o: James Sadler

B3 Problem Set 2   Ziyan Li

14.   Electric dipole radiation = Selection rules :

$\Delta J = 0, \pm 1$ $(J = 0 \not\leftrightarrow 0)$ (total angular momentum)
                                    ↳ forbidden ✓

$\Delta M_J = 0, \pm 1$ (z-direction of total angular momentum) ✓

$\Delta l = \pm 1$ (orbital Angular momentum of a single
                                electron) ✓

$\Delta L = 0, \pm 1$ $(L = 0 \not\leftrightarrow 0)$ (total orbital angular momentum)
                                    ↳ forbidden ✓

$\Delta S = 0$ (total spin angular momentum) ✓

$\Delta n = $ anything   (principle quantum number) ✓

Justifications :

① $\Delta l = \pm 1$ is resulted from the facts
that a photon carries angular momentum
of 1 unit (of $\hbar$), and that the expectation
value for the dipole term is only non-zero
if the initial and final states are different
in parity. ~~so $\Delta l = \pm$~~. Parity is determined
by ~~$\Leftrightarrow$~~ $(-1)^l$ so $\Delta l = 0$ is not possible.
Photon carries angular momentum ~~can only~~
~~carry~~ of 1, so Δl can only be $-1, 0, 1$

Together gives $\boxed{\Delta l = \pm 1}$ ✓

The expectation value for transitions of more than 1
electrons is 0, so this rule applies to one single
electron.

② $\Delta J = 0, \pm 1 \quad (J = 0 \nleftrightarrow 0)$

$\Delta L = 0, \pm 1 \quad \cancel{(J=0)} (L = 0 \nleftrightarrow 0)$

If $J \neq 0$
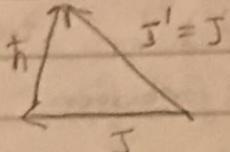
If $J = 0$

A photon carries angular momentum of 1, and J is quantised in the initial and final states, so $\boxed{\Delta J = 0, \pm 1}$ ✓

If J starts to be 0, then adding a vector of length 1 must change the magnitude of J, so $\cancel{\Delta J} \boxed{J = 0 \nleftrightarrow 0}$ ✓

Similar ~~argo~~ argument applies for L

③ $\boxed{\Delta S = 0}$ because the dipole operator does not operate on the spin part of the wavefunction. Electron spin plays ~~not~~ no part in the spatial oscillation. ✓

The transitions:

$$1s^2 2p \ ^2P_{1/2} - 1s^2 3d \ ^2D_{5/2}$$

$\Delta l = 1$ ✓ $\Delta L = 1$ ✓ $\Delta S = 0$ ✓ $\Delta J = 2$ ✗

$\Rightarrow$ <u>Disobey</u> ✓

$1s^2 2p$ $1s^2 2s2p^1 P_1 - 1s^2 2p3p^1 P_1$

$\Delta l = 1$ ✓ $\Delta L = 0$ ✓ $\Delta S = 0$ ✓ $\Delta J = 0$ ✓

$\Rightarrow$ obey ✓

$1s^2 2s^2 {}^1 S_0$ $-$ $1s^2 2p^2 {}^3 P_1$
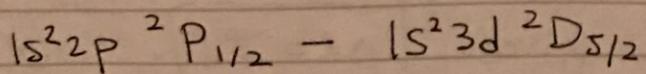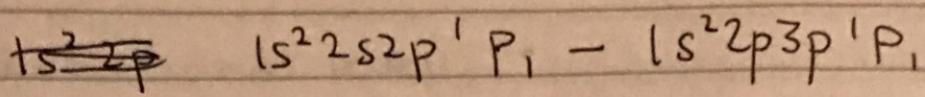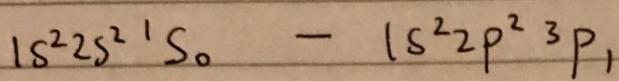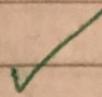
two electrons transition X $\Delta S \neq 0$ X ✓

$\Rightarrow$ disobey
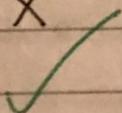
15 terms and levels :

$$4s^2 \rightarrow {}^1S_0 \qquad\qquad 4s5s \rightarrow {}^1S_0, {}^3S_1$$

$$4s4p \rightarrow {}^1P_1, {}^3P_2, {}^3P_1, {}^3P_0$$

Selection Rules :

$\rightarrow$ $\Delta l = \pm 1$ implies only $4s4p \rightarrow 4s^2$ and
$4s5s \rightarrow 4s4p$ are possible emission lines.

$\rightarrow$ For $4s4p \rightarrow 4s^2$, since $\Delta S = 0$, $\Delta J = 0, \pm 1$
$(J = 0 \not\leftrightarrow 0)$

$\Rightarrow$ only ~~$4s5s$~~ $4s4p\,{}^1P_1 \rightarrow 4s^2\,{}^1S_0$
is possible

$\rightarrow$ For $4s5s \rightarrow 4s4p$, since $\Delta S = 0$, $\Delta L = 0, \pm 1$
$(L = 0 \not\leftrightarrow 0)$, $\Delta J = 0, \pm 1$ $(J = 0 \not\leftrightarrow 0)$

$\Rightarrow$ allowed transitions are

$4s5s\,{}^1S_0 \rightarrow 4s4p\,{}^1P_1$

$4s5s\,{}^3S_1 \rightarrow 4s4p\,{}^3P_2$

$4s5s\,{}^3S_1 \rightarrow 4s4p\,{}^3P_1$

$4s5s\,{}^3S_{0,1} \rightarrow 4s4p\,{}^3P_0$

These are 5 emission lines ✓

→ The absorption line must start from the ground state, so the $4s4p\,{}^1P_1 \rightarrow 4s^2\,{}^1S_0$ line has wavelength 422.8 nm

→ The 610.4 nm, 612.4 nm, 616.4 nm triplet is clearly the transition from $4s5s\,{}^3S_1$ to $4s4p\,{}^3P$ ~~odd~~ states. ~~According interval rule~~ ~~In LS coupling scheme~~ :

$$\frac{616.4 - 612.4}{612.4 - 610.4} = \frac{4}{2} = 2 \quad , \quad \text{compare with}$$

$$\frac{E_{J=2} - E_{J=1}}{E_{J=1} - E_{J=0}} = \frac{\beta \cdot 2}{\beta \cdot 1} = 2$$

we get ${}^3P_2 \rightarrow$

In LS coupling scheme the energy of states $4s4p\,{}^3P$ are in the order ${}^3P_2 > {}^3P_1 > {}^3P_0$ because energy shift depends on

$$\frac{1}{2}\left(J(J+1) - L(L+1) - S(S+1) \right).$$

Larger $J \rightarrow$ Larger energy under fixed L, S

So transition to

$${}^3P_2 \rightarrow 616.4 \text{ nm}$$

$${}^3P_1 \rightarrow 612.4 \text{ nm}$$

$${}^3P_0 \rightarrow 610.4 \text{ nm}$$

Hence, the energy for each line:
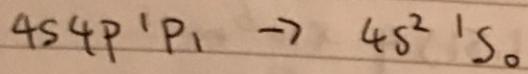
$4s4p\ ^1P_1 \rightarrow 4s^2\ ^1S_0$
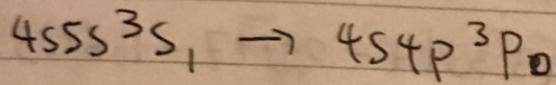
$$\Rightarrow \lambda = 422.8\ nm$$
$$\nu = \frac{1}{\lambda} = 2.3652 \times 10^6\ m^{-1}$$

