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

↝ nuclear

$$|\Psi\rangle = |\Psi_e\rangle \otimes |\Phi\rangle$$

↳ eletrónica

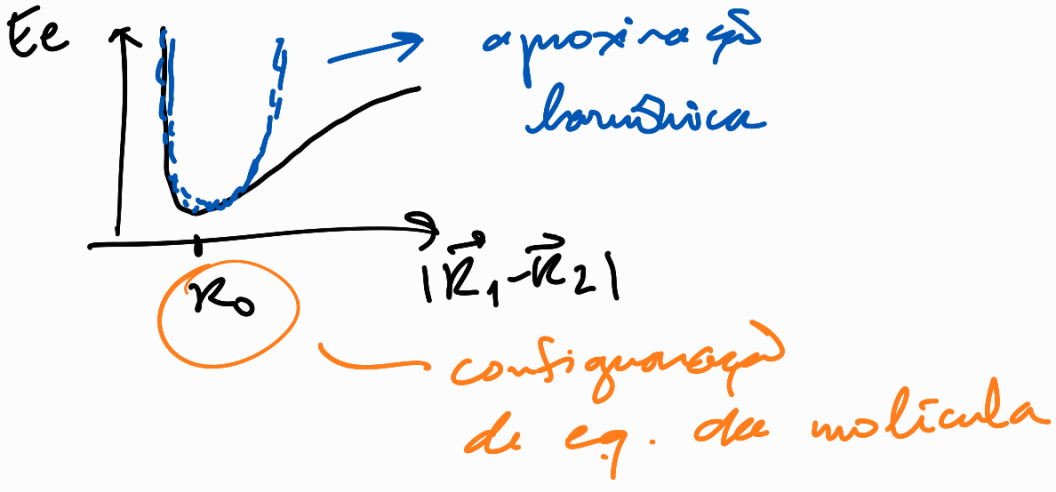
ESPECTRO DOS NÚCLEOS

$$\left[-\sum_{a=1}^{n} \frac{\nabla_a^2}{2M_a} + E_e(\{\vec{R}_a\}) \right] |\Phi\rangle = E_T |\Phi\rangle$$

energia eletrónica

energia total

* Aproximação de Born-Oppenheimer



APROXIMAÇÃO HARMÓNICA

$$E_e(\{\vec{R}_a\}) \approx E_e(\{\vec{R}_a^{(0)}\}) + \sum_a^n \frac{\partial E_e}{\partial \vec{R}_a}\Big|_{\vec{R}_a^{(0)}} \cdot (\vec{R}_a - \vec{R}_a^{(0)}) + \frac{1}{2!} \sum_a \sum_b \frac{\partial^2 E_e}{\partial \vec{R}_a \partial \vec{R}_b} (\vec{R}_a - \vec{R}_a^{(0)})(\vec{R}_b - \vec{R}_b^{(0)}) + \mathcal{O}(\vec{R}_a^3)$$

($\frac{\partial E_e}{\partial \vec{R}_a}$ → 0)

posições de equilíbrio

de modo

$$\hat{H}_n = \left[-\sum_a \frac{\nabla_a^2}{2M_a} + \underbrace{E_e(\{\vec{R}_a^{(0)}\})}_{= E_e^{(0)}} + \frac{1}{2}\sum_a\sum_b (\vec{R}_a - \vec{R}_a^{(0)}) \frac{\partial^2 E_e}{\partial \vec{R}_a \partial \vec{R}_b} (\vec{R}_b - \vec{R}_b^{(0)}) \right]$$

$$\hat{H}_n |\Xi_n\rangle = E_T |\Xi_n\rangle$$

$$\left[-\sum_a \frac{\nabla_a^2}{2M_a} + \frac{1}{2}\sum_a\sum_b \Delta\vec{R}_a \frac{\partial^2 E_e}{\partial \vec{R}_a \partial \vec{R}_b} \Delta\vec{R}_b \right] |\Xi_n\rangle = E_n |\Xi_n\rangle$$

onde $E_n = E_T - E_e^{(0)}$

$$\frac{\partial^2 E_e}{\partial \vec{R}_a \partial \vec{R}_b} = 3M \left(\begin{array}{ccc} a_1 & a_2 & a_3 \\ \vdots & \vdots & \vdots \end{array} \right) \quad (3M \times 3M)$$

$$\frac{\partial^2 E_e}{\partial a_i \partial a_j} = \left(\begin{array}{c} \\ 3M \end{array} \right)$$

$$|\Xi_n\rangle = |\Xi_T\rangle \otimes |\Xi_R\rangle \otimes |\Xi_\nu\rangle$$

TRANSLAÇÃO

$$\begin{cases} \hat{P}_{cm} |\Xi_T\rangle = \vec{P}_{cm} |\Xi_T\rangle \\ \dfrac{\hat{P}_{cm}^2}{2M_T} |\Xi_T\rangle = E_{cin} |\Xi_T\rangle \end{cases}$$

