

Exercice 2A :

1. liant  $\Rightarrow \sigma_F, \pi_F$   
antiliant  $\Rightarrow \sigma_F^*, \pi_F^*$   
non-liant  $\Rightarrow n_p$

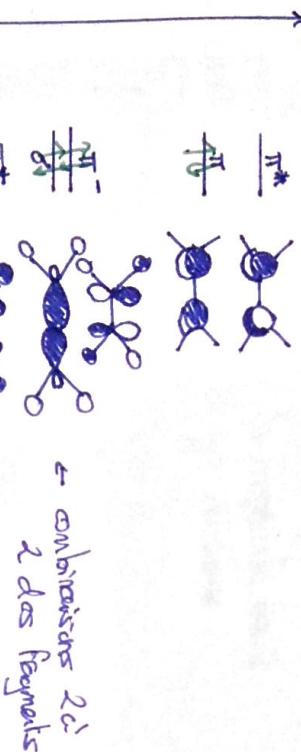
2.  $n_p$  est l'orbite  $2p_z$  du carbone

3. Selon les fragments



Non liante car le recouvrement entre les orbitales du carbone et l'su est très faible de O

4. Diagramme d'énergie de  $C_2H_4$ :



b) Orbite antiliante : orbite qui destabilise plus le système que les orbitales qui en sort à l'origine.

$$n_I = \frac{n_b e^- \text{ liant} - n_b e^- \text{ anti}}{2}$$

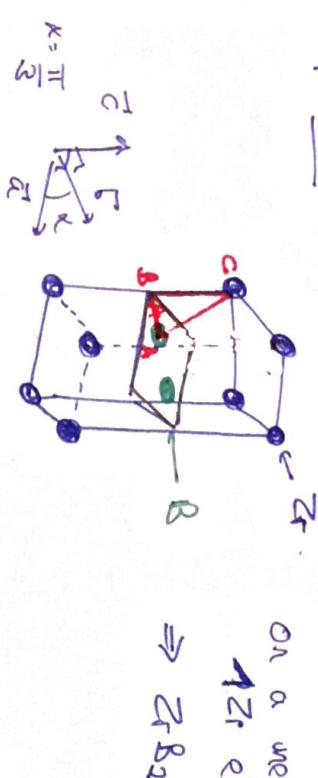
$$|n_I| = \frac{8-4}{2} = 2$$

7) Une radiation amplificate une excitation du système hors de son niveau fondamental avec  $n_I \downarrow$ . On observe alors un schéma de levage de la ligne.

$$|K_C - C_K| \Leftrightarrow |n_I| = 1$$

Exercice 4A :

1) Maille:



$$\text{On a une maille composée de } 1Zr \text{ et } 2B$$

2) Condition de contact:

$$\bullet \frac{Zr}{2r} : \frac{2r}{2R_{Zr}} = \frac{a}{2R_{Zr}} = \frac{a}{2r}$$

