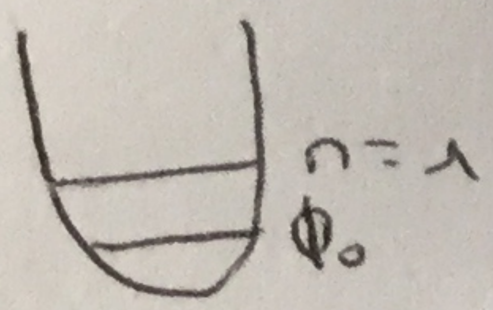
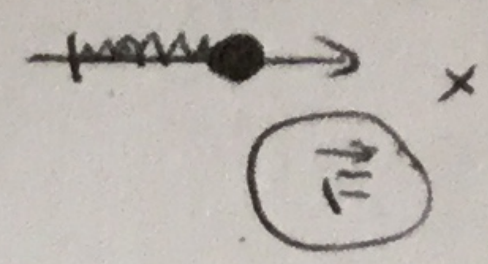
T7 : Problemes

AP.





Polarizado

1. Transició $\neq 0$

$$\langle \Phi_1 \mid \hat{d_x}\, \Phi_0 \rangle \neq 0$$

$\hat{d_y}$

$\hat{d_z}$

$d_x = q\,x$

$$\int_{-\infty}^{+\infty} \left(\frac{4\alpha^3}{\pi}\right)^{1/4} \cdot x\, e^{-\alpha x^2/2} \cdot \hat{d_x} \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}\, \underline{\underline{dx}}$$

$$\int_{-\infty}^{+\infty} \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x\, e^{-\alpha x^2/2}\, q\,x \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}\, dx$$

$$N_1 N_0 q \int_{-\infty}^{+\infty} x^2 e^{-\alpha x^2}\, dx = 2 \left(\frac{4\alpha^4}{\pi^2}\right)^{1/4} q \int_0^{\infty} x^2 e^{-\alpha x^2}\, dx$$

lim simetricos!!

$$= 2\alpha q \left(\frac{\alpha}{\pi}\right)^{1/2} \left(\frac{1}{2^2} \sqrt{\frac{\pi}{\alpha^3}}\right)$$

$$= \frac{2}{4}\alpha q \left(\frac{2}{\alpha^3}\right)^{1/2} = \frac{1}{2} q \sqrt{\frac{2}{\alpha}} \neq 0 \quad \text{permitida!!}$$

$$= q\sqrt{\frac{1}{2\alpha}} \neq 0$$

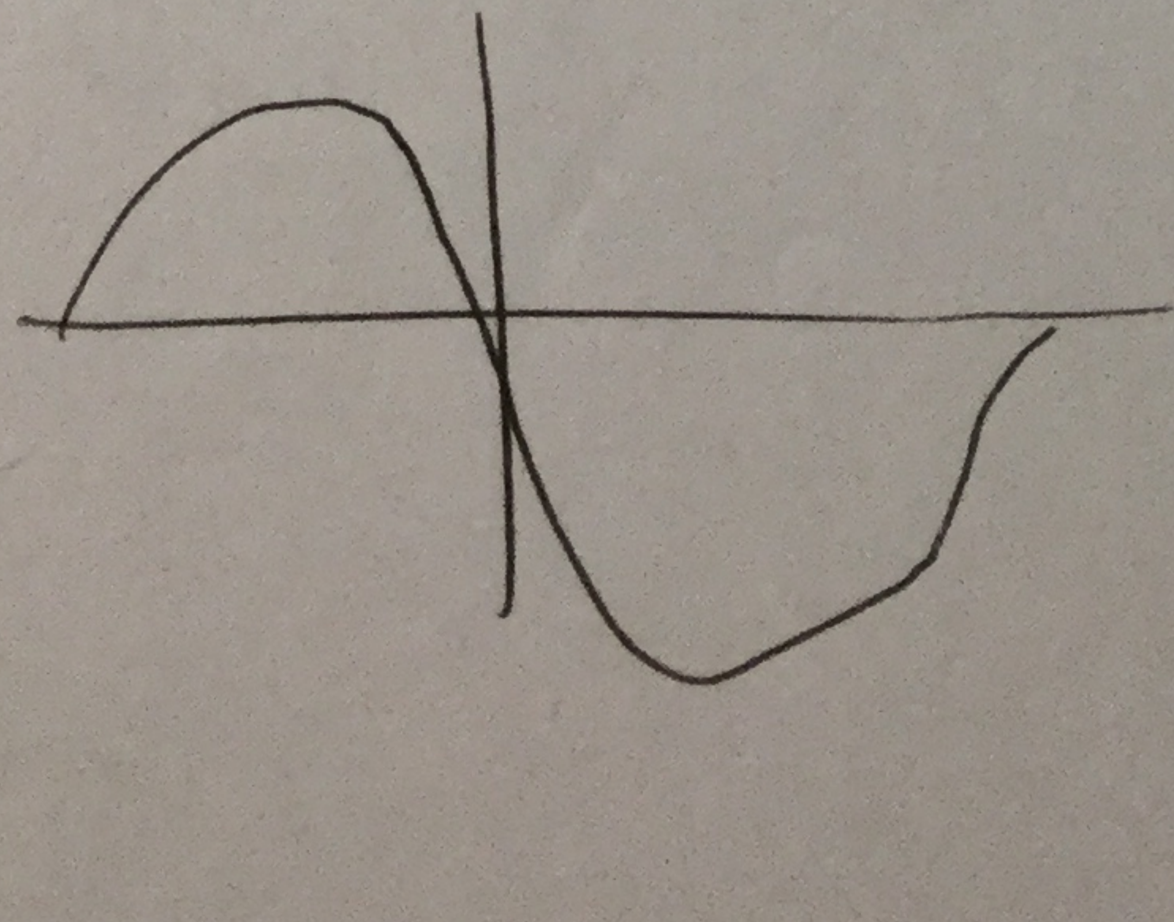
$$\int_{-\infty}^{+\infty} N\, y\, dy = 0$$