ROTAÇÃO

$$\hat{J}_z|\phi_k\rangle = m_j|\phi_k\rangle$$

$$\hat{J}^2|\phi_k\rangle = j(j+1)|\phi_k\rangle$$

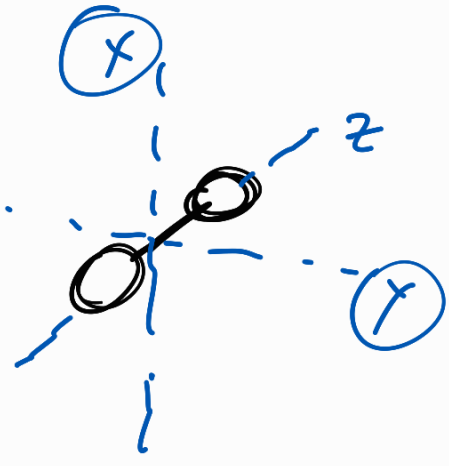
$\vec{J}$: operador de momento angular da molécula

$$\frac{\hat{J}^2}{2I_{ij}}|\phi_k\rangle = E_{rot}|\phi_k\rangle$$

Sobrarão $3N-6$ graus de liberdade

para moléculas lineares $3N-5$

moléculas planares $3N-4$

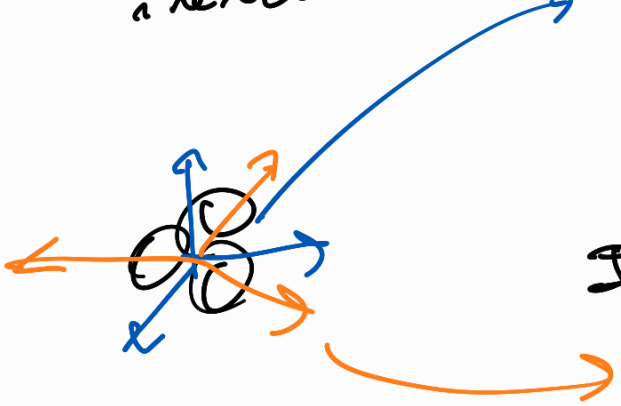


H_2: $3\times 2-5 =$ 1 modo de vib.

CH_4: $3\times 5-6 =$ 9 modos de vib.

Momento de inércia

$$I_{ij}^{(CM)} = \begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{pmatrix}$$



$$I_{ij}^{(CM)} = \begin{pmatrix} I_{xx} & 0 & 0 \\ 0 & I_{yy} & 0 \\ 0 & 0 & I_{zz} \end{pmatrix}$$

Voltando a $\dfrac{\partial^2 E_e}{\partial \vec{R}_a \partial \vec{R}_b} = \dfrac{\partial}{\partial \vec{R}_a}\left(\dfrac{\partial E_e}{\partial \vec{R}_b}\right)$

↓ calculado

Diagonalizando, temos o seguinte

$$(\vec{R}_a - \vec{R}_a^{(0)}) \frac{\partial^2 E_e}{\partial \vec{R}_a \partial \vec{R}_b} (\vec{R}_b - \vec{R}_b^{(0)}) = K_\alpha Q_\alpha^2$$

$$\vec{Q}_\alpha = \sum_a \lambda_{\alpha a} (\vec{R}_a - \vec{R}_a^{(0)})$$

↳ novas coordenadas de vibração.

$$\sum_{\alpha=1}^{3N-6} \left[-\frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2 + \frac{1}{2} K_\alpha Q_\alpha^2 \right] |E_v\rangle = E_v |E_v\rangle$$

note que $\nabla_\alpha^2 = \dfrac{\partial^2}{\partial \vec{Q}_\alpha}$

↳ Eq. de Schrodinger do oscilador harmônico com $3N-6$ coordenadas.

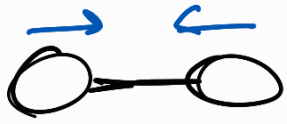
α: modos de vibração

$$E_v = \sum_{\alpha=1}^{3N-6} \hbar \omega_\alpha \left(v_\alpha + \frac{1}{2} \right)$$

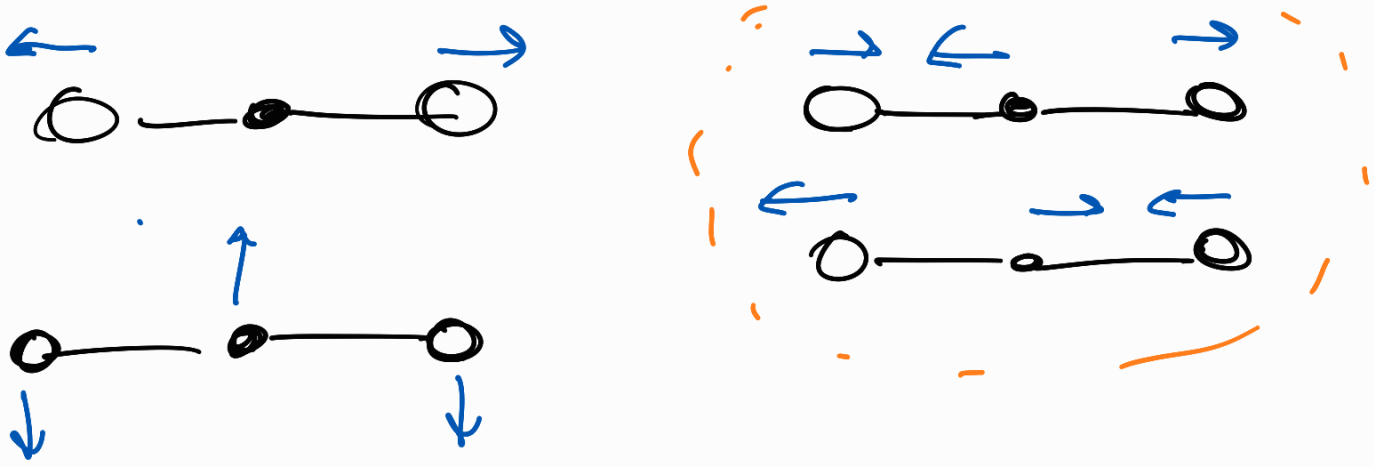
com $v_\alpha = 0, 1, 2, 3, \ldots$

$$\omega_\alpha = \sqrt{\frac{K_\alpha}{M_\alpha}}$$

Molécula de H_2:



Molécula de CO_2 ($3 \times 3 - 5 = 4$)



Molécula de H_2O ($3 \times 3 - 6 = 3$)