Applications du principe variationnel et de la condition de stationnarité

1. Atome d'hydrogène

a) • $E \longrightarrow$ joules

• $\vec{r} \equiv (x, y, z)$ — x : mètres, y : mètres, z : mètres

• $\underbrace{\int_{\mathbb{R}^3} d\vec{r}}_{m^3} \; \underbrace{\psi^2(\vec{r})}_{m^{-3}} = 1 \rightarrow$ sans unité

donc $\psi(\vec{r})$ est en $m^{-\frac{3}{2}}$.

• $\tilde{E} = \dfrac{E}{2E_I} \longrightarrow$ sans unité

• $\tilde{\vec{r}} \equiv (\tilde{x}, \tilde{y}, \tilde{z}) = (x/a_0, y/a_0, z/a_0)$ → sans unité

• $\tilde{\psi}(\tilde{\vec{r}}) = \underbrace{a_0^{3/2}}_{m^{3/2}} \underbrace{\psi(a_0 \tilde{\vec{r}})}_{m^{-3/2}} \longrightarrow$ sans unité !

b) Changement de variables
$\tilde{x} = x/a_0, \quad \tilde{y} = y/a_0, \quad \tilde{z} = z/a_0$

d'où $1 = \int_{\mathbb{R}^3} d\vec{r}\, \psi^2(\vec{r}) = \int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dy \int_{-\infty}^{+\infty} dz\, \psi^2(x,y,z)$

$$= a_0^3 \int_{-\infty}^{+\infty} d\tilde{x} \int_{-\infty}^{+\infty} d\tilde{y} \int_{-\infty}^{+\infty} d\tilde{z}\, \psi^2(a_0\tilde{x}, a_0\tilde{y}, a_0\tilde{z})$$

$$= \int_{\mathbb{R}^3} d\tilde{\vec{r}}\; a_0^3\, \psi^2(a_0 \tilde{\vec{r}})$$

soit $\boxed{\int_{\mathbb{R}^3} d\tilde{\vec{r}} \left[\tilde{\psi}(\tilde{\vec{r}})\right]^2 = 1}$

c) $2E_I = \dfrac{m_e e^4}{(4\pi\varepsilon_0)^2 \hbar^2} = \dfrac{m_e^2 e^4}{(4\pi\varepsilon_0)^2 \hbar^4} \times \dfrac{1}{m_e} \times \hbar^2 = \dfrac{\hbar^2}{m_e a_0^2} = 2E_I$

$$= \frac{e^2}{4\pi\varepsilon_0} \times \frac{m_e e^2}{4\pi\varepsilon_0 \hbar^2} = \frac{e^2}{4\pi\varepsilon_0} \frac{1}{a_0} = 2E_I$$

d) $\psi(\vec{r}) = \psi\left(a_0 \dfrac{\vec{r}}{a_0}\right) = a_0^{-3/2}\, \tilde{\psi}\left(\dfrac{\vec{r}}{a_0}\right)$

d'où $\nabla^2_{\vec{r}} \psi(\vec{r}) = \nabla^2_{\vec{r}} \left[a_0^{-3/2} \tilde{\psi}(\vec{r}/a_0)\right]$

or $\dfrac{\partial}{\partial x} \tilde{\psi}\left(\dfrac{x}{a_0}, y/a_0, z/a_0\right) = \dfrac{\partial}{\partial x}\left(\dfrac{x}{a_0}\right) \dfrac{\partial \tilde{\psi}}{\partial \tilde{x}}(\vec{r}/a_0) + \cancel{\dfrac{\partial}{\partial x}(y/a_0)} \dfrac{\partial \tilde{\psi}}{\partial \tilde{y}}(\vec{r}/a_0)$
$+ \cancel{\dfrac{\partial}{\partial x}(z/a_0)} \dfrac{\partial \tilde{\psi}}{\partial \tilde{z}}(\vec{r}/a_0) = \dfrac{1}{a_0} \dfrac{\partial \tilde{\psi}}{\partial \tilde{x}}(\vec{r}/a_0)$

$\Rightarrow \dfrac{\partial^2 \tilde{\psi}}{\partial x^2}(x/a_0, y/a_0, z/a_0) = \dfrac{1}{a_0^2} \dfrac{\partial^2 \tilde{\psi}}{\partial \tilde{x}^2}(\vec{r}/a_0)$

De même $\frac{\partial^2 \tilde{\psi}}{\partial y^2}(x/a_0, y/a_0, z/a_0) = \frac{1}{a_0^2} \frac{\partial^2 \tilde{\psi}}{\partial \tilde{y}^2}(\vec{r}/a_0)$

et $\frac{\partial^2 \tilde{\psi}}{\partial z^2}(x/a_0, y/a_0, z/a_0) = \frac{1}{a_0^2} \frac{\partial^2 \tilde{\psi}}{\partial \tilde{z}^2}(\vec{r}/a_0)$

de sorte que

$$\nabla^2_{\vec{r}} \psi(\vec{r}) = a_0^{-3/2} \times \frac{1}{a_0^2}\left[\frac{\partial^2 \tilde{\psi}}{\partial \tilde{x}^2}(\vec{r}/a_0) + \frac{\partial^2 \tilde{\psi}}{\partial \tilde{y}^2}(\vec{r}/a_0) + \frac{\partial^2 \tilde{\psi}}{\partial \tilde{z}^2}(\vec{r}/a_0)\right]$$

$$= a_0^{-3/2} \times \frac{1}{a_0^2}(\nabla^2_{\tilde{\vec{r}}} \tilde{\psi})(\tilde{\vec{r}})$$

L'équation de Schrödinger s'écrit donc

$$\frac{-\hbar^2}{2m_e} \times \cancel{a_0^{-3/2}} \times \frac{1}{a_0^2}(\nabla^2_{\tilde{\vec{r}}} \tilde{\psi})(\tilde{\vec{r}}) - \frac{e^2}{4\pi\varepsilon_0 r} \times \cancel{a_0^{-3/2}} \tilde{\psi}(\tilde{\vec{r}}) = E \times \cancel{a_0^{-3/2}} \tilde{\psi}(\tilde{\vec{r}})$$

$$\rightarrow \; -\frac{1}{2}(\nabla^2_{\tilde{\vec{r}}} \tilde{\psi})(\tilde{\vec{r}}) \times \underbrace{\frac{\hbar^2}{m_e a_0^2}}_{2E_I} - \underbrace{\frac{e^2}{4\pi\varepsilon_0 a_0}}_{2E_I} \underbrace{\frac{a_0}{r}}_{\frac{1}{\tilde{r}}} \tilde{\psi}(\tilde{\vec{r}}) = E\tilde{\psi}(\tilde{\vec{r}})$$

d'où $$\boxed{-\frac{1}{2}(\nabla^2_{\tilde{\vec{r}}} \tilde{\psi})(\tilde{\vec{r}}) - \frac{1}{\tilde{r}}\tilde{\psi}(\tilde{\vec{r}}) = \tilde{E}\tilde{\psi}(\tilde{\vec{r}})}$$

