

I- Description classiques des atomes hydrogénoïdes¹

I-1 - De l'origine des forces et de leur magnitude

Force gravitationnelle: $F = G \times \frac{m \cdot m'}{d^2} \approx 10^{-47} \text{ N}$

où G en $\text{m}^3 \text{kg}^{-1} \text{s}^{-2}$

m_p en kg

m_e en kg

d en m

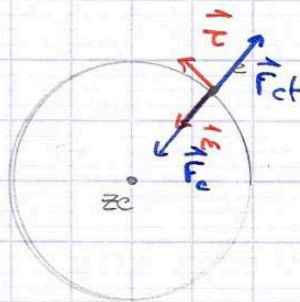
$$[F] = [\text{m}^3 \text{kg}^{-1} \text{s}^{-2}] \times \frac{[\text{kg}][\text{kg}]}{[\text{m}^2]}$$

Force coulombienne: $F = \frac{qq'}{4\pi\epsilon_0} \times \frac{1}{d^2} \approx 10^{-8} \text{ N}$

$$[F] = \frac{[\text{A} \cdot \text{s}]^2}{[\text{m}^{-3} \cdot \text{kg}^{-1} \text{s}^4 \text{A}^2]} \times \frac{1}{[\text{m}^2]} = [\text{N}]$$

donc $F_c \gg F_g$.

I-2 . Modèle de Rutherford



Énergie potentielle coulombienne

$$V = - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r}$$

$$\rightarrow F_c = - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r^2}$$

$$F_{ct} = m \frac{v^2}{r}$$

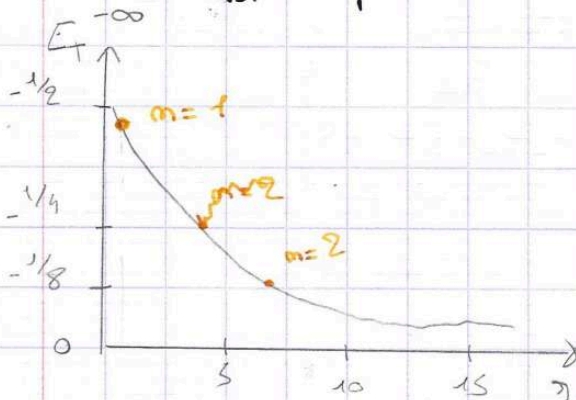
D'après l'équation de Newton dans le repère de Fermi : $\vec{F} = m\vec{a}$

$$\begin{aligned}\vec{a} &= a_r \vec{r} + a_\theta \vec{\theta} \\ &= \frac{dv}{dt} \frac{1}{r} + \frac{v^2}{r} \vec{\theta} \quad \text{on } v = c\alpha\end{aligned}$$

$$\text{donc } \vec{F} = m \frac{v^2}{r} \vec{\theta} = \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r^2} \vec{\theta}$$

$$\Rightarrow \frac{1}{2} mv^2 = \frac{Ze^2}{8\pi\epsilon_0 r}$$

$$\text{donc } E_{\text{tot}} = E_p + E_c = - \frac{1}{8\pi\epsilon_0} \frac{Ze^2}{r}$$



I-3. Modèle de Bohr

- Les orbites sont définies par la quantification du moment cinétique $mv r = n\hbar$

À partir du postulat 2 : $v = \frac{n\hbar}{m r}$

$$E_c = \frac{1}{2} mv^2 = \frac{1}{2} m \frac{n^2 \hbar^2}{m^2 r^2} = \frac{n^2 v^2}{8\pi^2 m r^2}$$

on d'après Rutherford on a $E_c = \frac{e^2}{8\pi r \epsilon_0}$

$$E_c = \frac{1}{2} mv^2 = \frac{e^2}{8\pi r \epsilon_0} \Leftrightarrow v^2 = \frac{e^2}{4\pi m \epsilon_0 r}$$

$$v = \frac{e}{\sqrt{4\pi\epsilon_0 m E_0}} = \frac{m h}{m^2 \pi \hbar}$$

$$\Leftrightarrow \frac{e^2}{4\pi\epsilon_0 m E_0} = \frac{m^2 h^2}{m^2 4\pi^2 \hbar^2}$$

$$\Rightarrow \frac{e^2}{E_0} = \frac{m^2 h^2}{\pi \hbar}$$

$$\hbar = \frac{m^2 h^2 E_0}{\pi e^2 m} \Leftrightarrow \hbar = a_0 \frac{m^2}{Z}$$

D'après Rutherford:

$$L_T = -\frac{1}{8} \frac{Z e^2}{\pi \epsilon_0 \hbar}$$

$$\hbar = a_0 \frac{m^2}{Z}$$

$$L_T = -\frac{1}{8} \frac{e^4 m}{h^2 \epsilon_0^2} \cdot \frac{Z^2}{m^2}$$

$$= K \cdot \frac{Z^2}{m^2}$$

$$[\hbar] = \frac{[J \cdot s]^2 [F \cdot m^{-1}]}{[kg] \cdot [C^2]} = \frac{[kg^2 \cdot m^4 \cdot s^{-2}] [m^{-3} kg^{-1} s^4 A^2]}{[kg] [A^2 s^2]}$$

$$= [m]$$

$$= 5,29 \cdot 10^{-11} \text{ m}$$

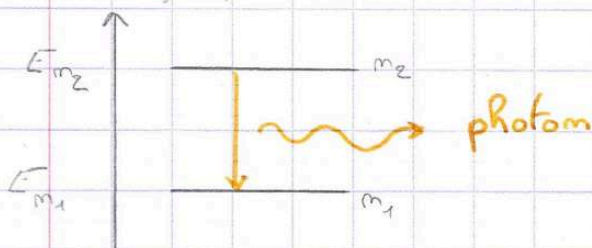
$$[K] = \frac{[A^4 s^4] [kg]}{kg^2 m^2 s^{-4} s^2 m^{-4} kg^{-2} s^8 A^4 m^{-2}} = [J]$$

