ATOMS, MOLECULES & REACTIONS

QUANTUM MECHANICS - SPRING '06 - WEEK 4 HW

Chapter 13

(26) H atom in 3d state $\;{}^2D_{5/2} \qquad {}^2D_{3/2}$

Spin-orbit ~~splitting~~ energy $= A\vec{L}\cdot\vec{S}$

$$= \frac{A\hbar^2}{2}\left[J(J+1) - L(L+1) - S(S+1)\right]$$

${}^2D_{5/2}$ state : $\quad S = \frac{1}{2} \quad L = 2 \quad J = 5/2$

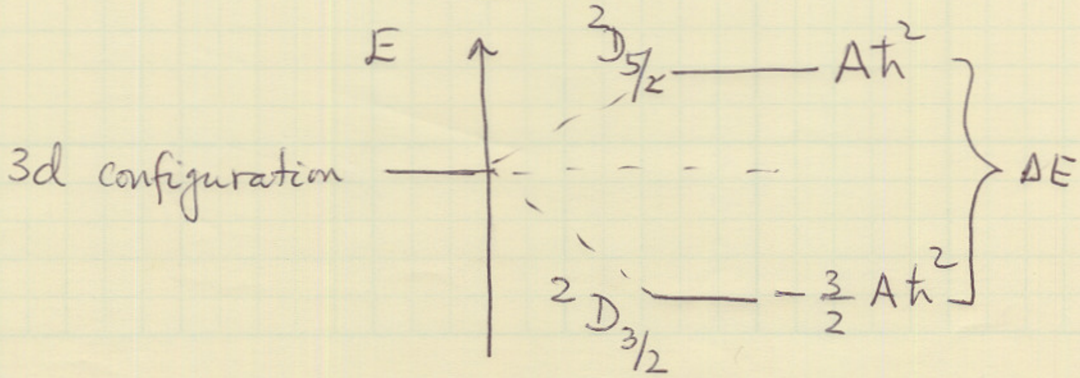
$$\therefore A\vec{L}\cdot\vec{S} = \frac{A\hbar^2}{2}\left[\frac{5}{2}\cdot\frac{7}{2} - 2\cdot 3 - \frac{1}{2}\cdot\frac{3}{2}\right]$$

$$= A\hbar^2$$

${}^2D_{3/2}$ state : $\quad S = 1/2 \quad L = 2 \quad J = 3/2$

$$\therefore A\vec{L}\cdot\vec{S} = \frac{A\hbar^2}{2}\left[\frac{3}{2}\cdot\frac{5}{2} - 2\cdot 3 - \frac{1}{2}\cdot\frac{3}{2}\right]$$

$$= -\frac{3}{2}A\hbar^2$$



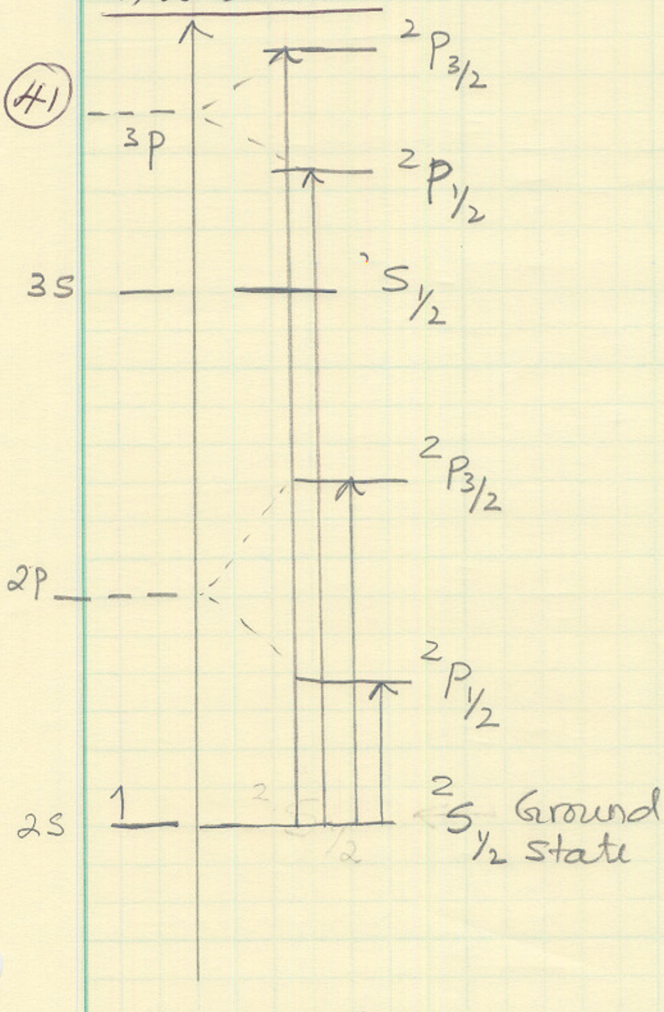
$$\text{spin-orbit splitting} = \Delta E = A\hbar^2 - \left(-\frac{3}{2}A\hbar^2\right) = \left(A + \frac{3}{2}A\right)\hbar^2$$