L'hamiltonien s'écrit donc en unités atomiques

$$\hat{H} \equiv -\frac{1}{2}\nabla^2_{\vec{r}} - \frac{1}{r} \times$$

c) $\hat{H}\psi(\vec{r}) = E\psi(\vec{r}) \quad \forall \vec{r} \in R^3$

$$\rightarrow \; -\frac{1}{2}\underbrace{(\nabla^2_{\vec{r}}\psi)(\vec{r})}_{\downarrow} - \frac{1}{r}\psi(r) = E\psi(r)$$

$$\frac{1}{r}\frac{d^2}{dr^2}(r\psi(r)) = \frac{1}{r}\frac{d}{dr}\left[\psi(r) + r\frac{d\psi(r)}{dr}\right]$$

$$= \frac{1}{r}\frac{d\psi(r)}{dr} + \frac{1}{r}\left[\frac{d\psi}{dr}(r) + r\frac{d^2\psi(r)}{dr^2}\right]$$

$$= \frac{2}{r}\frac{d\psi(r)}{dr} + \frac{d^2\psi(r)}{dr^2}$$

D'où

$$-\frac{1}{2}\frac{d^2\psi(r)}{dr^2} \underbrace{- \frac{1}{r}\frac{d\psi(r)}{dr} - \frac{1}{r}\psi(r)}_{-\frac{1}{r}\left[\frac{d\psi(r)}{dr} + \psi(r)\right]} = E\psi(r)$$

Cette équation doit être satisfaite $\forall r \in R$, en particulier lorsque $r = 0$.

Comme $\frac{1}{r} \xrightarrow[r \to 0^+]{} +\infty$ et que $E\psi(r) + \frac{1}{2}\frac{d^2\psi(r)}{dr^2}$ est en principe une fonction continue et bornée, on en déduit que

↳ puisque $\int_{R^3} d\vec{r}\, \psi^2(\vec{r}) = 1$

$\left(\frac{d\psi}{dr}(r) + \psi(r)\right)$ doit tendre vers 0 lorsque $r \to 0^+$

soit $\boxed{\left.\frac{d\psi(r)}{dr}\right|_{r=0} = -\psi(0)}$

f) • $\psi_\alpha(\vec{r}) = \psi_\alpha(r) = e^{-\alpha r}$ où $\alpha \in \mathbb{R}_+^*$

$\frac{d\psi_\alpha(r)}{dr} = -\alpha e^{-\alpha r} \to \left.\frac{d\psi_\alpha(r)}{dr}\right|_{r=0} = -\alpha$

et $\psi_\alpha(0) = 1$.

La condition de cusp nucléaire est donc satisfaite lorsque $\alpha = 1$.

• $E(\alpha) = \frac{\langle\psi_\alpha|\hat{H}|\psi_\alpha\rangle}{\langle\psi_\alpha|\psi_\alpha\rangle}$ où $\hat{H} = -\frac{1}{r}\frac{d}{dr} - \frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r}\times$

$\langle\psi_\alpha|\psi_\alpha\rangle = \int_{\mathbb{R}^3} d\vec{r}\, \psi_\alpha^2(\vec{r}) = 4\pi\int_0^{+\infty} dr\, \psi_\alpha^2(r)\, r^2$

soit $\langle\psi_\alpha|\psi_\alpha\rangle = 4\pi\underbrace{\int_0^{+\infty} dr\, r^2 e^{-2\alpha r}}_{\frac{2}{(2\alpha)^3}} = \frac{\pi}{\alpha^3}$

De plus $\langle\psi_\alpha|\hat{H}|\psi_\alpha\rangle = \int_{\mathbb{R}^3} d\vec{r}\, \psi_\alpha(\vec{r})\, \hat{H}\, \psi_\alpha(\vec{r})$

soit $\langle\psi_\alpha|\hat{H}|\psi_\alpha\rangle =$

$$\int_{\mathbb{R}^3} d\vec{r}\left[-\frac{\psi_\alpha(r)}{r}\frac{d\psi_\alpha(r)}{dr} - \frac{1}{2}\psi_\alpha(r)\frac{d^2\psi_\alpha(r)}{dr^2} - \frac{1}{r}\psi_\alpha^2(r)\right]$$

$$= \int_{\mathbb{R}^3} d\vec{r}\left[\frac{\alpha}{r}e^{-2\alpha r} - \frac{1}{2}\alpha^2 e^{-2\alpha r} - \frac{1}{r}e^{-2\alpha r}\right]$$

$$= 4\pi\int_0^{+\infty} dr\left[\alpha r e^{-2\alpha r} - \frac{\alpha^2}{2} r^2 e^{-2\alpha r} - r e^{-2\alpha r}\right]$$

or $\int_0^{+\infty} dr\, \underbrace{r}_{f}\, \underbrace{e^{-2\alpha r}}_{g'} = \left[r\frac{e^{-2\alpha r}}{-2\alpha}\right]_0^{+\infty} - \int_0^{+\infty}\frac{e^{-2\alpha r}}{-2\alpha}dr$

$= \frac{1}{2\alpha}\left[\frac{e^{-2\alpha r}}{-2\alpha}\right]_0^{+\infty}$

$= \frac{1}{4\alpha^2}$

d'où $\langle\psi_\alpha|\hat{H}|\psi_\alpha\rangle$

$\shortparallel$

$\cancel{4}\pi(\alpha-1)\frac{1}{\cancel{4}\alpha^2} - 4\pi\cdot\frac{\alpha^2}{\cancel{2}}\cdot\frac{\cancel{2}}{(2\alpha)^3} = \frac{\pi}{\alpha^3}\left[\alpha(\alpha-1) - \frac{\alpha^2}{2}\right]$

$\to \boxed{E(\alpha) = \frac{1}{2}\alpha^2 - \alpha = \alpha\left(\frac{\alpha}{2} - 1\right)}$

$E(\alpha)$ est minimale lorsque $\dfrac{dE(\alpha)}{d\alpha} = \alpha - 1 = 0 \Rightarrow \alpha = 1.$

Dans ce cas $\hat{H}\psi_1(\vec{r}) = -\dfrac{1}{r}\underbrace{\dfrac{d\psi_1(r)}{dr}}_{-e^{-r}} - \dfrac{1}{2}\underbrace{\dfrac{d^2\psi_1(r)}{dr^2}}_{e^{-r}} - \dfrac{1}{r}\underbrace{\psi_1(r)}_{e^{-r}}$

soit $\boxed{\hat{H}\psi_1(\vec{r}) = -\dfrac{1}{2}\psi_1(\vec{r})}$

$\psi_1(\vec{r})$ est bien la solution exacte.

L'énergie associée vaut $-0{,}5$ unités atomiques.

g) • $\psi_\alpha(\vec{r}) = e^{-\alpha r^2} = \psi_\alpha(r)$

• $\dfrac{d\psi_\alpha(r)}{dr} = -2\alpha r e^{-\alpha r^2}$

$\Rightarrow \left.\dfrac{d\psi_\alpha(r)}{dr}\right|_{r=0} = 0$

alors que $\psi_\alpha(0) = 1$

Une gaussienne ne satisfait pas la condition de cusp nucléaire $\Rightarrow$ elle ne peut donc pas être la solution exacte.

