begin{aligned} V_{30} &= -\int_0^\infty R_{30}(r) \frac{e^2}{4\pi\epsilon_0 r} R_{30}(r) r^2 dr = -\frac{e^2}{4\pi\epsilon_0} \left(\frac{Z}{a_0}\right)^3 \frac{1}{243} \int_0^\infty (6 - 6\alpha r + \alpha^2 r^2)^2 e^{-\alpha r} r dr \\ &= -\frac{e^2}{4\pi\epsilon_0} \left(\frac{Z}{a_0}\right)^3 \frac{1}{243} \int_0^\infty (36r - 72\alpha r^2 + 48\alpha^2 r^3 - 12\alpha^3 r^4 + \alpha^4 r^5) e^{-\alpha r} dr \end{aligned}$$

A very useful integral for this type of problem is given at the bottom of p. 259 and we find:

$$\begin{aligned} V_{30} &= -\frac{e^2}{4\pi\epsilon_0} \left(\frac{Z}{a_0}\right)^3 \frac{1}{243\alpha^2} \{36 - 144 + 288 - 288 + 120\} = -\frac{e^2}{4\pi\epsilon_0} \left(\frac{Z}{a_0}\right)^3 \frac{12}{243\alpha^2} \\ &= -\frac{e^2}{4\pi\epsilon_0} \left(\frac{Z}{a_0}\right)^3 \frac{12}{243} \cdot \frac{n^2 a_0^2}{4Z^2} = \frac{-Ze^2 n^2}{324\pi\epsilon_0 a_0} \end{aligned}$$

Substituting for a_0 and with $n = 3$ and $Z = 1$ we have:

$$V = -\frac{Ze^2 n^2}{324\pi\epsilon_0} \cdot \frac{m_e e^2}{4\pi\epsilon_0 \hbar^2} = -\frac{9e^2}{81\epsilon_0} \cdot \frac{m_e e^2 4\pi^2}{16\pi^2 \epsilon_0 \hbar^2} = -\frac{m_e e^4}{36\epsilon_0^2 \hbar^2}$$

Equation 5.1.1 with $n = 3$ gives

$$E = -\frac{m_e e^4}{8n^2 \epsilon_0^2 \hbar^2} = -\frac{m_e e^4}{72\epsilon_0^2 \hbar^2} = V/2$$

Problem 5.7

All the transitions are $s \rightarrow p$ transitions and the radial integration will be the same in all cases. Therefore, to obtain the relative intensities we need only perform the integrations over the angular functions, i.e. the spherical harmonics. A few examples of the procedure should suffice.

The s function	$ 0\ 0\rangle = \{1/4\pi\}^{1/2}$
The p_{+1} function	$ 1\ +1\rangle = -\{3/8\pi\}^{1/2} \sin\vartheta e^{+i\phi}$
The p_x function	$ 1\ x\rangle = \{3/4\pi\}^{1/2} \sin\vartheta \cos\phi$
The lcp transition moment operator	$m_- = \{1/2\}^{1/2} er \sin\vartheta e^{-i\phi}$
(lcp = left-circularly polarised light - see Chapter 8)	
The x transition moment operator	$m_x = er \sin\vartheta \cos\phi$

An lcp transition:

$$\begin{aligned} \langle 00 | m_- | 1+1 \rangle &= \frac{-1}{2\sqrt{\pi}} \cdot \frac{er}{\sqrt{2}} \cdot \sqrt{\frac{3}{8\pi}} \int_0^\pi \int_0^{2\pi} \sin\vartheta e^{-i\phi} \sin\vartheta e^{+i\phi} \sin\vartheta d\vartheta d\phi \\ &= -\frac{er\sqrt{3}}{8\pi} \int_0^\pi \sin^3\vartheta d\vartheta \int_0^{2\pi} e^0 d\phi = -\frac{er\sqrt{3}}{8\pi} \cdot \frac{4}{3} \cdot 2\pi = -\frac{er}{\sqrt{3}} \end{aligned}$$

A π -type transition:

$$\begin{aligned} \langle 00 | m_x | 1x \rangle &= \frac{1}{2\sqrt{\pi}} \cdot er \cdot \sqrt{\frac{3}{4\pi}} \int_0^\pi \int_0^{2\pi} \sin\vartheta \cos\phi \sin\vartheta \cos\phi \sin\vartheta d\vartheta d\phi \\ &= \frac{er\sqrt{3}}{4\pi} \int_0^\pi \sin^3\vartheta d\vartheta \int_0^{2\pi} \cos^2\phi d\phi = \frac{er\sqrt{3}}{4\pi} \cdot \frac{4}{3} \cdot \pi = \frac{er}{\sqrt{3}} \end{aligned}$$

A σ -type transition:

$$\begin{aligned} \langle 00 | m_x | 1+1 \rangle &= \frac{-1}{2\sqrt{\pi}} \cdot er \cdot \sqrt{\frac{3}{8\pi}} \int_0^\pi \int_0^{2\pi} \sin\vartheta \cos\phi \sin\vartheta e^{i\phi} \sin\vartheta d\vartheta d\phi \\ &= -\frac{\sqrt{3}}{2} \frac{er}{4\pi} \int_0^\pi \sin^3\vartheta d\vartheta \int_0^{2\pi} (\cos^2\phi + i \cos\phi \sin\phi) d\phi \\ &= -\sqrt{\frac{3}{2}} \frac{er}{4\pi} \cdot \frac{4}{3} (\pi - 0) = -\frac{er}{\sqrt{6}} \end{aligned}$$

The intensities of the lines are proportional to the squares of the above matrix elements, therefore,

$$\text{Intensity lcp} : \pi : \sigma = 2 : 2 : 1$$