I- Description classique des atomes hydrogénoïdes

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

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

où G en $m^3 kg^{-1} s^{-2}$

m_p en kg

m_e en kg

d en m

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

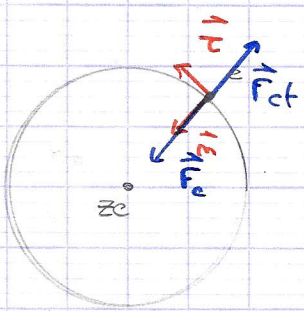
Force coulombienne : $F = \frac{qq'}{4\pi\varepsilon_0} \times \frac{1}{d^2} \simeq 10^{-8}\ N$

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

$= [N]$

donc $F_c \gg F_G$.

I-2 . Modèle de Rutherford



L'énergie potentielle coulombienne

$V = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$

$\rightarrow F_c = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r^2}$

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

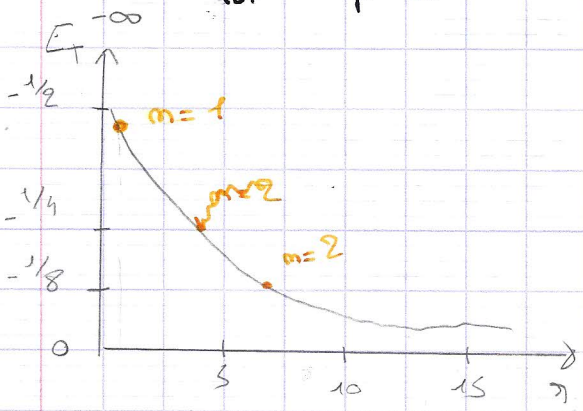
D'après l'équation de Newton dans le repère de Frenet : $\vec{F} = m\vec{a}$

$$\vec{a} = a_t \vec{t} + a_n \vec{n}$$
$$= \frac{dv}{dt}\vec{t} + \frac{v^2}{r}\vec{n} \quad \text{on } v = cte$$

donc $\vec{F} = m\frac{v^2}{r}\vec{n} = \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r^2}\vec{n}$

$$\Leftrightarrow \frac{1}{2}mv^2 = \frac{Ze^2}{8\pi\varepsilon_0 r}$$

donc $E_{tot} = E_p + E_c = -\frac{1}{8\pi\varepsilon_0}\frac{Ze^2}{r}$



I-3. Modèle de Bohr

- Les orbites sont définies par la quantification du moment cinétique $mvr = nh$

À partir du postulat 2 : $v = \frac{nh}{m\,2\pi r}$

$$E_c = \frac{1}{2}mv^2 = \frac{1}{2}m\frac{n^2h^2}{m^2 4\pi^2 r^2} = \frac{n^2v^2}{8\pi^2 m r^2}$$

or d'après Rutherford on a $E_c = \frac{e^2}{8\pi r\varepsilon_0}$

$$E_c = \frac{1}{2}mv^2 = \frac{e^2}{8\pi r\varepsilon_0} \Leftrightarrow v^2 = \frac{e^2}{4\pi r m\varepsilon_0}$$

$$v = \frac{e}{\sqrt{4\pi\varepsilon_0 m r}} = \frac{nh}{m 2\pi r}$$

$$\Leftrightarrow \frac{e^2}{4\pi\varepsilon_0 m r} = \frac{n^2 h^2}{m^2 4\pi^2 r^2}$$

$$\Leftrightarrow \frac{e^2}{\varepsilon_0} = \frac{n^2 h^2}{\pi r}$$

$$r = \frac{n^2 h^2 \varepsilon_0}{\pi e^2 m} \quad \Leftrightarrow \quad r = a_0 \frac{n^2}{Z}$$

D'après Rutherford :

$$\mathcal{L}_T = -\frac{1}{8} \cdot \frac{Ze^2}{\pi\varepsilon_0 r} \qquad \mathcal{L}_T = -\frac{1}{8} \frac{e^4 m}{h^2 \varepsilon_0^2} \cdot \frac{Z^2}{n^2}$$

$$r = a_0 \frac{n^2}{Z} \qquad = K \cdot \frac{Z^2}{2n^2}$$

$$[r] = \frac{[J.s]^2 [F.m^{-1}]}{[Kg] \cdot [C^2]} = \frac{[Kg^2 . m^4 . s^{-2}][m^{-3} Kg^{-1} s^4 A^2]}{[Kg]\,[A^2 s^2]}$$