• $\langle\psi_\alpha|\psi_\alpha\rangle = \displaystyle\int_{\mathbb{R}^3} d\vec{r}\; e^{-2\alpha r^2} = \left(\dfrac{\pi}{2\alpha}\right)^{3/2}$

• $\hat{H}\psi_\alpha(r) = -\dfrac{1}{2}\dfrac{d^2\psi_\alpha(r)}{dr^2} - \dfrac{1}{r}\left[\psi_\alpha(r) + \dfrac{d\psi_\alpha(r)}{dr}\right]$

Comme $\dfrac{d^2\psi_\alpha(r)}{dr^2} = -2\alpha\left(e^{-\alpha r^2} - 2\alpha r^2 e^{-\alpha r^2}\right)$ 4.1 P V

$= -2\alpha e^{-\alpha r^2}(1 - 2\alpha r^2)$

il vient

$\hat{H}\psi_\alpha(r) = \alpha e^{-\alpha r^2}(1 - 2\alpha r^2) - \dfrac{e^{-\alpha r^2}}{r} + 2\alpha e^{-\alpha r^2}$

$= 3\alpha e^{-\alpha r^2} - 2\alpha^2 r^2 e^{-\alpha r^2} - \dfrac{e^{-\alpha r^2}}{r}$

$\rightarrow \psi_\alpha(r)\hat{H}\psi_\alpha(r) = e^{-2\alpha r^2}\left[3\alpha - 2\alpha^2 r^2 - \dfrac{1}{r}\right]$

$\langle\psi_\alpha|\psi_\alpha\rangle E(\alpha) = 3\alpha\displaystyle\int_{\mathbb{R}^3} d\vec{r}\; e^{-2\alpha r^2} - 2\alpha^2\underbrace{\int_{\mathbb{R}^3} d\vec{r}\; r^2 e^{-2\alpha r^2}}_{I} - \underbrace{\int_{\mathbb{R}^3} d\vec{r}\;\dfrac{e^{-2\alpha r^2}}{r}}_{J}$

$I = 4\pi\displaystyle\int_0^{+\infty} dr\; \underbrace{r^4 e^{-2\alpha r^2}}_{f\,g'} = 4\pi\left(\cancel{\left[r^3\dfrac{e^{-2\alpha r^2}}{-4\alpha}\right]_0^{+\infty}} - \int_0^{+\infty} dr\; 3r^2\dfrac{e^{-2\alpha r^2}}{-4\alpha}\right)$

$f \rightarrow r^3$, $g' \rightarrow r e^{-2\alpha r^2}$

$I = \dfrac{3\pi}{\alpha}\displaystyle\int_0^{+\infty} dr\; \underbrace{r}_{f}\,\underbrace{r e^{-2\alpha r^2}}_{g'} = \dfrac{3\pi}{\alpha}\left(\cancel{\left[r\dfrac{e^{-2\alpha r^2}}{-4\alpha}\right]_0^{+\infty}} - \int_0^{+\infty} dr\;\dfrac{e^{-2\alpha r^2}}{-4\alpha}\right)$

$= \dfrac{3\pi}{\alpha}\dfrac{1}{4\alpha}\underbrace{\displaystyle\int_0^{+\infty} dr\; e^{-2\alpha r^2}}_{\frac{1}{2}\left(\frac{\pi}{2\alpha}\right)^{1/2}} \Rightarrow \boxed{I = \dfrac{3\pi}{8\alpha^2}\left(\dfrac{\pi}{2\alpha}\right)^{1/2}}$

$$J = 4\pi \int_0^{+\infty} dr\, r\, e^{-2\alpha r^2} = 4\pi \left[\frac{e^{-2\alpha r^2}}{-4\alpha} \right]_0^{+\infty} = \frac{\pi}{\alpha}$$

d'où $E(\alpha) = \left(\frac{2\alpha}{\pi}\right)^{3/2} \cdot \left[3\alpha \left(\frac{\pi}{2\alpha}\right)^{3/2} - \frac{6\pi}{8}\left(\frac{\pi}{2\alpha}\right)^{1/2} - \frac{\pi}{\alpha} \right]$

$$= 3\alpha - \frac{6\cancel{\pi}}{8} \cdot \frac{2\alpha}{\cancel{\pi}} - 2^{3/2}\left(\frac{\alpha}{\pi}\right)^{1/2}$$

$$\boxed{E(\alpha) = \frac{3}{2}\alpha - 2\left(\frac{2\alpha}{\pi}\right)^{1/2}}$$

$E(\alpha)$ est minimale lorsque $\frac{dE(\alpha)}{d\alpha} = 0 = \frac{3}{2} - 2\left(\frac{2}{\pi}\right)^{1/2} \times \frac{1}{2}\alpha^{-\frac{1}{2}}$

$\Rightarrow 2\sqrt{2\pi}\, \alpha^{-\frac{1}{2}} = 3$

$\Rightarrow \alpha^{1/2} = \frac{2}{3}\sqrt{\frac{2}{\pi}} = \left(\frac{8}{9\pi}\right)^{1/2}$

$\Rightarrow \boxed{\alpha = \left(\frac{8}{9\pi}\right)} \simeq 0{,}28$

L'énergie associée vaut

$$E\left(\alpha = \frac{8}{9\pi}\right) = \frac{3}{2}\,\frac{8}{9\pi} - 2 \times \underbrace{\left(\frac{16}{9\pi^2}\right)^{1/2}}_{\frac{4}{3\pi}} = -\frac{4}{3\pi} \simeq -0{,}4244 > -\frac{1}{2}$$

énergie exacte

2. Méthode des variations et déterminant séculaire

a) $\underline{\tilde{C}} = \begin{bmatrix} \tilde{C}_1 \\ \tilde{C}_2 \\ \vdots \\ \tilde{C}_M \end{bmatrix}$

$$E(\underline{\tilde{C}}) = \frac{\langle \Psi(\underline{\tilde{C}}) | \hat{H} | \Psi(\underline{\tilde{C}}) \rangle}{\langle \Psi(\underline{\tilde{C}}) | \Psi(\underline{\tilde{C}}) \rangle}$$

Comme $\langle \Psi(\underline{\tilde{C}}) | \hat{H} | \Psi(\underline{\tilde{C}}) \rangle = \sum_{I=1}^{M} \tilde{C}_I \langle \Psi(\underline{\tilde{C}}) | \hat{H} | \Phi_I \rangle$

$$= \sum_{I,J=1}^{M} \tilde{C}_I \tilde{C}_J \underbrace{\langle \Phi_J | \hat{H} | \Phi_I \rangle}_{H_{JI}}$$

$$= \sum_{J=1}^{M} \tilde{C}_J (H\underline{\tilde{C}})_J$$

d'où $\langle \Psi(\underline{\tilde{C}}) | \hat{H} | \Psi(\underline{\tilde{C}}) \rangle = \underline{\tilde{C}}^T H \underline{\tilde{C}}$

