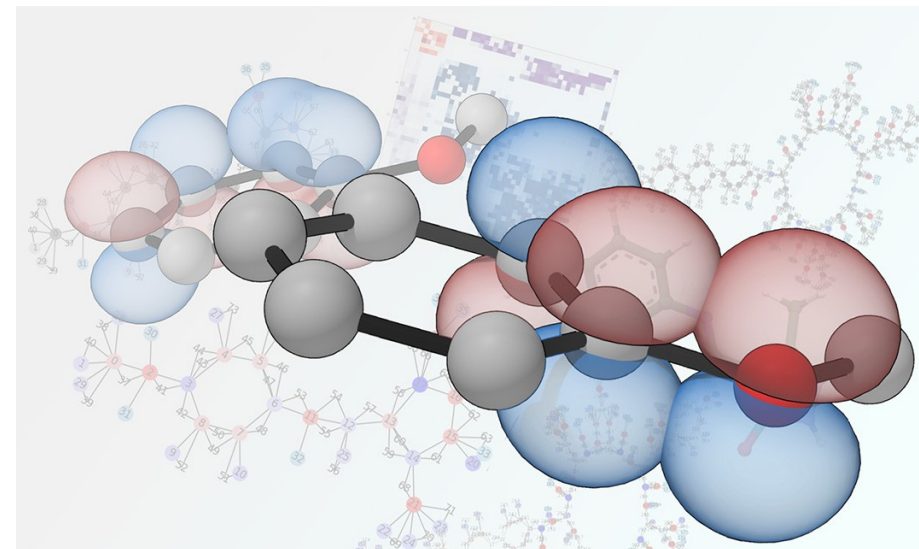


Aula 02 – Espectro Molecular

Prof. Elvis Soares
elvis@peq.coppe.ufrj.br



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

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

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

Aproximação de Born-Oppenheimer

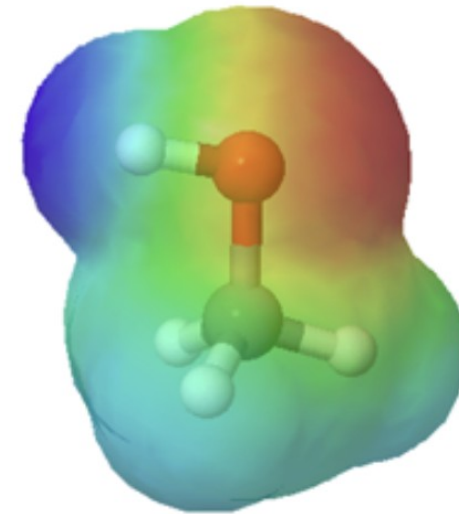
$$\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_A\}) = \sum_e \Psi_e(\{\mathbf{r}_i\}) \Phi_e(\{\mathbf{R}_A\})$$

- Dinâmica dos Elétrons

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

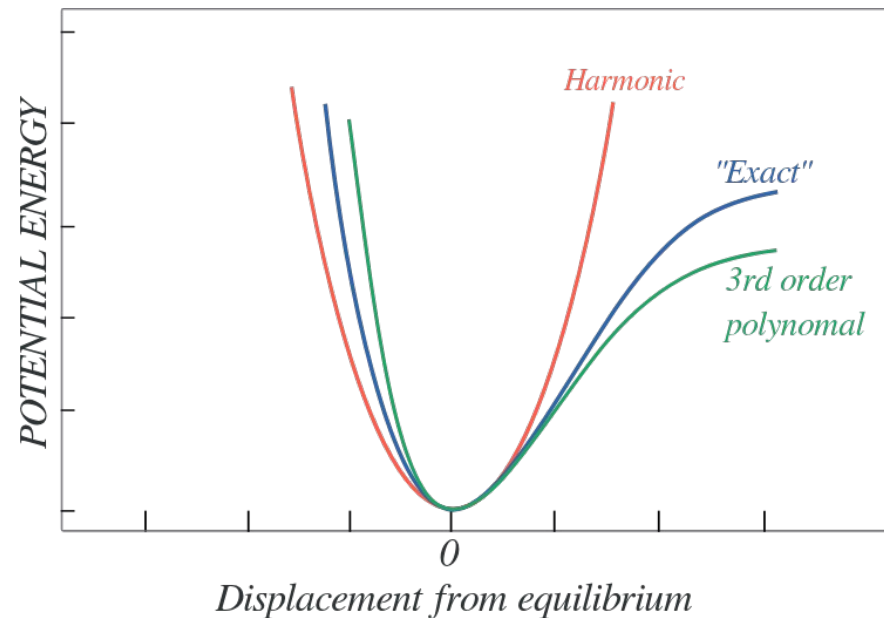
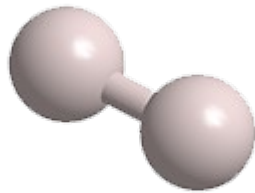
- Dinâmica dos Núcleos Atômicos