$$= [m]$$

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

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

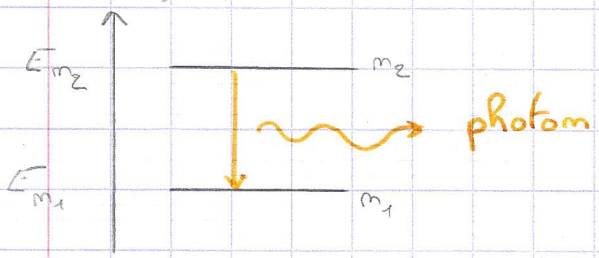
$$= [J]$$

I-4. Interprétations

	r_n (ua)	$\mathcal{L}_n$ (ua)
$n=1$	1	$-1/2$
$=2$	4	$-1/8$
$=3$	9	$-1/18$
$=4$	16	$-1/32$

II - Spectroscopie et niveaux d'énergies

II-1 - La constante de Rydberg.



Formule de Rydberg :

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

$$R_H = \left(\frac{1}{4\pi\varepsilon_0} \right)^2 \frac{me^4}{2\hbar^2} \times \frac{1}{hc} \quad \text{en } m^{-1}$$

$$= 1,097 \cdot 10^7 \text{ m}$$

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

$1,09668829 \cdot 10^{-4}$

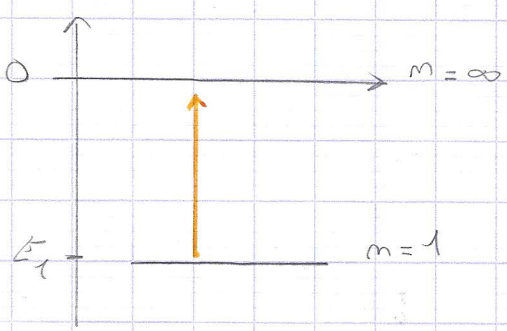
$1,09668829 \cdot 10^{4}$

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

$$A \xrightarrow{I_1} A^+ + 1e^-$$

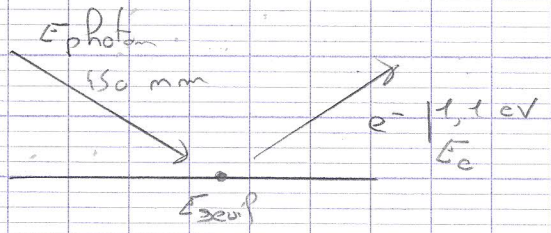
$$I_1 = \mathcal{E}_{A^+} - \mathcal{E}_A$$

$$= 0$$



$\Rightarrow Z = 1$

II - 3 Effet Photoélectrique



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

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

$\lambda_{seuil} = 747$ nm $\qquad \lambda_{dec} = 1,16$ nm

II - Énergie de dissociation

$$E = 2,57 . 10^{-19}$$
$$= 1,61 \text{ eV}$$
$$= \frac{hc}{\lambda} \Rightarrow \lambda = 770 \text{ nm} \qquad \nu = 3,89 . 10^{14} \text{ Hz}$$
$$\frac{1}{\lambda} = 12\,965 \text{ cm}^{-1}$$

III - Concepts

Concepts de mécanique quantique

Longueur d'onde de Broglie

a) $\lambda = 10^{-34}$ m
b) $\lambda = 10^{-36}$ m
c) $\lambda = 1,61.10^{-10}$ m
d) $\lambda = 2,3.10^{-8}$ m

$\lambda = \frac{h}{m.v}$

$= \frac{h.c}{E}$

Le principe d'incertitude d'Heisenberg.

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

bille : $\Delta v = 10^{-25}$ m.s^{-1}

electron : $\Delta v = 5,8.10^{5}$ m.s^{-1}

Notion d'opérateur

fonction propre : $\hat{A} f = \lambda f$

1) 0 x
2) ~~5x~~ x
3) $3xy^2$ x

$\hat{A} f = \frac{d}{dx^2}(x^2) + 2\frac{d}{dx}(x^2) + 3(x^2)$

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

Fonctions propre et valeurs propres associés du opérateur.

