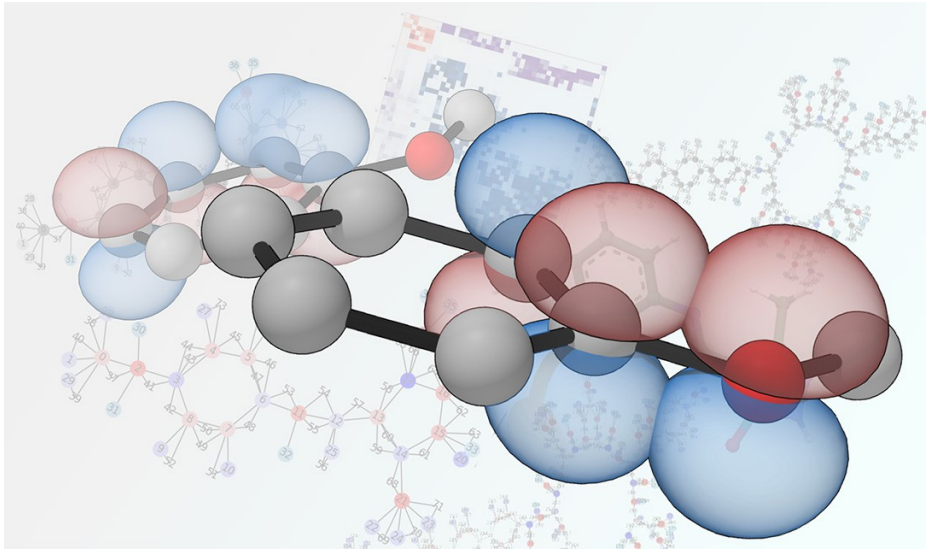
Aula 02 – Espectro Molecular



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$$i\hbar\frac{\partial}{\partial t}\left|\Psi\right\rangle = \hat{H}\left|\Psi\right\rangle$$

$$\left|\Psi\right\rangle = \left|\psi\right\rangle e^{-iEt/\hbar}$$

$$\hat{H}\left|\psi\right\rangle = E\left|\psi\right\rangle$$

Aproximação de Born-Oppenheimer

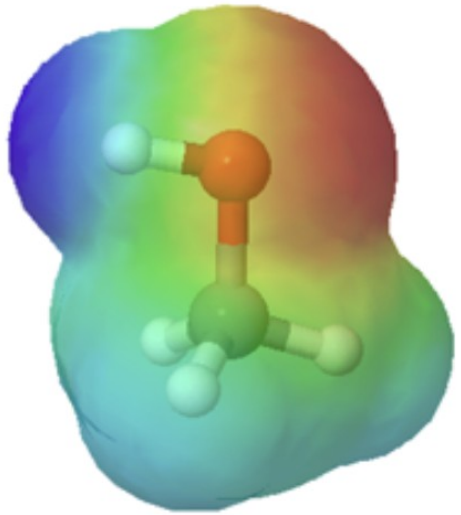
$$\Psi(\{\boldsymbol{r}_i\},\{\boldsymbol{R}_A\}) = \sum_e \Psi_e(\{\boldsymbol{r}_i\})\Phi_e(\{\boldsymbol{R}_A\})$$

- Dinâmica dos Elétrons

$$\hat{H}_e \left|\Psi_e\right\rangle = E_e \left|\Psi_e\right\rangle$$

- Dinâmica dos Núcleos Atômicos

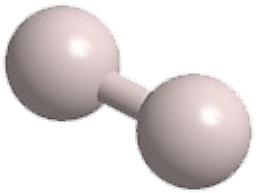
$$\left[-\frac{1}{2}\sum_{A=1}^{M}\frac{\nabla^2}{M_A} + E_e\right]\left|\Phi\right\rangle = E_T\left|\Phi\right\rangle$$

