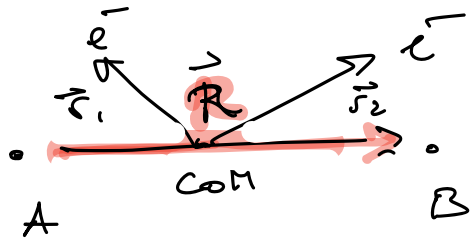
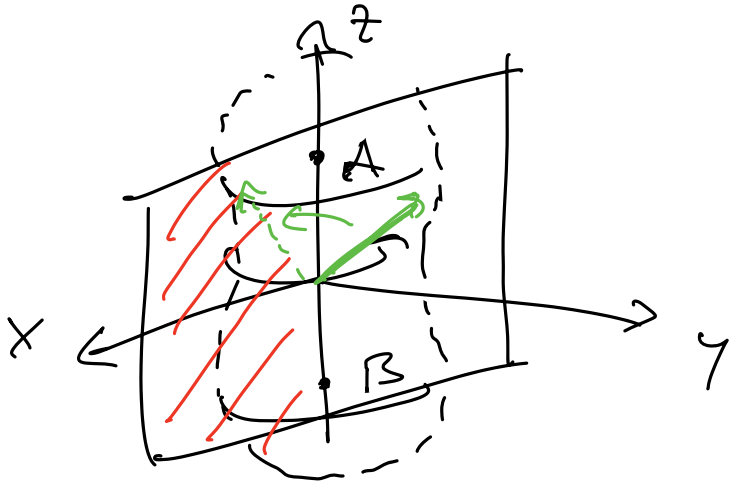
Molécules : États électroniques / nucléaires



$$\Psi(\{\vec{r}_i\}, \vec{R}) \simeq F_s(\vec{R})\, \Phi_s(\{\vec{r}_i\}; \vec{R})$$

BO

États électroniques $\Phi_s(\{\vec{r}_i\}; \vec{R})$



référentiel moléculaire

Symétries → quantités conservées → nombres quantiques

1) rotations autour de z

2) réflexion par rapport au plan xz

3) $A \equiv B$ (molécule homonucléaire)

inversion autour du centre de la molécule

(4) conservation du spin total $\vec{S} = \sum_i \vec{s}_i$)

1) rotations autour de z

$$L^z = \sum_i l_i^z \qquad [L^z, \mathcal{H}_{el}] = 0$$

$$L^z \Phi_s = \hbar M \Phi_s \qquad M = 0, \pm 1, \pm 2, \ldots$$

$$M = \pm \Lambda \qquad \Lambda = |M|$$

Λ , $\pm$ (↑) nombres quantiques

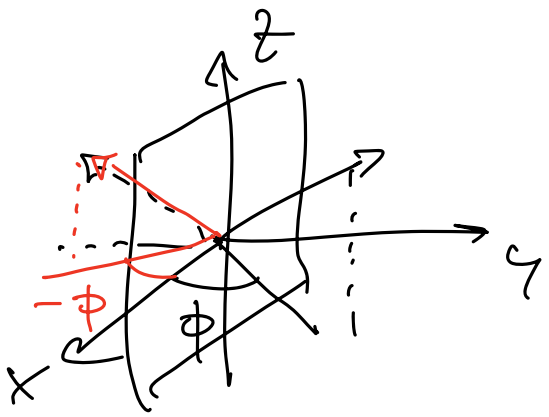
notation spectroscopique

$\Lambda =$	0	1	2	--
	Σ	Π	Δ	--

molécule mono-électroniques | σ | π | δ

H_2^+

2) inversion par rapport au plan xz



$y \to -y$
$\phi \to -\phi$

$$A_y^2 = 1$$

$$A_y f(x,y,z) = f(x,-y,z)$$

$$A_y \Phi_s(\{\vec{r}_i\}; \vec{R}) = \pm \Phi_s(\{\vec{r}_i\}; \vec{R})$$

[état propre de L^z : 1 électron

$$L^z \Phi_s(\vec{r}) = m \Phi_s(\vec{r}) \qquad L^z = -i\hbar \frac{\partial}{\partial \phi}$$

$$\Phi_s(\vec{r}) = \Phi_m(\vec{r}) = \psi(r,\theta)\, e^{im\phi}$$

$$A_y \Phi_m(\vec{r}) \neq \pm \Phi_m(\vec{r})$$

$$= \Phi_{-m}(\vec{r}) \quad \text{sauf si } m=0$$]

$$A_y \left(\Phi_m \pm \Phi_{-m}\right) = \pm \left(\Phi_m \pm \Phi_{-m}\right)$$