I-4. Interpretations

	$n_m(u_a)$	$L_m(u_a)$
$m=1$	1	$-1/2$
$=2$	4	$-1/8$
$=3$	9	$-1/18$
$=4$	16	$-1/32$

II - Spectroscopie et niveaux d'énergie

II-1 - La constante de Rydberg



Formule de Rydberg:

$$\frac{1}{\lambda} = R_H \left(\frac{1}{m_2^2} - \frac{1}{m_1^2} \right) \quad \text{en } m^{-1}$$

$$R_H = \left(\frac{1}{4\pi\epsilon_0} \right)^2 \frac{me^4}{2h^2} \times \frac{1}{hc} \quad \text{en } m^{-1}$$

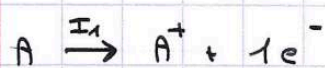
$$= 1,097 \cdot 10^7 m$$

Pour Li^{2+} on a $R_{Li^{2+}} = 9R_H =$

$$1,0968829 \cdot 10^8 m^{-1}$$

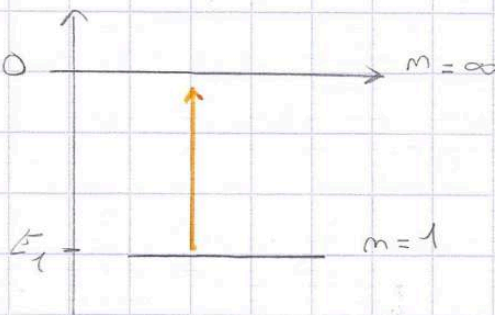
$$1,0968829 \cdot 10^8 m^{-1}$$

II-2. Énergie d'ionisation d'un système hydrogénoïde

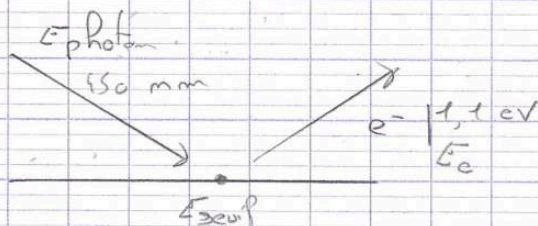


$$I_1 = \overset{0}{\underset{0}{E_{A^+}}} - E_A$$

$$\Rightarrow Z = 4$$



II - 3 Effet Photoélectrique



$$E_{\text{photon}} = E_{\text{seuil}} + E_c$$
$$E_c = \frac{1}{2}mv^2$$
$$\Rightarrow v = \sqrt{\frac{2E_c}{m}} = 622 \text{ } 062 \text{ m.s}^{-1}$$

$$E_{\text{seuil}} = \frac{h \cdot c}{\lambda} - E_c$$
$$= 1,66 \text{ eV}$$

$$\lambda_{\text{seuil}} = 747 \text{ nm}$$

$$\lambda_{\text{dec}} = 1,16 \text{ nm}$$

II - Énergie de dissociation

$$E = 2,57 \cdot 10^{-19}$$

$$= 1,61 \text{ eV}$$

$$= \frac{hc}{\lambda} \Rightarrow \lambda = 770 \text{ nm}$$

$$\frac{1}{\lambda} = 12 \text{ } 965 \text{ cm}^{-1}$$

$$\nu = 3,83 \cdot 10^{14} \text{ Hz}$$

III - Concepts

Concepts de mécanique quantique

Longueur d'onde de Broglie

$$\begin{aligned} \text{a) } \lambda &= 10^{-31} \text{ m} & \lambda &= \frac{h}{m \cdot v} \\ \text{b) } \lambda &= 10^{-36} \text{ m} & & \\ \text{c) } \lambda &= 1,61 \cdot 10^{-10} \text{ m} & &= \frac{h \cdot c}{E} \\ \text{d) } \lambda &= 2,3 \cdot 10^{-8} \text{ m} & & \end{aligned}$$

Le principe d'incertitude d'Heisenberg.

$$\Delta x \Delta v \gg \frac{h}{4\pi m}$$

bille : $\Delta v = 10^{-25} \text{ m.s}^{-1}$
 électron : $\Delta v = 5,8 \cdot 10^5 \text{ m.s}^{-1}$

Notion d'opérateur

Fonction propre :

$$\hat{A}g = \lambda g$$

$$\begin{aligned} 1) \quad 0 & \quad \times \\ 2) \quad 5x & \quad \times \quad \hat{A}g = \frac{d}{dx^2}(x^2) + 2 \frac{d}{dx}(x^2) + 3(x^2) \\ 3) \quad 3xy^2 & \quad \times \end{aligned}$$

$$= 2 + 4x + 3x^2$$

Fonctions propres et valeurs propres associées de l'opérateur.

- $\hat{p} = -i\hbar \frac{\partial}{\partial x}$
- $g(x) = A e^{ikx}$
- $$\begin{aligned} p_x(g(x)) &= -i\hbar (ikA \exp(ikx)) \\ &= \hbar k A \exp(ikx) \\ &= \hbar k g(x) \end{aligned}$$

$\hbar k$ valeur propre

$$\hat{p}_x^2 = (-\hbar i)^2 \frac{\partial^2}{\partial x^2} = -\hbar^2 \frac{\partial^2}{\partial x^2}$$

$$\hat{p}_x^2(g(x)) = \left(\frac{\hbar^2 m}{2a}\right)^2 g(x)$$

$\left(\frac{\hbar m}{2a}\right)^2$ est la valeur propre

Un système quantique simple : la particule sur un cercle.

$$\hat{H} = \hat{T} = -\frac{\hbar^2}{2mR^2} \frac{\partial^2}{\partial \varphi^2}$$