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

$\hbar k$ valeur propre

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

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

$\left(\frac{hm}{2a}\right)^2$ 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 : $\psi(\varphi) = Ae^{iq\varphi}$

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

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

Quantification $\leftrightarrow$ conditions aux limites

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

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

$e^{iq2\pi} = 1$

$\cos(2\pi q) + i\sin(2\pi q) = 1$

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

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

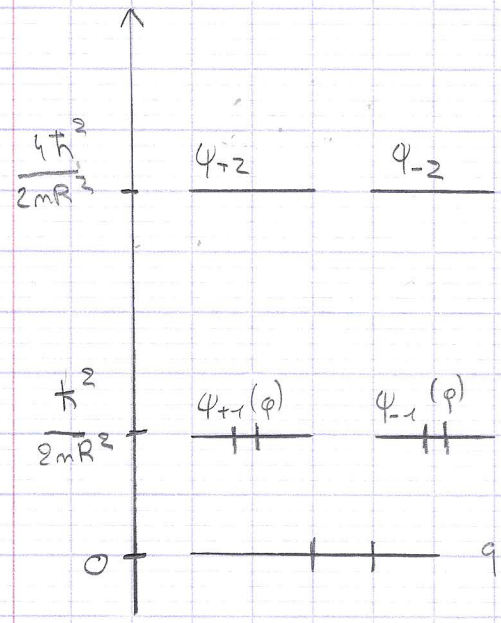
$$E_q = \frac{q^2\hbar^2}{2mR^2} \qquad \psi_q(\varphi) = Ae^{iq\varphi}$$

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

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

$2\pi A^2 = 1$

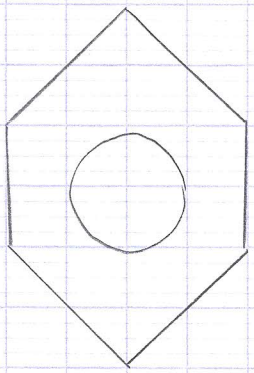
$A = \pm \frac{1}{\sqrt{2\pi}}$



Application

$R = 1,39\ \text{Å}$

$6\,e^-\pi$



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

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

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

$$= 210\ \text{nm}$$

7- Manipulation des fonctions d'onde hydrogénoïdes

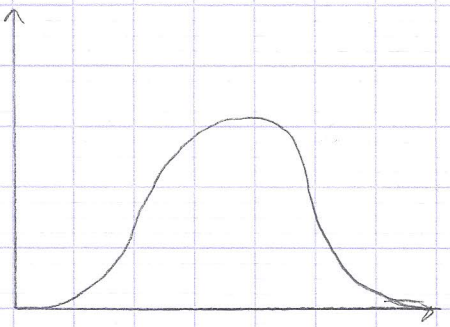
Exercice 1 : Fonction d'onde 1s des ions d'hydrogénoïdes.

$$\psi_{1s} = \psi_{100}(r,\theta,\varphi) = R_{10}(r)\,\Theta_{00}(\theta)\,\varphi_0(\varphi)$$
$$= \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\frac{Zr}{a_0}} = g(r)$$

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

$$= \int_0^\infty r^2 \psi_{1s}^2\, dr \; 4\pi$$

$$\frac{dP}{dr} = 4\pi r^2 \frac{1}{\pi}\left(\frac{Z}{a_0}\right)^3 \exp\left(-\frac{2Zr}{a_0}\right) = 4r^2\left(\frac{Z}{a_0}\right)^3 \exp\left(-\frac{2Zr}{a_0}\right)$$



On cherche $\frac{\partial}{\partial r}\left(\frac{dP}{dr}\right) = 0$

$$\Leftrightarrow \frac{\partial}{\partial r}\left(4(Z/a_0)^3 r^2 e^{-\frac{2Zr}{a_0}}\right) = 0$$

$$\Leftrightarrow 4(Z/a_0)^3\left(2r\exp\left(-\frac{2Zr}{a_0}\right) - r^2\frac{2Z}{a_0}\exp\left(-\frac{2Z}{a_0}r\right)\right) = 0$$

$$\Leftrightarrow 4\left(\frac{Z}{a_0}\right)^3 \exp\left(-\frac{2Zr}{a_0}\right)\left(2r - r^2\frac{2Z}{a_0}\right) = 0$$

$$\Rightarrow r^2 - \frac{a_0}{Z}r = 0 \Rightarrow r = \frac{a_0}{Z} \text{ ou } r = 0$$