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



Aproximação Harmônica

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

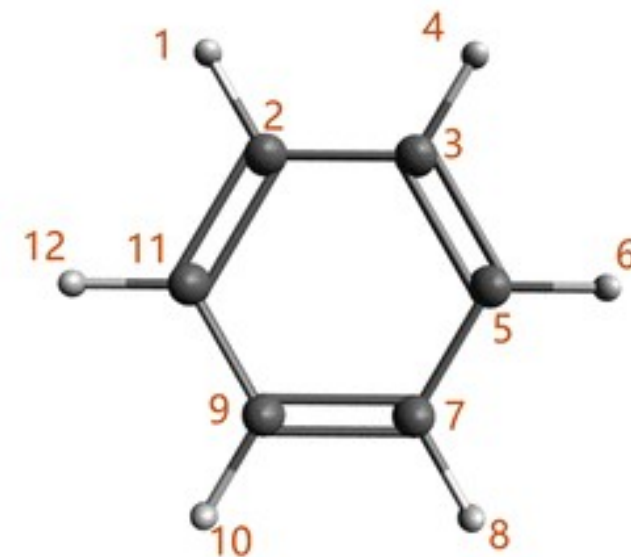
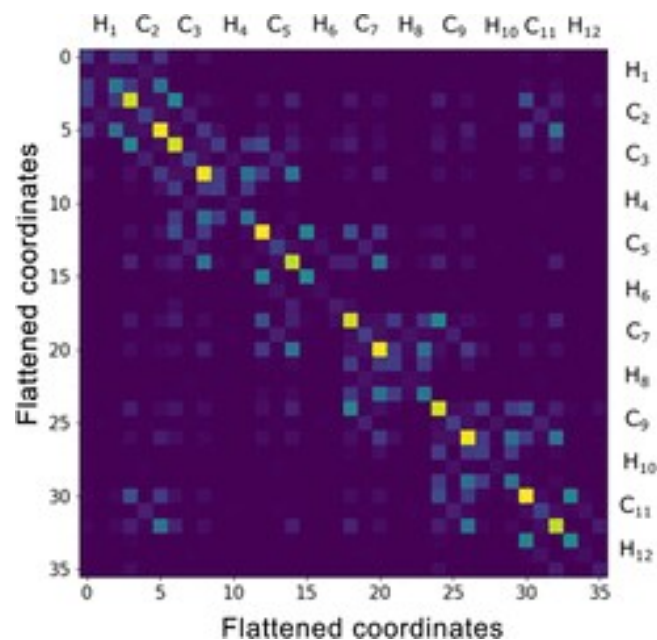


Hessiana

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

3M

3M



Separando Modos

Função de Onda Nuclear

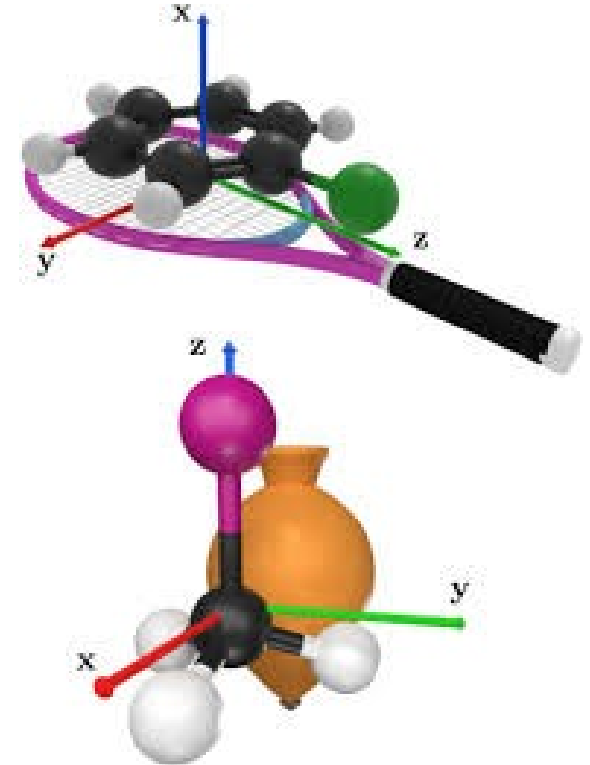
$$|\Phi\rangle = |\Phi_t\rangle \otimes |\Phi_r\rangle \otimes |\Phi_v\rangle$$