$$= \underline{\underline{\frac{5}{2}A\hbar^2}}$$

If the atom is He^+, the spin-orbit splitting is still $\underline{\underline{\frac{5}{2}A\hbar^2}}$

<u>HW sheet</u>

41



Note from this diagram that if a H-like atom is in a 2S orbital, it is in a $^2S_{1/2}$ state.

allowed transitions are

$$\left.\begin{array}{l} ^2S_{1/2} \longrightarrow {}^2P_{1/2} \\ \phantom{^2S_{1/2}} \longrightarrow {}^2P_{3/2} \end{array}\right\} \text{4 of them are marked on the figure.}$$

$^2S_{1/2} \longrightarrow {}^2S_{1/2}$ is not allowed since this is a $L=0 \longrightarrow L=0$ transition

(b) If the atom is in a 3p orbital, the terms arising from it are:

$^2P_{1/2}$ and $^2P_{3/2}$ where $\underline{^2P_{1/2}}$ will be the <u>ground state</u>

allowed transitions are:

$$^2P_{1/2} \longrightarrow {}^2P_{3/2}$$
$$\longrightarrow {}^2S_{1/2}$$
$$\longrightarrow {}^2D_{3/2}$$
$$\longrightarrow {}^2P_{1/2}$$

(c) If the H-like atom is in a 3d orbital, the terms arising from it are;

$^2D_{3/2}$ and $^2D_{5/2}$ of which the ground state is $\underline{^2D_{3/2}}$. Allowed transitions are:

$$^2D_{3/2} \longrightarrow {}^2D_{5/2} \longrightarrow {}^2F_{5/2}$$
$$\longrightarrow {}^2P_{1/2}$$
$$\longrightarrow {}^2P_{3/2}$$

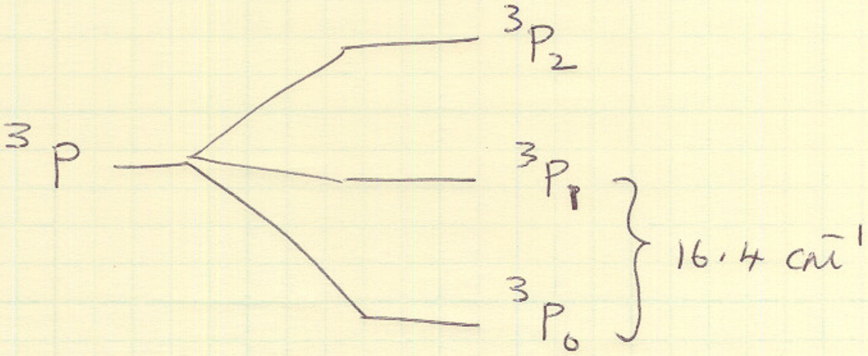
~~assigh~~

assigned sheet

① (a) ^3P state $S = 1$ $L = 1$ $J = 2, 1, 0$

$\therefore$ Spin-orbit terms are $^3P_0$, $^3P_1$, $^3P_2$

(b)



Spin-orbit energy term $= A\vec{L}\cdot\vec{S}$

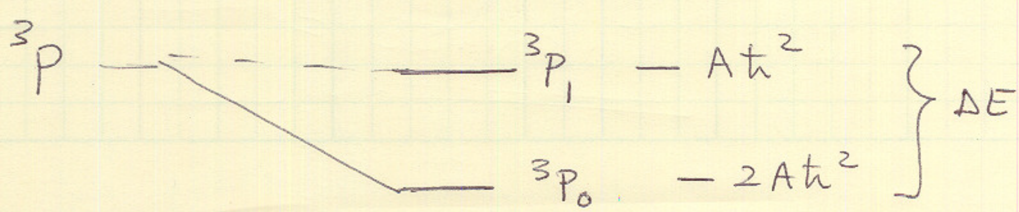
$= \frac{A\hbar^2}{2}\left[J(J+1) - L(L+1) - S(S\right.$

