

# 15 B3 Q1

central field approximation

General Hamiltonian for multi electron atom

$$H = \sum_{i=1}^N \left[ \left( -\frac{\hbar^2}{2me} \nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i} \right) + \sum_{j>i}^N \frac{e^2}{4\pi\epsilon_0 r_{ij}} \right]$$

where  $\underline{r}_i = |\underline{r}_i|$ ,  $r_{ij} = |\underline{r}_i - \underline{r}_j|$

We gather the terms that depend only on  $r_i$  to a single central potential  $V_{cf}(r_i)$  for each individual electron  $i$

$$H = \sum_{i=1}^N \left[ \left( -\frac{\hbar^2}{2me} \nabla_i^2 + V_{cf}(r_i) \right) \right]$$

$H_{cf}$

$$+ \sum_{i=1}^N \left[ -V_{cf}(r_i) - \frac{Ze^2}{4\pi\epsilon_0 r_i} + \sum_{j>i}^N \frac{e^2}{4\pi\epsilon_0 r_{ij}} \right]$$

$H_{res}$

$$H = H_{cf} + H_{res}$$

the central field Hamiltonian  $H_{cf}$  has no term that mixes  $i$  and  $j$  th electron, so we can get a separable solution for the Schrodinger equation

$$\Psi(r_1, r_2, \dots, r_N) = \Psi_1(r_1) \Psi_2(r_2) \dots \Psi_N(r_N)$$

Angular wavefunction same  $Y_{l,m}$ ,  
Radial wavefunction different

if we ignore  $H_{res}$ .

~~but~~ We choose a  $\psi_{CF}$  that minimises  $H_{res}$ , the ~~the~~ residual electrostatic interaction, so that  $H_{res}$  serves as a perturbation to  $H_{CF}$ .

This is the central field approximation.

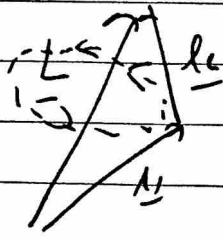
The ~~&~~ solution to Schrodinger equation involving only  $H_{CF}$  gives separable solutions as the product of wavefunction of each electron. So each electron occupies its own orbital. We can describe the solution by ~~Pauli exclusion principle~~ of the atomic wavefunction ~~as~~ by listing the orbital (quantum numbers  $n, l$ ) occupied by ~~each~~ each electron in the atom, subject to the Pauli exclusion principle. This gives the configuration of the atom.

Eg 2 electrons:  $n_1 l_1 n_2 l_2$

Next we use perturbation theory on the ~~res~~  $H_{res}$ . The interaction between electrons causes the angular momenta (orbital) of each electron to be not conserved.

▮ Their magnitude is constant but their direction is changing. The total ~~angular~~ orbital angular momentum of all electrons, however, is conserved. ~~So~~ using the vector

model, we see that  $\underline{l}_1, \underline{l}_2$  (2 electron atom as an example) precess around  $\underline{L} = \underline{l}_1 + \underline{l}_2$



So  $\underline{l}_1, \underline{l}_2 \dots$  are not good quantum numbers.  $\underline{l}_1, \underline{l}_2$  doesn't have known directions.  $m_{l1}, m_{l2}$  are not good quantum numbers.

— Spins couple together so that the overall wave function has correct symmetry

(2)

We instead find that  $L = \sum \underline{l}_i, S = \sum \underline{s}_i$  are good quantum numbers. The electronic states are now  $|L M_L S M_S\rangle$

This gives rise to terms  $2S+1$  as a perturbation to configuration.

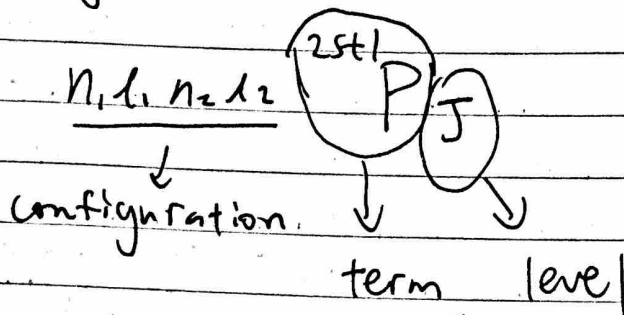
— Now the spin-orbit interaction serves as a further perturbation to the terms. The spin and orbital angular momenta,  $\underline{L}$  and  $\underline{S}$  can point to different directions relative to each other, this causes the total angular momentum  $\underline{J} = \underline{L} + \underline{S}$  to be different.