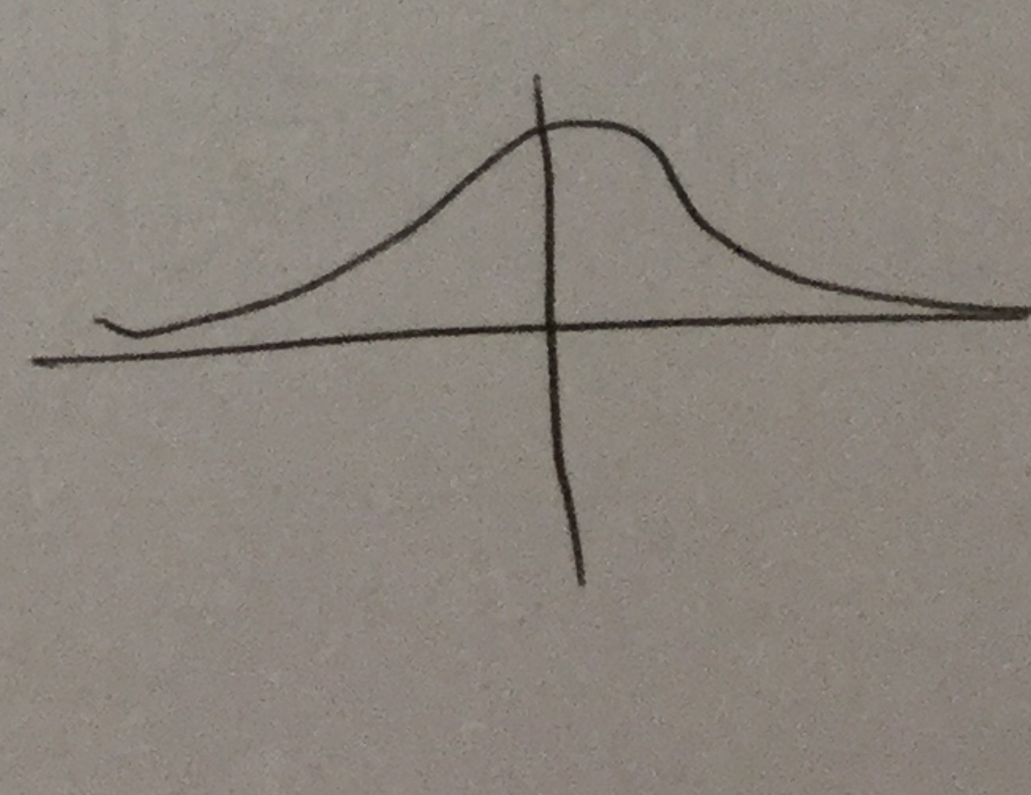
$y \quad dz \quad = 0$

$$\left(\frac{4\alpha^3}{\pi}\right)^{1/4} \int$$

$f(-y) = -f(y)$

$f(-x) = f(x)$

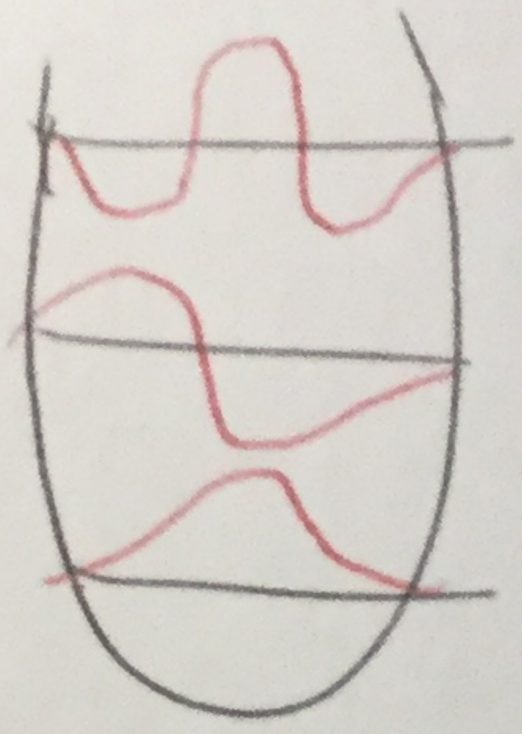




1. Hace ... $\hat{I}\ \Phi \rangle \neq 0$ Permitida

$n=0 \quad n=2 \qquad \langle \Phi_2 \mid d_x \Phi_0 \rangle = \int_{impar} = 0$

$\int$



$P \mid P = I = 0$

Transición $0 \to 2$ prohibida.