Fonction d'onde : $\psi(\varphi) = A e^{iq\varphi}$

$$\hat{H}\psi = E\psi = \left(\frac{\hbar^2 q^2}{2mR^2}\right) \psi$$

$$\frac{\partial^2 \psi(\varphi)}{\partial \varphi^2} = q^2 \psi(\varphi)$$

Quantification $\Leftrightarrow$ conditions aux limites

$$\psi(\varphi) = \psi(\varphi + 2\pi)$$

$$e^{iq\varphi} = e^{iq(\varphi + 2\pi)}$$

$$e^{iq2\pi} = 1$$

$$e^{i2\pi q} + i \sin(2\pi q) = 1$$

$$\Rightarrow q = 0, \pm 1, \pm 2, \dots, \pm \infty$$

$$\psi_0(\varphi) = A, E_0 = 0$$

$$E_q = \frac{q^2 \hbar^2}{2mR^2}$$

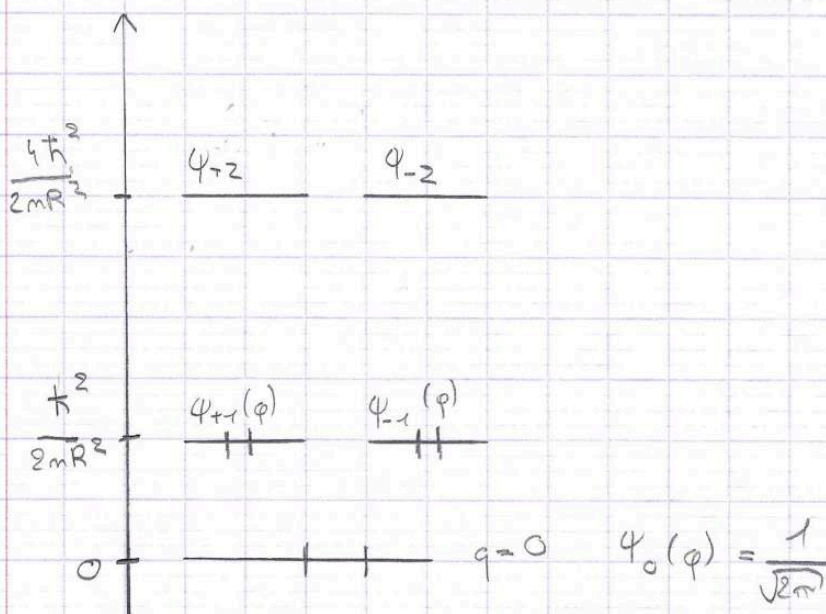
$$\psi_q(\varphi) = A e^{iq\varphi}$$

$$\int_0^{2\pi} \psi_q^*(\varphi) \psi_q(\varphi) d\varphi = 1$$

$$A^2 \int_0^{2\pi} d\varphi = 1$$

$$2\pi A^2 = 1$$

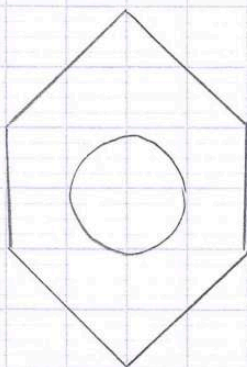
$$A = \pm \frac{1}{\sqrt{2\pi}}$$



Application

$$R = 1,39 \text{ \AA}$$

$$6e^{-}\pi$$



$$\psi(1,2,3,4,5,6) = \psi_0(1)\psi_0(2)\psi_1(3)\psi_{-1}(4)\psi_{-1}(5)\psi_1(6)$$

$$E_{\text{photon}} = \frac{hc}{\lambda} = E_2 - E_1 = \frac{3\hbar^2}{2mR^2}$$

$$\Rightarrow \lambda = \frac{8mR^2 e\pi^2}{3h}$$

$$= 210 \text{ nm}$$

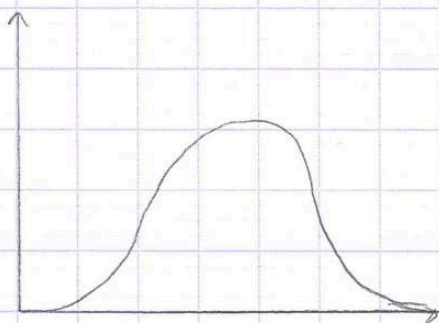
7- Manipulation des fonctions d'onde hydrogénoïdes

Exercice 1 : Fonction d'onde 1s des ions d'hydrogénénoïdes.

$$\begin{aligned}\psi_{1s} &= \psi_{100}(\eta, \theta, \varphi) = R_{10}(\eta) \Theta_0(\theta) \varphi_0(\varphi) \\ &= \frac{1}{\sqrt{\pi}} \left(\frac{z}{a_0}\right)^{3/2} e^{-\frac{z\eta}{a_0}} = f(\eta)\end{aligned}$$

$$P = \int_{\text{esp}} \psi_{1s}^* \psi_{1s} dV$$

$$\begin{aligned}&= \int_0^\infty \eta^2 \psi_{1s}^2 d\eta \quad 4\pi \\ \frac{dP}{d\eta} &= 4\pi \eta^2 \frac{1}{\pi} \left(\frac{z}{a_0}\right)^3 \exp\left(-\frac{2z\eta}{a_0}\right) = 4\eta^2 \left(\frac{z}{a_0}\right)^3 \exp\left(-\frac{2z\eta}{a_0}\right)\end{aligned}$$