De même $\langle \Psi(\underline{\tilde{C}}) | \Psi(\underline{\tilde{C}}) \rangle = \sum_{I=1}^{M} \tilde{C}_I \langle \Psi(\underline{\tilde{C}}) | \Phi_I \rangle$

$$= \sum_{I,J=1}^{M} \tilde{C}_I \tilde{C}_J \underbrace{\langle \Phi_J | \Phi_I \rangle}_{S_{JI}}$$

$$= \sum_{J=1}^{M} \tilde{C}_J (S\underline{\tilde{C}})_J$$

$$= \underline{\tilde{C}}^T S \underline{\tilde{C}}$$

donc $\boxed{E(\underline{\tilde{C}}) = \dfrac{\underline{\tilde{C}}^T H \underline{\tilde{C}}}{\underline{\tilde{C}}^T S \underline{\tilde{C}}}}$

b) $\dfrac{\partial \underline{\tilde{C}}}{\partial \tilde{C}_J} = \begin{bmatrix} 0 \\ 0 \\ \vdots \\ 1 \\ 0 \\ \vdots \\ 0 \end{bmatrix}$ ← $J^{\text{ème}}$ ligne

$$\frac{\partial}{\partial \tilde{C}_J}\left[\underline{\tilde{C}}^T H \underline{\tilde{C}} \right] = \left(\frac{\partial \underline{\tilde{C}}}{\partial \tilde{C}_J} \right)^T H \underline{\tilde{C}} + \underline{\tilde{C}}^T H \frac{\partial \underline{\tilde{C}}}{\partial \tilde{C}_J}$$

$$\xrightarrow{(1)} = (H\underline{\tilde{C}})_J + \left(\underline{\tilde{C}}^T H \frac{\partial \underline{\tilde{C}}}{\partial \tilde{C}_J} \right)^T$$

$$\xrightarrow{(2)} = (H\underline{\tilde{C}})_J + \left(\frac{\partial \underline{\tilde{C}}}{\partial \tilde{C}_J} \right)^T \underbrace{H^T}_{\xrightarrow{(3)}\ H} \underline{\tilde{C}}$$

(1) si x est un nombre $x^T = x$

(2) $(AB)^T = B^T A^T$ pour toutes matrices A et B dont on peut calculer le produit.

(3) $(H^T)_{IJ} = H_{JI} = \langle \Phi_J | \hat{H} | \Phi_I \rangle = \langle \Phi_J | \hat{H} | \Phi_I \rangle^*$ ← algèbre réelle!

$$\langle \Phi_J | \hat{H} | \Phi_I \rangle^* = \langle \hat{H}\Phi_I | \Phi_J \rangle \overset{\text{car } \hat{H} \text{ est hermitien}}{=} \langle \Phi_I | \hat{H} | \Phi_J \rangle = H_{IJ}$$

donc $H^T = H$

D'où $\boxed{\dfrac{\partial}{\partial \tilde{C}_J}\left(\underline{\tilde{C}}^T H \underline{\tilde{C}}\right) = 2\,(H\underline{\tilde{C}})_J}$

Comme $(S^T)_{IJ} = S_{JI} = \langle \Phi_J | \Phi_I \rangle = \langle \Phi_J | \Phi_I \rangle^* = \langle \Phi_I | \Phi_J \rangle = S_{IJ}$

algèbre réelle

$\Rightarrow$ $S^T = S$ et, par analogie,

$$\boxed{\frac{\partial}{\partial \tilde{C}_J}\left(\underline{\tilde{C}}^T S\, \underline{\tilde{C}}\right) = 2\,(S\underline{\tilde{C}})_J}$$

c) Condition de stationnarité :

$\forall J = 1, \dots, M \qquad \dfrac{\partial E(\underline{\tilde{C}})}{\partial \tilde{C}_J} = 0$

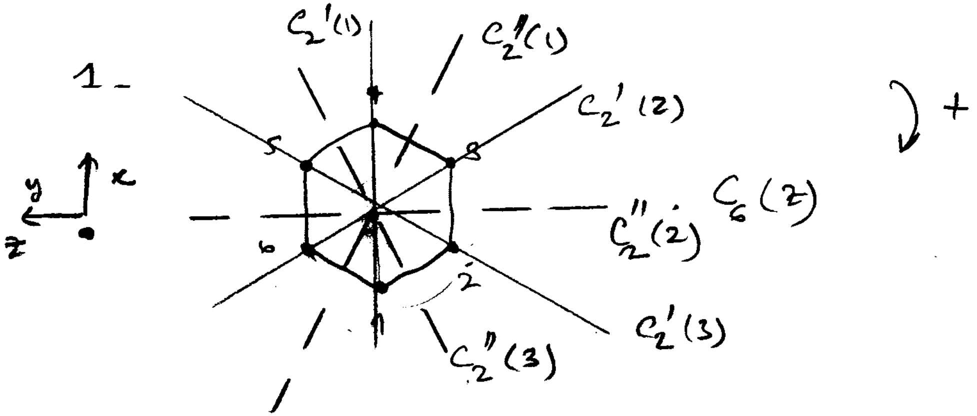
or $\quad (\underline{\tilde{C}}^T S \underline{\tilde{C}})\, E(\underline{\tilde{C}}) = \underline{\tilde{C}}^T H \underline{\tilde{C}}$

$$\Rightarrow \underbrace{\left[\frac{\partial}{\partial \tilde{C}_J}(\underline{\tilde{C}}^T S \underline{\tilde{C}})\right]}_{2(S\underline{\tilde{C}})_J} E(\underline{\tilde{C}}) + \underline{\tilde{C}}^T S \underline{\tilde{C}} \underbrace{\left(\frac{\partial E(\underline{\tilde{C}})}{\partial \tilde{C}_J}\right)}_{=0} = \underbrace{\frac{\partial}{\partial \tilde{C}_J}\left(\underline{\tilde{C}}^T H \underline{\tilde{C}}\right)}_{2(H\underline{\tilde{C}})_J}$$

donc $\forall J \quad (S\underline{\tilde{C}})_J\, E(\underline{\tilde{C}}) = (H\underline{\tilde{C}})_J \Leftrightarrow \boxed{H\underline{\tilde{C}} = E(\underline{\tilde{C}})\, S\underline{\tilde{C}}}$

TD benzene

1 –



$2C_6$ rotations $+\frac{2\pi}{6}$, $-\frac{2\pi}{6}$

$2C_3$ " $+\frac{2\pi}{3}$, $-\frac{2\pi}{3}$

1 – a

	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$
Γ	6	0	0	0	-2	0

1 – b –

$$\Gamma = \sum_i a_i \Gamma_i \, , \qquad a_i = \frac{1}{h} \sum_{\hat{R}} \chi_i(\hat{R}) \chi(\hat{R})$$