Atomes polyelectroniques

Exercice 1 : Atome de carbone

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

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

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

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

$E_{2s2p} = -\frac{1}{2}\frac{Z^*_{2s2p}{}^2}{2^2} = -\frac{1}{2}\frac{(6-2\times0,85-3\times0,35)^2}{4} = -1,32$ ua

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

$I_1 = E_C^+ - E_C$

$E_C^+ = 2E_{1s} + 3E_{2s2p}$
$= +2\times(-16,25) + 3\left(-\frac{1}{2}\frac{(6-2\times0,85-3\times0,85)^2}{4}\right)$
$= -37,36$ ua

$I_1 = 11,4$ eV
$= 0,42$ ua

Exercice 2 : Atome d'Azote

N : $Z = 7$ $\quad \underbrace{1s^2}\ \underbrace{2s^2 2p^3}$

$E_{1s} = \frac{1}{2}(7-0,3)^2 = -22,445$ ua

$E_{2s2p} = -\frac{1}{2}\frac{(7-2\times0,85-4\times0,35)^2}{9}$
$= -1,30$ ua

$$E_{tot}^{N} = 2E_{1s} + 5E_{2s2p} = -54,4 \text{ ua}$$

- $1s^2\ 2s^2 2p^2\ 3s^1$

$$\Leftrightarrow E_{tot}^{N^+} = 2E_{1s} + 4E_{2s2p} + 1E_{3s}$$
$$= -54,07 \text{ ua}$$

$$E_{2s2p} = -\frac{1}{2}\frac{(7 - 2\times 0,85 - 3\times 0,35)^2}{1} = -2,86 \text{ ua}$$

$$E_{3s} = -\frac{1}{2}\frac{(7 - 2\times 1 - 4\times 0,85)^2}{9} = -0,14 \text{ ua}$$

- $\Delta E = \frac{hc}{\lambda} \Leftrightarrow \lambda = \frac{hc}{\Delta E} = 113 \text{ nm}.$

$$\langle r \rangle = \int_{esp} r \, \psi_{1s}^2 \, dV$$
$$= 4\pi \int r^3 \frac{1}{\pi} \left(\frac{Z}{a_0}\right)^3 \exp\left(-\frac{2Zr}{a_0}\right) dr$$

$$= \frac{3}{2} \frac{a_0}{Z}$$

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

$$\psi_{210}(r, \theta, \varphi) = R_{21}(r)\, \theta_{10}(\theta)\, \varphi_0(\varphi)$$
$$= \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{5/2} r \cos\theta \exp\left(-Zr/2a_0\right)$$

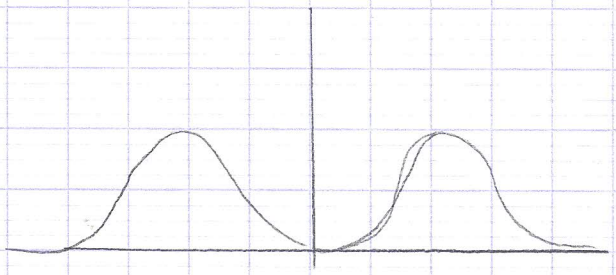
$$\frac{dP}{dV} = \frac{1}{32\pi} \left(\frac{Z}{a_0}\right)^5 r^2 \cos^2\theta \exp\left(-Zr/a_0\right)$$
$$= \frac{1}{32\pi} \left(\frac{Z}{a_0}\right)^2 r^2 \exp\left(-Zr/a_0\right)$$

on est sur l'axe z donc $\theta = \begin{cases} 0 \\ \pi \end{cases}$

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

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

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



Exercice 3 : Recherche de fonctions 2p réelles

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

$$\int_{esp} \Phi_1^* \Phi_1 \, d\tau = \frac{1}{2} \left[\int \varphi_{2l+1}^* \varphi_{2l+1} \, d\tau + \int \varphi_{2l+1}^* \varphi_{2l-1} \, d\tau + \int \varphi_{2l-1}^* \varphi_{2l+1} \, d\tau + \int \varphi_{2l-1}^* \varphi_{2l-1} \, d\tau \right]$$

$$= 1$$

$$\int_{esp} \Phi_2^* \Phi_2 \, d\tau = \frac{1}{2} \left[\int \varphi_{2l+1}^* \varphi_{2l+1} \, d\tau - \int \varphi_{2l+1}^* \varphi_{2l-1} \, d\tau - \int \varphi_{2l-1}^* \varphi_{2l+1} \, d\tau + \int \varphi_{2l-1}^* \varphi_{2l-1} \, d\tau \right]$$

$$= 1$$

$$\Phi_1 = K (e^{i\varphi} + e^{-i\varphi})$$
$$= K (2 \cos \varphi)$$
$$\Phi_2 = \frac{K}{i} (e^{i\varphi} - e^{-i\varphi})$$
$$= \frac{K}{i} (2i \sin \varphi)$$
$$= K 2 \sin \varphi$$