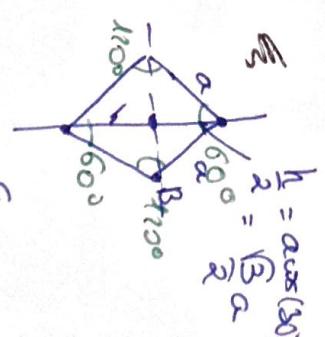
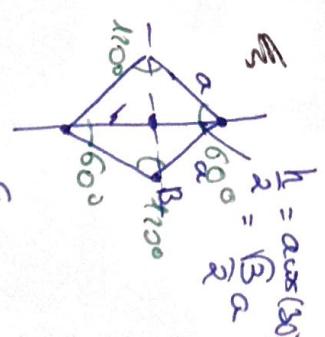
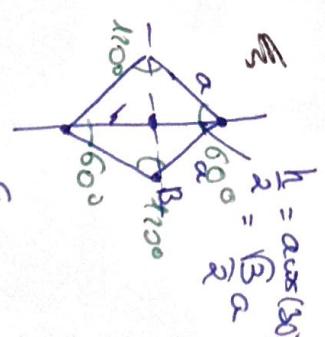
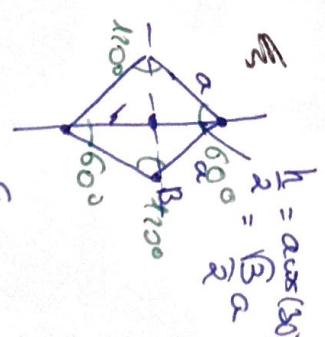
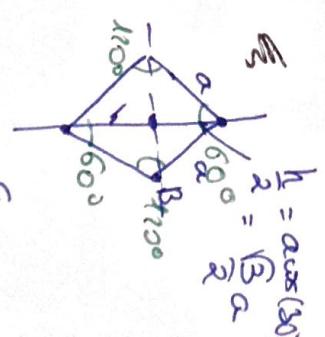
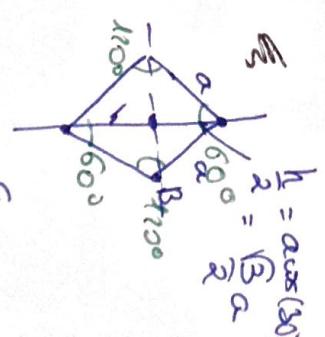
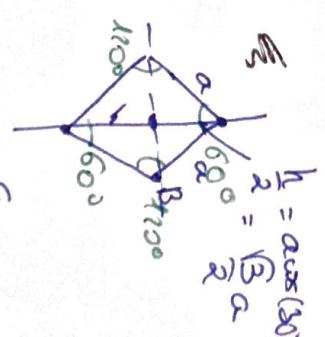
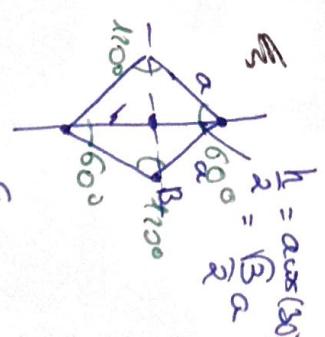
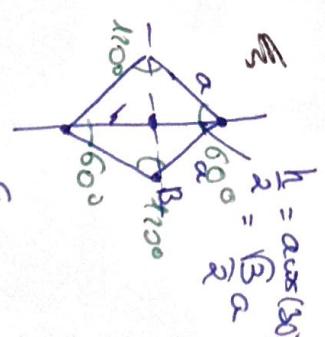
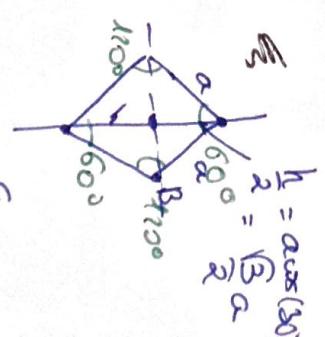
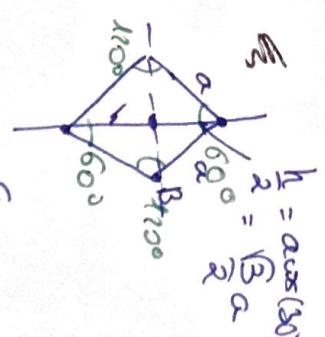
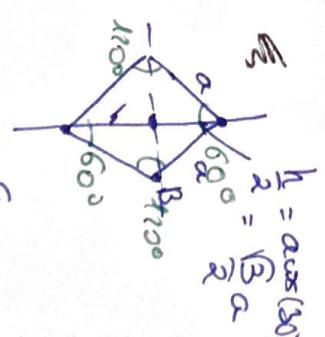
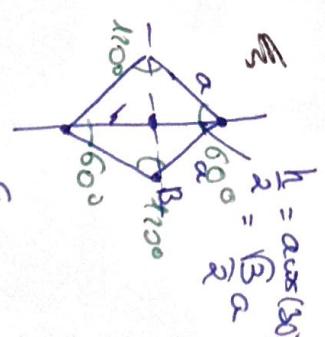
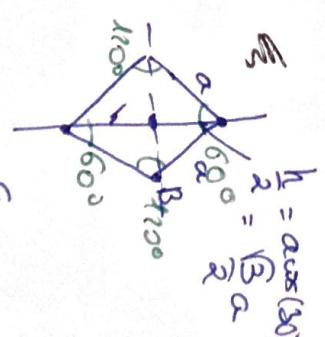
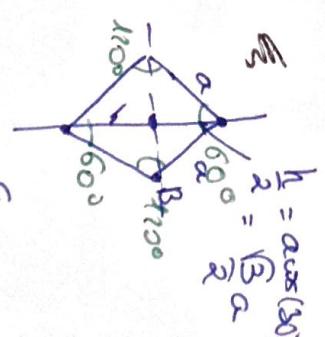
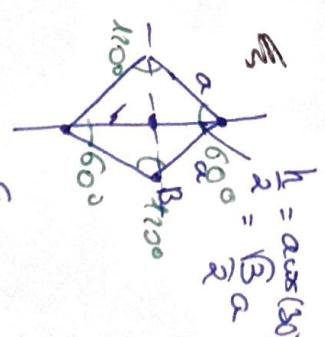
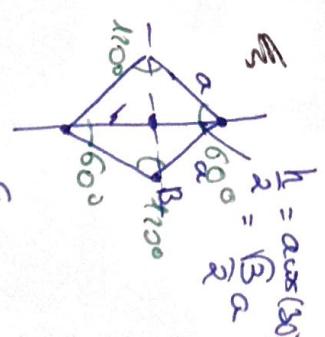
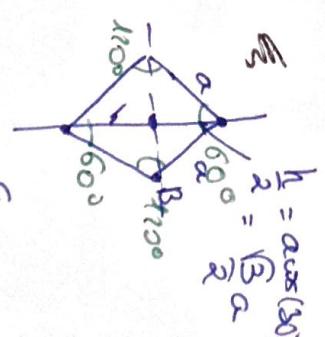
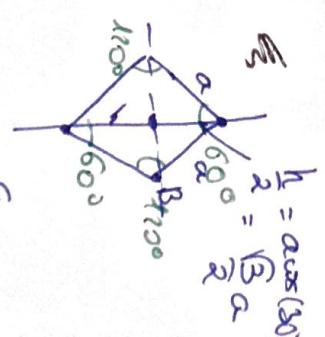