On cherche $\frac{\partial}{\partial \eta} \left(\frac{dP}{d\eta} \right) = 0$

$$\Leftrightarrow \frac{\partial}{\partial \eta} \left(4 \left(\frac{z}{a_0}\right)^3 \eta^2 e^{-\frac{2z\eta}{a_0}} \right) = 0$$

$$\Leftrightarrow 4 \left(\frac{z}{a_0}\right)^3 \left(2\eta \exp\left(-\frac{2z\eta}{a_0}\right) - \eta^2 \frac{2z}{a_0} \exp\left(-\frac{2z\eta}{a_0}\right) \right) = 0$$

$$\Leftrightarrow 4 \left(\frac{z}{a_0}\right)^3 \exp\left(-\frac{2z\eta}{a_0}\right) \left(2\eta - \eta^2 \frac{2z}{a_0} \right) = 0$$

$$\Rightarrow \eta^2 - \frac{a_0}{z} \eta = 0 \Rightarrow \eta = \frac{a_0}{z} \text{ ou } \eta = 0$$

Atomes polyélectroniques

Exercice 1: Atome de carbone

$$1s^2 2s^2 2p^2$$

Slater $\frac{1s^2}{2e^-} \frac{2s^2 2p^2}{4e^-}$

$$E_{\text{tot}} = 2E_{1s} + 4E_{2s2p}$$

$$E_{1s} = -\frac{1}{2} \frac{Z_{1s}^*{}^2}{1^2} = -\frac{1}{2} (6 - 0,30)^2 = -16,25 \text{ ua}$$

$$E_{2s2p} = -\frac{1}{2} \frac{Z_{2s2p}^*{}^2}{2^2} = -\frac{1}{2} \frac{(6 - 2 \times 0,85 - 3 \times 0,35)^2}{4} = -1,32 \text{ ua}$$

donc $E_{\text{tot}} = -37,77 \text{ ua}$

$$I_1 = E_C^+ - E_C$$

$$\begin{aligned} E_C^+ &= 2E_{1s} + 3E_{2s2p} \\ &= 2 \times (-16,25) + 3 \left(-\frac{1}{2} \frac{(6 - 2 \times 0,85 - 3 \times 0,35)^2}{4} \right) \\ &= -37,36 \text{ ua} \end{aligned}$$

$$I_1 = 11,4 \text{ eV}$$

$$= 0,42 \text{ ua}$$

Exercice 2: Atome d'Azote

N: $Z=7$ $1s^2 2s^2 2p^3$

$$E_{1s} = \frac{1}{2} (7 - 0,3)^2 = -22,45 \text{ ua}$$

$$\begin{aligned} E_{2s2p} &= -\frac{1}{2} \frac{(7 - 2 \times 0,85 - 1 \times 0,35)^2}{9} \\ &= -1,30 \text{ ua} \end{aligned}$$

$$L_{\text{tot}}^N = 2L_{12} + 5L_{232p} = -51,4 \text{ u.e.}$$

$$\begin{aligned} & \cdot 1s^2 2s^2 2p^2 3s^1 \\ & \Rightarrow L_{\text{tot}}^{N^+} = 2L_{12} + 5L_{232p} + 1L_{33} \\ & \quad = -54,07 \text{ u.e.} \end{aligned}$$

$$L_{232p} = -\frac{1}{2} \frac{(7 - 2 \times 0,85 - 3 \times 0,35)^2}{1} = -2,26 \text{ u.e.}$$

$$L_{33} = -\frac{1}{2} \frac{(7 - 2 \times 1 - 4 \times 0,85)^2}{9} = -0,11 \text{ u.e.}$$

$$\cdot \Delta E = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{hc}{\Delta E} = 113 \text{ nm.}$$

$$\begin{aligned}
 \langle r \rangle &= \int \psi^2 dV \\
 &= 4\pi \int_0^\infty \frac{1}{\pi} \left(\frac{z}{a_0}\right)^3 \exp\left(-\frac{2z}{a_0}\right) dz \\
 &= \frac{3}{2} \frac{a_0}{2}
 \end{aligned}$$

Exercice 2: Fonction d'onde $2p_z$ des ions hydrogénoïdes

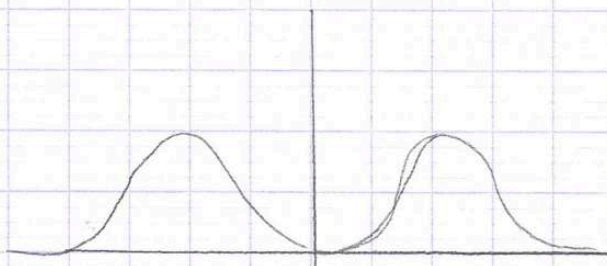
$$\begin{aligned}
 \psi_{210}(r, \theta, \varphi) &= R_{21}(r) \Theta_{10}(\theta) \varphi_0(\varphi) \\
 &= \frac{1}{4\sqrt{\pi}} \left(\frac{z}{a_0}\right)^{5/2} r \cos \theta \exp(-z/a_0)
 \end{aligned}$$

$$\begin{aligned}
 \frac{dP}{dV} &= \frac{1}{32\pi} \left(\frac{z}{a_0}\right)^5 r^2 \cos^2 \theta \exp(-z/a_0) \quad \text{on est sur l'axe} \\
 &= \frac{1}{32\pi} \left(\frac{z}{a_0}\right)^5 r^2 \exp(-z/a_0) \quad z \text{ donc } \theta = \begin{cases} 0 \\ \pi \end{cases}
 \end{aligned}$$

$$\frac{dP}{dr} \propto r^2 \exp(-z/a_0)$$

$$z > 0 \quad r = z \quad \frac{dP}{dr} \propto z^2 e^{-z/a_0}$$

$$z < 0 \quad r = -z \quad \frac{dP}{dr} \propto z^2 e^{z/a_0}$$



Exercice 3: Recherche de fonctions 2p normales

$$\Phi_1 = \frac{1}{\sqrt{2}} (\psi_{211} + \psi_{21-1})$$

$$\int_{\text{esp}} \Phi_1^* \Phi_1 d\tau = \frac{1}{2} \left[\int \psi_{211}^* \psi_{211} d\tau + \int \psi_{211}^* \psi_{21-1} d\tau + \int \psi_{21-1}^* \psi_{211} d\tau + \int \psi_{21-1}^* \psi_{21-1} d\tau \right]$$
$$= 1$$