Niveles consecutivos permitidos !!!

Indiqueu si són permeses per dipol e⁻

$\Psi_{110} \leftarrow \Psi_{000}$ i $\Psi_{010} \leftarrow \Psi_{000}$ osc. harm. 3D m, q, k_x, k_y, k_z.

$\Phi_{110} = \Phi_1(x)\Phi_1(x)\Phi_0(z)$

On s'observarà la transició abs./emissió?

1. primer mirem si és complex $\langle \Phi_{110} | \hat{d}_x \Phi_{000} \rangle \neq 0$ (y, z)

$$\int_{-\infty}^{+\infty} \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\frac{\alpha x^2}{2}} \left(\frac{4\alpha^3}{\pi}\right)^{1/2} y x^{2} e^{-\alpha x^2} \, x \, q \left(\frac{\alpha}{\pi}\right)^{3/4} e^{-\alpha x^2 \frac{3}{2}} \, dx\, dy\, dz$$

$$= \frac{\alpha}{\pi}\left(\frac{4\alpha^3}{\pi}\right)^{1/2} \int_{-\infty}^{+\infty} y^2 x^3 e^{-4\alpha x^2} \, dx\, dy\, dz$$ és imparell respecte x

$\hat{d_y} = qy$

$$= \int_{-\infty}^{+\infty} NN \, e^{-4\alpha x^2} \cdot y^2 x^2 z \, dx\, dy\, dz$$

$= \int \neq 0$ No està permesa!

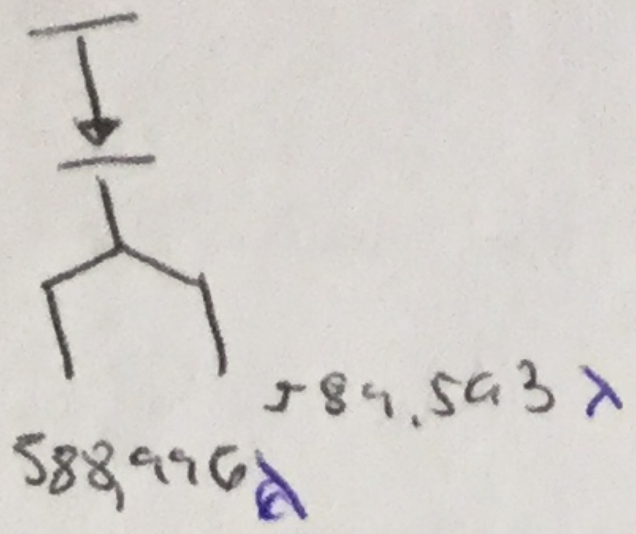
$$\langle \Phi_{010} \leftarrow \Phi_{000} \rangle = \int_{-\infty}^{+\infty}$$ per la y és parell

sí que està permesa per dipol elèctric.

$$\nu_{010} = \frac{E_2 - E_0}{h} = \frac{\cancel{h}\nu + \frac{3}{2}h\nu - \frac{3}{2}h\nu}{\cancel{h}}$$

$$\nu_{010} = \left(\frac{5}{2} - \frac{3}{2}\right)\nu = \nu = \frac{1}{2\pi}\sqrt{\frac{k_m}{m}}$$ harmònic.

7.2. Na



a) Sodi $1s^2\ 2s^2\ 2p^6\ 3s^1 \to 2S \to {}^2S_{1/2}$

$3p^1$

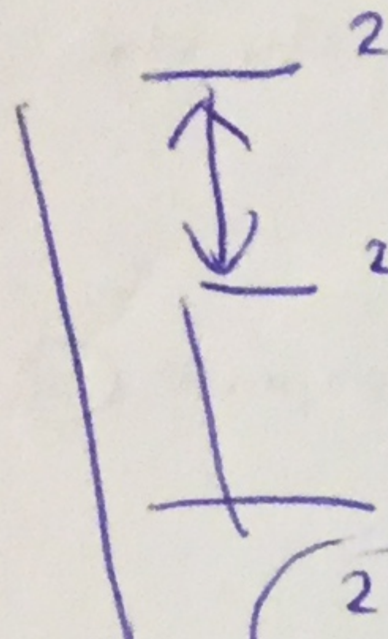
$3p \downarrow 2p$

$p^1 \to \left.\begin{array}{l} s = 1/2 \\ l = 1 \end{array}\right\} {}^2P$

$J_T = L + S = 3/2,\ 1/2$

$\bar{\nu}_1 = \frac{1}{\lambda} \cdot \frac{10^7\ \text{nm}}{1\ \text{cm}} = 16978$