The spin-orbit interaction is  $H_{so} = \beta \underline{L} \cdot \underline{S}$  because this energy arises from the magnetic moment of electron ( $\propto \underline{S}$ ) in the magnetic field created by the relative motion between electrons and the nucleus ( $\propto \underline{L}$ )

$\therefore \underline{S} \cdot \underline{L} = \frac{1}{2} (\hat{J}^2 - \hat{L}^2 - \hat{S}^2)$   $\therefore$  different  $J$  gives different energy

for given  $L$  and  $S$   $J = |L-S|, \dots, L+S$

this gives levels



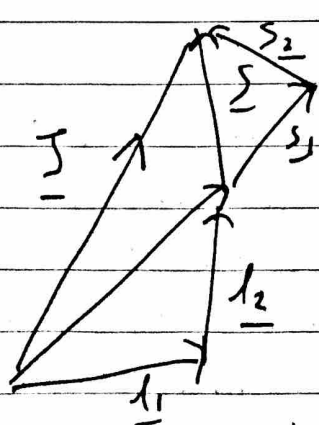
— LS coupling is the scheme that assumes the spin-orbit interaction is much less than residual electrostatic interaction

$H_{so} = \mu_B \langle L \cdot S \rangle \ll H_{res}$

$J = L + S$

If this is the case, then the orbital angular momenta of each electron couple to each other, and spin of each electron couple to each other. This two coupling are strong.  $l_1$  and  $l_2$  precess around

$\frac{4}{8}$



$L \ll$  fast due to  $H_{res}$

Then due to  $H_{so}$ ,  $L$  and  $S$  couples weakly. They precess about the total angular momentum  $J$  slowly.

The quantum states are  $|LSJM\rangle$   
 $L, S, J, M_J$  are good quantum numbers.

This is the LS coupling

- interval rule.

$$H_{so} = \beta \underline{L} \cdot \underline{S}$$

$$E_{so} = \beta \langle \underline{L} \cdot \underline{S} \rangle = \frac{1}{2} \beta (\underline{J}^2 - \underline{L}^2 - \underline{S}^2)$$

$$= \frac{1}{2} \beta (J(J+1) - L(L+1) - S(S+1))$$

∴ for spin-orbit energy in LS coupling,

-  $E_J - E_{J-1}$ , for the same L and S, is:

$$E_J - E_{J-1} = \frac{1}{2} \beta [ (J(J+1) - L(L+1) - S(S+1)) - ((J-1)J - L(L+1) - S(S+1)) ]$$

$$= \frac{1}{2} \beta [ J(J+1) - J(J-1) ] \quad (L, S \neq 0)$$

$$= \frac{1}{2} \beta [ \underbrace{J(J+1 - J + 1)}_2 ] = \beta J$$

∴  $E_J - E_{J-1} = \beta J$  ✓ interval rule

$$\frac{\Delta E_{J,J-1}}{\Delta E_{J+1,J}} = \frac{\beta J}{\beta(J-1)} = \frac{J}{J-1}$$

- Sr  $3s^2 3d$  state:

Energy difference  $E_2^1 = 35045 \text{ cm}^{-1}$

$E_1^1 = 35022 \text{ cm}^{-1}$

$E_0 = 35007 \text{ cm}^{-1}$

$S = 1.0$

difference

$$E'' - E' = 23 \text{ cm}^{-1}$$

$$E' - E = 15 \text{ cm}^{-1}$$

$$x = \frac{E'' - E'}{E' - E} = \frac{23}{15} = 1.533$$

By interval rule :

$$x = \frac{E_J - E_{J-1}}{E_{J-1} - E_{J-2}} = \frac{\beta J}{\beta(J-1)} = \frac{J}{J-1}$$

$$\therefore J = \frac{x}{x-1} \approx 3$$

$$\therefore E'' = E_3 \quad E' = E_2 \quad E = E_1$$

$J = 3, 2, 1$  in this triplet

$\therefore$   $S \leq J \leq$  state, ~~S electron~~ two electrons have spin  $\frac{1}{2}$  each