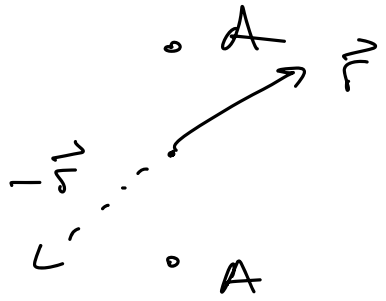
Étiquettes compatibles $\Lambda = |M|$

$\pm$ valeur propre de A_y

notation spectroscopique $\Lambda^{\pm}$

ex. Σ^+, Σ^-, Π^+, Π^- ...

3) $A \equiv B$: inversion par rapport au centre



paire :	gerade	(g)	(+)
impaire :	ungerade	(u)	(-)

notation spectroscop. : $^{2S+1}\Lambda^{\pm}_{g/u}$ (sym total)

(S)

Etat quantique des noyaux

$\mathcal{F}_s(\vec{R})$ $\qquad \mu_n = \frac{m_A m_B}{m_A + m_B}$

$$\left[-\frac{\hbar^2}{2\mu_n} \nabla^2_{\vec{R}} + \underbrace{E_s(R)}_{=} \right] \underbrace{f_s(\vec{R})}_{=} = \underbrace{E}_{=} \underbrace{f_s(\vec{R})}_{=}$$

$\vec{R} \rightarrow (R, \theta, \varphi)$ ↓

$$-\frac{\hbar^2}{2\mu_n} \nabla^2_R = -\frac{\hbar^2}{2\mu_n} \frac{1}{R^2} \frac{\partial}{\partial R}\left(R^2 \frac{\partial}{\partial R}(\cdot) \right) + \frac{\vec{N}^2}{2\mu_n R^2}$$

$\vec{N}^2 \rightarrow (\vec{R} \times \vec{P})^2$

$\vec{N}$ = moment angulaire nucléaire

$N^2 \Longrightarrow \hbar^2 N(N+1)$ $\qquad N = 0, 1, 2, \ldots$

$$f_s(\vec{R}) = \frac{\mathcal{F}^{(s)}_{vN}(R)}{R} \; U_{NM_N}(\theta, \varphi)$$

$\vec{N}^2$ $\quad$ N^2

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + \frac{\hbar^2 N(N+1)}{2\mu_n R^2} + E_s(R) \right] \mathcal{J}_{VN}^{(s)}(R)$$

$$= E_{SVN}\, \mathcal{J}_{VN}^{(s)}(R)$$

$\vec{N}$ $\longrightarrow$ $\vec{K} = \vec{N} + \vec{L}$

Mouv. orb. est
molécule

$\vec{N} = \vec{K} - \vec{L}$

$\vec{N}^2 = \vec{K}^2 - 2\vec{K}\cdot\vec{L} + \vec{L}^2$

$\vec{N} \perp$ axe moléculaire

$\vec{N}\cdot\vec{R} = 0$ $\qquad$ $\vec{N} = \vec{R} \times \vec{P}$

$\vec{L}$ est lié rigidement solidaire de $\vec{R}$

$\vec{K}\cdot\vec{L} \simeq K_R L_R = L_R^2 = \hbar^2 \Lambda^2$
$\perp \quad \perp$ $\qquad$ $=$ $\qquad$ $=$