$4s5s\ ^3S_1 \rightarrow 4s4p\ ^3P_0$

$$\Rightarrow \lambda = 610.4\ nm, \quad \nu = 1.6383 \times 10^6\ m^{-1}$$

$4s5s\ ^3S_1 \rightarrow 4s4p\ ^3P_1$

$$\Rightarrow \lambda = 612.4\ nm, \quad \nu = 1.6329 \times 10^6\ m^{-1}$$

$4s5s\ ^3S_1 \rightarrow 4s4p\ ^3P_2$
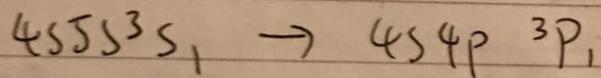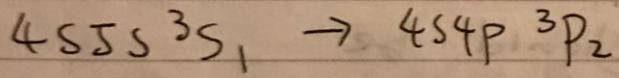
$$\Rightarrow \lambda = 616.4\ nm, \quad \nu = 1.6223 \times 10^6\ m^{-1}$$
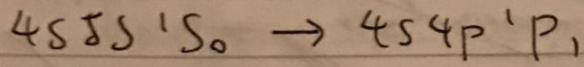
$4s5s\ ^1S_0 \rightarrow 4s4p\ ^1P_1$

$$\Rightarrow \lambda = 1035\ nm, \quad \nu = 0.9662 \times 10^6\ m^{-1}$$

So, if $4s^2\ ^1S_0$ has energy at 0,
then:

$4s4p\ ^1P_1$ is at $2.3652 \times 10^6\ m^{-1}$

$4s5s\ ^1S_0$ is at $(2.3652 + 0.9662) \times 10^6$
$$= 3.3314 \times 10^6\ m^{-1}$$

singlet triplet splitting ↓ for 4s5s

$4s4p\ ^3P_0$ is at $(3.3314 - 0.1777 - 1.6383) \times 10^6$

$$= 1.5154 \times 10^6\,m^{-1}$$

$4s4p\ ^3P_1$ is at $(3.3314 - 0.1777 - 1.6329) \times 10^6\,m^{-1}$

$$= 1.5208 \times 10^6\,m^{-1}$$

$4s4p\ ^3P_2$ is at $(3.3314 - 0.1777 - 1.6223) \times 10^6\,m^{-1}$

$$= 1.5314 \times 10^{+6}\,m^{-1}$$

$4s5s\ ^3S_1$ is at $(3.3314 - 0.1777) \times 10^6\,m^{-1}$
$$= 3.1537 \times 10^6\,m^{-1}$$

The diagram should be

$\nu \times 10^6\,m^{-1}$	$4s^2$	$4s4p$	$4s5s$
3.3314		$^1S_0$	
3.1537			
2.3652	$^1P_1$		$^3S_1$ ✓
			$0.1777 \times 10^{+6}\,m^{-1}$
1.5314	$^3P_2$		
1.5208		$^3P_1$	
1.5154	$^3P_0$		
0	$^1S_0$		

Energy

✓ All correct
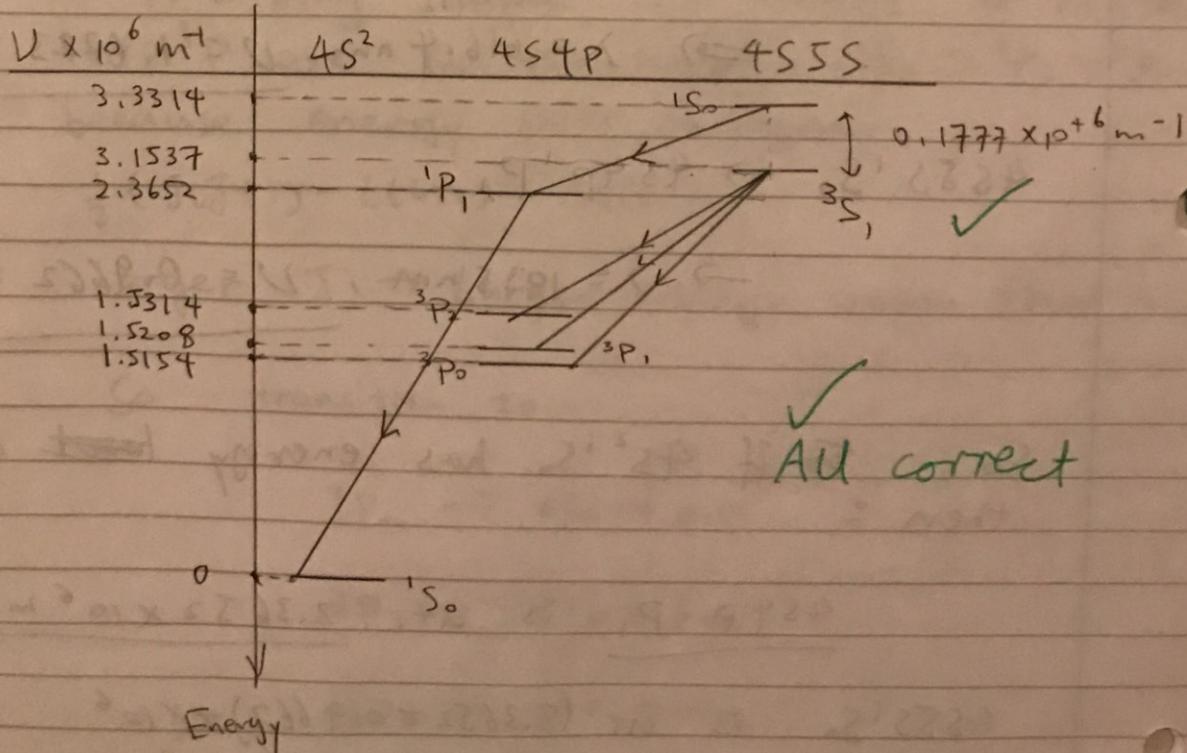
16. The nucleus has nuclear spin $\underline{I}$ and magnetic moment $\underline{\mu_I}$ given by:

$$\underline{\mu_I} = g_I \mu_N \underline{I} \qquad \checkmark$$
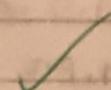
For s-electrons the magnetic field $\underline{B_e}$ it produces is ~~per~~ proportional to $\underline{S}$. So the hyperfine structure energy $E = \langle -\underline{\mu_I} \cdot \underline{B_e} \rangle$ ~~to~~ has the form

$$E_{HFS} \propto \underline{I} \cdot \underline{S} = \underline{I} \cdot \underline{J}$$

