SOLUTIONS TO HOMEWORK 5

1) a) energy $E_n = -\frac{1}{2n^2}$ a.u. $= \frac{4.3598\times10^{-18}}{2n^2}$ J

$\Rightarrow E_2 = -5.4498\times10^{-19}$ J, $E_3 = -2.4221\times10^{-19}$ J, $E_4 = -1.3624\times10^{-19}$

b) Frequencies are $\nu = E/h$; wavelengths $\lambda = 10^{10} c/\nu$ Å

TRANSITION	E(J)	ν	λ.
4-2	4.0874×10^{-19}	6.1686×10^{14}	4860.
4-3	1.0597×10^{-19}	1.5993×10^{14}	18745.
3-2	3.0277×10^{-19}	4.5693×10^{14}	6561.0

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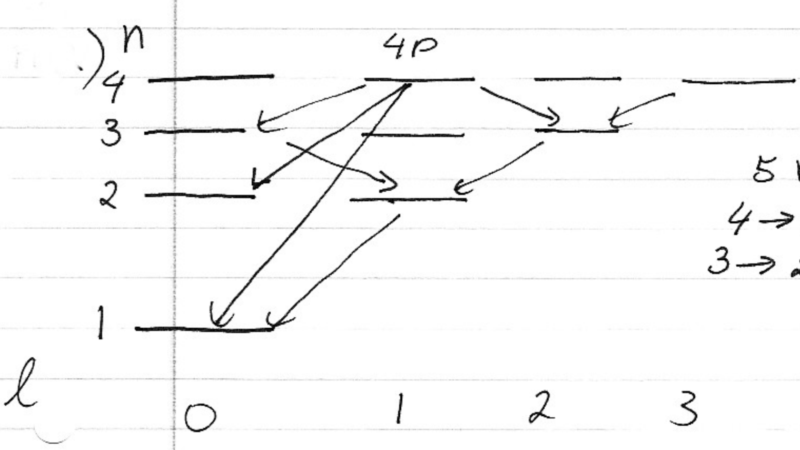

SELECTION RULES

$\Delta n =$ any

$\Delta l = \pm 1$

5 POSSIBLE WAVELENGTHS

$4\to3$, $4\to2$, $4\to1$

$3\to2$, $2\to1$

b) still 5, but transitions are

$4\to3$, $4\to2$, $3\to2$, $3\to1$, $2\to1$

(ie $4\to1$ absent, $3\to1$ present)

3) For a configuration 3d4p we have $\ell_1 = 2, \ell_2 = 1$ and $S_1 = S_2 = 1/2$

Hence $|\ell_1 - \ell_2| \leqslant L \leqslant \ell_1 + \ell_2$ and $L = 1, 2, 3.$

Also $|S_1 - S_2| \leqslant S \leqslant S_1 + S_2$ so $S = 0, 1.$

Then, $|S - L| \leqslant J \leqslant L + S$

$L = 1, S = 0 \Rightarrow J = 1$

$L = 1, S = 1 \Rightarrow J = 0, 1, 2$

$L = 2, S = 0 \Rightarrow J = 2$

$L = 2, S = 1 \Rightarrow J = 1, 2, 3$

$L = 3, S = 0 \Rightarrow J = 3$

$L = 3, S = 1 \Rightarrow J = 2, 3, 4$. There are 12 levels in total. **[10]**

4) for the $3p \to 2s$ transition, $\lambda = 6561$ Å so

$2.026 \times 10^{18}/\lambda^3 = .7173 \times 10^7$ **[5]**

The dipole matrix element has a radial part and an angular part.
Since

$$M = \int R_{3p}\, r\, R_{2s}\, r^2 dr \cdot \int Y_{1m}^* \cos\theta\, Y_{00} \sin\theta\, d\theta . d\phi$$

Now since the dipole (which is polarised along z) has no ϕ dependence, we have the selection rule $\Delta m = 0$ since else the angular integral is zero. Hence instead of Y_{1m}^* we are only allowed $m = 0$. The angular integral is

$$A = \int Y_{10}^* \cos\theta \cdot 1/\sqrt{4\pi}\, \sin\theta\, d\theta\, d\phi = \sqrt{4\pi/3} \int |Y_{10}|^2 \sin\theta\, d\theta\, d\phi$$

(since $Y_{10} = \sqrt{3/4\pi}\cos\theta$). **[5]**

Hence $A = 1/\sqrt{3}$.

The radial integral $R = \int_0^\infty r^4 R_{3p} \cdot R_{2s}\, dr$ =

$$\frac{2}{3\sqrt{3}} \int_0^\infty r^4 (1 - r/6)(1 - r/2)\, e^{-5/6\, r} dr =$$ **[5]**

$$\frac{2}{3\sqrt{3}} \left[\frac{4!}{(5/6)^5} - \frac{2 \cdot 5!}{3(5/6)^6} + \frac{6!}{12(5/6)^7} \right] = 13.8$$

Hence multiplying by A we obtain $M^2 = (7.96)^2$

SO

The probability = $.7173 \times 10^7 \times (7.96)^2 = 4.54 \times 10^8 s^{-1}$ **[5]**