$^3P_0$ state : $L = 1$ $S = 1$ $J = 0$

$$\therefore A\vec{L}\cdot\vec{S} = \frac{A\hbar^2}{2}\left[0 - 1.2 - 1.2\right] = -2A\hbar^2$$

$^3P_1$ state : $L = 1$ $S = 1$ $J = 1$

$$\therefore A\vec{L}\cdot\vec{S} = \frac{A\hbar^2}{2}\left[1.2 - 1.2 - 1.2\right] = -A\hbar^2$$



$$\therefore \ \Delta E = -A\hbar^2 - \left(-2A\hbar^2\right) = A\hbar^2$$

But $\Delta E = h\nu = \dfrac{hc}{\lambda} = hc\left(\dfrac{1}{\lambda}\right)$

$$= hc\left(16.4\ cm^{-1}\right)$$

$$\therefore \ hc\left(16.4\ cm^{-1}\right) = A\hbar^2$$

$$A = \frac{hc\left(16.4\ cm^{-1}\right)}{\hbar^2}$$

$$= \frac{\left(6.626 \times 10^{-34}\ Js\right)\left(2.99 \times 10^{10}\ cm\,s^{-1}\right)\left(16.4\ cm^{-1}\right)}{\left(1.055 \times 10^{-34}\ Js\right)^2}$$

$$\underline{\underline{A = 2.919 \times 10^{46}\ J^{-1}\,s^{-2}}}$$

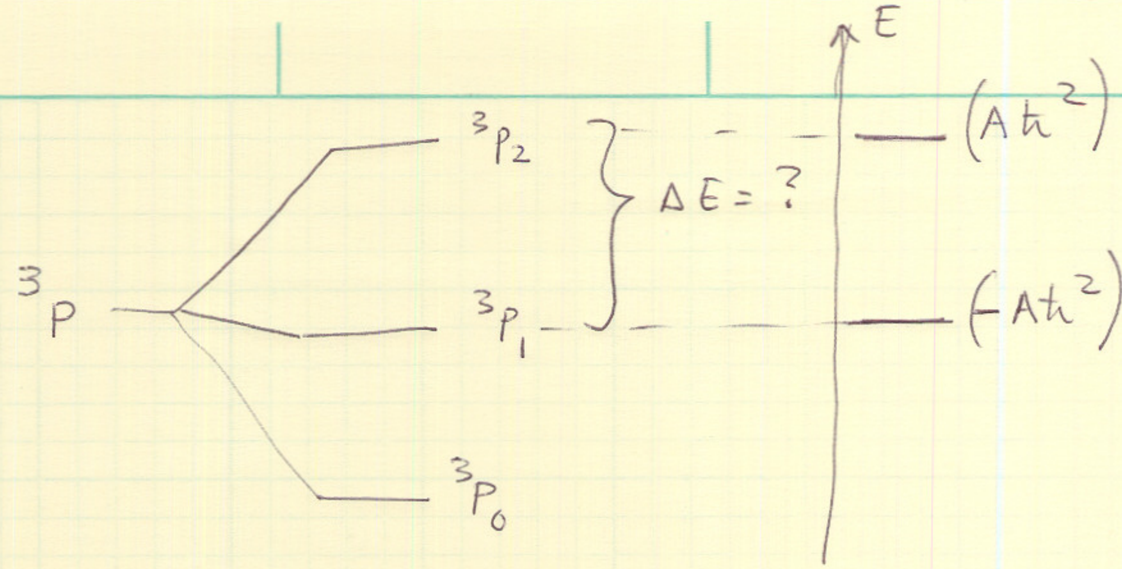
need not do this to get credit.

A is <u>usually</u> expressed in cm^{-1} units. To convert, do the following.

$$A = \left(2.919 \times 10^{46}\ J^{-1}\,s^{-2}\right)\frac{h}{c} = \frac{\left(2.919 \times 10^{46}\ J^{-1}\,s^{-2}\right)\left(6.626 \times 10^{-34}\ Js\right)}{\left(2.99 \times 10^{10}\ cm\,s^{-1}\right)}$$

$$= \underline{\underline{646.91\ cm^{-1}}}$$

(c)