$h = 12$

$a_{A_1} = \frac{1}{12}(6 \times 1 - 6) = 0$, $a_{A_2} = 1$, $a_{B_1} = 0$, $a_{B_2} = 1$, $a_{E_1} = \frac{1}{12} \times 12 = 1$, $a_{E_2} = 1$

$$\boxed{\Gamma = A_2 \oplus B_2 \oplus E_1 \oplus E_2}$$

2/benzen

A_2: $\hat{P}_i = \sum_{\hat{R}} \chi_i(\hat{R})\hat{R}$

$$\hat{P}_{A_2}(p_1) = \overset{\hat{E}}{\cancel{1\times(p_1)}} + \overset{\hat{C}_6(+\frac{2\pi}{6})}{1\times(p_6)} + \overset{\hat{C}_6(-\frac{2\pi}{6})}{\cancel{1\times(p_2)}} + \overset{\hat{C}_3(+\frac{2\pi}{3})}{\cancel{1\times(p_5)}} + \overset{\hat{C}_3(-\frac{2\pi}{3})}{\cancel{1\times(p_3)}} + \overset{\hat{C}_2}{\cancel{1\times(p_4)}} - \overset{C_2'(1)}{\cancel{1\times(p_1)}} - \overset{C_2'(2)}{\cancel{1\times(-p_5)}}$$

$$- \underset{C_2'(3)}{\cancel{1\times(-p_3)}} - \underset{C_2''(1)}{\cancel{1\times(-p_6)}} - \underset{C_2''(2)}{\cancel{1\times(-p_4)}} - \underset{C_2''(3)}{\cancel{1\times(-p_2)}}$$

$$= 2p_6 + 2p_2 + 2p_5 + 2p_3 + 2p_4 + 2p_1$$

$$\boxed{\psi_{A_2} = \frac{1}{\sqrt{6}}(p_1 + p_2 + p_3 + p_4 + p_5 + p_6)}$$

B_2:

$$\hat{P}_{B_2}(p_1) = \cancel{1\times(p_1)} - \cancel{1\times(p_6)} - \cancel{1\times(p_2)} + \cancel{1\times(p_5)} + \cancel{1\times(p_3)} - \cancel{1\times(p_4)} - \cancel{1\times(-p_1)} - \cancel{1\times(-p_5)} - \cancel{1\times(-p_3)}$$

$$+ \cancel{1\times(-p_6)} + \cancel{1\times(-p_4)} + \cancel{1\times(-p_2)}$$

$$= 2p_1 - 2p_2 + 2p_3 - 2p_4 + 2p_5 - 2p_6$$

$$\boxed{\psi_{B_2} = \frac{1}{\sqrt{6}}(p_1 - p_2 + p_3 - p_4 + p_5 - p_6)}$$

E_1:

$$\hat{P}_{E_1}(p_1) = \cancel{2\times(p_1)} + 1\times(p_6) + \cancel{1\times(p_2)} - \cancel{1\times(p_5)} - \cancel{1\times(p_3)} - \cancel{2\times(p_4)} = 2p_1 + p_2 - p_3 - 2p_4 - p_5 + p_6$$

$$\boxed{\psi_{E_1,1} = \frac{1}{\sqrt{12}}(2p_1 + p_2 - p_3 - 2p_4 - p_5 + p_6)}$$

$$\hat{P}_{E_1}(p_2) = \cancel{2\times(p_2)} + \cancel{1\times(p_1)} + \cancel{1\times(p_3)} - \cancel{1\times(p_6)} - \cancel{1\times(p_4)} - \cancel{2\times(p_5)} = p_1 + 2p_2 + p_3 - p_4 - 2p_5 - p_6$$

$$\boxed{\psi_{E_1,2} = \frac{1}{\sqrt{12}}(p_1 + 2p_2 + p_3 - p_4 - 2p_5 - p_6)}$$

In the representation E_1, we want an orthonormal basis

$$|\psi_{E1,1}\rangle, |\psi_{E1,2}\rangle \longrightarrow |\psi_{E1,1}\rangle, |\psi'_{E1,2}\rangle$$

where $$|\psi'_{E1,2}\rangle = \Big(\underbrace{|\psi_{E1,2}\rangle - |\psi_{E1,1}\rangle\langle\psi_{E1,1}|\psi_{E1,2}\rangle}_{|\psi_u\rangle}\Big) \frac{1}{\sqrt{\langle\psi_u|\psi_u\rangle}}$$

Note that $$\langle\psi_{E1,1}|\psi'_{E1,2}\rangle = \langle\psi_{E1,1}|\psi_{E1,2}\rangle - \underbrace{\langle\psi_{E1,1}|\psi_{E1,1}\rangle}_{1}\langle\psi_{E1,1}|\psi_{E1,2}\rangle = 0$$

$$\langle\psi_{E1,1}|\psi_{E1,2}\rangle = \frac{1}{12}(2+2-1+2+2-1) = \frac{1}{2}$$

$$\psi_u = \frac{1}{\sqrt{12}}\left(\cancel{p_1} + 2p_2 + p_3 - \cancel{p_4} - 2p_5 - p_6 - \cancel{p_1} - \tfrac{1}{2}p_2 + \tfrac{1}{2}p_3 + \cancel{p_4} + \tfrac{1}{2}p_5 - \tfrac{1}{2}p_6\right)$$
$$= \frac{1}{\sqrt{12}}\left(\tfrac{3}{2}p_2 + \tfrac{3}{2}p_3 - \tfrac{3}{2}p_5 - \tfrac{3}{2}p_6\right) = \frac{3}{2\sqrt{12}}(p_2 + p_3 - p_5 - p_6)$$

$$\rightarrow \boxed{\psi'_{E1,2} = \tfrac{1}{2}(p_2 + p_3 - p_5 - p_6)}$$

E_2 $$\hat{P}_{E_2}(p_1) = 2\times(p_1) - 1\times(p_4) - 1\times(p_2) - 1\times(p_5) - 1\times(p_3) + 2\times(p_4) = 2p_1 - p_2 - p_3 + 2p_4 - p_5 - p_6$$

$$\boxed{\psi_{E_2,1} = \frac{1}{\sqrt{12}}(2p_1 - p_2 - p_3 + 2p_4 - p_5 - p_6)}$$

$$\hat{P}_{E_2}(p_2) = 2\times(p_2) - 1\times(p_1) - 1\times(p_3) - 1\times(p_6) - 1\times(p_4) + 2\times(p_5) = -p_1 + 2p_2 - p_3 - p_4 + 2p_5 - p_6$$

$$\Rightarrow \boxed{\psi_{E_2,2} = \frac{1}{\sqrt{12}}(p_1 - 2p_2 + p_3 + p_4 - 2p_5 + p_6)}$$

In the E_2 representation, we want an orthonormal basis

$$|\psi_{E_2,1}\rangle, |\psi_{E_2,2}\rangle \longrightarrow |\psi_{E_2,1}\rangle, |\psi'_{E_2,2}\rangle$$

where (1) $|\psi'_{E_2,2}\rangle = \underbrace{|\psi_{E_2,2}\rangle - |\psi_{E_2,1}\rangle\langle\psi_{E_2,1}|\psi_{E_2,2}\rangle}_{|\psi_v\rangle} \cdot \frac{1}{\sqrt{\langle\psi_v|\psi_v\rangle}}$

$\langle\psi_{E_2,1}|\psi'_{E_2,2}\rangle = 0$

$$\langle\psi_{E_2,1}|\psi_{E_2,2}\rangle = \frac{1}{12}(2+2-1+2+2-1) = \frac{1}{2}$$

$$\psi_v = \frac{1}{\sqrt{12}}(\cancel{p_1} - 2p_2 + p_3 \cancel{+p_4} - 2p_5 + p_6 - \cancel{p_1} + \tfrac{1}{2}p_2 + \tfrac{1}{2}p_3 - \cancel{p_4} + \tfrac{1}{2}p_5 + \tfrac{1}{2}p_6) = \frac{1}{\sqrt{12}}(-\tfrac{3}{2}p_2 + \tfrac{3}{2}p_3 - \tfrac{3}{2}p_5 + \tfrac{3}{2}p_6)$$