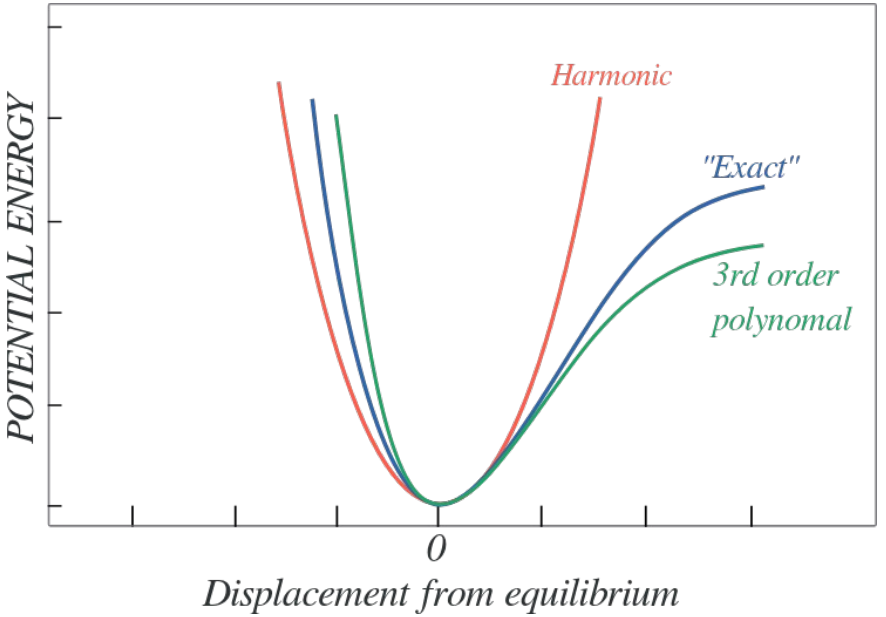


Aproximação Harmônica

$$E_e[\{\boldsymbol{R}_A\}] = E_e[\{\boldsymbol{R}_A^{(0)}\}] + \sum_{A=1}^{M} \left.\frac{\partial E_e}{\partial \boldsymbol{R}_A}\right|_{\boldsymbol{R}_A=\boldsymbol{R}_A^{(0)}} (\boldsymbol{R}_A - \boldsymbol{R}_A^{(0)}) = 0$$

$$+\frac{1}{2|} \sum_{A=1}^{M}\sum_{B=1}^{M} (\boldsymbol{R}_A - \boldsymbol{R}_A^{(0)}) \left.\frac{\partial^2 E_e}{\partial \boldsymbol{R}_A \partial \boldsymbol{R}_B}\right|_{\boldsymbol{R}_A=\boldsymbol{R}_A^{(0)},\boldsymbol{R}_B=\boldsymbol{R}_B^{(0)}} (\boldsymbol{R}_B - \boldsymbol{R}_B^{(0)})$$