<u>For $^3P_2$ state:</u> $\quad L = 1 \quad S = 1 \quad J = 2$

$$A\,\vec{L}\cdot\vec{S} = \frac{A\hbar^2}{2}\left[2\cdot 3 - 1\cdot 2 - 1\cdot 2\right] = A\hbar^2$$

$$\left.\begin{array}{l}\Delta E = \text{energy gap} \\ \text{between } {}^3P_2 \text{ and } {}^3P_1\end{array}\right\} = A\hbar^2 - (-A\hbar^2)$$

$$= 2A\hbar^2$$

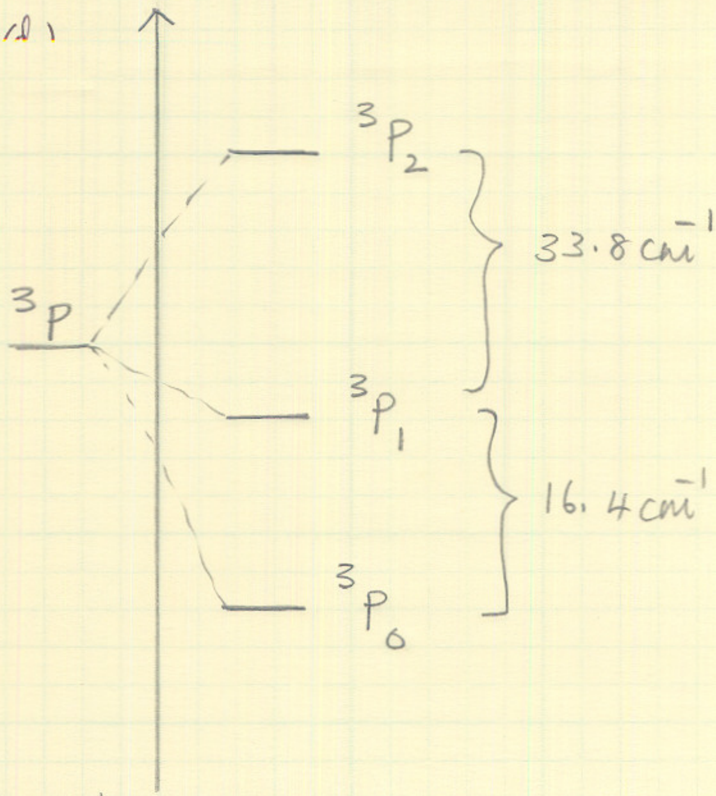
$$= 2\left(2.919\times10^{46}\ J^{-1}s^{-2}\right)\left(1.055\times10^{-34}\ Js\right)^2$$

$$\Delta E = 6.4978\times10^{-22}\ J = \frac{hc}{\lambda}$$

$$\therefore \frac{1}{\lambda} = \frac{\Delta E}{hc} = \frac{6.4978\times10^{-22}\ J}{(6.626\times10^{-34}\ Js)(2.99\times10^{10}\ cm\,s^{-1})}$$

$$= \underline{\underline{33.82\ cm^{-1}}}$$

(d)



(e) transitions that are allowed :

$^3P_0 \longrightarrow {}^3P_1$ allowed $\Delta L = 0,\ \Delta S = 0$, $\Delta J = 1$

$^3P_0 \not\longrightarrow {}^3P_2$ forbidden $\Delta S = 0 \quad \Delta L = 0$, $\Delta J = 2$

② (a) Na $\underbrace{1s^2\, 2s^2\, 2p^6}_{[Ne]}\, 3s^1 = [Ne]\, 3s^1$ $\quad \frac{1}{3s}$

$M_L = 0 \quad M_S = \frac{1}{2} \Rightarrow L = 0,\ S = \frac{1}{2} \Rightarrow J = \frac{1}{2}$

$\underline{\underline{^2S_{1/2}}}$ ground state term. No spin-orbit terms.

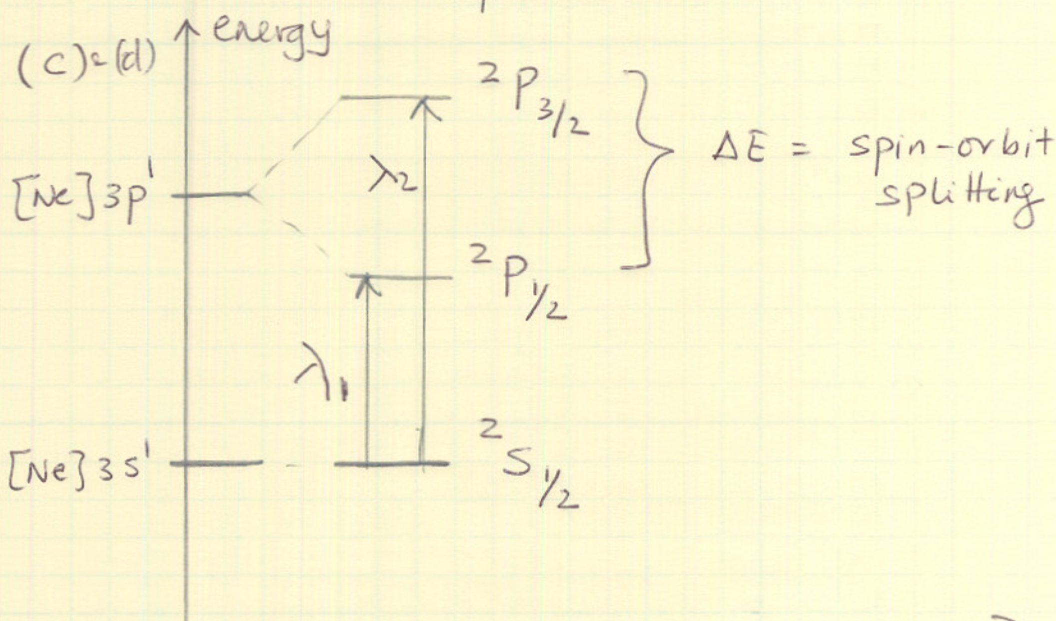
(b) $\underbrace{1s^2\, 2s^2\, 2p^6}_{\text{closed shell}}\ 3p^1$