$$\int_{\text{esp}} \Phi_2^* \Phi_2 d\tau = \frac{1}{2} \left[\int \psi_{211}^* \psi_{211} d\tau - \int \psi_{211}^* \psi_{21-1} d\tau - \int \psi_{21-1}^* \psi_{211} d\tau + \int \psi_{21-1}^* \psi_{21-1} d\tau \right]$$
$$= 1$$

$$\Phi_1 = K (e^{i\varphi} + e^{-i\varphi})$$

$$= K (2 \cos \varphi)$$

$$\Phi_2 = \frac{K}{i} (e^{i\varphi} - e^{-i\varphi})$$

$$= \frac{K}{i} (2i \sin \varphi)$$

$$= K 2 \sin \varphi$$

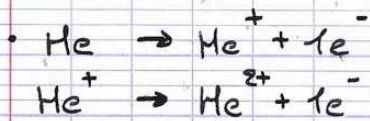
$$\hat{H} \Phi_1 = \hat{H} \left[\frac{1}{\sqrt{2}} (\psi_{211} + \psi_{21-1}) \right]$$

$$= \frac{1}{\sqrt{2}} [\hat{H} \psi_{211} + \hat{H} \psi_{21-1}]$$

$$= \epsilon_2 \Phi_1$$

$$\text{idem } \hat{H} \Phi_2 = \epsilon_2 \Phi_2$$

Exercice 2: Système à 2 électrons : He et Li^{2+}



$$I_1 = E_{\text{He}^+} - E_{\text{He}}$$

$$I_2 = E_{\text{He}^{2+}} - E_{\text{He}^+}$$

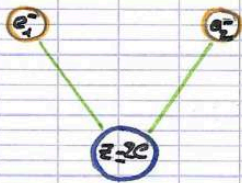
ou $E_{\text{He}^{2+}} = 0$ (plus d'électron)

donc

$$E_{\text{He}} = -I_1 - I_2 = -79 \text{ eV}$$

$$E_{\text{He}^+} = -54,4 \text{ eV}$$

$$E_{\text{He}^{2+}} = 0$$



$$E_{\text{He}} = 2 \cdot E_{\text{He}^+}$$

$$= -\frac{Z^2}{n^2}$$

$$= -108,8 \text{ eV}$$

$$Z = 2, n = 1$$

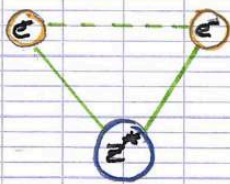
$$E_{\text{He}^+} = -54,4 \text{ eV}$$

$$E_{\text{He}^{2+}} = 0$$

$$I_1 = 54,4 \text{ eV}$$

$$I_2 = 54,4 \text{ eV}$$

(pas d'interaction, un électron)



$$\text{He} : 1s^2$$

$$E_{\text{tot}} = 2E_{1s}$$

$$= -\frac{Z^2}{2} \left(\frac{2-0,30}{1} \right)^2 = -1,415 \text{ ua} \times 2$$

$$= -2,83 \text{ ua}$$

$$= -78,61 \text{ eV}$$

$$I_1 = 24,51 \text{ eV}$$

$$I_2 = 54,4 \text{ eV}$$

$$E_{\text{He}^+} (1 \text{ électron}) = 54,4 \text{ eV}$$

Pour Li:

$$\cdot E_{Li} = -\frac{1}{2} \frac{2(3-0,30)^2}{1} = -7,29 \text{ u} = -198,36 \text{ eV}$$

$$E_{Li, 2s} = -122,1 \text{ eV}$$

$$I_2 = 76,05 \text{ eV}$$

$$I_3 = 122,1 \text{ eV}$$

Exercice 1: Modèle variationnel d'un système de deux électrons en interactions

$$\langle E \rangle = \int \psi^* H \psi dV$$

$$\hat{H} = -\frac{1}{2} \Delta_1 - \frac{Z}{r_1} - \frac{1}{2} \Delta_2 - \frac{Z}{r_2} + \frac{1}{r_{12}}$$

$$\langle E \rangle = \int_{\Omega_p} \psi_1(r_1) \psi_2(r_2) \hat{H} \psi_1(r_1) \psi_2(r_2) d\tau$$
$$= \underline{I_1} + \underline{I_2} + \underline{J} = \underline{2I} + \underline{J}$$

$$= -\alpha^2 + 2\alpha(Z - 2) + \frac{5}{8}\alpha$$

$$\frac{\partial \langle E \rangle}{\partial \alpha} = 0 = -2\alpha + 2Z - 5/8$$

$$2\alpha = 2Z - 5/8$$

$$\alpha = Z - 5/16$$



Propriétés des fonctions d'onde

Principe d'indiscernabilité, l'Antisymétrie

$\psi_1(1, 2)$: symétrique (ne convient pas pour décrire des électrons).