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

$$= \frac{1}{\sqrt{2}} \left[\hat{H} \psi_{2l+1} + \hat{H} \psi_{2l-1} \right]$$

$$= \varepsilon_2 \Phi_1$$

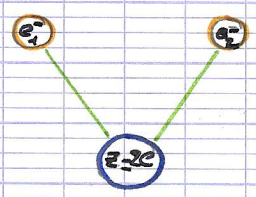
idem $\hat{H} \Phi_2 = \varepsilon_2 \Phi_2$

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

- $He \rightarrow He^+ + 1e^-$
  $He^+ \rightarrow He^{2+} + 1e^-$

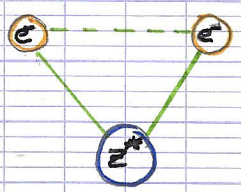
$I_1 = \mathcal{E}_{He^+} - \mathcal{E}_{He}$
$I_2 = \mathcal{E}_{He^{2+}} - \mathcal{E}_{He^+}$
on $\mathcal{E}_{He^{2+}} = 0$ (plus d'électron)

donc $\mathcal{E}_{He} = -I_1 - I_2 = -79$ eV
$\mathcal{E}_{He^+} = -54,4$ eV
$\mathcal{E}_{He^{2+}} = 0$

- 

$\mathcal{E}_{He} = 2 . \mathcal{E}_{He^+}$
$= -\frac{Z^2}{n^2}$ $Z = 2$, $n = 1$
$= -108,8$ eV

$\mathcal{E}_{He^+} = -54,4$ eV (pas d'intéraction, un électron)
$\mathcal{E}_{He^{2+}} = 0$
$I_1 = 54,4$ eV
$I_2 = 54,4$ eV

- 

$I_1 = 24,51$ eV
$I_2 = 54,4$ eV

$He : 1s^2$
$\mathcal{E}_{tot} = 2\mathcal{E}_{1s}$
$= -\frac{Z}{2}\left(\frac{Z - 0,30}{1}\right)^2 = -1,445$ ua $\times 2$
$= -2,89$ ua
$= -78,61$ eV

$\mathcal{E}_{He^+}$ (1 électron) $= 54,4$ eV

Pour Li :

- $E_{Li^+} = -\frac{1}{2}\frac{2(3-0,30)^2}{1} = -7,89\ ua = -198,36\ eV$

$E_{Li^{2+}} = -122,4\ eV$

$I_2 = 76,05\ eV$

$I_3 = 122,4\ eV$

Exercice 4 : Modèle variationnel d'un système de deux électrons en interactions

$$\langle E \rangle = \int \Psi^* H \Psi \, dV$$

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

$$\langle E \rangle = \int_{esp} 1s(1)\,1s(2)\,\hat{H}\,1s(1)\,1s(2)\,d\tau$$

$$= I_1 + I_2 + J = 2I + J$$

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

$$\frac{\partial \langle E \rangle}{\partial \alpha} = 0 = -2\alpha + 4\alpha - 2Z + 5/8$$

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

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

Propriétés des fonctions d'ondes

Principe d'indiscernabilité, l'Antisymétrie

$\Psi_1(1,2)$: symétrique (ne convient pas pour décrire des électrons).

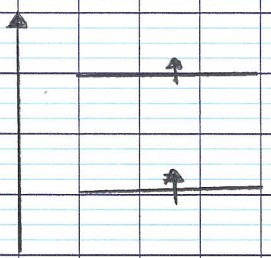
Ψ_2 : rien

Ψ_3 : antisymétrique (partie de spin)

Ψ_4 : antisymétrique (partie espace)

Ψ_5 : " (partie spin)

Ψ_6 : " (partie espace).



He^* $1s(1)\alpha(1)$ $2s(2)\alpha(2)$

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

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

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

Indiscernabilité et particules indépendants.