$\underline{J} = \underline{S}$ for s-electrons since $\underline{L} = 0$

For electrons with $l \neq 0$ the terms in the expression for $\underline{B_e}$ that are perpendicular to $\underline{J}$ will be averaged to 0 in the vector model. So $\underline{B_e} \propto \underline{J}$

$$\Rightarrow E_{HFS} = -\langle \underline{\mu_I} \cdot \underline{B_e} \rangle \propto \underline{I} \cdot \underline{J}$$

$\Rightarrow$ In both cases, $\hat{H}_{HFS} = A_J \underline{I} \cdot \underline{J}$, this term describes the energy shift caused by the ~~hyperf~~ interaction between nuclear spin and the magnetic field produced by the orbiting electrons (hyperfine structure) $\checkmark$

The hyperfine structure energy for ~~the~~ total atomic angular momentum F is:

$$E_F = \langle I J F M_F | \hat{H}_{HFS} | I J F M_F \rangle$$

$$= A_J \langle \underline{I} \cdot \underline{J} \rangle = \frac{A_J}{2} [F(F+1) - J(J+1) - I(I+1)]$$

$$\rightarrow \quad \Delta E_{F, F-1} = \bar{E}_F - \bar{E}_{F-1} = A_J \cdot \frac{1}{2}\left((F)(F+1) - (F)(F-1)\right)$$

$$= A_J F$$

$$\rightarrow \quad \Delta E_{F-1, F-2} = \bar{E}_{F-1} - \bar{E}_{F-2} = A_J (F-1)$$

$$\Rightarrow \quad \frac{\Delta E_{F, F-1}}{\Delta E_{F-1, F-2}} = \frac{F}{F-1} \qquad \text{Q.E.D} \quad \checkmark$$

→ The contribution to the hyperfine structure is dominated by the S-electrons because the S-electrons can come very close to the nucleus ($|\psi_{ns}(\text{at } r=0)|^2 \neq 0$). The electrons with $l \neq 0$ are futher away from the nucleus and thus their contributions to the magnetic field are small compare to ~~that~~ those of S-electrons.

⇒ let $x = \dfrac{\Delta E_{F, F-1}}{\Delta E_{F-1, F-2}} = \dfrac{F}{F-1}$, then

rearranging gives $F = \dfrac{x}{x-1}$

∵ $5p^5 6s$ has one unpaired S-electron but $5p^5 6p$ does not

∴ $5p^5 6s$ has much larger hyperfine splitting than $5p^5 6p$ does

→ we neglect the small hyperfine structure of the $5p^5 6p$ state
→ the 5 wavenumbers are all due to the 5 hyperfine ~~leve~~ levels of $5p^5 6s$ state

The 5 lines are $\{0.0 \, m^{-1}, \, 8.1 \, m^{-1}, \, 19.5 \, m^{-1}, \, 33.7 \, m^{-1},$
$51.3 \, m^{-1}\}$

experimental uncertainty $\approx 0.1 \, m^{-1}$

$\Rightarrow$ we modify the 5 lines to be: (within error)

$$\{\nu\} = \{0.0 \, m^{-1}, \, 8.1 \, m^{-1}, \, 19.4 \, m^{-1}, \, 33.8 \, m^{-1}, \, 51.4 \, m^{-1}\}$$

If state with ~~atomic~~ total atomic angular ~~momentum~~ momentum F has wavenumber ν_F, then

$$E_F = hc\,\nu_F$$

$$\rightarrow \quad X = \frac{E_F - E_{F-1}}{E_{F-1} - E_{F-2}} = \frac{hc}{hc}\,\frac{\nu_F - \nu_{F-1}}{\nu_{F-1} - \nu_{F-2}} = \frac{\nu_F - \nu_{F-1}}{\nu_{F-1} - \nu_{F-2}}$$

In set $\{\nu\}$, $0.0 \, m^{-1}$ is the energy with lowest F
~~since~~, and $51.4 \, m^{-1}$ is the energy with highest F.
Because $E_{HFS} = \frac{1}{2}$ $E_F = \frac{A_J}{2}\left[F(F+1) - I(I+1) - J(J+1)\right]$

Given I, J, larger F gives larger energy.

(Here we assert that $A_J > 0$ because the hyperfine
structure is mainly due to the s-electron. and
for s-electrons:

$$E_F \Rightarrow E_{HFS} = g\frac{2}{3}\, g_I \mu_N \, g_S \mu_0 \, \mu_B \, |\psi_{ns}(0)|^2 \, \underline{I} \cdot \underline{S}$$
$$\underbrace{\qquad\qquad\qquad}_{A_J}$$

$$= A_J \, \underline{I} \cdot \underline{J} \quad , \quad A_J \text{ is clearly positive)}$$

$$\underline{J} = \underline{S}$$

wavenumber (m⁻¹)	$\nu_F - \nu_{F-1}$ (m⁻¹)	x	$\frac{x}{x-1}$
0.0	—	—	—
8.1	8.1	—	—
19.4	11.3	1.395	3.53
33.8	14.4	1.274	4.65
51.4	17.6	1.222	5.50

$\Rightarrow$ # the ~~hyper~~ 3 hyperfine states with highest F ~~has~~ have predicted F values to be $\{F\} = \{\frac{x}{x-1}\} = \{3.53, 4.65, 5.50\}$

they correspond ~~to~~ to ~~{F}~~

$\{F\} = \{3.5, 4.5, 5.5\}$ because F can be ~~interg~~ integers or half integers and must be separated by 1.