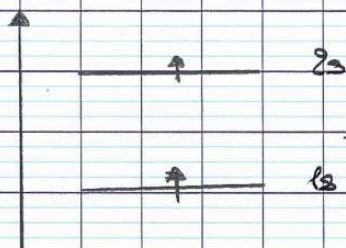
ψ_2 : rien

ψ_3 : antisymétrique (partie de spin)

ψ_4 : antisymétrique (partie espace)

ψ_5 : " (partie spin)

ψ_6 : " (partie espace)



$\text{He}^* \quad 1s(1)\alpha(1) \quad 2s(2)\alpha(2)$

$$\frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 2s(2)\alpha(2) \end{vmatrix}$$

$$= \frac{1}{\sqrt{2}} (1s(1)\alpha(1) 2s(2)\alpha(2) - 2s(1)\alpha(1) 1s(2)\alpha(2))$$

$$= \frac{1}{\sqrt{2}} \alpha(1)\alpha(2) (1s(1)2s(2) - 2s(1)1s(2))$$

Indiscernabilité et particules indépendantes.

$$\hat{H} = \hat{h}_1 + \hat{h}_2$$

$$\hat{h}_1 \chi_i = \epsilon_1 \chi_i$$

$$\hat{h}_2 \chi_j = \epsilon_2 \chi_j$$

$$\begin{aligned} \hat{H}(\chi_i \chi_j) &= (\hat{h}_1 + \hat{h}_2)(\chi_i \chi_j) = \hat{h}_1 \chi_i \chi_j + \hat{h}_2 \chi_i \chi_j \\ &= \chi_j [\hat{h}_1 \chi_i] + \chi_i [\hat{h}_2 \chi_j] \\ &= (\epsilon_1 + \epsilon_2) \chi_i \chi_j \end{aligned}$$

$$\begin{aligned} & \cdot (\hat{h}_1 + \hat{h}_2)(\chi_i(1)\chi_j(2) - \chi_i(2)\chi_j(1)) \\ &= \hat{h}_1(\chi_i(1)\chi_j(2) - \chi_i(2)\chi_j(1)) + \hat{h}_2(\chi_i(1)\chi_j(2) - \chi_i(2)\chi_j(1)) \\ &= (\epsilon_1 + \epsilon_2)(\chi_i(1)\chi_j(2) - \chi_i(2)\chi_j(1)) \end{aligned}$$



$$N^2 \int_{\text{exp}} (\chi_i(1) \chi_j(2) - \chi_i(2) \chi_j(1))^2 dV = 1$$

$$\Rightarrow \int (\chi_i(1) \chi_j(2))^2 dV + \int (\chi_i(2) \chi_j(1))^2 dV$$

$$- 2 \int \chi_i(1) \chi_j(2) \chi_i(2) \chi_j(1) dV = 1/N^2$$

$$\Rightarrow \int_{\text{exp}} \chi_i(1)^2 dV \int_{\text{exp}} \chi_j(2)^2 dV + \int_{\text{exp}} \chi_i(2)^2 dV + \int_{\text{exp}} \chi_j(1)^2 dV$$

$$N = \frac{1}{\sqrt{2}}$$

X-Configurations électroniques

Règle de Hund

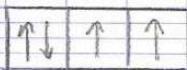
$$\hat{H} = \sum_{i=1}^N \left(-\frac{1}{2} \Delta - \frac{Z}{r_i} \right) + \sum_{i,j} \frac{1}{r_{ij}}$$

$$\langle \bar{E} \rangle = \langle \Psi | \hat{H} | \Psi \rangle$$

$$\Psi = \frac{1}{R} \Phi_R$$

intégrales I énergie des électrons N
J interférence coulombienne $\frac{N(N-1)}{2}$
K échange ?

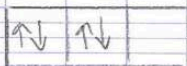
On a 6 façons de remplir les 3 cases avec 4 électrons



A

$$\bar{E}_A = 4I + 5J_1 + J_2 - 3K$$

3 façons



B

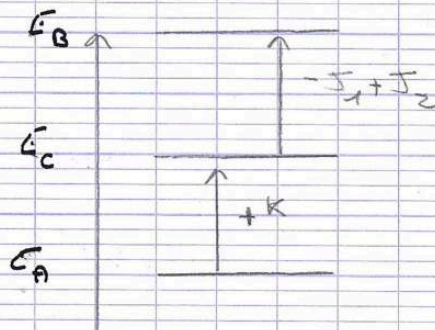
$$\bar{E}_B = 4I + 4J_1 + 2J_2 - 2K$$

6 façons

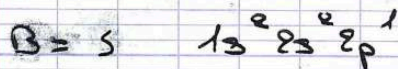


C

$$\bar{E}_C = 4I + 5J_1 + J_2 - 2K$$

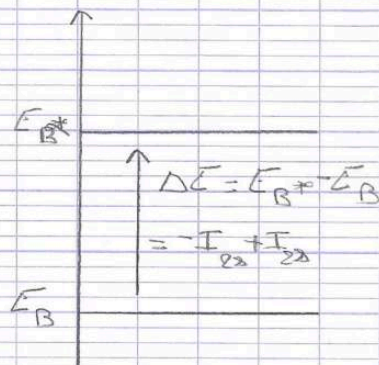


Application des règles de Hund à l'atome de Bore



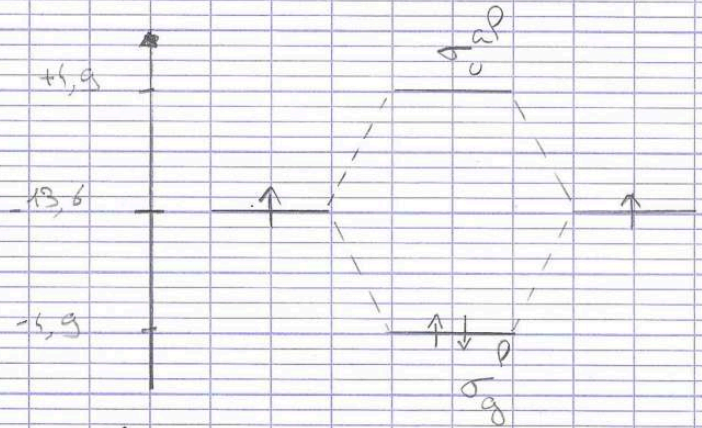
B	6	$\uparrow\downarrow$	$\uparrow$
B*	X	$\uparrow$	$\uparrow \quad \uparrow$
	X	$\uparrow$	$\uparrow \quad \downarrow$
	X	$\uparrow$	$\uparrow\downarrow$

$$\begin{aligned} & 2I_{2s} + I_{2p} + 2J_1 + J_2 - K \\ & I_{2s} + 2I_{2p} + 3J_1 - 3K \\ & I_{2s} + 2I_{2p} + 3J_1 - K \\ & I_{2s} + 2I_{2p} + 2J_1 + J_2 - K \end{aligned}$$