$$\vec{N}^2 = \vec{k}^2 - 2\hbar^2\Lambda^2 + \vec{L}^2$$

propriété de l'état électronique

$$\frac{\vec{N}^2}{2\mu_n R^2} + E_s(R) = \frac{\vec{k}^2}{2\mu_n R^2} + \frac{\vec{L}^2 - 2\hbar^2\Lambda^2}{2\mu_n R^2} + E_s(R)$$

$$\tilde{E}_s(R)$$

$N \to k$

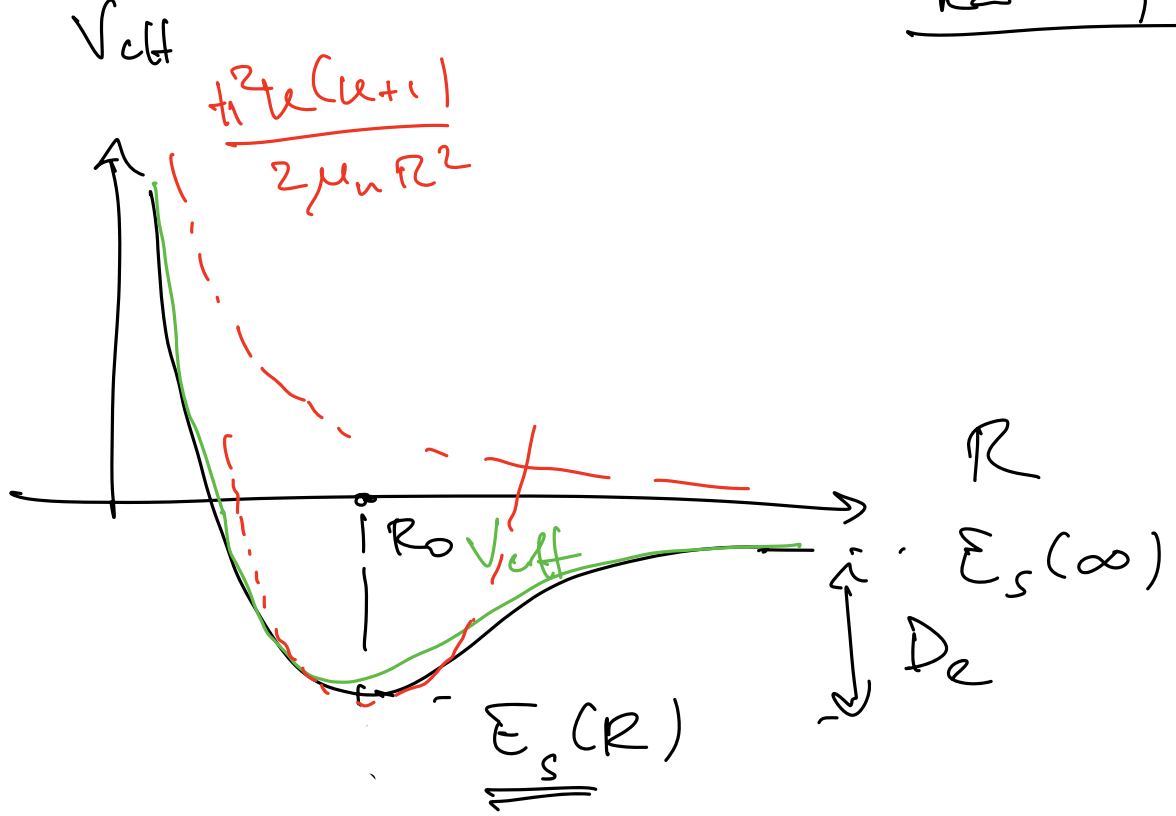
$$\left[-\frac{\hbar^2}{2\mu_n}\frac{d^2}{dR^2} + \frac{\hbar^2 k(k+1)}{2\mu_n R^2} + V_{eH}(R) + \tilde{E}_s(R) \right] \mathcal{J}^{(s)'}_{\nu k}(R) = E_{s\nu k}\, \mathcal{J}^{(s)}_{\nu k}(R)$$

$$f_s(\vec{R}) = \frac{\mathcal{J}^{(s)}_{\nu k}(R)}{R}\, \mathcal{Y}_{kM_k}(\Theta, \Phi)$$