$\Rightarrow$ the F values for the 5 states are

$\{F\} = \{1.5, 2.5, 3.5, 4.5, 5.5\}$

$\Rightarrow$ ∵ $\underline{F} = \underline{I} + \underline{J}$ ∴ $I + J = 5.5$

$|I - J| = 1.5$

$\Rightarrow$ two solutions are possible

$\begin{cases} I = \frac{7}{2} \\ J = 2 \end{cases}$ ✓ or $\begin{cases} I = 2 \\ J = \frac{7}{2} \end{cases}$ ✗

~~J is integer because even number of valence electrons~~

$\Rightarrow$ ~~J is integer and I is always integer.~~

Now consider the state itself. The electron configuration is $5p^5 6s$

→ the 6s electron has $l_s = 0$, $S_s = \frac{1}{2}$

→ electrons in the $5p^5$ states behave like a fully filled $5p^6$ ~~state~~ Sub-shell minus an electron with orbital angular momentum $l = 1$ and spin $S = \frac{1}{2}$

The fully filled $5p^6$ ~~shell~~ Subshell has $L = 0$, $S = 0$

∴ $5p^5$ ~~shell~~ Subshell has ~~l~~ $l_p = 1$, $S_p = \frac{1}{2}$

total orbital and spin angular momenta :

$\underline{L} = \underline{l_s} + \underline{l_p}$ ⇒ ~~l~~ $l_s = 0$, $l_p = 1$ ⇒ $L = 1$

$\underline{S} = \underline{S_s} + \underline{S_p}$ ⇒ $S_s = \frac{1}{2}$, $S_p = \frac{1}{2}$ ⇒ $S = 0$ or 1

⇒ ~~if~~ $\underline{J} = \underline{L} + \underline{S}$

if ~~$S = 0$~~ $S = 0$, then $J = 1$

if $S = 1$, then $J = 0, 1, 2$

⇒ possible values for J are

$J = 0, 1, 2$ ✓
  Good ✓

$\Rightarrow$ $J \neq \frac{7}{2}$, we can ~~ot~~ only have

$$\boxed{I = \frac{7}{2} \quad , \quad J = 2 \quad \text{for } 5p^5 6s}$$

✓
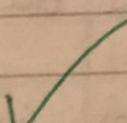
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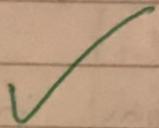
17. When an atom is placed in a uniform external magnetic field:

Atom's magnetic moment: $\underline{\mu}$

$$\underline{\mu} = -\mu_B \underline{L} - g_s \mu_B \underline{S} = -\mu_B (\underline{L} + 2\underline{S})$$

$$\underbrace{}_{g_s \approx 2}$$

If $\underline{B}$ is along $\hat{z}$ direction, then we project the magnetic moment onto $\underline{J}$ gives the Zeeman Hamiltonian

$$\hat{H}_{ze} = -\underline{\mu} \cdot \hat{B} = -\frac{\langle \underline{\mu} \cdot \underline{J} \rangle}{J(J+1)} \underbrace{\underline{J} \cdot \underline{B}}_{J_z}$$

$$= \underbrace{\frac{\langle \underline{L} \cdot \underline{J} \rangle + 2\langle \underline{S} \cdot \underline{J} \rangle}{J(J+1)}}_{g_J} \mu_B B \hat{J}_z$$

$$= g_J \mu_B B \hat{J}_z$$

→ the Zeeman energy shift $\underline{E_{ze} = g_J \mu_B B M_J}$

for state $|LSJM_J\rangle$

The Landé g-factor $\boxed{g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}}$

If $S = 0 \Rightarrow J = L$. $g_J = \frac{3}{2} - \frac{1}{2} = 1$

the Landé g-factor $\boxed{g_J = \frac{\langle \underline{L} \cdot \underline{J} \rangle + g_s \langle \underline{S} \cdot \underline{J} \rangle}{J(J+1)}}$

In basis $|LSJM_J\rangle$:

$$\langle \underline{L}\cdot\underline{J}\rangle = \tfrac{1}{2}\langle J^2 + L^2 - S^2\rangle$$

$$= \tfrac{1}{2}\left[J(J+1) + L(L+1) - S(S+1)\right].$$

$$g_s\langle \underline{S}\cdot\underline{J}\rangle = \tfrac{g_s}{2}\langle J^2 + S^2 - L^2\rangle \approx \langle J^2 + S^2 - L^2\rangle$$

$$\underbrace{}_{g_s \approx 2}$$

$$= J(J+1) + S(S+1) - L(L+1)$$

$$\Rightarrow g_J = \frac{1}{J(J+1)}\left[\frac{3}{2}J(J+1) + \tfrac{1}{2}S(S+1) - \tfrac{1}{2}L(L+1)\right]$$

$$= \boxed{\frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}} \quad \checkmark$$

If $S=0 \Rightarrow J=L \Rightarrow \cancel{g_J = 0}\ g_J = \frac{3}{2} - \frac{1}{2} = 1$

The splitting only depends on M_J

$\Rightarrow$ Normal Zeeman effect $\checkmark$

If $S \neq 0 \Rightarrow g_J$ depends on J

~~The~~ The splitting depends on both J and M_J

$\Rightarrow$ Anomalous zeeman effect. $\checkmark$

$$\therefore \quad g_{\bar{J}} = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

For $g_J < 0$ we need $\dfrac{S(S+1) - L(L+1)}{2J(J+1)} < -\dfrac{3}{2}$

So clearly $L > S$ $(\because J \geqslant 0)$

maximum absolute value of $\dfrac{S(S+1) - L(L+1)}{2J(J+1)}$ needs

minimum J, so choose $J = |L-S| = L-S$

$\Rightarrow \quad g_J < 0 \iff \dfrac{L(L+1) - S(S+1)}{(L-S)(L-S+1)} > 3$

$L(L+1) - S(S+1) = L^2 + L - S^2 - S$

$\qquad = (L^2 - S^2) + (L-S) = (L-S)(L+S) + (L-S)$

$\qquad = (L-S)(L+S+1)$

$\Rightarrow \quad \dfrac{(L-S)(L+S+1)}{(L-S)(L-S+1)} > 3$

$\Rightarrow \quad L+S+1 > 3L - 3S + 3$

$\Rightarrow \quad 4S > 2L + 2 \quad \Rightarrow \quad \boxed{S > \frac{1}{2}(L+1)}$

$\Rightarrow \quad \boxed{2S - L > 1}$ is the condition

possibly

for g_J to be $\checkmark$ negative ϖ

$\boxed{(\text{need } J = L-S, \; L > S)}$

~~choose $S=\frac{3}{2}$, $L=1$~~

ℓ choose $\boxed{S=\frac{5}{2}, \quad L=3}$

it satisfies $L > S$ and $2S - L > 1$

choose $J = L - S = \frac{1}{2}$, then

$$g_J = \frac{3}{2} + \frac{\frac{7}{2} \cdot \frac{7}{2} - 3 \cdot 4}{2 \cdot \frac{1}{2} \cdot \frac{3}{2}} = \frac{3}{2} \boxed{-\frac{2}{3}} < 0$$

$\Rightarrow \boxed{{}^6F_{1/2}}$ ✓ is an example that ~~has~~ has $g_J < 0$

For the ${}^4D_{1/2}$ level, $S = \frac{3}{2}$, $L = 2$, $J = \frac{1}{2}$

$\Rightarrow g_J = \frac{3}{2} + \frac{\frac{3}{2} \cdot \frac{5}{2} - 2 \cdot 3}{2 \cdot \frac{1}{2} \cdot \frac{3}{2}} = \frac{3}{2} - \frac{3}{2} = \boxed{0} \rightarrow QED$

vector model explanation for $g_J < 0$:

∵ $g_s \approx 2$

$\Rightarrow \underline{N}_S \propto 2\underline{S}$

$\underline{N}_L \propto \underline{L}$

$\Rightarrow \underline{J}$ and $\underline{N}_J$ are not anti-aligned
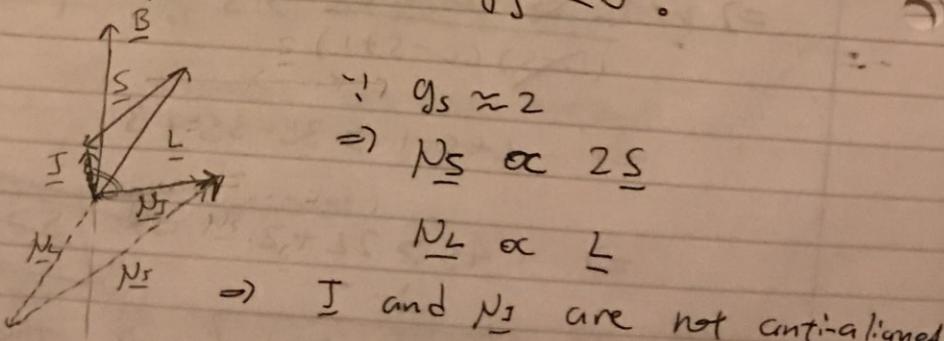
∴ The diagram shows a case that the angle θ between $\underline{N}_J$ and $\underline{J}$ is less than $90°$

$\Rightarrow$ the projection $\langle -\mu \cdot \underline{J} \rangle$ is negative

$\Rightarrow \quad g_J < 0$ ✓

Atomic nitrogen $(Z=7)$, so ground state
configuration is $1s^2 2s^2 2p^3$

the Zeeman shift $E_{ze} = g_J \mu_B B M_J$

∴ energy gap between adjacent Zeeman levels is
$(\Delta M_J = 1)$ is

$$\Delta E_z = g_J \mu_B B$$

→ The frequency separation is

$$f_z = \frac{\Delta E_z}{h} = \frac{g_J \mu_B B}{h}$$

• $f_z = 28 \times 10^9 \, Hz$, $\mu_B = 9.274 \times 10^{-24} \, J \cdot T^{-1}$

$h = 6.63 \times 10^{-34} \, J \cdot S$, $B = 1T$

$$\Rightarrow g_J = \frac{f_z h}{\mu_B B} = 2 \checkmark$$

∵ There are 4 Zeeman levels

∴ $2J + 1 \leq 4 \Rightarrow \boxed{J = \frac{3}{2}}$ ✓

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} \qquad ∵ J = \frac{3}{2}, \; g_J = 2$$

∴ $S(S+1) - L(L+1) = \frac{3}{2}(\frac{3}{2}+1)$

(S, L are integers or half integers)

∴ There are 3 valence electrons with sp..

∴ maximum value for S is $3 \times \frac{1}{2} =$

$\rightarrow S \leq \frac{3}{2}$

∴ $L \geq 0$, $S(S+1) - L(L+1) = \frac{3}{2}(\frac{3}{2}+1)$

$\Rightarrow S \geq \frac{3}{2}$

∴ ∵ $S \leq \frac{3}{2}$ and $S \geq \frac{3}{2}$

∴ $\boxed{S = \frac{3}{2}}$

∵ $J = \frac{3}{2}$, $S = \frac{3}{2}$ ∴ $\boxed{L = 0}$

$\Rightarrow \boxed{J = \frac{3}{2}, \quad L = 0, \quad S = \frac{3}{2}}$ ✓

In strong external magnetic field the
interaction of the orbit and spin with the
external field is stronger than the interaction
of the orbit and the spin. the magnetic moments
$\underline{\mu}_L$ and $\underline{\mu}_S$ will individually precess more rapidly
around B-field rather than they do around
each other. The total angular momentum
J is no longer a constant of motion
so J and M_J are not good quantum
numbers. The components of $\underline{L}$ and
$\underline{S}$ along $\underline{B}$ are conserved so now
M_L and M_S are good quantum
numbers. The eigenstates are now $|LSM_LM_S\rangle$

This is the Paschen - Back effect

in the basis $|LSM_LM_S\rangle$, the energy shift
due to magnetic field is

$$E_{PB} = \langle -\underline{\mu} \cdot \underline{B} \rangle = \langle \frac{g \mu}{} (\mu_B B L_z + g_s \mu_B B S_z) \rangle$$

$$= (M_L + 2M_S) \mu_B B \quad \checkmark$$

The spin-orbit interaction now becomes the
perturbation

$$\hat{H}_{SO} = \beta_{LS} \underline{\hat{L}} \cdot \underline{\hat{S}}$$

energy shift is $E_{SO} = \beta_{LS} \langle \underline{\hat{L}} \cdot \underline{\hat{S}} \rangle$

components perpendicular to the B-field ($\hat{z}$-direction)
are averaged to 0

$$\rightarrow \quad E_{SO} = \beta_{LS} M_L M_S$$

$\Rightarrow$ total energy shift

$$E = (M_L + 2M_S) \mu_B B + \beta_{LS} M_L M_S$$

$\rightarrow$ Energy separation between $^4P_{5/2}$ and $^4P_{1/2}$ of nitrogen
is 0.01 eV $\quad \checkmark$

This separation is due to spin-orbit interaction
in the LS-coupling scheme

The requirement for Paschen - Back effect re
is the spin-orbit interaction energy $beco$
less than the energy shift due to magnetic f

energy due to magnetic field $\sim \mu_B B$

$$\Rightarrow \quad \mu_B B \sim 0.01 \, eV = 1.6\times10^{-21} \, J \Rightarrow \boxed{B = 172 \, T.}$$

$$\Rightarrow \quad B \quad \boxed{B \sim 200 \, T}$$
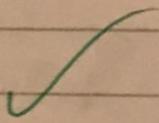
This is very difficult to achieve in lab
conditions.