- $\hat{H} = \hat{h}_1 + \hat{h}_2$ $\qquad \hat{h}_1\chi_i = \varepsilon_i\chi_i$, $\hat{h}_2\chi_j = \varepsilon_j\chi_j$

$$\hat{H}(\chi_1\chi_2) = (\hat{h}_1+\hat{h}_2)(\chi_1\chi_2) = \hat{h}_1\chi_1\chi_2 + \hat{h}_2\chi_1\chi_2$$
$$= \chi_2[\hat{h}_1\chi_1] + \chi_1[\hat{h}_2\chi_2]$$
$$= (\varepsilon_1+\varepsilon_2)\chi_1\chi_2$$

- $(\hat{h}_1+\hat{h}_2)(\chi_i(1)\chi_j(2) - \chi_i(2)\chi_j(1))$
$= \hat{h}_1(\chi_i(1)\chi_j(2) - \chi_i(2)\chi_j(1)) + \hat{h}_2(\chi_i(1)\chi_j(2) - \chi_i(2)\chi_j(1))$
$= (\varepsilon_i+\varepsilon_j)(\chi_i(1)\chi_j(2) - \chi_i(2)\chi_j(1))$

$$N^2 \int_{esp} \left(\chi_i(1)\chi_j(2) - \chi_i(1)\chi_j(2) \right)^2 dV = 1$$

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

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

$$\Leftrightarrow \int_{esp} \chi_i(1)^2 dV \int_{esp} \chi_j(2)^2 dV + \int_{esp} \chi_i(2)^2 dV + \int_{esp} \chi_j(1)^2 dV$$

$$= 1/N^2$$

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

X - Configurations électroniques

Règle de Hund

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

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

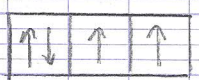
$\Psi = \prod_R \varphi_R$

intégrales I énergie des électrons N

J ~~interférence~~ coulombienne $\frac{N(N-1)}{2}$

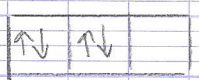
K échange ?

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



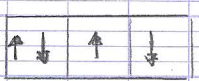
A $\quad E_A = 4I + 5J_1 + J_2 - 3K$

3 façons

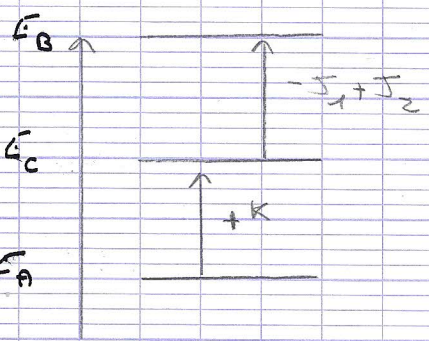


B $\quad E_B = 4I + 4J_1 + 2J_2 - 2K$

6 façons



C $\quad E_C = 4I + 5J_1 + J_2 - 2K$



Application des règles de Hund à l'atome de Bore

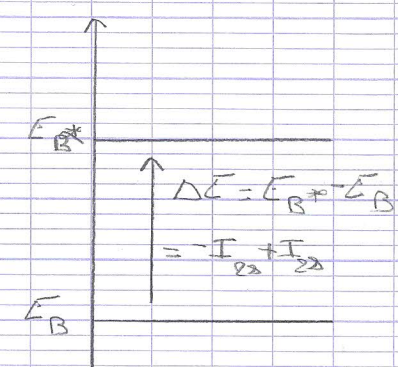
$B = 5 \quad 1s^2 2s^2 2p^1$

B 6 $\uparrow\downarrow \quad \uparrow$ $\quad 2I_{2s} + I_{2p} + 2J_1 + J_2 - K$

B^* ✗ $\uparrow \quad \uparrow \quad \uparrow$ $\quad I_{2s} + 2I_{2p} + 3J_1 - 3K$

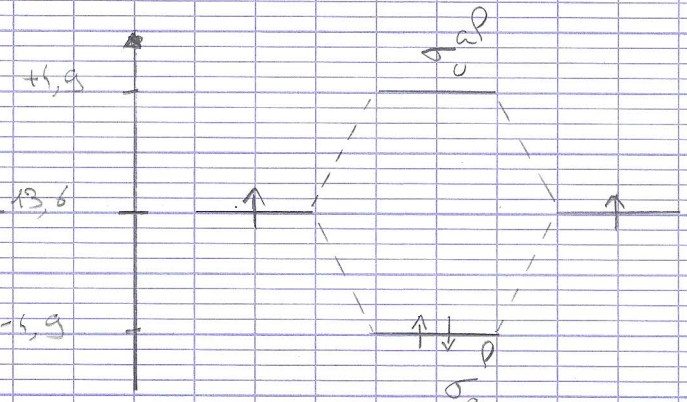
✗ $\uparrow \quad \uparrow \quad \downarrow$ $\quad I_{2s} + 2I_{2p} + 3J_1 - K$