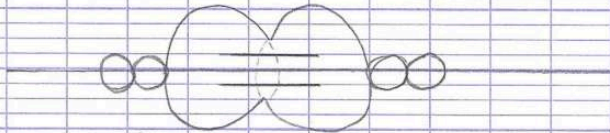


$$\psi_1 = \frac{1}{\sqrt{2}} (\varphi_{1s}^A + \varphi_{1s}^B)$$

$$\psi_2 = \frac{1}{\sqrt{2}} (\varphi_{1s}^A - \varphi_{1s}^B)$$



$$\psi_1 = \underbrace{0,65 s_{C_1} + 0,23 p_{x_{C_1}}}_{\text{hybridisation}} + \underbrace{0,65 s_{C_2} - 0,23 p_{x_{C_2}}}_{\text{hybridisation}} + 0,17 s_{H_3} + 0,17 s_{H_4}$$



$$D_{S_{C_1}} = 2 \times (0,6193)^2 + 2 \times (0,1532)^2 + 2 \times (0,0714)^2 = 1,25$$

$$D_{p_{x_{C_1}}} = 2 \times (0,225)^2 + 2 \times (0,3531)^2 + 2 \times (0,5512)^2 = 1,96$$

$$D_{p_{y_{C_1}}} = 2 \times \left(\frac{1}{\sqrt{2}}\right)^2 + 2 \times \left(\frac{1}{\sqrt{2}}\right)^2 = 2$$

$$D_{p_{z_{C_1}}} = 2$$

$$\begin{aligned} D_{C_1} &= D_{S_{C_1}} + D_{p_{x_{C_1}}} + D_{p_{y_{C_1}}} \\ &\quad + D_{p_{z_{C_1}}} \quad 1,25 \quad 1,96 \quad 1 \quad 1 \\ &= 1,25 + 1,96 + 2 + 2 \\ &= 6,25 \quad 1,22 \end{aligned}$$

XI - Méthode des variations linéaires

$$\hat{H}\psi = E\psi$$

→ recherches des solutions approchées

$$\psi = \sum_i c_i \Omega_i \quad \Omega_i \text{ normalisées et non orthogonales}$$

$$\text{Soient } \int_{\Omega_p} \Omega_i^* \Omega_j d\tau = 1 = S_{ii} \quad (\text{normalisées})$$

$$\int_{\Omega_p} \Omega_i^* \Omega_j d\tau = S_{ij} \neq 0 \quad (\text{non } \perp)$$

$$\langle E \rangle = \int_{\Omega_p} \psi^* \psi d\tau = \sum_i c_i^* c_i H_{ii} + \sum_{i \neq j} \sum_j c_i^* c_j H_{ij}$$

$$H_{ii} = \int_{\Omega_p} \Omega_i^* \hat{H} \Omega_i d\tau \quad \text{et} \quad H_{ij} = \int_{\Omega_p} \Omega_i^* \hat{H} \Omega_j d\tau$$

Méthode de la variation

→ Chercher le minimum de $\langle E \rangle$

• Sans la contrainte

$$\int_{\Omega_p} \psi^* \psi d\tau = 1$$

$$\Rightarrow \sum_i c_i^* c_i \underbrace{S_{ii}}_{=1} + \sum_{i \neq j} \sum_j c_i^* c_j \underbrace{S_{ij}}_{\neq 1}$$

Lagrangien

$$\langle L \rangle = \langle E \rangle + \lambda [1 - (\sum_i c_i^* c_i + \sum_{i \neq j} \sum_j c_i^* c_j S_{ij})]$$

$$\rightarrow \frac{d\langle L \rangle}{dc_R} = 0$$

$$\begin{pmatrix} H_{11} & \dots & H_{1m} \\ \vdots & & \vdots \\ H_{m1} & \dots & H_{mm} \end{pmatrix} \begin{pmatrix} c_1 \\ \vdots \\ c_m \end{pmatrix} = \lambda \begin{pmatrix} S_{11} & \dots & S_{1m} \\ \vdots & & \vdots \\ S_{m1} & \dots & S_{mm} \end{pmatrix} \begin{pmatrix} c_1 \\ \vdots \\ c_m \end{pmatrix}$$

$$HC = \lambda SC$$

→ on cherche les λ (énergies)

→ coefficients

→ nommer les ψ_i

$$\psi = C_1 \Omega_1 + C_2 \Omega_2$$

2 fonctions $\left\{ \begin{array}{l} \text{dégenérées} \\ \text{orthogonales} \end{array} \right.$

$$H_{11} = \int_{\Omega} \Omega_1^* \hat{H} \Omega_1 d\tau = H_{11}$$

$$H_{22} = \int_{\Omega} \Omega_2^* \hat{H} \Omega_2 d\tau = H_{22}$$

orthogonales

$$S_{11} = 1$$

$$S_{12} = 0$$

$$S_{22} = 1$$

$$S_{21} = 0$$

$$S = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$HC = \lambda SC$$

$$HC = \lambda C$$

$$\Rightarrow \begin{pmatrix} H_{11} & H_{12} \\ H_{12} & H_{22} \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = \lambda \begin{pmatrix} C_1 \\ C_2 \end{pmatrix}$$

$$\Rightarrow \begin{pmatrix} H_{11} - \lambda & H_{12} \\ H_{12} & H_{22} - \lambda \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$\Rightarrow \begin{vmatrix} H_{11} - \lambda & H_{12} \\ H_{12} & H_{22} - \lambda \end{vmatrix} = 0$$