$$\underset{+1}{\underline{1}}\ \underset{0}{\underline{\ \ }}\ \underset{-1}{\underline{\ \ }}$$
3p

$M_L = 1 \quad M_S = 1/2 \Rightarrow L = 1,\ S = 1/2 \Rightarrow J = 3/2,\ 1/2$

Terms $\underbrace{{}^2P_{1/2} \qquad {}^2P_{3/2}}_{\text{spin-orbit terms.}}$

(c)+(d)



(e) $^2S_{1/2} \longrightarrow {}^2P_{1/2} \quad \lambda_1 = 616.07\,nm$

$^2S_{1/2} \longrightarrow {}^2P_{3/2} \quad \lambda_2 = 615.42\,nm$

sodium d-lines

ΔE = spin-orbit splitting of the ^2P state $= (616.07 - 615.42)\,nm$

$= 0.65\,nm \longleftarrow$ X

$$\Delta E = \frac{hc}{\lambda} = \frac{(6.626\times10^{-34}\ Js)(2.99\times10^{8}\ ms^{-1})}{(0.65\times10^{-9}\ m)}$$

$$\left.\begin{array}{l}\text{Energy of the } {}^2S_{1/2} \to {}^2P_{1/2} \\ \text{transition}\end{array}\right\} = E_1 = \frac{hc}{\lambda_1}$$

$$\left.\begin{array}{l}\text{Energy of the } {}^2S_{1/2} \to {}^2P_{3/2} \\ \text{transition}\end{array}\right\} = E_2 = \frac{hc}{\lambda_2}$$

$$\therefore \Delta E = \left.\begin{array}{l}\text{spin-orbit splitting} \\ \text{of the excited} \\ \text{electronic state}\end{array}\right\} = E_2 - E_1$$

$$= hc\left[\frac{1}{\lambda_2} - \frac{1}{\lambda_1}\right]$$

$$= \frac{(6.626 \times 10^{-34}\,\mathrm{Js})(2.99 \times 10^{8}\,\mathrm{m\,s^{-1}})}{(10^{-9}\,\mathrm{m/nm})}\left[\frac{1}{615.42\,\mathrm{nm}} - \frac{1}{616.07\,\mathrm{nm}}\right]$$

$$= 3.396 \times 10^{-22}\,\mathrm{J}$$

<u>${}^2P_{1/2}$ state</u> $\quad L = 1 \quad S = 1/2 \quad J = 1/2$

$$\text{Spin-orbit energy} = A\vec{L}\cdot\vec{S} = \frac{A\hbar^2}{2}\left[J(J+1) - L(L+1) - S(S+1)\right]$$

$$= -A\hbar^2$$

<u>${}^2P_{3/2}$ state</u> $\quad L = 1 \quad S = 1/2 \quad J = 3/2$

$$\text{spin orbit energy} = A\vec{L}\cdot\vec{S} = \frac{A\hbar^2}{2}$$

$$\Delta E = \frac{A\hbar^2}{2} - (-A\hbar^2) = \frac{3A\hbar^2}{2}$$

$$\therefore \frac{3A\hbar^2}{2} = 3.396 \times 10^{-22}\ J$$

$$A = \frac{2(3.396 \times 10^{-22}\ J)}{3(1.055 \times 10^{-34}\ Js)^2}$$

$$= 2.634 \times 10^{46}\ J^{-1}\ s^{-2} \left[\frac{6.626 \times 10^{-34}\ Js}{2.99 \times 10^{10}\ cm\ s^{-1}}\right]$$

$$\underline{A = 450.77\ cm^{-1}}$$