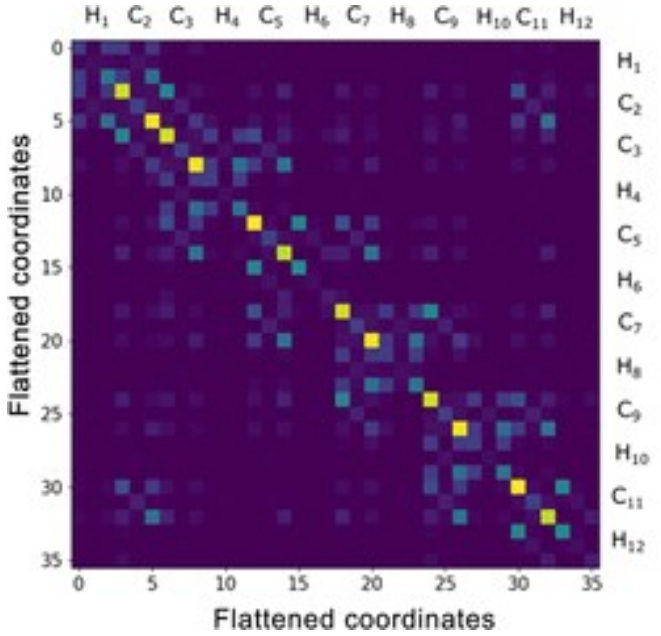


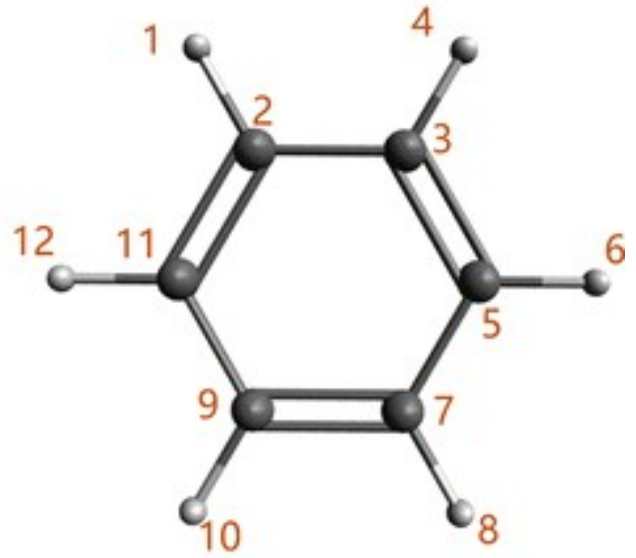
Hessiana

$$\frac{\partial^2 E_e}{\partial \boldsymbol{R}_A \partial \boldsymbol{R}_B} = \begin{pmatrix} \frac{\partial^2 E_e}{\partial \boldsymbol{R}_1 \partial \boldsymbol{R}_1} & \cdots & \frac{\partial^2 E_e}{\partial \boldsymbol{R}_1 \partial \boldsymbol{R}_M} \\ \vdots & \ddots & \vdots \\ \frac{\partial^2 E_e}{\partial \boldsymbol{R}_M \partial \boldsymbol{R}_1} & \cdots & \frac{\partial^2 E_e}{\partial \boldsymbol{R}_M \partial \boldsymbol{R}_M} \end{pmatrix}$$

3M

3M





Yang, X., Ma, H., Lu, Q., & Bian, W. (2024). Efficient method for numerical calculations of molecular vibrational frequencies by exploiting sparseness of Hessian matrix. The Journal of Physical Chemistry A, 128(15), 3024-3032.

Separando Modos

Função de Onda Nuclear

$$|\Phi\rangle = |\Phi_t\rangle \otimes |\Phi_r\rangle \otimes |\Phi_v\rangle$$

Translação

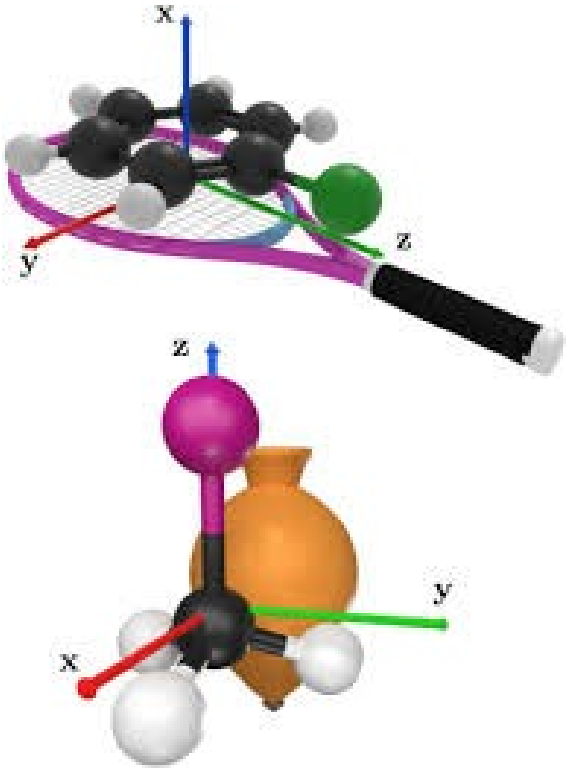
$$\hat{\boldsymbol{P}}_{cm} |\Phi_t\rangle = \boldsymbol{P}_{cm} |\Phi_t\rangle \rightarrow \frac{\hat{\boldsymbol{P}}^2_{cm}}{2M_T} |\Phi_t\rangle = E_t |\Phi_t\rangle$$

Rotação

$$\hat{J}_z |\Phi_r\rangle = m_j |\Phi_r\rangle \rightarrow$$

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

$$\frac{\hat{J}^2}{2I} |\Phi_r\rangle = E_r |\Phi_r\rangle$$

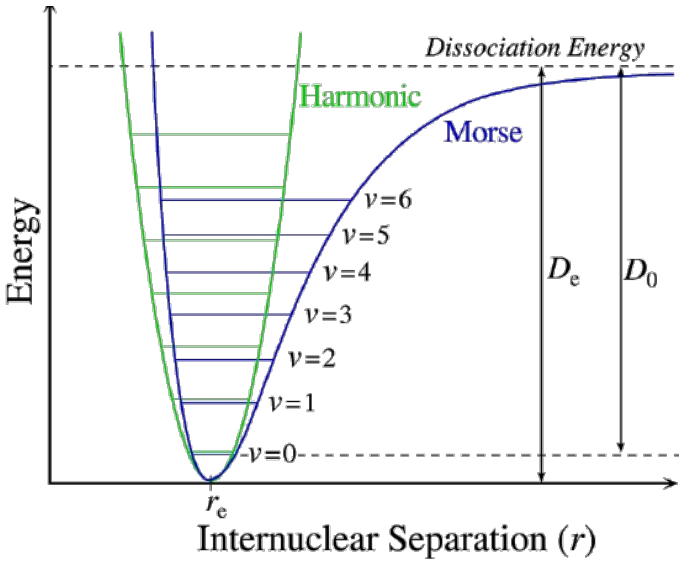


Modos Vibracionais

3 modos de translação

3 modos de rotação (2 modos para moléculas lineares e 0 modos para molécula pontual)