✗ $\uparrow \quad \uparrow\downarrow$ $\quad I_{2s} + 2I_{2p} + 2J_1 + J_2 - K$

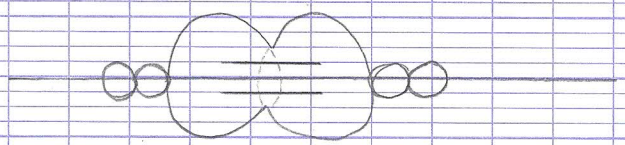


$$\psi_1 = \frac{1}{\sqrt{2}} (\varphi_{1s}^{A} + \varphi_{1s}^{B})$$

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



$$\psi_1 = \underbrace{0,658\, s_{C_1} + 0,23\, p_x C_1}_{\text{hybridation}} + \underbrace{0,65\, s_{C_2} - 0,23\, p_x C_2}_{\text{hybridation}} + 0,19\, s_{H_3} + 0,19\, s_{H_4}$$



$$D_{s C_1} = 2 \times (0,6473)^2 + 2 \times (0,1532)^2 + 2 \times (0,0714)^2 = 1,25$$

$$D_{p_x C_1} = 2 \times (0,285)^2 + 2 \times (0,3531)^2 + 2 \times (0,5512)^2 = \cancel{1}\ 0,96$$

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

$$D_{p_z C_1} = \cancel{2}\ 1$$

$$D_{C_1} = D_{s C_1} + D_{p_x C_1} + D_{p_y C_1} + D_{p_z C_1}$$
$$= 1,25 + \cancel{1} + \cancel{1} + 1$$
$$= \cancel{6,25}\ 4,22$$

XI - Méthode des variations linéaires

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

↳ recherche des solutions approchées

$\Psi = \sum_i c_i \Omega_i$ $\quad$ Ω_i normées et non orthogonales

Soient $\int_{esp} \Omega_i^* \Omega_i \, d\tau = 1 = S_{ii}$ (normées)

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

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

$H_{ii} = \int_{esp} \Omega_i^* \hat{H} \Omega_i \, d\tau$ et $H_{ij} = \int_{esp} \Omega_i^* \hat{H} \Omega_j \, d\tau$

Méthode de la variation

- Chercher le minimum de $\langle E \rangle$
- Sous la contrainte

$\int_{esp} \Psi^* \Psi \, d\tau = 1$

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

Lagrangien

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

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

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

$$HC = \lambda SC$$

→ on cherche les λ (énergies)

→ coefficients

→ normer les ψ_i $\qquad \psi = C_1 \Omega_1 + C_2 \Omega_2$

2 fonctions { dégénérées / orthogonales

$$H_{11} = \int_{esp} \Omega_1^* \hat{H} \Omega_1 \, d\tau = H_{11}$$
$$H_{22} = \int_{esp} \Omega_2^* \hat{H} \Omega_2 \, d\tau = H_{22}$$

orthogonales $\qquad S_{11} = 1 \qquad S_{12} = 0$

$\qquad\qquad\qquad S_{22} = 1 \qquad S_{21} = 0$

$$S \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad HC = \lambda SC$$
$$HC = \lambda C$$

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

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

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

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

$$\begin{cases} \lambda_1 = H_{11} + H_{12} \\ \lambda_2 = H_{11} - H_{12} \end{cases}$$