18. transition $1s^2 2s\ {}^2S_{1/2} \longrightarrow 1s^2 2p\ {}^2P_{3/2}$
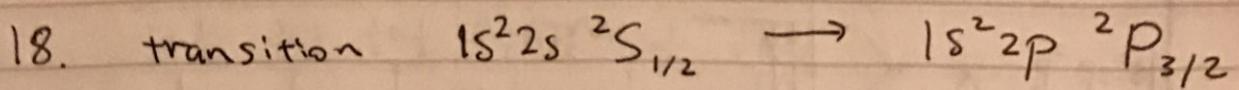
In a weak magnetic field B, the Zeeman splittings are:

$$E_{ze} = g_J \mu_B B M_J, \qquad g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

For $1s^2 2s\ {}^2S_{1/2} \rightarrow L=0 \quad S=\frac{1}{2} \quad J=\frac{1}{2}$
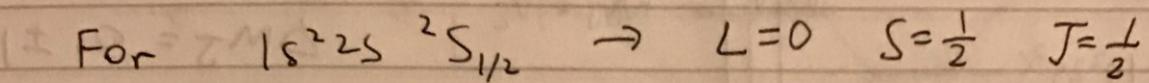
$$\therefore \quad M_J = \frac{1}{2}, -\frac{1}{2}$$

$$g_J = \frac{3}{2} + \frac{\frac{1}{2}\cdot\frac{3}{2} - 0\cdot 1}{2\cdot\frac{1}{2}\cdot\frac{3}{2}} = 2 \quad \checkmark$$

$$\therefore \Delta E_S = \pm 2 \cdot \mu_B B \cdot \frac{1}{2} = \underline{\pm \mu_B B}$$

For $1s^2 2p\ {}^2P_{3/2} \rightarrow L=1 \quad S=\frac{1}{2} \quad J=\frac{3}{2}$
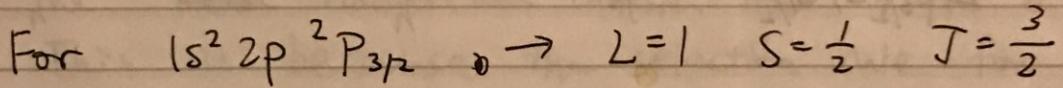
$$M_J = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$$

$$g_J = \frac{3}{2} + \frac{\frac{1}{2}\cdot\frac{3}{2} - 1\cdot 2}{2\cdot\frac{3}{2}\cdot\frac{5}{2}} = \frac{4}{3} \quad \checkmark$$

$$\Delta E_p(\pm\tfrac{3}{2}) = \pm\frac{4}{3}\mu_B B \frac{3}{2} = \underline{\pm 2\mu_B B}$$

$$\Delta E_p(\pm\tfrac{1}{2}) = \pm\frac{4}{3}\mu_B B \cdot \frac{1}{2} = \underline{\pm\frac{2}{3}\mu_B B}$$

~~Energy of~~ the Bohr magneton $\mu_B = \frac{e\hbar}{2m_e}$

$$\rightarrow \quad \mu_B = \frac{eh}{4\pi m_e} \quad \Rightarrow \quad \text{1 unit of frequency}$$

$$= \frac{eB}{4\pi m_e} = \boxed{\frac{\mu_B B}{h}}$$

$M_J = 3/2$

$M_J = 1/2$

$M_J = -1/2$

$M_J = -3/2$

$1s^2 2p\ ^2P_{3/2}$

$\lambda_0 = 671\,nm$

$1s^2 2s\ ^2S_{1/2}$

$M_J = 1/2$

$M_J = -1/2$
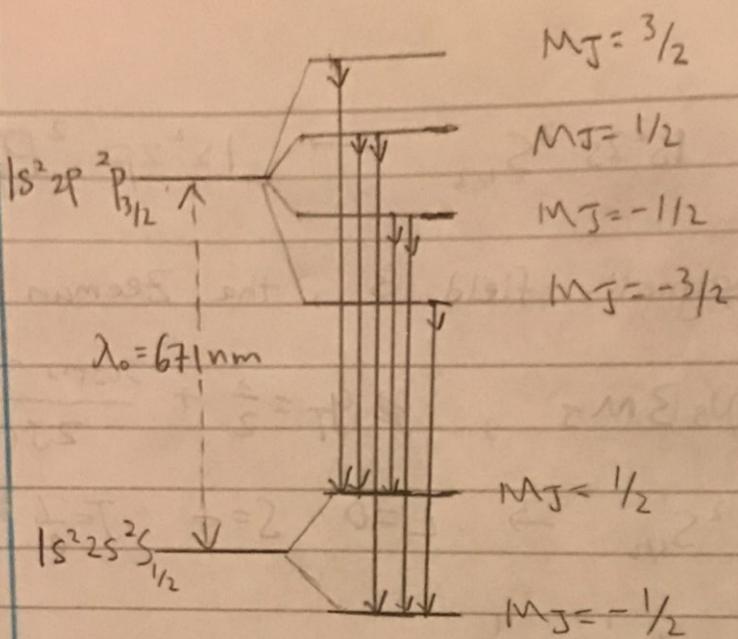
Selection rule:

$$\Delta M_J = 0, \pm 1$$

frequency gap between original $1s^2 2s\ \&\ ^2S_{1/2}$ and $1s^2 2p\ ^2P_{3/2}$ is $\leq f_0 = \dfrac{c}{\lambda_0}$ $(\lambda_0 = 671\,nm)$

Six transitions have frequency gaps: $(E = hf)$

$$\Delta f_{3/2 \to 1/2} = f_0 + \frac{2\mu_0 B - \mu_B B}{h} = f_0 + \frac{\mu_B B}{h}$$

$$\cancel{\Delta f_{1/2 \to -1/2} = f_0 + \frac{2\mu_B B \mp \mu_B B}{h} = f_0 + \frac{3\mu_B B}{h}}$$

$$\Delta f_{1/2 \to 1/2} = f_0 + \frac{2/3\,\mu_B B - \mu_B B}{h} = f_0 \mp \frac{1}{3}\frac{\mu_B B}{h}$$

$$\Delta f_{1/2 \to -1/2} = f_0 + \frac{2/3\,\mu_B B + \mu_B B}{h} = f_0 + \frac{5}{3}\frac{\mu_B B}{h}$$

$$\Delta f_{-1/2 \to 1/2} = f_0 + \frac{-2/3\,\mu_B B - \mu_B B}{h} = f_0 - \frac{5}{3}\frac{\mu_B B}{h}$$

$$\Delta f_{-1/2 \to -1/2} = f_0 + \frac{-2/3\,\mu_B B + \mu_B B}{h} = f_0 + \frac{1}{3}\frac{\mu_B B}{h} \checkmark$$

$$\Delta f_{-3/2 \to -1/2} = f_0 + \frac{-2\mu_B B + \mu_B B}{h} = f_0 - \frac{\mu_B B}{h} \checkmark$$

Intensity

the frequency interval is $\boxed{\Delta f = \dfrac{2}{3} \dfrac{eB}{4\pi m_e}}$ ✓

→ The 2 π-transitions, namely transitions from $M_J = \frac{1}{2}$ to $M_J = \frac{1}{2}$, and transition from $M_J = -\frac{1}{2}$ to $M_J = -\frac{1}{2}$ will not occur if we look at the ~~clear~~ radiation from the field direction. This is because the selection rule for ΔM_J along the field direction is $\Delta M_J = \pm 1$. In this case $\Delta M_J = 0$ is forbidden. ✓

The fine-structure splitting of $1s^2 2p \; {}^2P$ term is $\Delta f_{so} = 10 \times 10^9 \, Hz$. The splitting due to external magnetic field is on the order of $\Delta f_{ze} \sim \dfrac{\mu_B B}{h}$

For weak field need $\Delta f_{ze} \ll \Delta f_{so}$

~~f_{ze}~~ So $\dfrac{\mu_B B}{h} \ll 10 \times 10^9 \, Hz$ ✓ $< 10^8 \, Hz$ is OK

choose $\dfrac{\mu_B B}{h} = 10 \times 10^7 \, Hz$, then $\because \mu_B = 9.274 \times 10^{-24} \, J \cdot T^{-1}$
$h = 6.63 \times 10^{-34} \, J \cdot s$

→ $\underline{B = 0.0072 \, T}$

19.