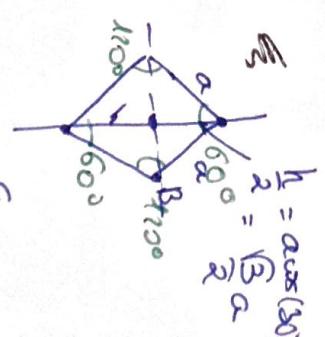
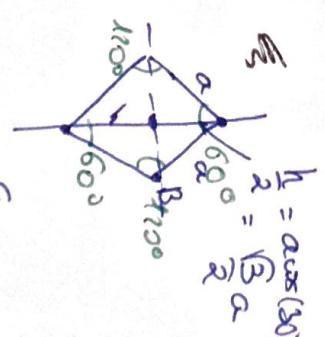
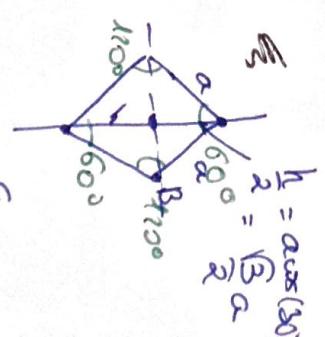
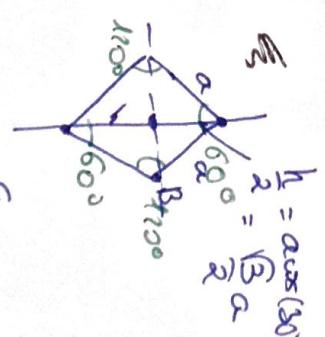
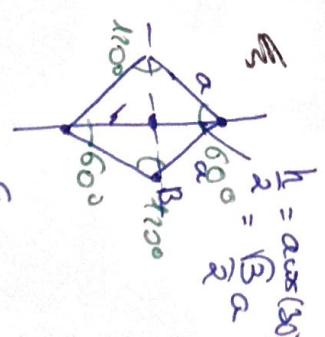
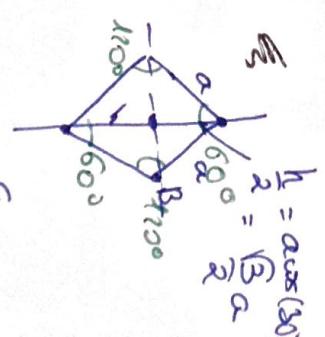
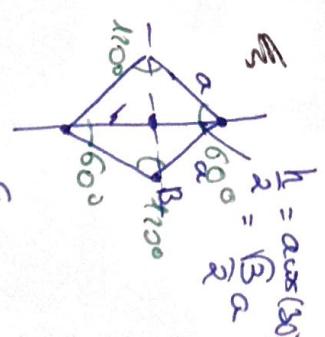
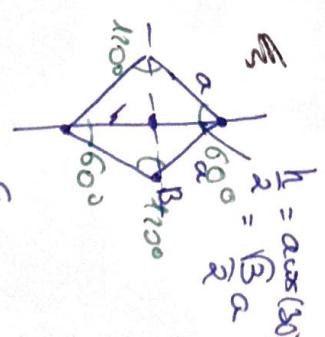
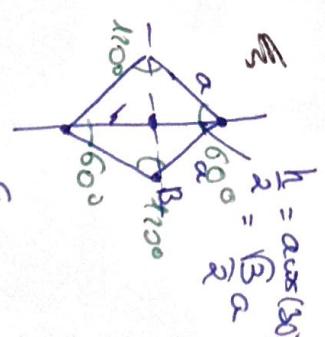
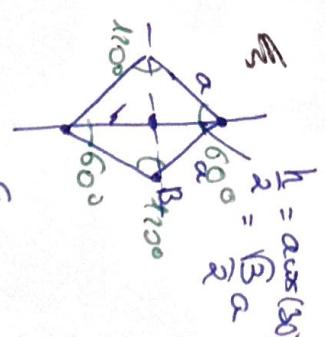
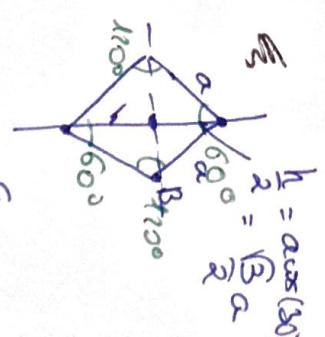
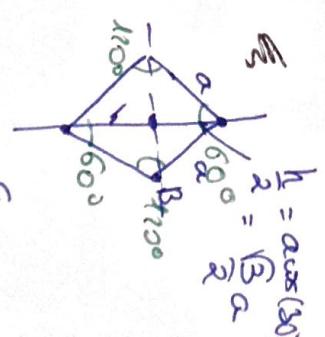
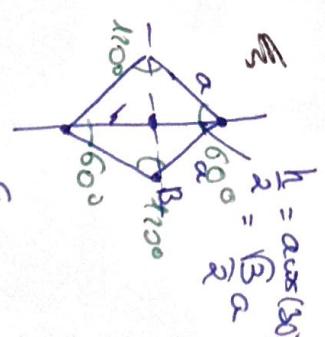
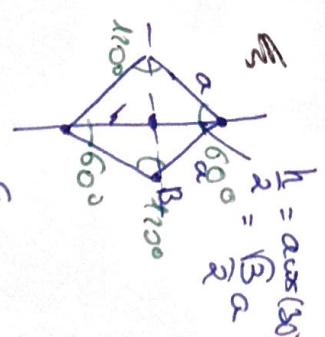
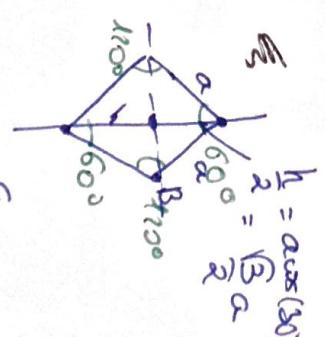
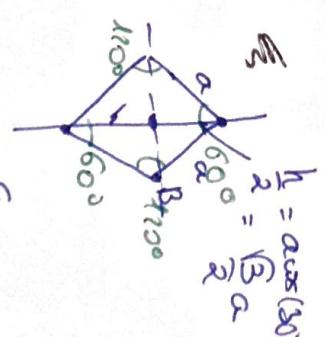
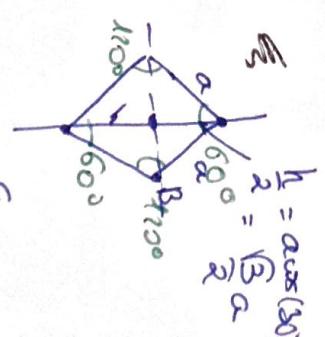
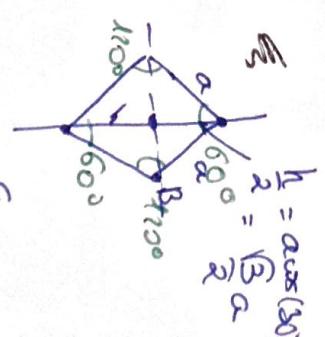
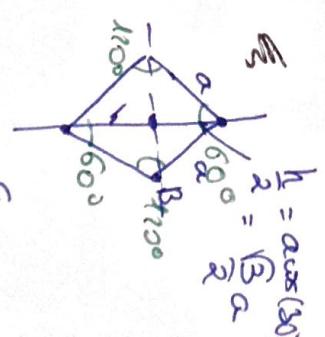