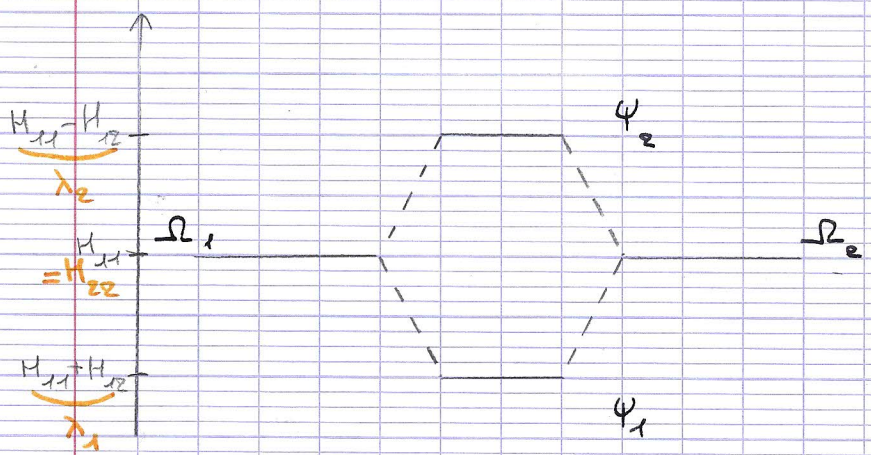
$\Rightarrow$ $\begin{cases} \psi_1 \text{ à l'énergie } \lambda_1 \\ \psi_2 \text{ à l'énergie } \lambda_2 \end{cases}$ $\Rightarrow$ normes ψ_1 et ψ_2

λ_1 : $\begin{cases} (H_{11} - H_{11} - H_{12})\, C_1 + H_{12}\, C_2 = 0 \\ H_{12}\, C_1 + (H_{12} - H_{11} + H_{12})\, C_2 = 0 \end{cases}$ $\Rightarrow C_1 = C_2$

$\Rightarrow \psi_1 = A(\Omega_1 + \Omega_2)$ normes ψ_1

λ_2 : $C_1 = -C_2$

$\Rightarrow \psi_2 = B(\Omega_1 - \Omega_2)$ normes ψ_2



normalisation

- $A^2 \int (\Omega_1 + \Omega_2)^* (\Omega_1 + \Omega_2)\, d\tau = 1$

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

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

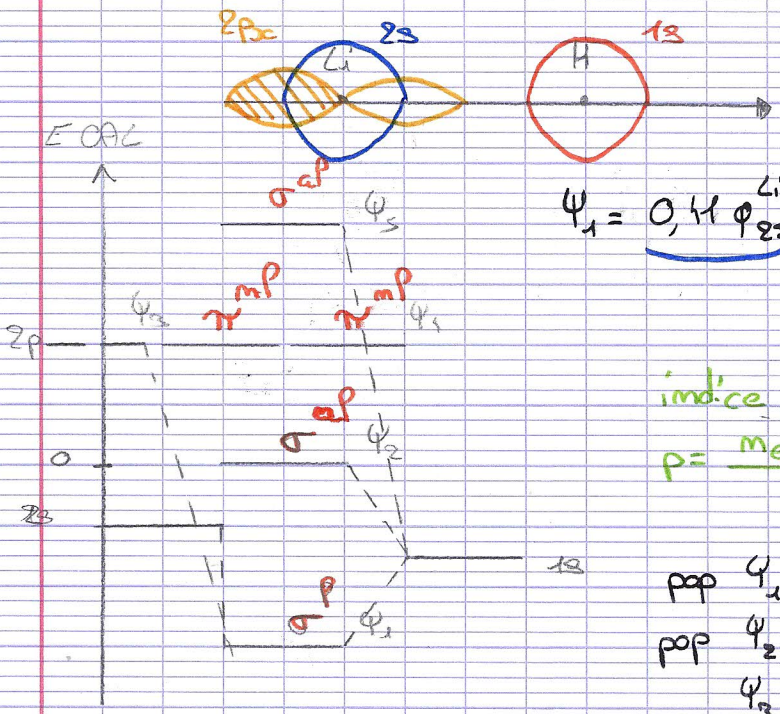
XII - Étude de la molécule LiH

CLOA → e^- valence

H $1s^1$ 1 e^-V

Li $1s^2\ 2s^1\ 2p^0$ 1 e^-V

5 OA → 5 OM { 1 OM occupé / 4 OM virtuelle



$\Psi_1 = 0,44\,\varphi^{Li}_{2s} + 0,33\,\varphi^{Li}_{2p_z} + 0,85\,\varphi^{H}_{1s}$

indice p de cp liaison

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

pop $\Psi_1 = 2$

pop $\Psi_2 = 0$

Ψ_3

Ψ_4

Ψ_5

pop(H) = 1,438

= 0,848 × 0,848 × 2

pop(Li) = 0,562

= (0,4141 × 0,4141 + 0,33 × 0,33) × 2

(Li) — (H)

−0,562 + 1 −1,438 + 1

= 0,438 = −0,438