$\nu_2 = 16960{,}9\ \text{cm}^{-1}$



${}^2P_{3/2} \to {}^2S_{1/2}$

${}^2P_{1/2}$

${}^2P_{3/2} \to {}^2S_{1/2}$ $\lambda_1 = 588{,}996$ nm

${}^2P_{1/2} \to {}^2S_{1/2}$ $\lambda = 589{,}593$ nm

OK

$\Delta E =$ ${}^2P_{3/2} \downarrow {}^2S_{1/2}$

$$A = \frac{2\Delta E_{SO}}{J(J+1) - L(L+1) - S(S+1)} \quad (-2)$$

$$A = \frac{2\Delta E_{SO}}{\frac{3}{2}\left(\frac{5}{2}\right) - 2 - \frac{1}{2}\frac{3}{2}} = \frac{hc(\nu_1 - \nu_2)}{1+2} =$$

$\frac{15}{4} - 2 - \frac{3}{4} = 1$

$\frac{1}{2} \cdot \frac{3}{2} - 2 - \frac{1}{2} \cdot \frac{3}{2}$

$1 -$

$$A = \frac{2hc(\nu_1 - \nu_2)}{3} = 2{,}27 \cdot 10^{-22}\ \text{J}$$

Okey

Transicions permeses?/ Nombre de línies.