$\therefore$  total  $S = 0$  or  $1$

For triplet  $S = 1 \quad \therefore J = 3, 2, 1$

$\therefore L = 2 \Rightarrow \text{d} \quad l = d$

$SSd =$  configuration

∴ 4 levels

$5s 5d \ ^3D_3$        $S=1$      $L=2$      $J=3$     ✓

$5s 5d \ ^3D_2$        $S=1$      $L=2$      $J=2$     ✓

$5s 5d \ ^3D_1$        $S=1$      $L=2$      $J=1$     ✓

$5s 5d \ ^1D_2$        $S=0$      $L=2$      $J=2$     ✓

3/5

selection rules  $\Delta S=0$      $\Delta L=0, \pm 1$      $\Delta J=0, \pm 1$   
~~investigate the wave numbers:~~     $(0 \neq 0)$      $(0 \neq 0)$  ✓

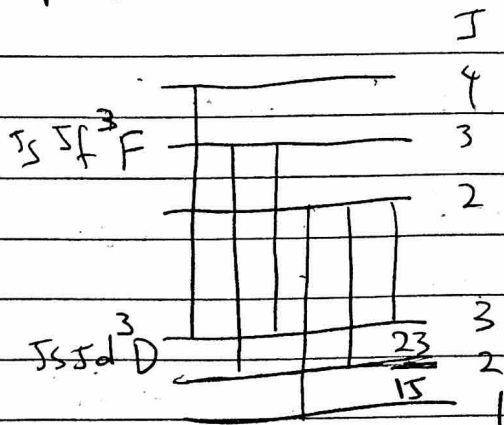
~~20108    20423    2046    20503    20689~~

∴  $l'$  can only be  $l'=1$  or  $3$  (since  $l=2$ )

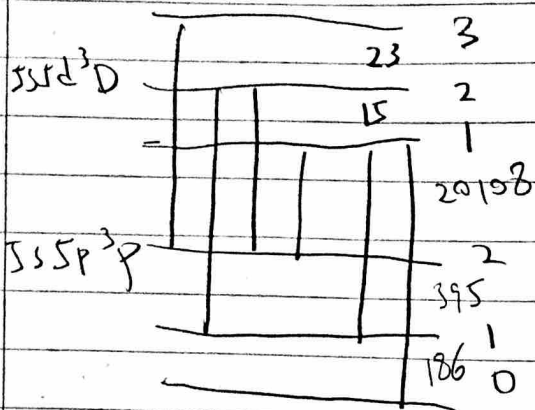
$S$  must be 1    ∴  $\Delta S=0$

we have two cases to consider

① triplet  $5s 5f \rightarrow$  triplet  $5s 5d$



② triplet  $5s5d$  to triplet  $5s5p$



But notice! there are two

pair of transitions differ by  $15 \text{ cm}^{-1}$

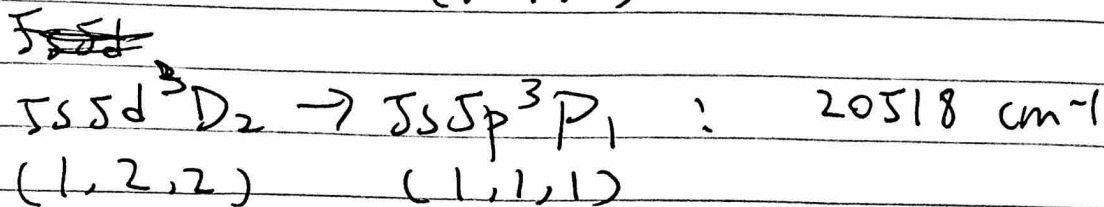
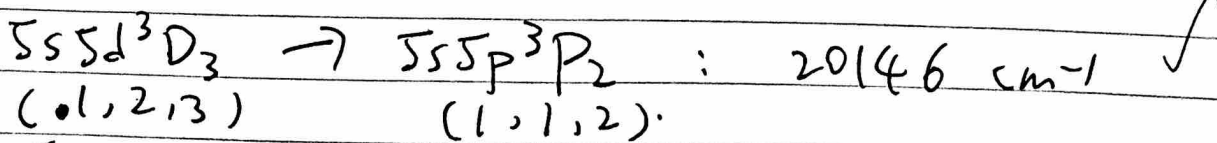
$$20123 - 20108 = 15$$