$\vec{L}^2, L^z$

$l = 0$ $\quad Y_{l m_l}(\theta, \varphi) = Y_{l m_l}(\theta, \varphi)$

harmonique sphérique



$D_e = E_s(\infty) - E_s(R_0)$ énergie de liaison

$\sim \frac{\hbar^2}{2 m R_0^2}$

barrière centrifuge $\sim \frac{\hbar^2}{2(\mu_n) R_0^2} \sim \left(\frac{m}{m_N}\right) D_e$

$\mu_n \sim m_N$

Mouvement de vibration des noyaux

$$V_{eff}(R) \simeq \underbrace{E_s(R_0) + \frac{1}{2}\mu_n \omega_s^2 (R-R_0)^2 + O(R-R_0)^3}_{\text{potentiel harmonique}} + \underbrace{\frac{\hbar^2}{2\mu_n R_0^2} k(k+1) - \frac{\hbar^2}{\mu_n R_0^3} k(k+1)(R-R_0)}_{\text{terme centrifuge}} + \frac{3}{4}\frac{\hbar^2 k(k+1)}{R_0^4}(R-R_0)^2 + \dots$$

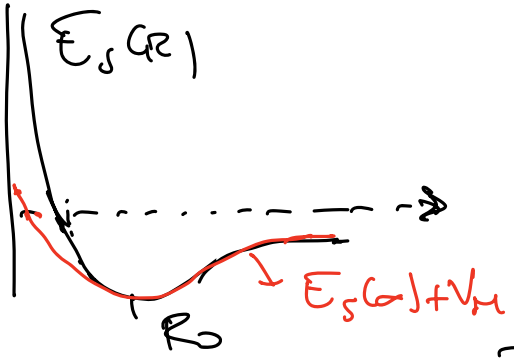
$k = 0 \rightarrow$ vibrations

$$\left[-\frac{\hbar^2}{2\mu_n}\frac{d^2}{dR^2} + \frac{1}{2}\mu_n \omega_s^2 (R-R_0)^2 + \dots \right] \mathcal{F}^{(s)}_{vk}(R) = \left(E_{svk} - E_s(R_0)\right) \mathcal{F}^{(s)}_{vk}$$

$$E_{svk} - E_s(R_0) \simeq \hbar\omega_s \left(v + \frac{1}{2}\right) \qquad v = 0, 1, 2, \dots$$

$$E_{svk} = E_s(R_0) + \hbar\omega_s \left(v + \frac{1}{2}\right) + \dots$$

corrections anharmoniques



potentiel de Morse

$$V_M(R) = D_e \left[\exp\left(-2\alpha(R-R_0)\right) - 2\exp\left(-\alpha(R-R_0)\right) \right]$$

$$E_s(R) \simeq E_s(\infty) + V_M(R) \qquad [\alpha] = \frac{1}{\ell}$$

$$V_M(R) \underset{R \simeq R_0}{\simeq} -D_e + \alpha^2 D_e (R-R_0)^2 + \dots$$

$$\frac{1}{2}\mu_M \omega_0^2$$

$$\omega_0 = \sqrt{\frac{2\alpha^2 D_e}{\mu_M}}$$

solution exacte

$$E_{sv\,u=0} = E_s(R_0) + \hbar\omega_0\left(v+\frac{1}{2}\right) - \hbar\omega_0 \beta \left(v+\frac{1}{2}\right)^2 + \dots$$

$$\beta = \frac{\hbar\omega_0}{4D_e} \sim \sqrt{\frac{m}{m_N}}$$

-> vibrations

-> mouv. électron.