$$(H_{11} - \lambda + H_{12})(H_{11} - \lambda - H_{12}) = 0$$

$$\lambda_1 = H_{11} + H_{12}$$

$$\lambda_2 = H_{11} - H_{12}$$

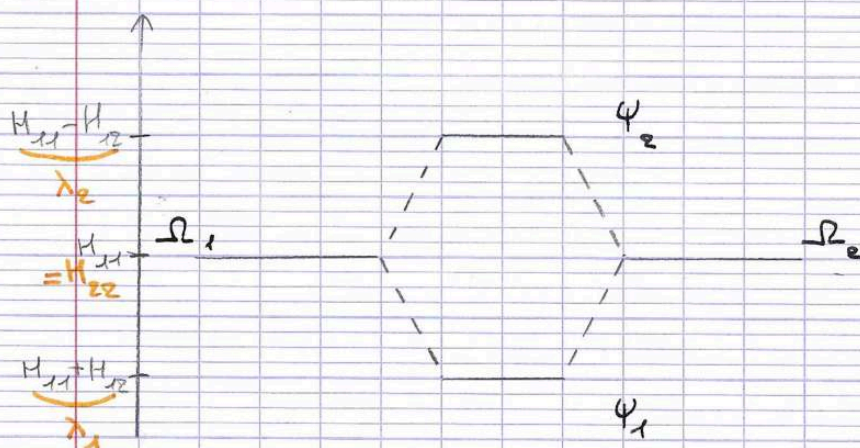
$$\Rightarrow \begin{cases} \psi_1 \text{ à l'énergie } \lambda_1 \\ \psi_2 \text{ à l'énergie } \lambda_2 \end{cases} \Rightarrow \text{normaliser } \psi_1 \text{ et } \psi_2$$

$$\lambda_1: \begin{cases} (H_{11} - H_{11} - H_{12}) C_1 + H_{12} C_2 = 0 \\ H_{12} C_1 + (H_{12} - H_{11} + H_{12}) C_2 = 0 \end{cases} \Rightarrow C_1 = C_2$$

$$\Rightarrow \psi_1 = A(\Omega_1 + \Omega_2) \quad \text{normaliser } \psi_1$$

$$\lambda_2: C_1 = -C_2$$

$$\Rightarrow \psi_2 = B(\Omega_1 - \Omega_2) \quad \text{normaliser } \psi_2$$



normalisation

$$A^2 \int (\Omega_1 + \Omega_2)^* (\Omega_1 + \Omega_2) dt = 1$$

$$\sum A^2 = 1 \Rightarrow A = \frac{1}{\sqrt{2}}$$

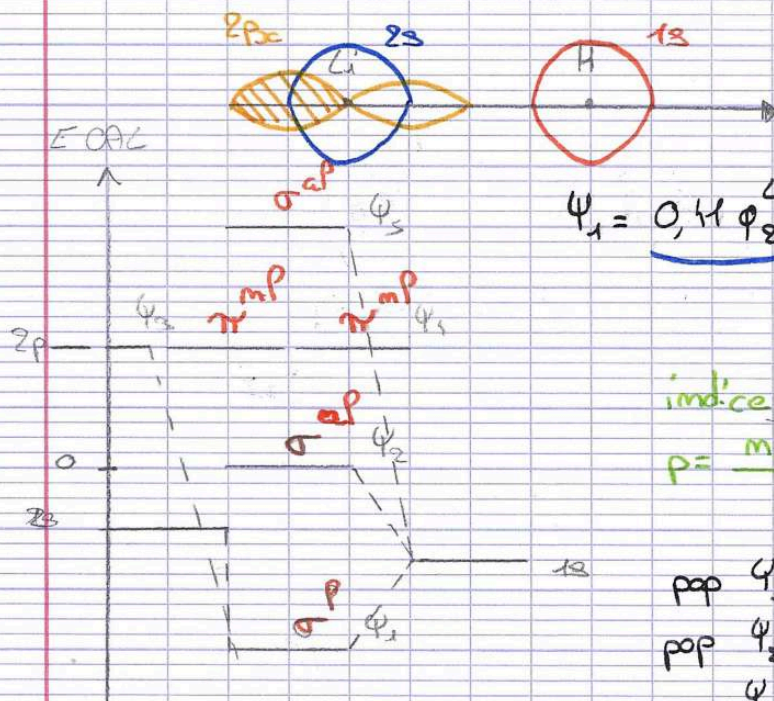
$$\text{idem} \Rightarrow B = \frac{1}{\sqrt{2}}$$

XIII - Étude de la molécule LiH

ClOA $\rightarrow$ e^- valence

H $1s^1$ $1e^-$
 Li $1s^2 2s^1 2p^0$ $1e^-$

5 OA $\rightarrow$ 5 OM $\begin{cases} 1 \text{ OM occupé} \\ 4 \text{ OM virtuelle} \end{cases}$



$$\psi_1 = 0,11 \phi_{2s}^{\text{Li}} + 0,33 \phi_{2p_z}^{\text{Li}} + 0,85 \phi_{1s}^{\text{H}}$$

indice p de p Liaison

$$p = \frac{m_e - m_c}{2} = \frac{2-0}{2} = 1$$

pop $\psi_1 = 2$
 pop $\psi_2 = 0$
 ψ_3
 ψ_4
 ψ_5

$$\text{pop(H)} = 1,438$$

$$= 0,848 \times 0,848 \times 2$$

$$\text{pop(Li)} = 0,562$$

$$= (0,544 \times 0,544 + 0,33 \times 0,33) \times 2$$

$\textcircled{\text{Li}}$	—	$\textcircled{\text{H}}$
$-0,562 + 1$		$-1,438 + 1$
$= 0,438$		$= -0,438$