$$20518 - 20503 = 15$$

16 ~~∴ must be~~ But from observation of above graphs, in ① only one pair is differ by  $15 \text{ cm}^{-1}$ .

∴ ② is correct

Six transitions are  $(S, L, J)$





$$\text{SsSd}^3D_2 \rightarrow \text{SsSp}^3P_2 : 20123 \quad \checkmark$$
$$(1, 2, 2) \rightarrow (1, 1, 2)$$

$$\text{SsSd}^3D_1 \rightarrow \text{SsSp}^3P_2 : 20108 \quad \checkmark$$
$$(1, 2, 1) \quad (1, 1, 2)$$

$$\text{SsSd}^3D_1 \rightarrow \text{SsSp}^3P_1 : 20503 \quad \checkmark$$
$$(1, 2, 1) \quad (1, 1, 1)$$

$$\text{SsSd}^3D_1 \rightarrow \text{SsSp}^3P_0 : 20689 \quad \checkmark$$
$$(1, 2, 1) \quad (1, 1, 0)$$

28

~~20~~  
25

15B3Q2

$$A_J \underline{I} \cdot \underline{J} + g_J \mu_B \underline{J} \cdot \underline{B}_{ext} - g_I \mu_N \underline{I} \cdot \underline{B}_{ext}$$

Hyperfine  
structure

energy of electron  
dipole moment  
in external  
magnetic field

energy of nuclear  
dipole moment in  
external magnetic  
field

~~the~~  $\therefore \mu_N \ll \mu_B$  ( $\mu_N = \frac{\mu_B}{1836} \ll \frac{m_p}{m_e}$ )

$$\therefore \underbrace{|g_I \mu_N \underline{I} \cdot \underline{B}_{ext}|}_{\rightarrow \text{negligible}} \ll |g_J \mu_B \underline{J} \cdot \underline{B}_{ext}|$$

for weak or strong field, we compare the hyperfine term with the electron dipole energy in  $\underline{B}_{ext}$ .

$$\text{If } |g_J \mu_B \underline{J} \cdot \underline{B}_{ext}| \ll |A_J \underline{I} \cdot \underline{J}|$$

field is weak

$\underline{I}, \underline{J}$  couple to  $\underline{E}$   
and precess around  $\underline{B}_{ext}$

$$\text{If } |g_J \mu_B \underline{J} \cdot \underline{B}_{ext}| \gg |A_J \underline{I} \cdot \underline{J}|$$

field is strong

$\underline{I}, \underline{J}$  precess around  $\underline{B}_{ext}$  separately.

- weak field limit

ignore  $-g_I \mu_N \underline{I} \cdot \underline{B}_{ext}$ , the Zeeman Hamiltonian is

$$H_{ZE} = g_J \mu_B \underline{J} \cdot \underline{B}_{ext} \quad \underline{\mu_J} = -g_J \mu_B \underline{J}$$

In Hyperfine structure, component of  $\underline{J}$  perpendicular to  $\underline{F} = \underline{I} + \underline{J}$  (total atomic angular momentum) averages to 0

we take  $\underline{B}_{ext} = (0, 0, B_{ext})^T$

$$H_{ZE} = g_J \mu_B \frac{\langle \underline{J} \cdot \underline{F} \rangle}{\langle F^2 \rangle} \underline{F} \cdot \underline{B}_{ext}$$

$$= g_J \mu_B \frac{\langle \underline{J} \cdot \underline{F} \rangle}{F(F+1)} B_{ext} \hat{F}_z$$

$$= \underbrace{\left( g_J \frac{\langle \underline{J} \cdot \underline{F} \rangle}{F(F+1)} \right)}_{g_F} \mu_B B_{ext} \hat{F}_z$$