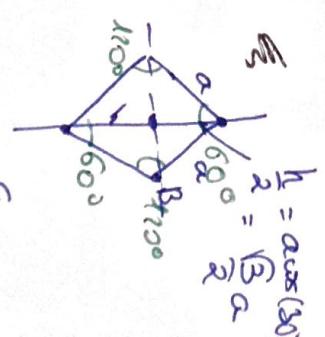
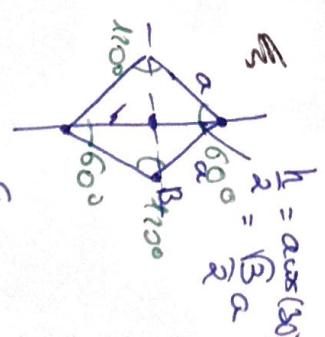
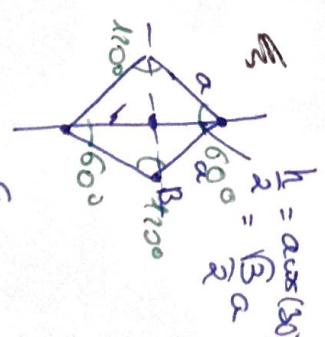
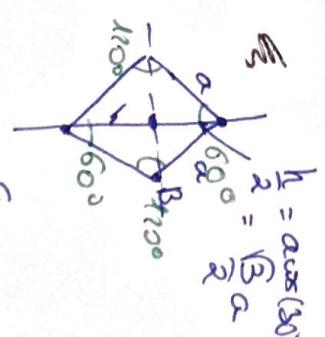
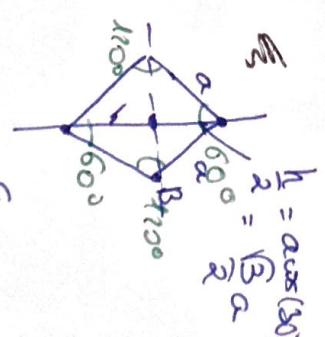
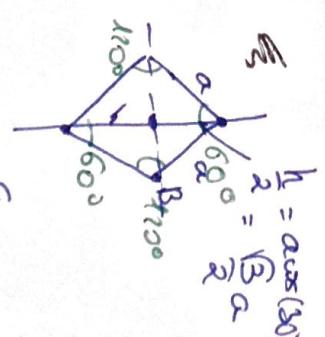
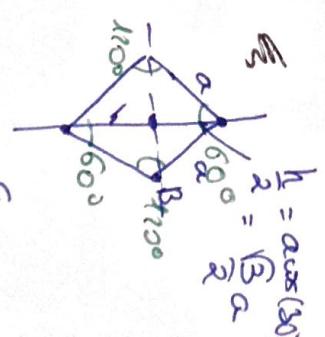
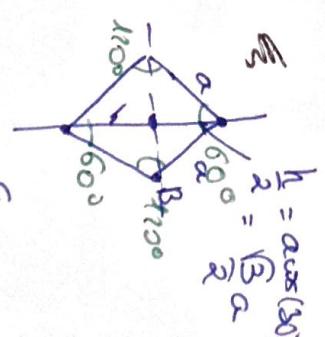
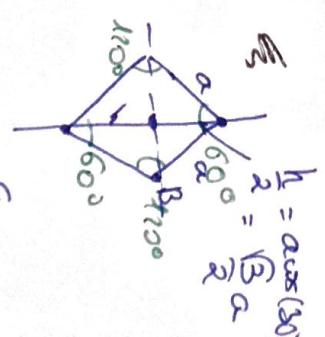
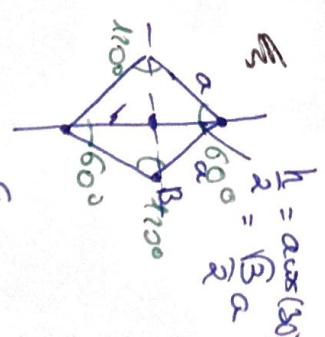
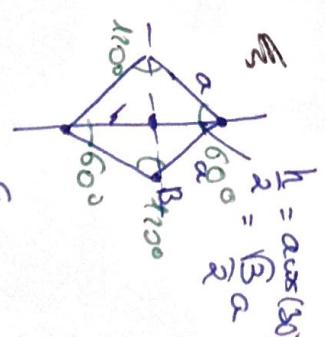
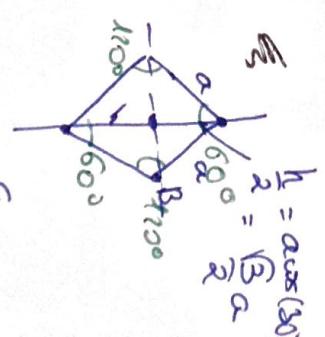
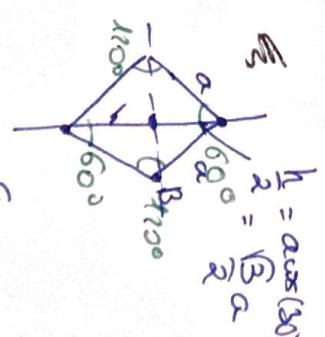
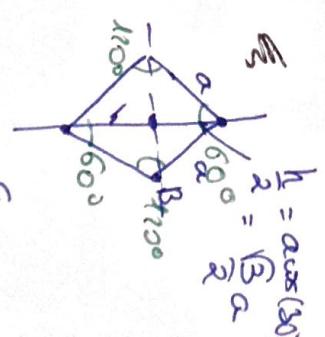
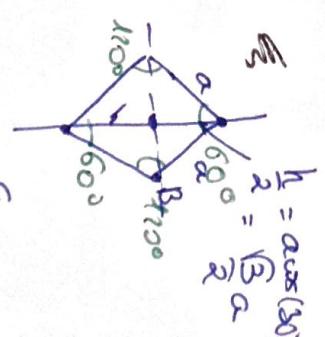
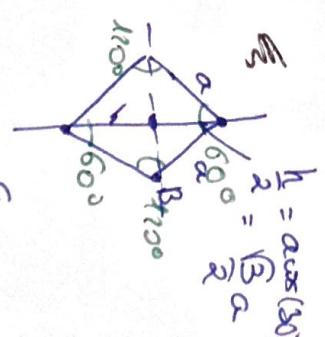
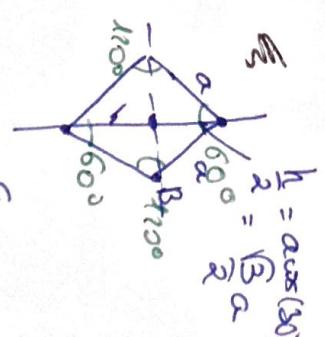
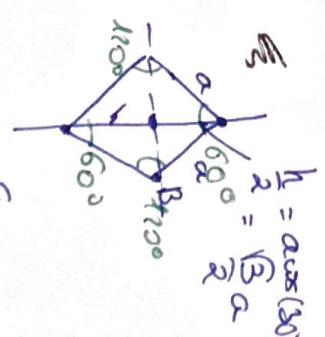
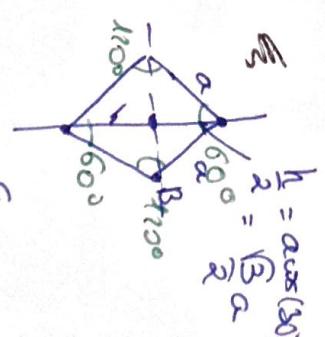