$(M_I = 1, M_J = \frac{1}{2})$
$(M_I = 0, M_J = \frac{1}{2})$
$(M_I = -1, M_J = \frac{1}{2})$ ✓

$I = 1$, $J = \frac{1}{2}$ ✓

$M_J = \frac{1}{2}, -\frac{1}{2}$

$M_I = -1, 0, 1$

$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} = 2 > 0$

$g_F > 0$ for $F = \frac{3}{2}$

$g_F < 0$ for $F = \frac{1}{2}$

$E_{ze} = g_F \mu_B B M_F$

$(M_I = -1, M_J = -\frac{1}{2})$
$(M_I = 0, M_J = -\frac{1}{2})$
$(M_I = 1, M_J = -\frac{1}{2})$ ✓
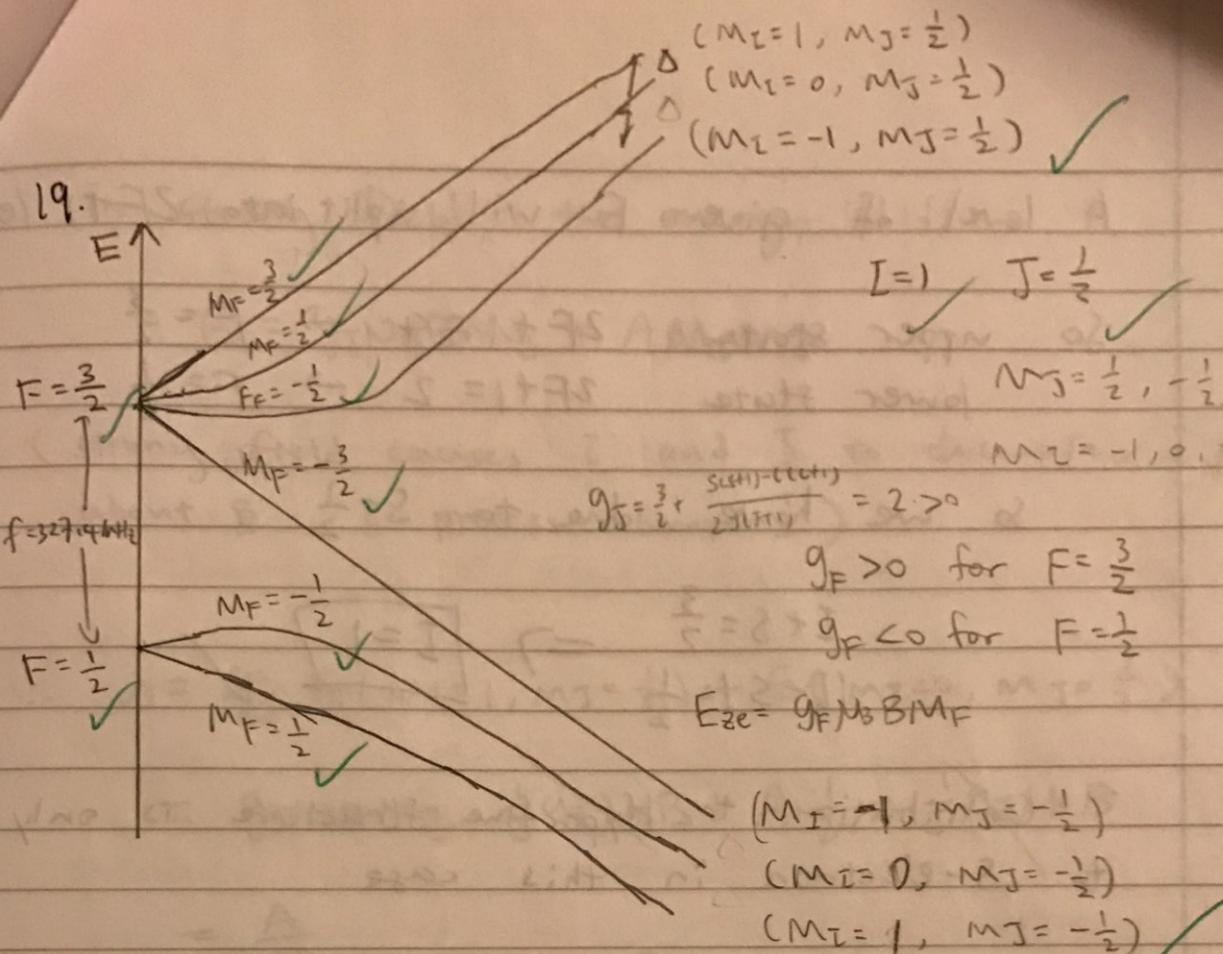
Ground level of isotope of Hydrogen
→ one electron
→ ~~L=0, S=½~~ L=1, S=½
$J = \frac{1}{2}$ has less energy than $J = \frac{3}{2}$, so $J = \frac{1}{2}$ is ground state

→ 1s

→ configuration: 1s

→ $L = 0$, $S = \frac{1}{2}$ → $J = \frac{1}{2}$ ✓

In weak field ⧉, the splitting is due to Zeeman effect is

$$E = g_F \mu_B B M_F$$

A level of given F will split into $2F+1$

So upper state $\quad 2F+1 = 4 \rightarrow F = \frac{3}{2}$
lower state $\quad 2F+1 = 2 \rightarrow F = \frac{1}{2}$

So we have, due to $S = \frac{1}{2}$,

$$I + S = \frac{3}{2}$$
$$|I - S| = \frac{1}{2} \implies \boxed{I = 1} \checkmark$$

∴ Contribution to Hyperfine structure is only due to S-electron in this case

∴ $H_{HFS} = g_I \mu_N \underline{I} \cdot \frac{2}{3} \mu_0 g_s \mu_B |\psi_{ns}(0)|^2 \underline{S}$

$$= A \underline{I} \cdot \underline{S} = A \underline{I} \cdot \underline{J}$$

● Hyperfine energy

$$E_{HFS} = A \langle \underline{I} \cdot \underline{J} \rangle = \frac{A}{2} \left[F(F+1) \overline{\Phi} J(J+1) - 2(I+1) \right]$$