~~[Ar] 3d¹⁰ 4s¹ 4p¹~~

1) $4s^1 4p^1$ ———— $^2S \; ^2P$ — $L_T = 1$, $S_T = 1, 0$ → $^3P \; ^1P$

3) $4s^1 3d^1$ ———— $^2S \; ^2D$ — $L_T = 2$, $S_T = 1, 0$ → $^3D \; ^1D$

$4s^1 4p^1$ ———— excitat — $^2S \; ^2P$ — $L_T = 1$, $S_T = 1, 0$ → $^3P \; ^1P$

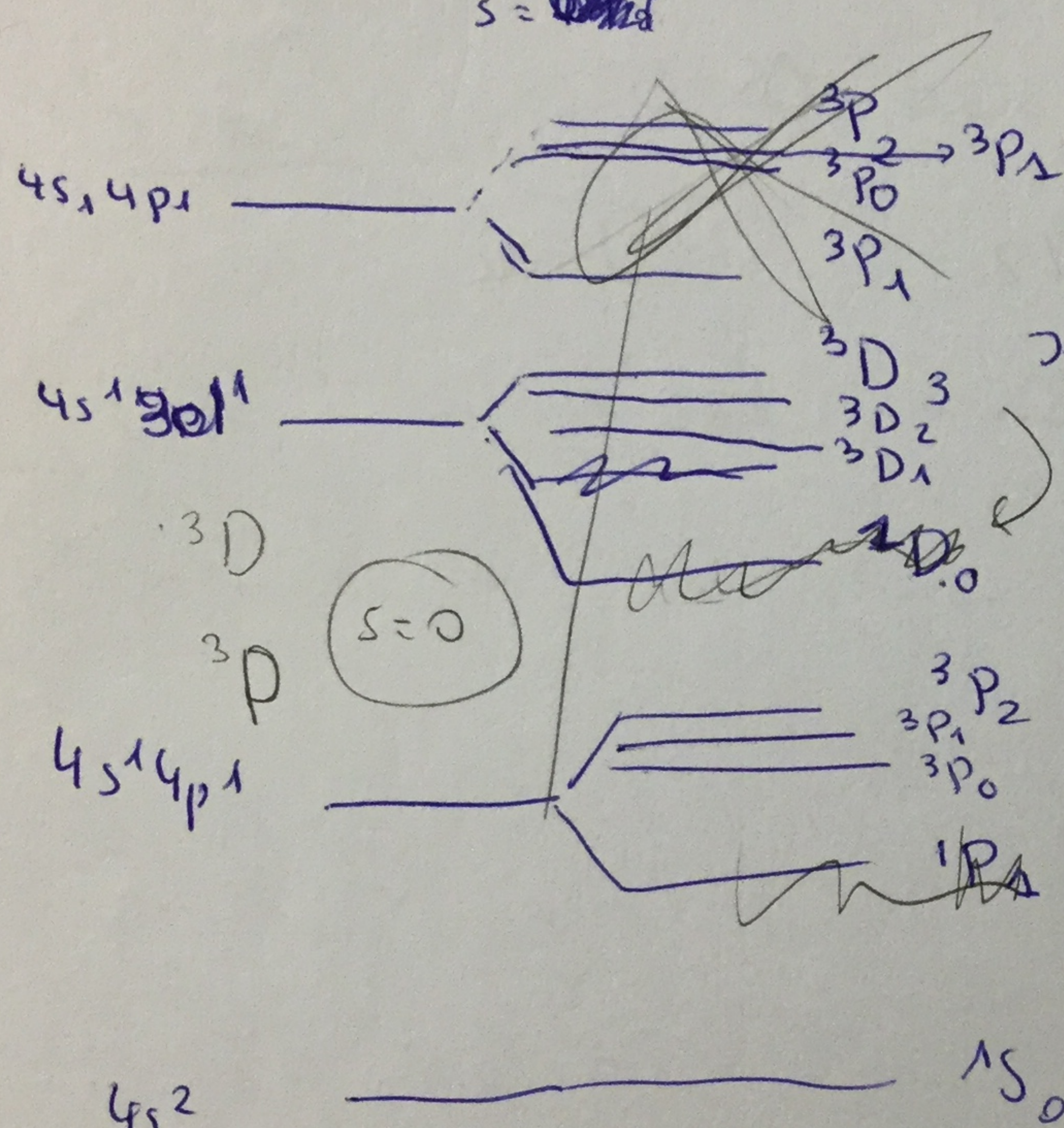
triplet

$4s^2$ ————

$s^2 \rightarrow \; ^1S_0$