We finally chose (change of sign compared to (1)) $\boxed{\psi'_{E_2,2} = \frac{1}{2}(p_2 - p_3 + p_5 - p_6)}$

$$\langle\psi_{A_2}|\hat{h}|\psi_{A_2}\rangle = \frac{1}{6}\big(\langle p_1|\hat{h}|p_1\rangle + \langle p_1|\hat{h}|p_2\rangle + \langle p_2|\hat{h}|p_1\rangle + \langle p_2|\hat{h}|p_2\rangle + \langle p_2|\hat{h}|p_3\rangle + \langle p_3|\hat{h}|p_2\rangle + \langle p_3|\hat{h}|p_3\rangle$$
$$+ \langle p_1|\hat{h}|p_6\rangle$$
$$+ \langle p_3|\hat{h}|p_4\rangle + \langle p_4|\hat{h}|p_3\rangle + \langle p_4|\hat{h}|p_4\rangle + \langle p_4|\hat{h}|p_5\rangle + (\alpha+2\beta) + (\alpha+2\beta)\big)$$
$$= \frac{1}{6} \times 6\,(\alpha+2\beta) = \alpha + 2\beta$$

$$\boxed{\varepsilon_{A_2} = \alpha + 2\beta}$$

$$\langle\psi_{B_2}|\hat{h}|\psi_{B_2}\rangle = \frac{1}{6}\big(\underbrace{\alpha - \beta - \beta}\ \underbrace{-\beta + \alpha - \beta}\ \underbrace{-\beta + \alpha - \beta} + \underbrace{\alpha - 2\beta} + (-2\beta + \alpha) + (-2\beta + \alpha)\big)$$

$$\boxed{\varepsilon_{B_2} = \alpha - 2\beta}$$

$$\langle \psi_{E1,1} | \hat{h} | \psi'_{E1,2} \rangle = \frac{1}{2\sqrt{12}} \underbrace{\langle 2p_1 + p_2 - p_3 - 2p_4 - p_5 + p_6 | \hat{h} | p_2 + p_3 - p_5 - p_6 \rangle}$$

$$\cancel{2\beta} + \cancel{\alpha} + \cancel{\beta} - \cancel{\beta} - \cancel{\alpha} - \cancel{2\beta} + \cancel{2\beta} + \cancel{\alpha} + \cancel{\beta} - \cancel{\beta} - \cancel{\alpha}$$

$$-2\beta, = 0$$

$$- \langle 2p_1 | \hat{h} | p_6 \rangle$$

$$\langle \psi_{E1,1} | \hat{h} | \psi_{E1,1} \rangle = \frac{1}{12}\left(4\alpha + 2\beta + 2\beta \quad + 2\beta + \alpha - \beta \quad - \beta + \alpha + 2\beta \quad + 2\beta + 4\alpha + 2\beta \quad + 2\beta - \beta + \alpha \quad + 2\beta - \beta + \alpha \right)$$

$$= \frac{1}{12}\left(8(\alpha+\beta) + 4(\alpha+\beta) \right) = \alpha + \beta$$

$$\langle \psi'_{E1,2} | \hat{h} | \psi'_{E1,2} \rangle = \frac{1}{4} \langle p_2 + p_3 - p_5 - p_6 | \hat{h} | p_2 + p_3 - p_5 - p_6 \rangle = \frac{1}{4}\left(\alpha + \beta + \beta + \alpha + \alpha + \beta + \beta + \alpha \right)$$

$$= (\alpha + \beta)$$

$$\langle \psi_{E2,1} | \hat{h} | \psi'_{E2,2} \rangle = \frac{1}{2\sqrt{12}} \underbrace{\langle 2p_1 - p_2 - p_3 + 2p_4 - p_5 - p_6 | \hat{h} | p_2 - p_3 + p_5 - p_6 \rangle} = 0$$

$$\cancel{2\beta} - \cancel{2\beta} \quad - \cancel{\alpha} + \cancel{\beta} \quad - \cancel{\beta} + \cancel{\alpha} \quad - \cancel{2\beta} + \cancel{2\beta} \quad - \cancel{\alpha} + \cancel{\beta} \quad - \cancel{\beta} + \cancel{\alpha}$$

$$\langle \psi_{E2,1} | \hat{h} | \psi_{E2,1} \rangle = \frac{1}{12}\left(4\alpha - 2\beta - 2\beta \quad - \cancel{2\beta} + \alpha + \cancel{\beta} \quad + \cancel{\beta} + \alpha - 2\beta \quad - 2\beta + 4\alpha - 2\beta \quad - 2\beta + \alpha + \cancel{\beta} \quad - \cancel{2\beta} + \cancel{\beta} + \alpha \right)$$

$$= \alpha - \beta$$

$$\langle \psi'_{E2,2} | \hat{h} | \psi'_{E2,2} \rangle = \frac{1}{4} \langle p_2 - p_3 + p_5 - p_6 | \hat{h} | p_2 - p_3 + p_5 - p_6 \rangle = \frac{1}{4}\left(\alpha - \beta - \beta + \alpha + \alpha - \beta - \beta + \alpha \right) = \alpha - \beta$$

b_2 — $\alpha - 2\beta$

$\beta < 0$

e_2 — — $\alpha - \beta$

e_1 ⥮ ⥮ $\alpha + \beta$

a_2 ⥮ $\alpha + 2\beta$

Ground state electronic configuration $(a_2)^2 (e_1)^4$

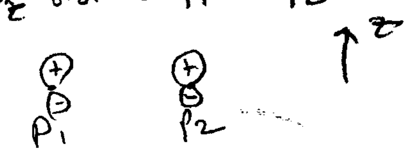
$$E_{total} = 2\times(\alpha + 2\beta) + 4(\alpha + \beta) = 6\alpha + 8\beta$$

independent π bonding orbitals energy $6\times(\alpha+\beta) = 6\alpha + 6\beta$ ⊛

$$E_{deloc} = E_{total} - E_{3\pi\,bonding} = +2\beta. < 0$$

⊛ Single independent π bond:

Consider 2 p_z orbitals p_1 and p_2



$$[\hat{h}] = \begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix}$$ eigenvalues $\alpha+\beta$ and $\alpha-\beta$

$$\hat{h}\left(\frac{1}{\sqrt{2}}(p_1 + p_2)\right) = \frac{1}{\sqrt{2}}(\alpha p_1 + \beta p_2 + \beta p_1 + \alpha p_2)$$

$$= \frac{(\alpha+\beta)}{\sqrt{2}}(p_1 + p_2)$$

$$\psi_{\alpha+\beta} = \frac{1}{\sqrt{2}}(p_1 + p_2) \quad \text{bonding orbital}$$

$$\frac{\hat{h}}{\sqrt{2}}(p_1 - p_2) = \frac{1}{\sqrt{2}}(\alpha p_1 + \beta p_2 - \beta p_1 - \alpha p_2)$$

$$= \frac{(\alpha-\beta)}{\sqrt{2}}(p_1 - p_2)$$

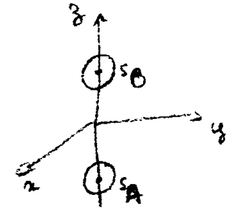
$$\psi_{\alpha-\beta} = \frac{1}{\sqrt{2}}(p_1 - p_2) \quad \text{antibonding orbital}$$

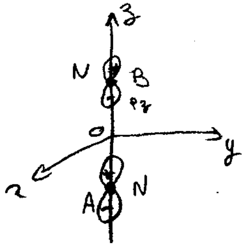
Benzene with 3 independent π bonds has an energy equal to $6\times(\alpha+\beta)$

N_2 , $d = 1{,}097$ Å

N . $1s^2\, 2s^2\, 2p^3$

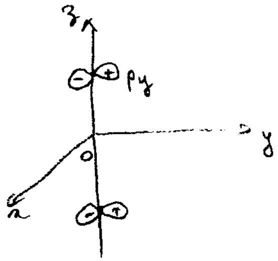
$\langle \varphi_i | \varphi_j \rangle = 0$.