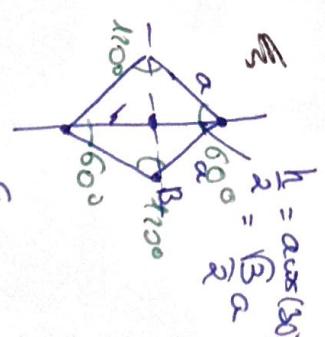
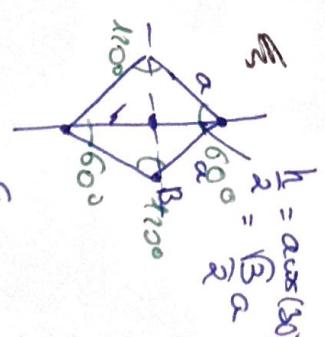
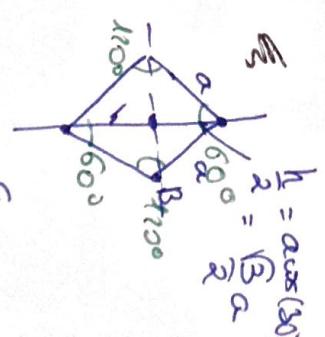
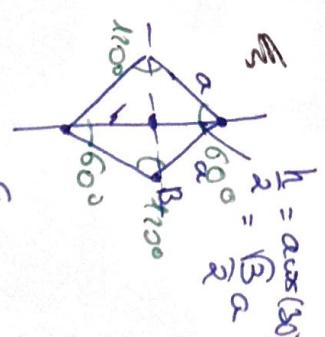
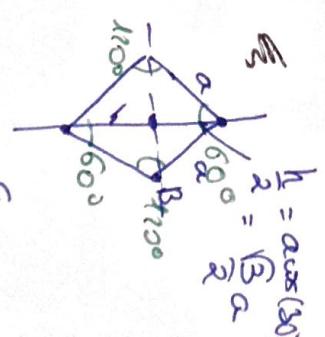
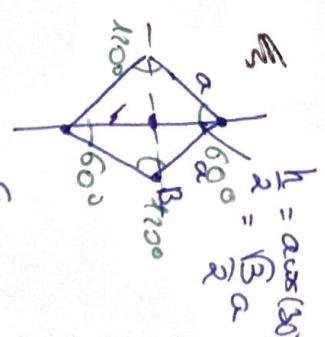
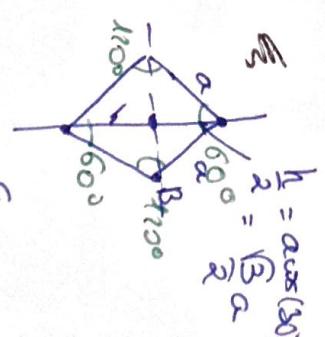
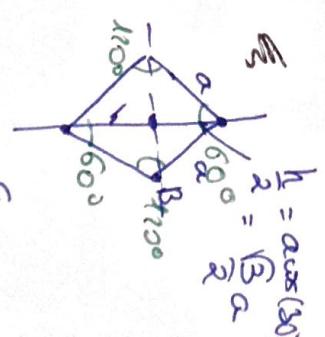
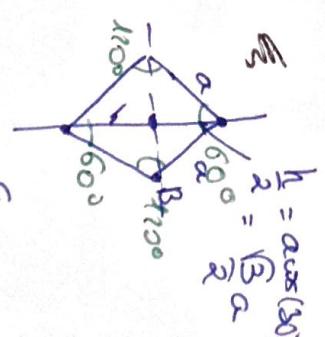
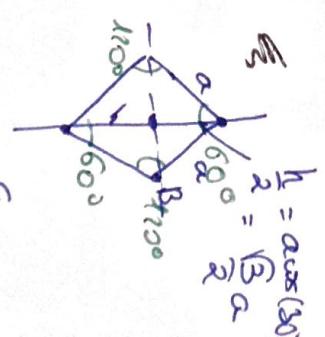
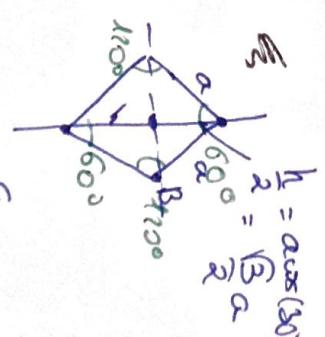
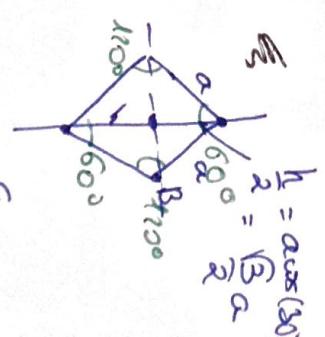
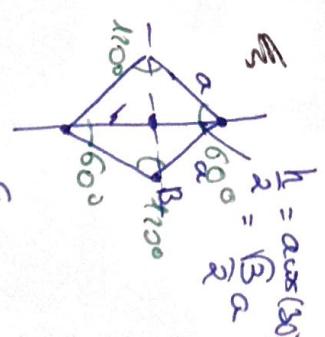
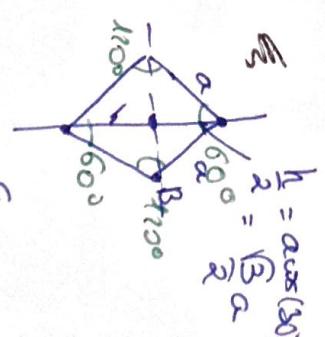
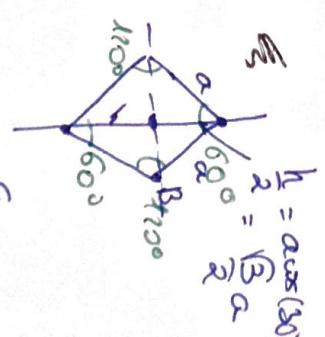
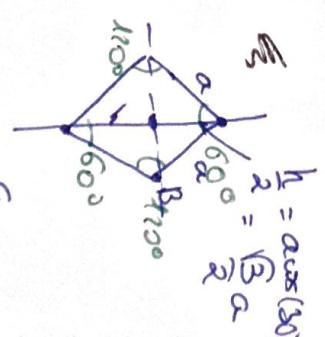
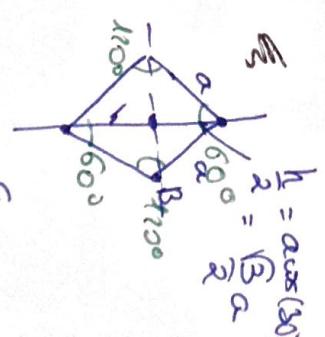
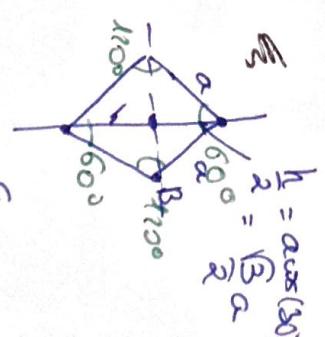
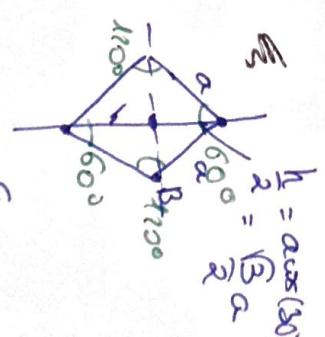