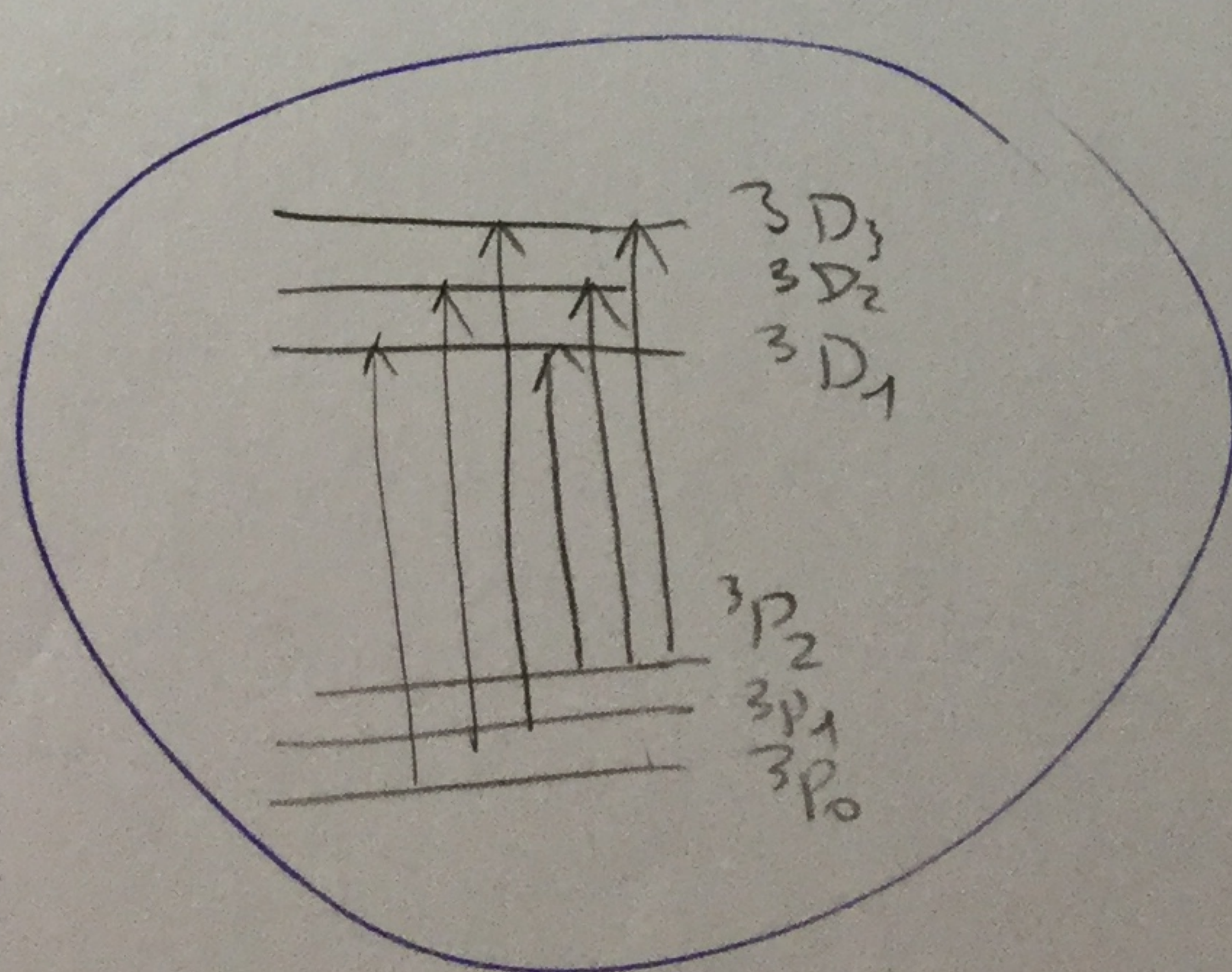
$L = 0$
$S = 0$

$J_T =$



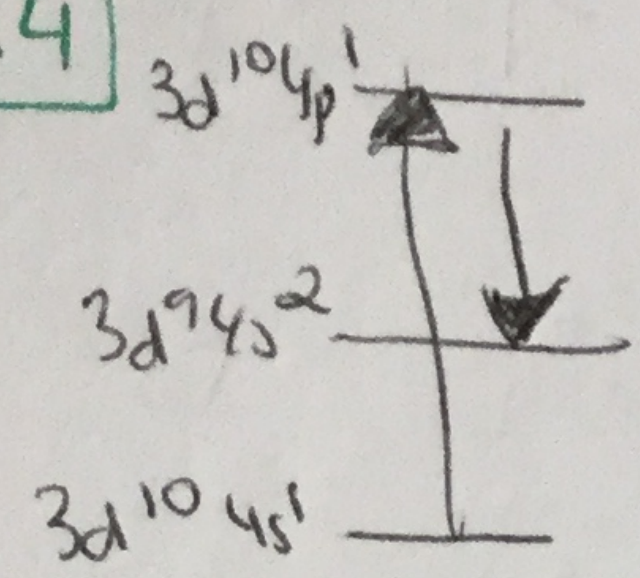
$J_T = 3, 2, 1$

$L_T = 2, 1, 0$



6 línies.

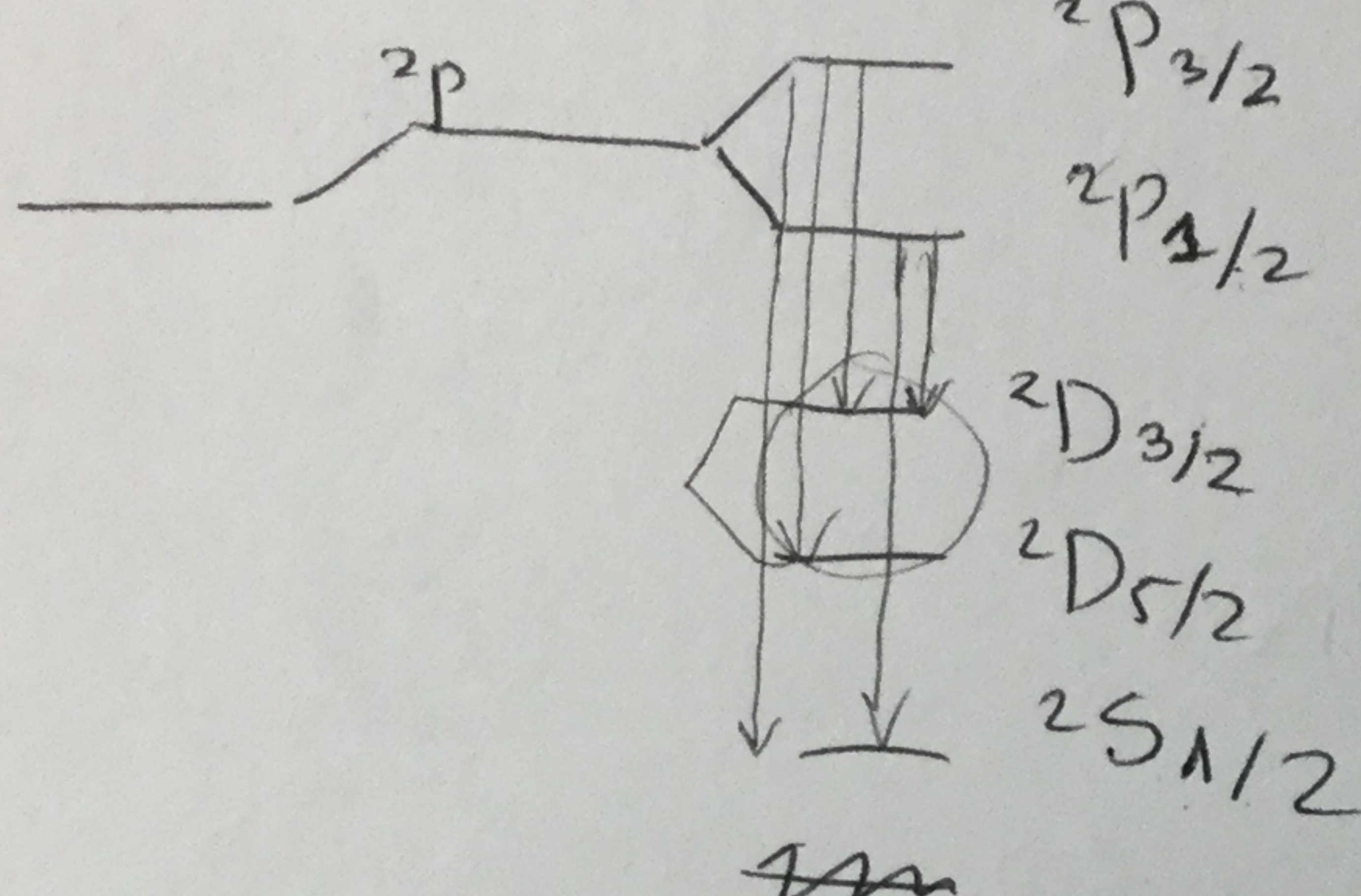
$\boxed{7.4}$



p^1 $\quad s = 1/2, \; l = 1 \quad {}^2P_{3/2} \quad {}^2P_{1/2}$

d^1 (inversión) $\quad s = 1/2, \; l = 2 \quad {}^2D \rightarrow {}^2D_{5/2} \quad {}^2D_{3/2}$