From the diagram we know $F = \frac{3}{2}$ has larger hyperfine energy than $F = \frac{1}{2}$

$\rightarrow$ A is positive $\implies \boxed{g_I > 0} \checkmark$

$$\boxed{A = g_I \mu_N \cdot \frac{2}{3} \cdot \mu_0 g_s \mu_B |\psi_{ns}(0)|^2}$$

$\rightarrow$ Strong field in this context means

$$\boxed{\mu_B B > A}$$

In strong field, the energy shift

$$E = g_J \mu_B B M_J + A M_I M_J$$

(strong field causes $\underline{I}$ and $\underline{J}$ to decouple, $\underline{J}$ precess about $\underline{B}$, $\underline{I}$ precess about $\underline{J}$)

$$\therefore \quad \Delta = \cancel{E} E(M_I = 1, M_J = \tfrac{1}{2}) - E(M_I = 0, M_J = \tfrac{1}{2})$$

$$= \cancel{g_J \mu_B B M_J} \; \tfrac{1}{2} g_J \mu_B B + A \cdot \tfrac{1}{2} - \cancel{\tfrac{1}{2} g_J \mu_B B}$$

$$= \frac{A}{2}$$

Zero field splitting $\qquad \left(E_{HFS} = \frac{A}{2} \left[F(F+1) - I(I+1) - J(J+1) \right] \right)$

$$E_0 = E_{HFS}(F = \tfrac{3}{2}) - E_{HFS}(F = \tfrac{1}{2})$$

$$= \frac{A}{2} \left[(\tfrac{3}{2})(\tfrac{3}{2}+1) - (\tfrac{1}{2})(\tfrac{1}{2}+1) \right]$$

$$= \frac{3}{2} A$$

$$\Rightarrow \quad \Delta = \frac{1}{3} E_0$$

in terms of frequency

$$\Delta = \tfrac{1}{3} \times 327.4 \text{ MHz} = \boxed{109.1 \text{ MHz}} \checkmark$$

20.

$$E_{n,m} = hcR\left(\frac{(Z-\sigma_n)^2}{n^2} - \frac{(Z-\sigma_m)^2}{n^2}\right)$$

$E_n = hcR\frac{(Z-\sigma_n)^2}{n^2}$ is the binding energy of an electron in a given shell of quantum number n. Same for m.

$E_{n,m} = E_n - E_m$ is the difference in binding energy, which corresponds to the energy of photon required for a transition between n and m states to occur.

→ σ_m and σ_n are ~~screen~~ screening factors. They accounts for the effect that as the ejected electron (the electron that is taken out to create vacancy in inner shell) moves outwards the remaining electrons togather screens some nuclear effect and ~~te~~ reduce the effective atomic number.

→ At voltage ~ 2.5kV, the incident electron has kinetic energy equal to the binding energy of ~~M ser~~ M (n=3) level, so an electron from M shell is ejected and there is a vacancy left in M shell. An electron from a higher level falls into that vacancy and emits ~~or~~ ~~ex~~ X-ray. At voltage ~ 12kV, the binding energy of L (n=2) shell is reached. So an electron from L shell is ejected and a vacancy is left. Transition from higher level

into that vacancy emits x-ray.

the $L\alpha$ line is $E = E_L - E_M = 12\,keV - 2.5\,keV$

$\qquad\qquad\qquad\qquad\qquad = 9.5\,keV$

wavelength $\lambda = \dfrac{hc}{\lambda_{LM}} = 9.5\,keV$

$\qquad\qquad \rightarrow \lambda_{LM} = 0.13\,nm$ which is observed

So the α-lines are the strongest lines of the L group. Assume that is also true for the K group.

The final group should be the K group. $(n=1)$

Binding energy $E_k = hcR\,\dfrac{(Z-\sigma_k)^2}{1^2}$

$\therefore \sigma_k \approx 2 \qquad Z = 74$

$\therefore E_k = 13.6\,eV \times (74-2)^2 = 70.5\,keV$

$\rightarrow$ Voltage should be $\boxed{70.5\,kV}$ ✓

The strongest line in the K group should be the $K\alpha$ line, which is transition from L shell to K shell.

$\dfrac{hc}{\lambda_{KL}} = E_k - E_L = 70.5\,keV - 12\,keV$

$\qquad\qquad = 58.5 \times 10^3\,eV$

$\rightarrow \boxed{\lambda_{KL} = 0.021\,nm}$ ✓

into that vacancy emits x-ray.

the $L\alpha$ line is $E_L - E_M = 12\,keV - 2.5\,keV$

$$= 9.5\,keV$$

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$\dfrac{hc}{\lambda_{KL}} = E_k - E_L = 70.5\,keV - 12\,keV$

$$= 58.5 \times 10^3\,eV$$

$\rightarrow \boxed{\lambda_{KL} = 0.021\,nm}$ ✓

→ The continous x-ray spectrum arises from the deceleration of the incident electrons as they hit the target. As electrons slow down their kinetic energy is transferred into photon energy. But the wavelength range is limited by the energy of electron.

→ The low wavelength cut off is determined by the maximum kinetic energy of incident electron.

If voltage $U = 60 \text{kV}$, then electron energy

$E_e = 60 \text{keV}$, low frequency cut off λ_{min} is

$$\frac{hc}{\lambda_{min}} = E_e \longrightarrow \lambda_{nm} = \frac{hc}{E_e} = \frac{6.63 \times 10^{-34} \times 3 \times 10^8}{60 \times 10^3 \times 1.8 \times 10^{-19}}$$

$$= \boxed{0.021 \text{nm}} \checkmark$$

→ Auger effect is the ejection of a second electron and emission of longer wavelength x-rays.

→ It is due to that the vacancy in the lower shell creates potential energy that is shared by all the ~~L-shell~~ higher ~~the~~ shell electrons. ~~When~~ Consider ~~the~~ transition between L and k. When 1 L-electron falls in the K-shell vacancy it can give up its energy ~~either~~ as ~~the~~ kinetic energy to another L-shell electron. If $(E_k - E_L) > E_L$, then this L-shell electron has enough kinetic energy to escape. The resulting ejected electron has kinetic energy $E_k - 2E_L$. There are now 2 vacancies in the L-shell that can be filled by electrons falling from higher shells $\checkmark$

This leads to emission of longer wavelength X-rays than the K-series or further Auger processes.

→ If $\boxed{E_k > 2E_L}$, then an Auger electron can be emitted from the L-shell in tungsten.

→ The minimum kinetic energy of such an electron is estimated to be

$$E_e = E_k - 2E_L = 70.5\,keV - 2 \times 12\,keV$$

$$= \boxed{46.5\,keV} \checkmark$$