Restam 3M-6 modos vibracionais na Hessiana
(3M-5 para moléculas lineares e 3M-3 para molécula pontual)



- Coordenadas de vibração

$$\boldsymbol{Q}_\alpha = \sum_{A=1}^{M} \lambda_{\alpha A}(\boldsymbol{R}_A - \boldsymbol{R}_A^{(0)})$$

$$\omega_\alpha = (k_\alpha / M_\alpha)^{1/2}$$

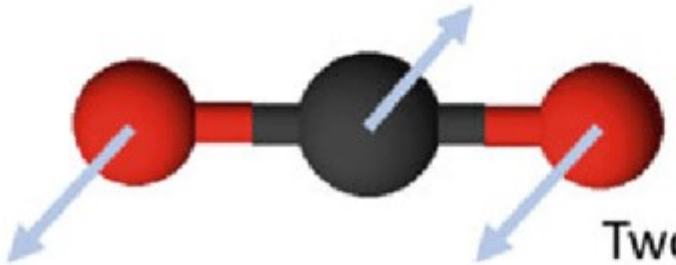
- Hamiltoniano de vibração

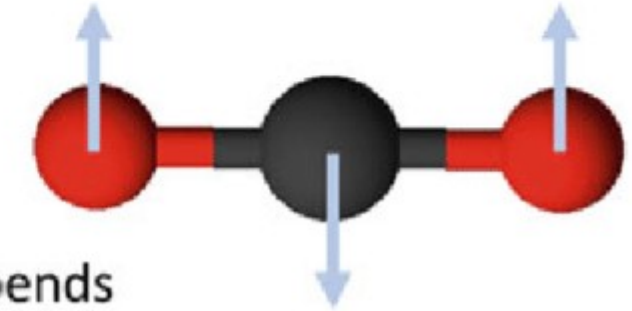
$$\left[-\frac{1}{2}\sum_{\alpha=1}^{3M-6}\frac{\nabla_\alpha^2}{M_\alpha} + \frac{1}{2}k_\alpha Q_\alpha^2\right]|\Phi_v\rangle = E_v\,|\Phi_v\rangle \longrightarrow E_v = \sum_{\alpha=1}^{3M-6}\hbar\omega_\alpha\left(n_\alpha + \frac{1}{2}\right)$$

Modos Vibracionais

Symmetric stretch
1388 cm^{-1}

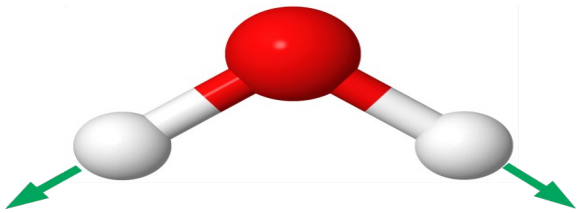
Antisymmetric stretch
2349 cm^{-1}





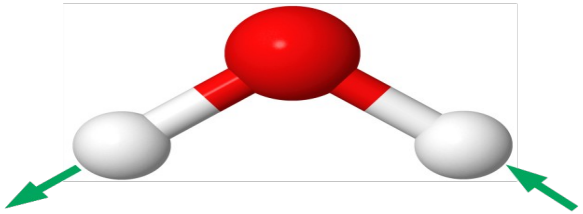
Two degenerate bends
667 cm^{-1}

Modos Vibracionais



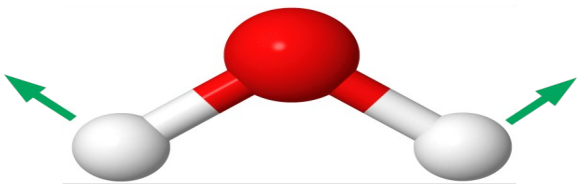
symmetric stretching

$3652\ \mathrm{cm}^{-1}$



asymmetric stretching

$3756\ \mathrm{cm}^{-1}$



bending

$1595\ \mathrm{cm}^{-1}$