Q  $\langle \underline{J} \cdot \underline{F} \rangle = \frac{1}{2} (F(F+1) + J(J+1) - I(I+1))$   $\underline{F} = \underline{I} + \underline{J} \therefore \underline{I} = \underline{F} - \underline{J}$

$$\therefore I^2 = F^2 + J^2 - 2\underline{F} \cdot \underline{J}$$

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

$$\therefore g_F = \frac{g_J}{2F(F+1)} (F(F+1) + J(J+1) - I(I+1))$$

$$H_{ZE} = g_F \mu_B B_{ext} \hat{F}_z$$

$$\therefore \Delta E_F = \langle H_{ZE} \rangle = \langle [J F M_F | H_{ZE} | [J F M_F] \rangle$$

(4/8)

$$\underline{\Delta E_F = g_F \mu_B B_{ext} M_F} \quad \checkmark$$

$^{39}\text{K}$  4s state. has  $S = \frac{1}{2}$ ,  $L = 0$

$$\therefore J = \frac{1}{2}$$

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

$$\therefore L=0 \quad \therefore S=J \quad \therefore \frac{S(S+1)}{2J(J+1)} = \frac{1}{2}$$

$$\therefore g_J = \frac{3}{2} + \frac{1}{2} = \underline{\underline{2}} \quad \checkmark$$

$$\therefore J = \frac{1}{2}, \quad I = \frac{3}{2} \quad \therefore F = 1, 2$$

- the  $g_F$ 's :

$$g_1 = \frac{2}{2(1)(2)} \left( (1)(2) + \left(\frac{1}{2}\right)\left(\frac{3}{2}\right) - \left(\frac{3}{2}\right)\left(\frac{5}{2}\right) \right)$$

$$= \underline{\underline{-\frac{1}{2}}} \quad \checkmark$$

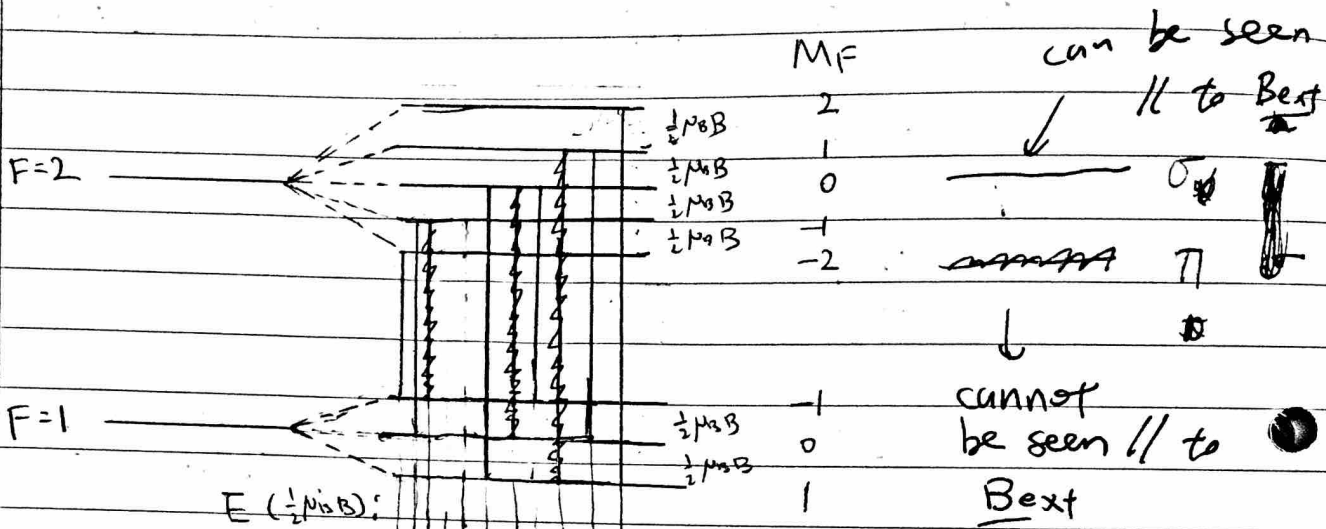
$$g_2 = \frac{2}{2(2)(3)} \left( (2)(3) + \left(\frac{1}{2}\right)\left(\frac{3}{2}\right) - \left(\frac{3}{2}\right)\left(\frac{5}{2}\right) \right)$$