$s^1 \rightarrow \left.\begin{matrix} s = 1/2 \\ l = 0 \end{matrix}\right\} \; {}^2S$



$\Delta L = 0, \pm 1$

$\Delta J = 0, \pm 1$

$\Delta S = 0$

5 ok

5 $^{12}C\,^{16}O$ estat vib. fonamental v=0

0 1 2

115271,2 ; 230537,97 , 345795,9

No saben que J comença !!

$$\frac{230537,97}{115271,2} = \frac{hB_e(J+2)(J+3) - hB(J+1)(J+2)}{hB(J+1)(J+2) - hB(J(J+1))}$$

$$2 = \frac{J^2+5J+6-J^2-3J-2}{J^2+3J+2-J^2-J} = \frac{2J+4}{2J+2}$$

$$2J+2 = J+2 \rightarrow J=0$$ aci

7.9 C_2H_4 → 3 12 = 18-6 -

→ not pur.

($\frac{4\alpha}{\pi}$

^{12}C ^{16}O | NH_3

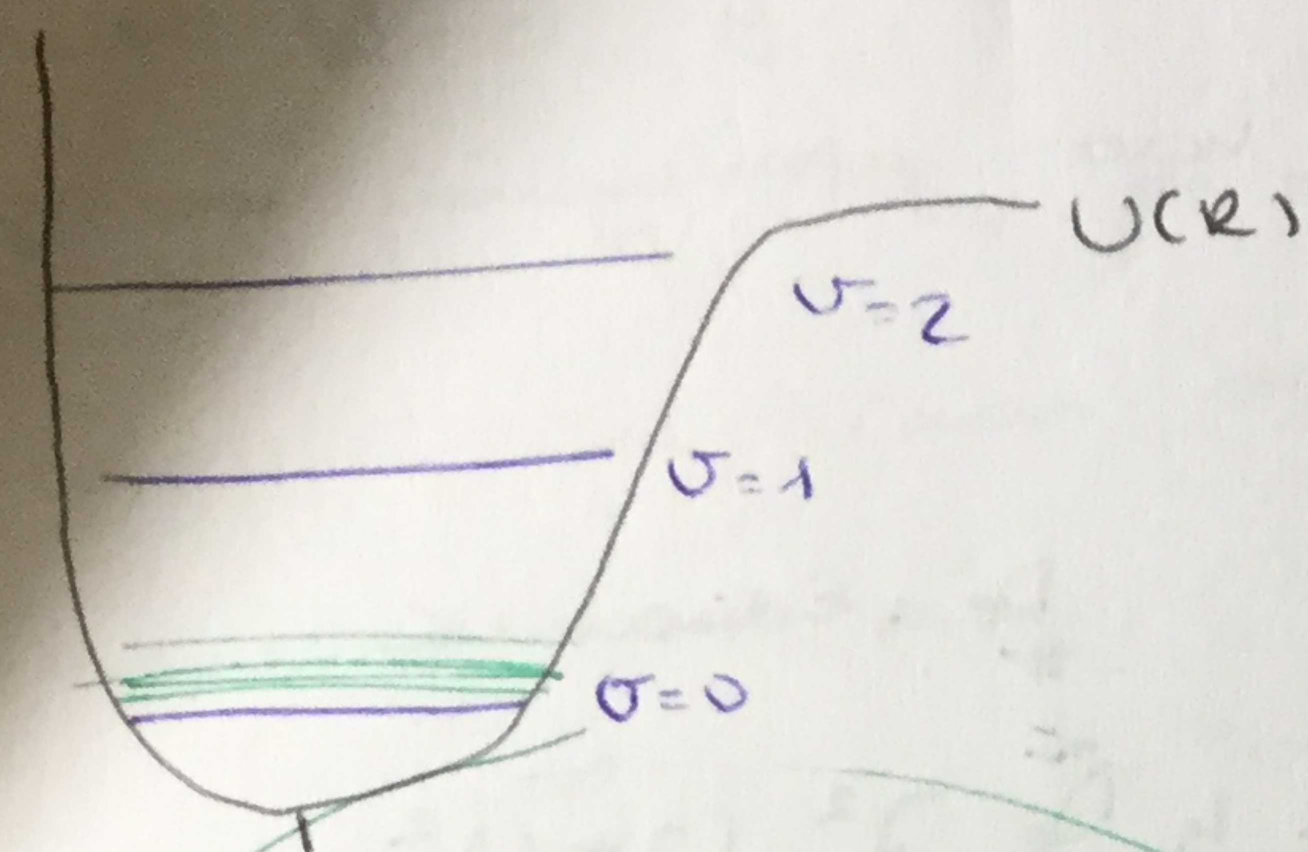
0 | 228438

E_{rot} | Rot. Microondas o IR lejano

pesadas

Espectro de rot puro: sólo cambian

a)



Reglas de selección:

① 1ª regla de selección: si la molécula no tiene μ permanente no tiene espectro de absorción, ni rotacional, ni vibracional (homonucleares)

Para presentar espectro de vibración / rotación $\vec{d}e \neq 0$

② $\Delta v = (0, \underbrace{\pm 1, \pm 2 \ldots}_{\text{esp. vibracional}})$ a medida que ↑ Δv se observan a ν + bajas.

rot.