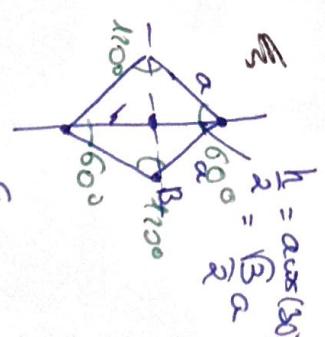
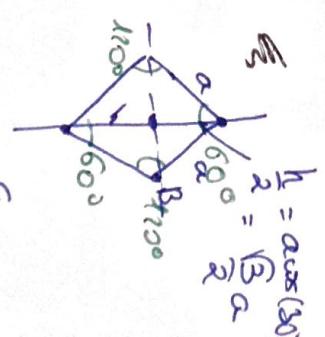
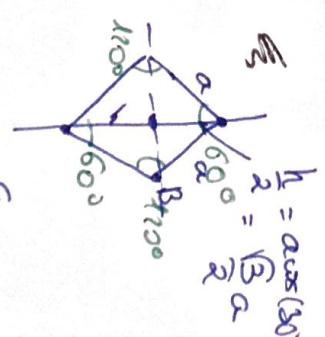
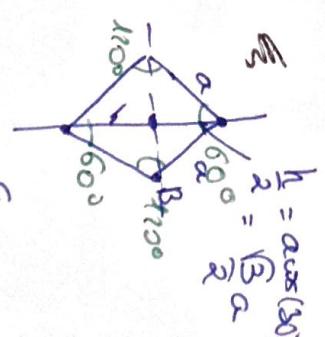
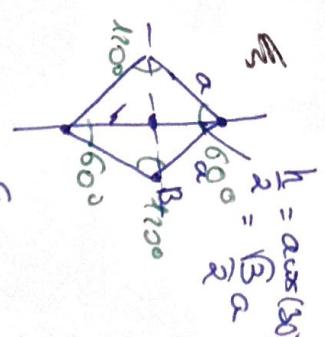
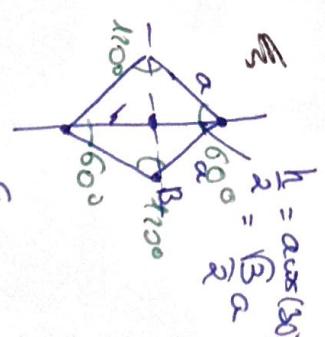
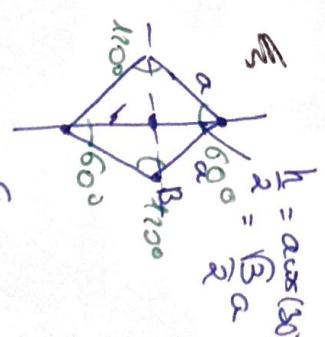
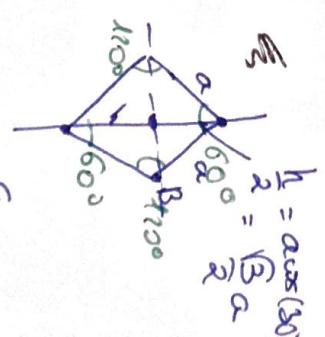
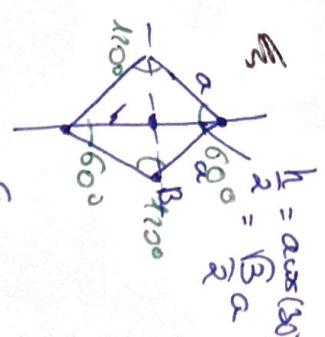
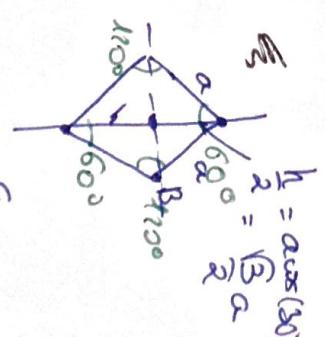
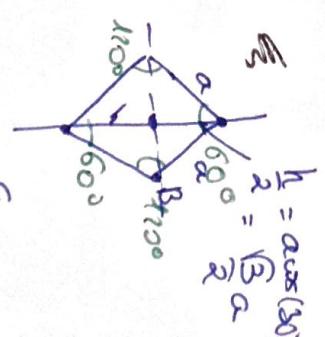
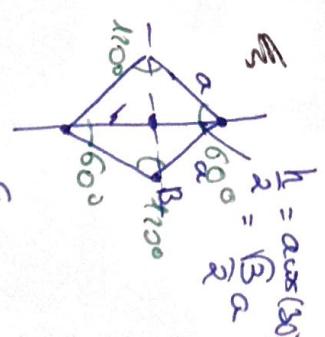
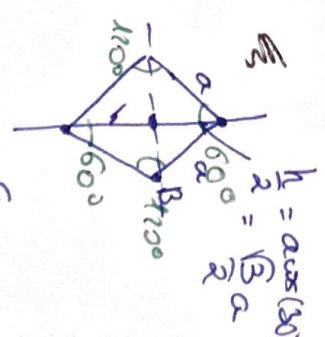
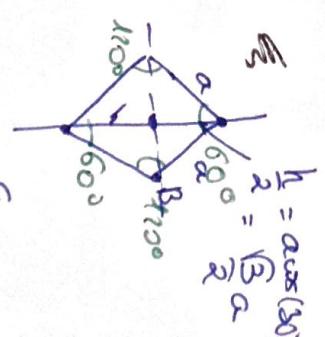
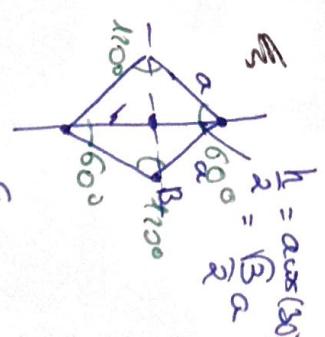
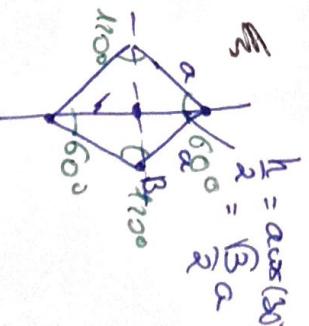
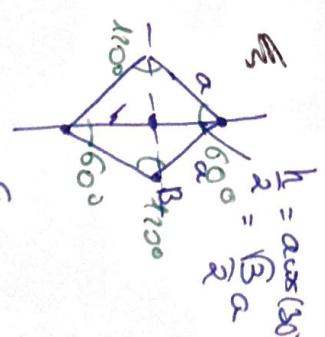
$$\bullet \frac{B}{2r} : \frac{2R_B}{2r} = \frac{1}{3} h = \frac{\sqrt{3}a}{3}$$