Mouvement de rotation

$$E_{sol} = E_{vib} + \frac{\hbar^2}{2\mu_m R_0^2} k(k+1) + \dots$$

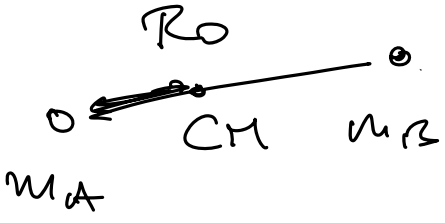
spectre rovibrationnel de la molécule

E_{vib} : $E_s(R_0) + \hbar\omega_0\left(v+\frac{1}{2}\right)$

$\frac{\hbar^2}{2\mu_m R_0^2}$: $\hat{H}_{rot} = \frac{\vec{k}^2}{2I}$

rotateur rigide de mom. d'inertie I

$$I = \mu_m R_0^2$$



$$\rightarrow I = \mu_m R_0^2$$

mom. d'inertie

$$= m_A(R_A - R_{CM})^2 + m_B(R_B - R_{CM})^2$$

Couplage entre rotations et vibrations

→ distortion centrifuge

Potentiel de Morse + $\frac{\hbar^2}{2\mu_m R^2} k(k+1)$

→ DL

$$E_s(\infty) + V_M(R) +$$

$$\simeq$$

$$\simeq E_s(R_0) + \frac{1}{2}\mu_n \omega_1(k)\left[R - R_1(k)\right]^2$$

$$\begin{cases} \omega_1(k) = \omega_0 + \dfrac{3}{4}\dfrac{\hbar^2 k(k+1)\,\omega_0}{2\alpha^2 D_e \mu_n R_0^4} \\ R_1(k) = R_0 + \dfrac{\hbar^2}{2\mu_n}\dfrac{k(k+1)}{\alpha^2 R_0^3 D_e} \end{cases}$$

Spectre rovibrationnel avec corrections anharmoniques

$$E_{vk} = E_s(R_0) + \left[\hbar\omega_0 - a\,k(k+1)\right]\left(v+\frac{1}{2}\right) - \left[\hbar\omega_0\left(v+\frac{1}{2}\right)\right]^2 + \frac{\hbar^2}{2\mu R_0^2}k(k+1) - \frac{5}{4}k^2(k+1)^2 + \cdots$$

$$a = \frac{3\hbar^3\omega_0}{4\mu_n \alpha R_0^3 D_e}\left(1 - \frac{1}{\alpha R_0}\right)$$

$$\delta = \frac{\hbar^2}{4\mu_n^2 \alpha^2 R_0^6 D_e}$$

Règles de sélection pour les transitions moléculaires

$$\Psi_{svk} = \Phi_s(\{\vec{r}_i\}, \vec{R}) \frac{f_{vk}^{(s)}(R)}{R} \mathcal{Y}_{KM_n}^{(\Theta,\Phi)}$$

$svk \longrightarrow s'v'k'$

approximation du dipole

$$\vec{D} = -e\sum_i \vec{r}_i + Z_A e \vec{R}_A + Z_B e \vec{R}_B$$

elect.

transition permise si $M = \langle svk | (\vec{D}\cdot\vec{\mathcal{E}}) | s'v'k' \rangle$

$$\int \left(\prod_i d^3r_i\right) d^3R \; \Psi^*_{svk} (\vec{D}\cdot\vec{\mathcal{E}}) \Psi_{s'v'k'} \neq 0$$

$S = S'$ et $M \neq 0$ interdit

(S) $\uparrow$ $\Lambda = 0$ $\rightarrow$ (S') $\uparrow$ $\Lambda' = 0$

$\Lambda = 0$

$$\mathcal{U}_{kM_k} = \mathcal{Y}_{kM_k}$$

$$\int (\Pi \cdot d^2\sigma) \int d^2R \, (\ldots) \; \mathcal{Y}^*_{kM_k} (\vec{D} \cdot \vec{\mathcal{E}}) \, \mathcal{Y}_{k'M_{k'}}$$

$\uparrow$

$\Delta k = \pm 1$ écart de la parité des harmoniques sphériques

$\Delta M_k = 0, \pm 1$ (dipôle de $\vec{\mathcal{E}}$)

$\vec{L} \neq 0$ ou $\vec{L}' \neq 0$

$\Delta l = 0, \pm 1$

$\Delta M_l = 0, \pm 1$