$$= \underline{\underline{\frac{1}{2}}} \quad \checkmark$$

$\frac{4}{4}$

For  $F=2$   $M_F = 2, 1, -1, 2, 0$   $g_F > 0$

$F=1$   $M_F = 1, -1, 0$   $g_F < 0$

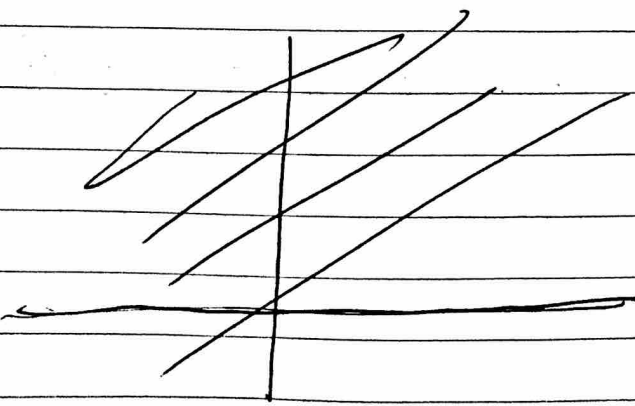


selection rules  $\Delta F = 0, \pm 1$  ( $0 \rightarrow 0$ )  
 $2 \rightarrow 1$  ✓

$\Delta M_F = 0, \pm 1$   
 $\pi$   $\sigma$

- 9 transitions, but since  $|g_1| = |g_2|$

only 7 frequencies.  $(0, 1, 2, 3, 4, 5, 6 \times (\frac{1}{2}\mu_B B) + \Delta E[(2, -2) \rightarrow (1, -1)])$



$\frac{12}{25}$

Q. 1. 2  $\frac{22}{50}$   $\frac{44}{50}$

$\frac{0}{7}$

# ISB3 Q3

energy

③ rotational energy

$$E = E_e(R_0) + (n + \frac{1}{2})h\nu_v + B(K)(K+1)$$

① electronic energy level

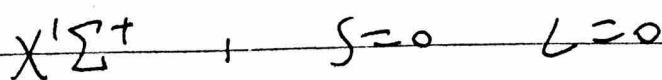
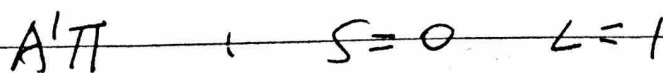
② vibrational energy

① From the coulomb interaction and kinetic energy of electrons around the two nuclei: Born-Oppenheimer approximation gives  $E_e$  as a function of separation of  $R$  between nuclei. This  $E_e(R_0)$  is  $E_e$  evaluated at equilibrium separation.

② vibrational energy derived from the oscillation between two nuclei under the potential created by the electronic energy  $E_e(R)$  this accounts for the deviation from  $R_0$  (but small).

③ rotational energy levels are derived from the total nuclei angular momentum operator in the Hamiltonian. It describes the energy of rotation of the nuclei around an axis perpendicular to the axis of joining the nuclei.

terms (molecular)



- P Branch  $\Delta K = +1 \quad \therefore K'' - K' = +1$

$$\therefore K' = K'' - 1$$

energy difference  $\Delta E = h\nu_p$   ~~$\Delta E = h$~~   
 $\Delta E_e + \Delta E_v = h\nu_{00}$

$$\begin{aligned} \therefore h\nu_p &= h\nu_{00} + B'K'(K'+1) - B''K''(K''+1) \\ &= h\nu_{00} + B'(K''-1)(K'') - B''K''(K''+1) \\ &= h\nu_{00} - (B' + B'')K'' + (B' - B'')K''^2 \end{aligned}$$