$$\bullet \frac{Zr}{B} : \frac{R_B}{\sqrt{3}} = \frac{R_{Zr}}{a}$$

On a alors:

$$(R_{Zr} + R_B)^2 = \left(\frac{a}{2}\right)^2 + \left(\frac{a}{3}\right)^2$$

$$\frac{a^2}{4} \left(1 + \frac{1}{3}\right) = \frac{a^2}{12}$$



$$d\omega = \boxed{\frac{c}{a} = \sqrt{\frac{2}{3}}}$$

Δ Détail :  $\frac{a^2}{R} \left[ \left( 1 + \frac{1}{\sqrt{3}} \right)^2 - \frac{4}{3} \right] = \frac{c^2}{R}$

$\Rightarrow a^2 \frac{2}{3} = c^2 \Rightarrow \boxed{\frac{c}{a} = \sqrt{\frac{2}{3}}}$

$$3) \rho = \frac{n_{\text{maille}}}{V_{\text{maille}}} = \frac{H(r) + 2H(B)}{N_A a_c^2 \sin\left(\frac{\pi}{3}\right)} = \frac{H(r) + 2H(B)}{N_A a^3 \sqrt{\frac{2}{3}} \sin\left(\frac{\pi}{3}\right)}$$

A.N.:  $P_{\text{RB2}} = 5.6 \times 10^3 \text{ Pa} \cdot \text{m}^{-3}$

4)  $C = \frac{V_r + 2V_B}{V_{\text{maille}}}$

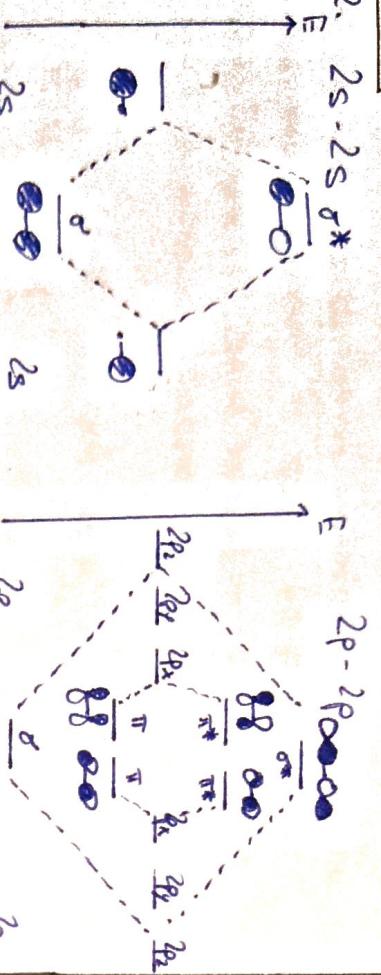
$$= \frac{4\pi}{3} \frac{R^3 + 2R^3}{a^3 \sqrt{\frac{2}{3}} \sin\left(\frac{\pi}{3}\right)} = \frac{\frac{4\pi}{3} \times \frac{1}{3} \left( 1 + \frac{1}{3\sqrt{3}} \right)}{\sqrt{\frac{2}{3}} \times \frac{\sqrt{3}}{2}}$$

A.N.:  $C \approx 0.78$

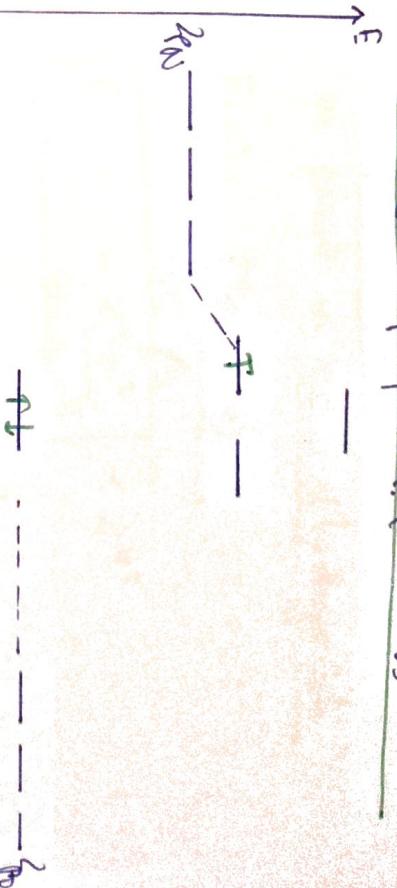
La compacté  $C > 0.74$  la compacté limite des structures complexes à 1 type d'atomes

### Exercice 1B:

1.2.  $2s - 2s \sigma^*$



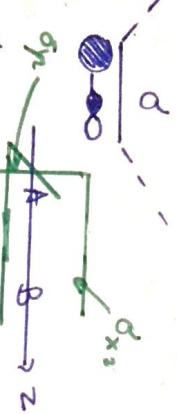
4.



dans le cas de l'oxygène.  
||| lors de la réalisation des diagrammes, on considérera séparément les interactions  $2s$  et  $2p$  par  $\sigma_2$ . (= documenté)

### Détail des symétries

| 2s   | $\sigma_{x^2}$ | $\sigma_{y^2}$ |
|------|----------------|----------------|
| 2p_x | S              | S              |
| 2p_y | A              | S              |
| 2p_z | S              | S              |



- interaction  $2s - 2s$ ,  $2p_x - 2p_x$ ,  $2p_y - 2p_y$
- interaction  $2p_z - 2p_z$
- $- 2p_x - 2p_y$

On a S: symétrique  
A: anti-symétrique

3. On va calculer  $|\Delta E| = E(C\text{ep}) - E(2s)$

$$\begin{aligned} O &: |\Delta E| = 16.5 \text{ eV} \\ N &: |\Delta E| = 12.7 \text{ eV} \end{aligned}$$

L'écart en énergie  $|\Delta E|$  est bien plus élevé pour O que pour N. On aura donc une réaction  $2s - 2p$  bien plus facile.

Le résultat  $\Rightarrow$  espèce paramagnétique ( $s = \frac{1}{2}$ )  
Du point de vue chimique, NO est un radical.  
Lorsque:

$$N = O$$

$$\begin{aligned} N &= 5e^- & O &= 6e^- \\ f_b &= \dots & O &= \dots \end{aligned}$$

### Exercice 1B:

La règle de Hund: La configuration électronique la plus stable est celle maximisant le spin. En pratique, cela signifie que l'on "remplit" les orbitales en cherchant à créer un minimum détection.

b)  $[O]: [He]^2 2s^2 2p^4$  dans les règles de l'Aufbau.

$[S]: [Ne]^2 3s^2 3p^4$

c) Oxygène: 2e ligne / 16e colonne.

Souche: 3e ligne / 16e colonne.

d)  $n_o = 2$  alors que  $n_s = 3 \Rightarrow R(O) > R(S)$

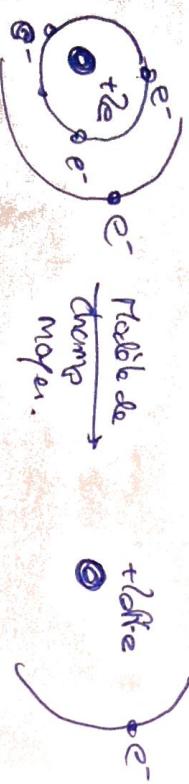
Nombre quantique n<sub>m</sub>

2) a)  $n \nearrow \Rightarrow R_n \nearrow \Rightarrow R_2(O) < R_3(S)$

b) Il s'agit de la cause de la largeur électronique C se déformant sous l'action d'un champ électrique  $\Rightarrow$  obtention d'un monat dipolaire dû à l'induit.

c)  $\sigma_S > \sigma_O$  ce qui est en accord avec le fait que le souche est plus gros que l'oxygène ( $R_{SO} = 1.10$ ). Notion atomique de Thomason conduit à  $R_3 \propto q\pi = \kappa$

3) a) La charge effective est la charge renseinte exercée par un électron externe pour échapper du noyau par les élections plus profond.



b) On a

$$P_n = \frac{n^2}{Z^2} \alpha_0$$

en prenant un modèle d'hydrogénide.