↳ también se llama espectro de v/rotación

③ $\Delta J = \pm 1$ (en $^1\Sigma$) → para capas cerradas (SINGULETES) σ.

(+)

Asignar las líneas: entre que J se ...

↳ Buscamos la J (núm entero) → rotor rígido (error). Buscamos núm entero es igual.

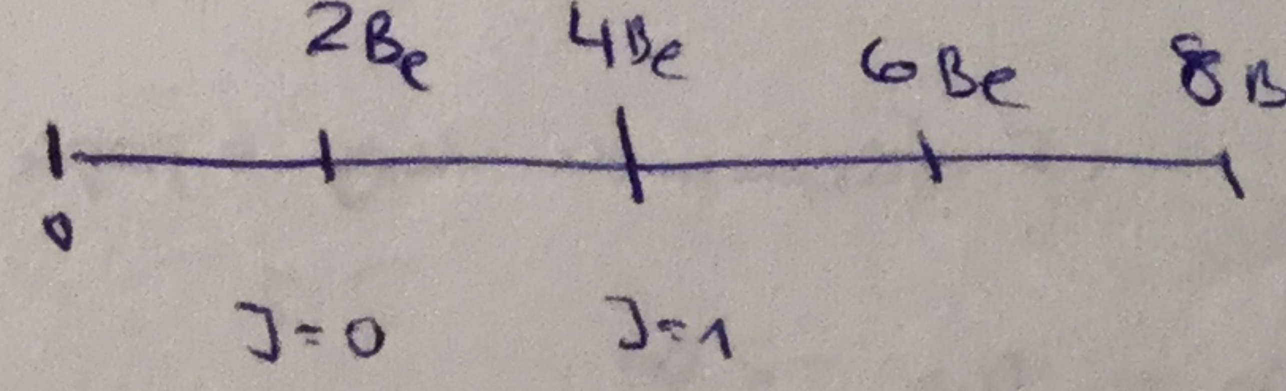
Rotor rígido: $E_{rot}(J) = h B_e J(J+1)$ $J = 0, 1, 2 \ldots$

Transición $J \xrightarrow[h\nu]{} J+1$ $\xrightarrow{E_{rot}}$, $\nu = \dfrac{E(J+1) - E(J)}{h}$

$h\nu = E(J+1) - E(J)$

$\nu = \dfrac{E(J+1) - E(J)}{h} = \dfrac{h B_e}{h} (J+1)(J+2) - B_e(J(J+1))$

$= B_e (J+1) 2$



Cada nueva línea está a $2B_e$ de la anterior. (Cada vez se van juntando más a núm. muy grandes!)

7.10. ν_e m.n.v. 3 atòmica no lineal $3\times3-6=3$ m.n.v.

$\bar{\nu}_{1e} = 1304\ cm^{-1}$ | ν_{aprox} origen bandas esp. IR:

$\bar{\nu}_{2e} = 981\ cm^{-1}$ | a) $(1,2,0) \leftarrow (0,0,0)$

$\bar{\nu}_{3e} = 512\ cm^{-1}$ | estat fundamental.

$$\bar{\nu} = \frac{\Delta E}{hc} = \frac{E_v(1,2,0) - E_v(0,0,0)}{hc}$$

E vibracional = ox. armònic pero 3 coor.

$$\bar{\nu} = \frac{(1+1/2)\cancel{hc}\,\bar{\nu}_1 + (2+1/2)\cancel{hc}\,\bar{\nu}_2 + \cancel{1/2\,hc\bar{\nu}_3} - 1/2\,\cancel{hc}(\bar{\nu}_1+\bar{\nu}_2\cancel{+\bar{\nu}_3})}{\cancel{hc}}$$

$$\bar{\nu} = \left(\frac{3}{2}\right)\bar{\nu}_1 - \frac{1}{2}\bar{\nu}_1 + \left(\frac{5}{2}-\frac{1}{2}\right)\bar{\nu}_2 = \underline{\underline{\bar{\nu}_1 + 2\bar{\nu}_2}}$$

$\boxed{7.11}$ IR abs H_2O $3N-6 = 3$ m.n.v.

$\bar{\nu}_1 = 1595\ cm^{-1}$ $\quad \bar{\nu}_2 = 1580\ cm^{-1}$

$(0,1,0) \leftarrow (0,0,0)$ o. $(0,2,0) \leftarrow (0,1,0)$

S