- Q Branch  $\Delta K = 0 \quad \therefore K' = K''$

$$\begin{aligned} \therefore h\nu_p &= h\nu_{00} + B'K''(K''+1) - B''K''(K''+1) \\ &= h\nu_{00} + (B' - B'')K'' + (B' - B'')K''^2 \end{aligned}$$

- R Branch  $\Delta K = -1 \quad \therefore K'' - K' = -1$

$$\therefore K' = K'' + 1$$

$$\begin{aligned} \therefore h\nu_p &= h\nu_{00} + B'(K''+1)(K''+2) - B''K''(K''+1) \\ &= h\nu_{00} + B'(K''^2 + 3K'' + 2) - B''(K''^2 + K'') \\ &= h\nu_{00} + (3B' - B'')K'' + (B' - B'')K''^2 \end{aligned}$$

absorb  
the  $2B'$  into  
this

the band head, occurs at  $K'' = 15$ , is when

$$0 = \frac{d(h\nu_p)}{dK''} = (3B' - B'') + 2K''(B' - B'')$$

$$= 3B' - B'' + 30B' - 30B''$$

$$= 33B' - 31B''$$

$$\therefore B'' = \frac{33}{31} B'$$

$$\therefore \left( \frac{B''}{hc} \right) = \frac{33}{31} \left( \frac{B'}{hc} \right)$$

$$= \underline{\underline{6.0034 \text{ cm}^{-1}}}$$

from graph  $\nu_{00} = 23470 \text{ cm}^{-1}$  (at  $K'' = 0$

correspond to P, Q, not R).

- separation  $R_0$  :

- upper level  $B' = \frac{\hbar^2}{2I} = \frac{\hbar^2}{2\mu R_0^2}$

$$\mu = \frac{1}{M_A} + \frac{1}{M_H} \sim \frac{1}{M_H} \sim \frac{1}{m_p} \therefore \mu \sim m_p$$

$$\therefore B' = \frac{\hbar^2}{2m_p R_0^2} \quad R_0 = \left( \frac{\sqrt{2m_p B'}}{\hbar} \right)^{-1} = \underline{\underline{1.663 \text{ \AA}}}$$

- lower level  $B'' = \frac{\hbar^2}{2m_p R_0^2} \Rightarrow R_0 \approx \sqrt{\frac{31}{33}} \times 1.663$   
 $= \underline{\underline{1.612 \text{ \AA}}}$



15B3Q4

$$E_{nm} = h c R_{\infty} \left[ \frac{(Z - \sigma_n)^2}{n^2} - \frac{(Z - \sigma_m)^2}{m^2} \right]$$

$\nearrow$  nuclear charge

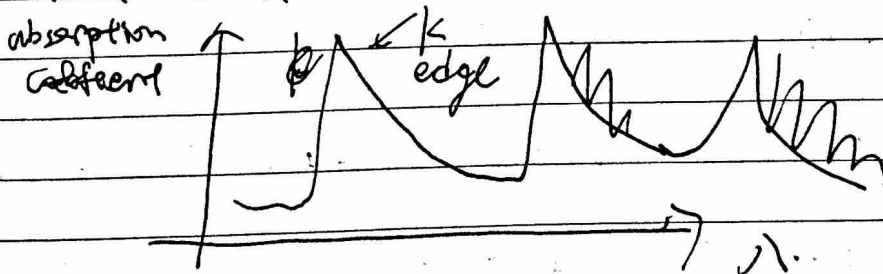
$\downarrow$                        $\downarrow$                        $\downarrow$   
 is the Rydberg constant      energy level of lower state      energy level of higher state

$\sigma_n, \sigma_m$  are screening factors that account for the screening effects of other electrons in the atom.

This is the X-ray transition between energy level  $m$  to energy level  $n$ .