$$E(R) = \frac{Z^* e \times (-e)}{4\pi \epsilon_0 R^2}$$

$$\propto Z^2$$

$$E_n = -\frac{Z^* e^2}{4\pi \epsilon_0 n^2}$$

$$\text{On posera } \frac{e^2}{4\pi \epsilon_0} = \frac{1}{2} \text{ (passage en unité abrégée)}$$

$$\Rightarrow E_{\text{tot}} = -\frac{Z^* e^2}{8\pi \epsilon_0 n^2}$$

d) Calcul de la charge effective:

$$Z^* = Z_0 - \sigma_0$$

$$\text{avec } \sigma_0 = 2\sigma_{n-1} + 5\sigma_n$$

AN:

$$\sigma_0 = 2 \times 0.85 + 5 \times 0.35$$

$$\sigma_0 = 3.45$$

$$\sigma^* = 8 - 3.45 = 4.55$$

. De même, avec S

$$Z_S^* = Z_S - \sigma_S$$

$$\text{et } \sigma_S = 2\sigma_{n-2} + 8\sigma_{n-1} + 5\sigma_n$$

$$\text{AN: } \sigma_S = 2 \times 4 + 8 \times 0.85 + 5 \times 0.35$$

$$\sigma_S = 10.55$$

$$Z_S^* = 16 - 10.55 = 5.45$$

\* Notamment un calcul sur un seul électron

$$\left| \frac{E_{\text{tot}}(O)}{E_{\text{tot}}(S)} = \left( \frac{Z^*}{Z_0} \right)^2 \times \left( \frac{n_S}{n_O} \right)^2 = \left( \frac{4}{5} \right)^2 = 1.57 \right.$$

On a expérimentalement  $|R(O)/R(S)| \approx 1.31 \Rightarrow$  différence moyen des proportions du modèle de

### Exercice 1C :

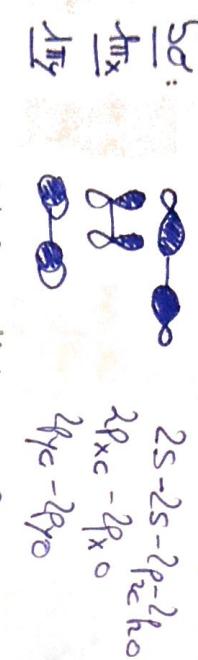
1. Schéma de Lewis:

$$C \equiv O^{\oplus}$$

2. Non, à priori on devrait avoir une autre distribution de charge (O sur O et O sur C) puisque  $r_O > r_C$

3. Structure électronique:  $(3s)^2 (4s)^1 (1\pi_x)^2 (1\pi_y)^2 (5s)^2$

4. Orbitalles moléculaires:



5. Orbitalles moléculaires:

7. On a alors:

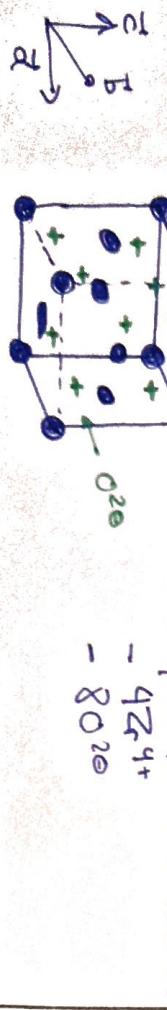
6. On a par CLOA:  $\left| \begin{array}{l} \Delta p_x = c_1 p_x(C) + c_2 p_x(O) \\ c_2 > c_1 \end{array} \right.$

7. On a alors:

8. La densité électronique est sur l'oxygène majoritairement, cette orbite n'est pas celle à considérer / Qd. Il faut donc prendre la  $\frac{1}{2}$  de  $c_2$  à  $\frac{1}{2}$

Exercice 1C

1. Maille élémentaire type fluorine



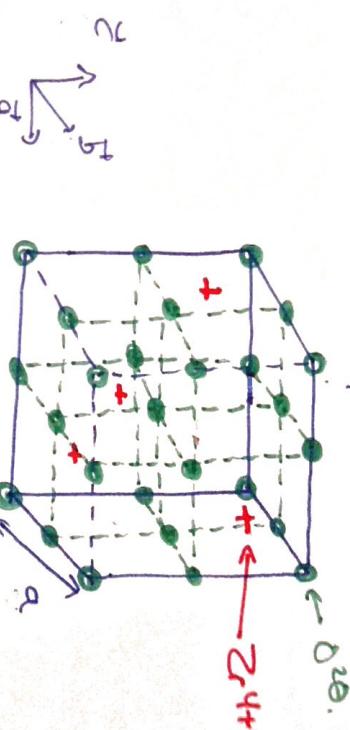
2. Il y a par maille élémentaire:

$$= 4Zr^{4+}$$

$$= 8O^{2-}$$

3. Le sous réseau formé par O<sup>2-</sup> est un réseau cubique simple avec un paramètre de maille  $a$ . Ce réseau est décalé d'un vecteur  $\vec{R} = \frac{\vec{a} + \vec{b} + \vec{c}}{2}$  par rapport au réseau de Zr<sup>4+</sup>.

4. Maille élémentaire déplacée de  $\vec{R}$ :



5. Coordonnées sont:

$$\left[ Zr^{4+} / O^{2-} \right] = 8$$

$$\left[ O^{2-} / Zr^{4+} \right] = 4$$

$$\left[ O^{2-} / O^{2-} \right] = 6$$

6. Condition de contact:

- $R(Td) + R(Zr^{4+}) = \frac{a\sqrt{3}}{4}$  (grande diagonale)

- $4R(Zr^{4+}) = \frac{a\sqrt{3}}{4}$  (faces)

- $R(ch) + R(Zr^{4+}) = \frac{a}{2}$  (arête)

A.N.:  $R(Td) = \frac{a\sqrt{3}}{4} - R(Zr^{4+})$

$$= 508 \times \frac{\sqrt{3}}{4} - 79 \approx 191 \text{ pm}$$

$$R(ch) = \frac{a}{2} - R(Zr^{4+})$$

$$= \frac{508}{2} - 79 = 175 \text{ pm}$$

On a  $R(Td)$  et  $R(ch) > R(O^{2-})$ . En plus, les deux sites peuvent être occupés par O<sup>2-</sup>. En résumé, tout les sites Td sont occupés.

7. On a alors :

- 1 Oh au centre de la maille élémentaire
  - 12 Oh partagé entre 4 mailles élémentaires
- $\Rightarrow$  4 sites Oh par maille élémentaire

La maille fluorine contient environ  $4 \times 4 = 16$  charges positives.

Il y a possibilité d'avoir  $-2 \times 8 = -16$  charges négatives si tous les sites Td sont occupés.

$$-4 \times 2 = -8 \text{ charges}$$

À bilan, l'électronégativité est assurée par les sites Td non occupés.

8. On a un composé de substitution où les ions  $Zr^{4+}$

sont remplacé par les ions  $Y^{3+}$ . Or le rayon atomique de  $Y^{3+}$  est supérieur de  $Zr^{4+}$ , ce qui implique un accroissement du paramètre de maille ( $a' > a$ )

9. Calcul de la masse volumique:

$$\rho' = \frac{m_{\text{maille}}}{V_{\text{maille}}} = 4 \left\{ 0.91 M(ZrO_2) + 0.09 M(YO_3)_2 \right\} \frac{N_A}{a^3}$$

A.N:  $\rho' = 5980 \text{ kg.m}^{-3}$