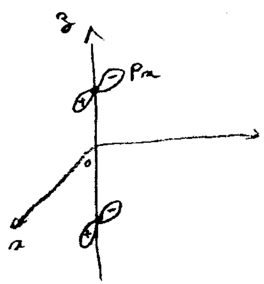




1- a)

	E	C_{2z}	C_{2y}	C_{2x}	i	σ_{xy}	σ_{xz}	σ_{yz}
$\Gamma_1(1s_A, 1s_B)$	2	2	0	0	0	0	2	2
$\Gamma_2(2s_A, 2s_B)$	2	2	0	0	0	0	2	2
$\Gamma_{2z}(2p_{zA}, 2p_{zB})$	2	2	0	0	0	0	2	2
$\Gamma_{2y}(2p_{yA}, 2p_{yB})$	2	-2	0	0	0	0	-2	2
$\Gamma_{2x}(2p_{xA}, 2p_{xB})$	2	-2	0	0	0	0	2	-2





. Décomposition en représentations irréductibles. R= opération symétrie

$$\Gamma = \sum_i a_i \Gamma_i \quad \text{avec} \quad a_i = \frac{1}{h} \sum_R \chi(R)\chi_i(R)$$

h est l'ordre du groupe $= \sum_i (\dim_i)^2$ — dimension $= \chi(E)$ pour chaque représentation irréductible

ici $h = 8 \times 1^2 = 8$.

- Pour $\Gamma_1(1s_A, 1s_B)$: $a_{A_g} = \frac{1}{8}\left(2\times1 + 2\times1 + 4\times(0\times1) + 2\times1 + 2\times1\right) = 1$

$a_{B_{1u}} = \frac{1}{8}\left(2\times1 + 2\times1 + 4\times(0\times(-1)) + 2\times1 + 2\times1\right) = 1$

$\Rightarrow$ $\underline{\Gamma_1(1s_A, 1s_B) = A_g \oplus B_{1u}}$

idem pour Γ_2 et Γ_{2z} (même symétrie)

$\Gamma_2(2s_A, 2s_B) = A_g \oplus B_{1u}$, $\Gamma_{2z}(2p_{zA}, 2p_{zB}) = A_g \oplus B_{1u}$

- pour $\Gamma_{2y}(2p_{yA}, 2p_{yB})$: $a_{B_{2u}} = \frac{1}{8}\big(2\times1 + (-2)\times(-1) + 0\times1 + 0\times(-1) + 0\times(-1) + 0\times1 + (-2)\times(-1) + 2\times1\big) = 1$

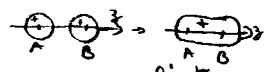
et $a_{B_{3g}} = 1$

$\underline{\Gamma_{2y}(2p_{yA}, 2p_{yB}) = B_{2u} \oplus B_{3g}}$

- de même pour $\underline{\Gamma_{2x}(2p_{xA}, 2p_{xB}) = B_{3u} \oplus B_{2g}}$

b) Orbitales de symétrie qui sont bases de représentations irréductibles :

* Γ_1 : $\underline{A_g}$: entièrement symétrique → $\underline{(1s_A) + (1s_B)}$



liante

$\underline{B_{1u}}$: on utilise le projecteur

C1

$$\begin{array}{cccccccccc} & E & C_{2z} & C_{2y} & C_{2x} & i & \sigma_{xy} & \sigma_{xz} & \sigma_{yz} \\ \hat{P}_{B_{1u}}(1s_A) = & 1s_A + & 1s_A & -1s_B & -1s_B & -1s_B & -1s_B & +1s_A & +1s_A \end{array}$$

$= \underline{4(1s_A) - 4(1s_B)}$

antiliante

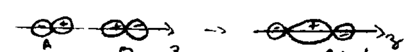
Rq. 2 OA → 2 OS , on garde le même nbre d'orbitales

Γ_2 idem $A_g \rightarrow (2s_A) + (2s_B)$

$B_{1u} \rightarrow 4(2s_A) - 4(2s_B)$

$$\begin{array}{cccccccccc} & E & C_{2z} & C_{2y} & C_{2x} & i & \sigma_{xy} & \sigma_{xz} & \sigma_{yz} \\ \Gamma_{2z} : \hat{P}_{A_g}(2p_{zA}) = & 2p_{zA} + & 2p_{zA} & -2p_{zB} & -2p_{zB} & -2p_{zB} & -2p_{zB} & +2p_{zA} & +2p_{zA} \end{array}$$

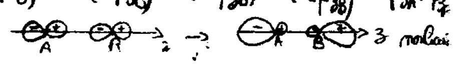
$= \underline{4(2p_{zA}) - 4(2p_{zB})}$



liante

$\hat{P}_{B_{1u}}(2p_{zA}) = 1\times2p_{zA} + 1\times2p_{zA} - 1\times(-2p_{zB}) - 1\times(-2p_{zB}) - 1\times(-2p_{zB}) - 1\times(-2p_{zB}) + 2p_{zA} + 2p_{zA}$

$= \underline{4(2p_{zA}) + 4(2p_{zB})}$



non lia

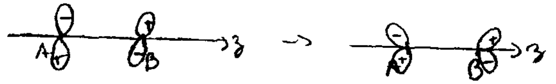
Γ_{2y} : $\hat{P}_{B_{2u}}(2p_{yA}) = \overset{E}{2p_{yA}} \overset{C_{2z}}{-1\times(2p_{yA})} \overset{C_{2y}}{+1\times(2p_{yB})} \overset{C_{2x}}{-1\times(-2p_{yB})} \overset{i}{-1\times(-2p_{yB})}$

$\overset{\sigma_{xy}}{+1\times(2p_{yB})} \overset{\sigma_{xz}}{-1\times(-2p_{yA})} \overset{\sigma_{yz}}{+1\times(2p_{yA})} = \underline{4(2p_{yA}) + 4(2p_{yB})}$

liante

$\hat{P}_{B_{3g}}(2p_{yA}) = 2p_{yA} - 1\times(-2p_{yA}) - 1\times(2p_{yB}) + 1\times(-2p_{yB}) + 1\times(-2p_{yB}) - 1\times(+2p_{yB})$