$K_{\alpha}$  transitions are transitions from  $2p$  to  $1s$  state, (or  $1s$  to  $2p$  for absorption)

$K$  edge is when the electron from the  $n=1$  shell can be ionised.



$K$  edge

$$4039 = E_K = h c R_{\infty} \frac{(Z - \sigma_1)^2}{1^2} = (13.6) \frac{(20 - \sigma_1)^2}{1^2}$$

$$\therefore \sigma_1 = 2.77$$

$$3692 \text{ eV} = E_{K\alpha} = (13.6) \left[ \frac{(20-2.77)^2}{1^2} - \frac{(20-0.5m)^2}{2^2} \right]$$

$$= 4039 - 13.6 \frac{(20-0.5m)^2}{2^2}$$

$$\underline{\underline{\sigma_m = 9.90}}$$

most effective absorption occurs when at K-edge, when  $n=1$  electrons can be ionised. This is because (1), at ionisation energy or above all ~~have~~ a continuous spectrum of wavelengths can be absorbed. ~~We do not need to~~ But for discrete absorption lines (less than ionisation), ~~we~~ only certain wavelengths can be ~~absorb~~ absorbed. Also, photons (2) are more likely to excite  $n=1$  electrons because it is easier to transfer momentum to the ~~nuclea~~ nucleus by interacting with  $n=1$  electrons than others.

$K\alpha$  radiation ~~is~~ can go ~~over~~ over the K-edge

$$h c R_{\infty} \left[ \frac{(Z-\sigma_1)^2}{1^2} - \frac{(Z-\sigma_2)^2}{2^2} \right] > h c R_{\infty} \frac{(Z-1-\sigma_1)^2}{1^2}$$

$$\therefore Z^2 - 2Z\sigma_1 + \sigma_1^2 - \frac{1}{4}(Z^2 - 2Z\sigma_2 + \sigma_2^2) > Z^2 - 2(Z+1)Z + (\sigma_1+1)^2$$

~~∴~~

$$-\frac{1}{4}z^2 + \frac{1}{2}\sigma_2 z + \sigma_1^2 - \frac{1}{4}\sigma_2^2 > -2z + \sigma_1^2 + 2\sigma_1 + 1.$$

$$\therefore \frac{1}{4}z^2 - \frac{1}{2}\sigma_2 z - \sigma_1^2 + \frac{1}{4}\sigma_2^2 - 2z + \sigma_1^2 + 2\sigma_1 + 1 < 0$$

$$\therefore \cancel{z^2 - 2\sigma_2 z}$$

$$z^2 - (2\sigma_2 + 8)z + (\sigma_2^2 + 8\sigma_1 + 4) < 0$$

~~∴ for equal sign~~  
⇒

If LHS = 0

$$z = \frac{1}{2} \left[ (2\sigma_2 + 8) \pm \sqrt{(2\sigma_2 + 8)^2 - 4(\sigma_2^2 + 8\sigma_1 + 4)} \right]$$
$$= \sigma_2 + 4 \pm \sqrt{(\sigma_2 + 4)^2 - (\sigma_2^2 + 8\sigma_1 + 4)}$$

$$\therefore z < \sigma_2 + 4 + \sqrt{(\sigma_2 + 4)^2 - (\sigma_2^2 + 8\sigma_1 + 4)}$$

for  $\sigma_1 = 2.77$ ,  $\sigma_2 = 9.90$ , then

$$z' = \sigma_2 + 4 + \sqrt{(\sigma_2 + 4)^2 - (\sigma_2^2 + 8\sigma_1 + 4)}$$

$$= \underline{\underline{22}}$$

For this  $Z=22$ .

$$E_{K\alpha} = (13.6) \left[ \frac{(22-2.77)^2}{1^2} - \frac{(22-9.50)^2}{2^2} \right]$$

$$= \underline{\underline{4531 \text{ eV}}}$$

k-edge:

$$E_k = 13.6 \left[ \frac{(22-1-2.77)^2}{1^2} \right]$$

$$= \underline{\underline{4519 \text{ eV}}}$$

$$\therefore \Delta E = \underline{\underline{17 \text{ eV}}}$$