$-1(-2p_{yA}) - 1\times(-2p_{yA}) + 1\times(2p_{yA}) = \underline{4(2p_{yA}) - 4(2p_{yB})}$



antiliante

Γ_{2x} : de même : $4(2p_{xA}) + 4(2p_{xB}) \leftarrow B_{3u}$ liante

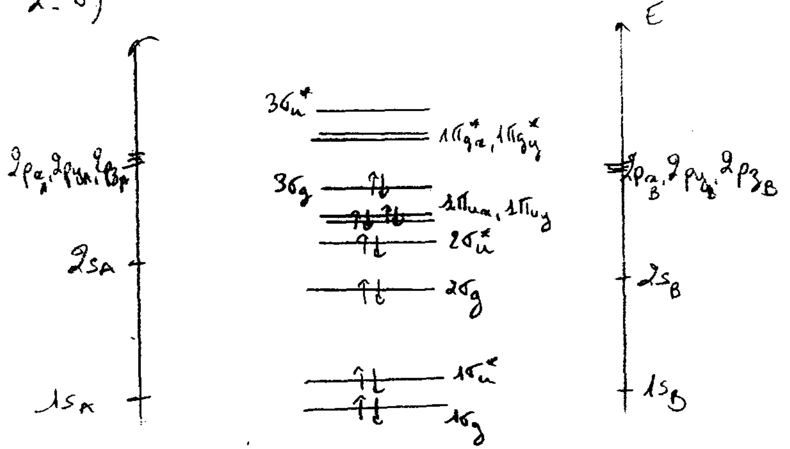
$4(2p_{xA}) - 4(2p_{xB}) \leftarrow B_{2g}$ antiliante

2_ Hartree-Fock (Note that the HF MOs in the DALTON outfile are not always normalized)

a) D'après le fichier Dalton :

- $1\sigma_g = 0{,}7068(1s_A + 1s_B)$ liante $E_{1\sigma_g} = -15{,}953$
- $1\sigma_u = 0{,}7076(1s_B - 1s_A)$ antiliante $E_{1\sigma_u} = -15{,}950$
- $2\sigma_g = 0{,}448(2s_A + 2s_B) + 0{,}2775(2p_{zB} - 2p_{zA})$ liante $E_{2\sigma_g} = -1{,}625$
- $2\sigma_u = 0{,}7037(2s_B - 2s_A) - 0{,}2617(2p_{zA} + 2p_{zB})$ antiliante $E_{2\sigma_u} = -0{,}869$
- $1\pi_{ux} = 0{,}0131(2p_{xA} + 2p_{xB})$ liante $E_{1\pi_{ux}} = -0{,}717$
- $1\pi_{uy} = 0{,}0131(2p_{yA} + 2p_{yB})$ liante $E_{1\pi_{uy}} = -0{,}717$
- $3\sigma_g = 0{,}4407(2s_A + 2s_B) - 0{,}6440(2p_{zB} - 2p_{zA})$ $E_{3\sigma_g} = -0{,}696$
- $1\pi_{gx} = 0{,}8895(2p_{xB} - 2p_{xA})$ antiliante $E_{1\pi_{gx}} = 0{,}078$
- $1\pi_{gy} = 0{,}8895(2p_{yA} - 2p_{yB})$ antiliante $E_{1\pi_{gy}} = 0{,}078$
- $3\sigma_u = 1{,}225(2s_A - 2s_B) - 0{,}121(2p_{zA} + 2p_{zB})$ $E_{3\sigma_u} = 0{,}821$

2.b)



N_2 : $(1\sigma_g)^2 (1\sigma_u^*)^2 (2\sigma_g)^2 (2\sigma_u^*)^2 (1\pi_{ux}, 1\pi_{uy})^4 (3\sigma_g)^2$ pas d'e^- non apparié → diamagnétique

d) Bond order : $p = \dfrac{n_{liant} - n_{antiliant}}{2} = \dfrac{10-4}{2} = 3$

Rq. les orbitales moléculaires sont des combinaisons linéaires d'orbitales de même symétrie.

3_ Analyse du calcul Hartree-Fock

a) $\hat{F}\Psi_i = \varepsilon_i \Psi_i$ avec $\langle \psi^{\Gamma_i} | \hat{F} | \psi^{\Gamma_j} \rangle = 0$ avec Γ_i et $\Gamma_j \in$ différentes représentations irréductibles

Il y a couplage entre les orbitales de symétrie $(2s_A + 2s_B)$ et $(2p_{zA} - 2p_{zB})$ (A_g)

et $(2s_A - 2s_B)$ et $(2p_{zA} + 2p_{zB})$ (B_{1u})

b) $\varepsilon_{1\sigma_g}, \dots$ sont les valeurs des énergies de $1\sigma_g$ $\dfrac{\langle 1\sigma_g | \hat{F} | 1\sigma_g \rangle}{\langle 1\sigma_g | 1\sigma_g \rangle}$

c) Il faut diagonaliser les matrices $\begin{pmatrix} \alpha_{g1} & \beta_g \\ \beta_g & \alpha_{g2} \end{pmatrix}$ et $\begin{pmatrix} \alpha_{u1} & \beta_u \\ \beta_u & \alpha_{u2} \end{pmatrix}$

afin de réécrire $[\hat{F}]$ dans la base des orbitales moléculaires HF

C_2 d) $\Sigma(OM)_{occupées} = -73{,}05$ u.a au lieu de -132 u.a pour l'énergie électronique HF

C1 • projection operator onto the space associated to the irreducible representation Γ_i^{irrep}

$$\hat{P}_i = \sum_{\hat{R}} \chi_i(\hat{R})\,\hat{R}$$

$\hat{R}$: symmetry operation

with $\chi_i(\hat{R})$: character associated $\forall \hat{R}$ for the irreducible representation Γ_i^{irrep}

• The symmetry orbitals should be normalized (we assume the overlap integrals are equal to zero)

for $\Gamma_1 \longrightarrow \psi_{b_{1u}} = \frac{1}{\sqrt{2}}(1s_A - 1s_B)$, $\psi_{a_g} = \frac{1}{\sqrt{2}}(1s_A + 1s_B)$

$\Gamma_2 \longrightarrow \psi_{a_g} = \frac{1}{\sqrt{2}}(2s_A + 2s_B)$, $\psi_{b_{1u}} = \frac{1}{\sqrt{2}}(2s_A - 2s_B)$

$\Gamma_{2z} \rightarrow \psi_{a_g} = \frac{1}{\sqrt{2}}(2p_{zA} - 2p_{zB})$, $\psi_{b_{1u}} = \frac{1}{\sqrt{2}}(2p_{zA} + 2p_{zB})$

$\Gamma_{2y} \rightarrow \psi_{b_{2u}} = \frac{1}{\sqrt{2}}(2p_{yA} + 2p_{yB})$, $\psi_{b_{3g}} = \frac{1}{\sqrt{2}}(2p_{yA} - 2p_{yB})$

$\Gamma_{2x} \rightarrow \psi_{b_{3u}} = \frac{1}{\sqrt{2}}(2p_{xA} + 2p_{xB})$, $\psi_{b_{2g}} = \frac{1}{\sqrt{2}}(2p_{xA} - 2p_{xB})$

C2 Pour deux électrons, on sait que

$$E_{HF} = 2\varepsilon_{HF} - \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} d\vec{r}\,d\vec{r}'\, \frac{\rho_{HF}^2(\vec{r})\,\rho_{HF}^2(\vec{r}')}{|\vec{r}-\vec{r}'|}$$

$$\neq 2\varepsilon_{HF}$$

Il n'y a a priori aucune raison pour que la somme des énergies des orbitales moléculaires HF occupées soit égale à l'énergie HF dans N_2.