Translação

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

Rotação

$$\begin{aligned} \hat{J}_z |\Phi_r\rangle &= m_j |\Phi_r\rangle \longrightarrow \\ \hat{J}^2 |\Phi_r\rangle &= j(j+1) |\Phi_r\rangle \longrightarrow \end{aligned} \quad \frac{\hat{J}^2}{2I} |\Phi_r\rangle = E_r |\Phi_r\rangle$$



Modos Vibracionais

3 modos de translação

3 modos de rotação (2 modos para moléculas lineares e 1 modo para molécula pontual)

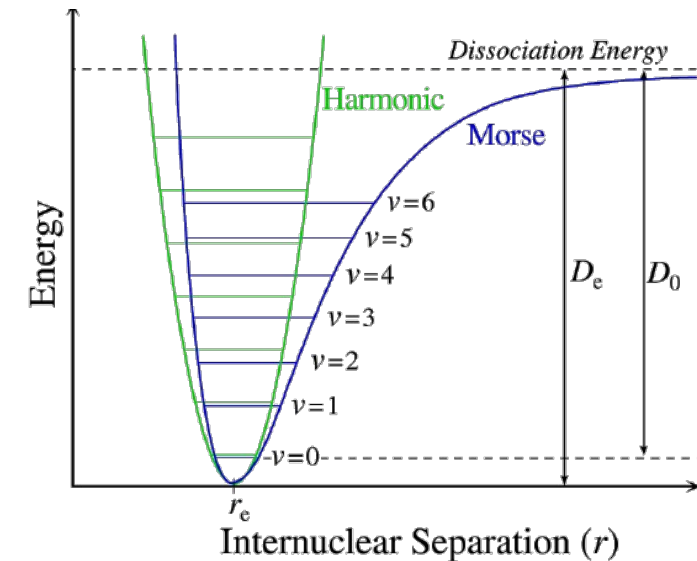
- Coordenadas de vibração

$$Q_\alpha = \sum_{A=1}^M \lambda_{\alpha A} (\mathbf{R}_A - \mathbf{R}_A^{(0)})$$

- Hamiltoniano de vibração

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

Restam 3M-6 modos vibracionais na Hessiana
(3M-5 para moléculas lineares e 3M-4 para molécula pontual)



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

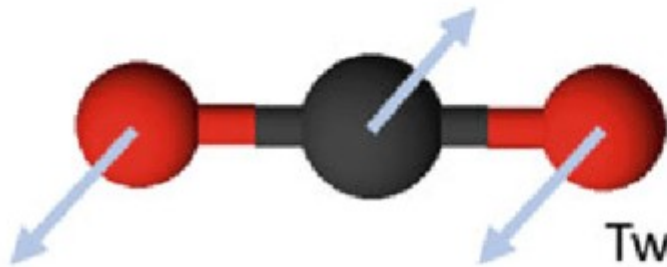
$$E_v = \sum_{\alpha=1}^{3M-6} \hbar \omega_\alpha \left(n_\alpha + \frac{1}{2} \right)$$

Modos Vibracionais

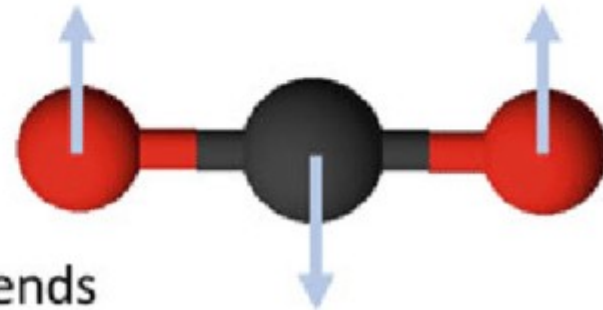
Symmetric stretch
 1388 cm^{-1}



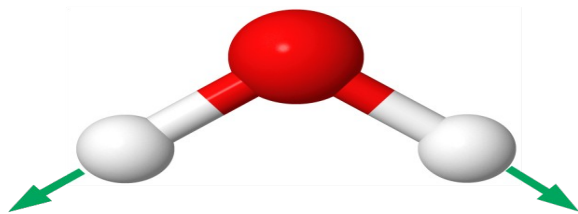
Antisymmetric stretch
 2349 cm^{-1}



Two degenerate bends
 667 cm^{-1}

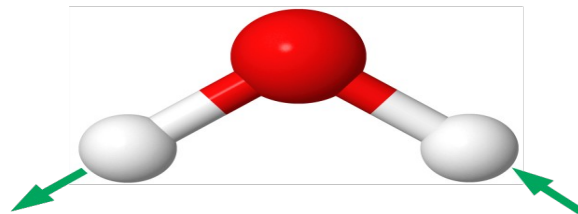


Modos Vibracionais



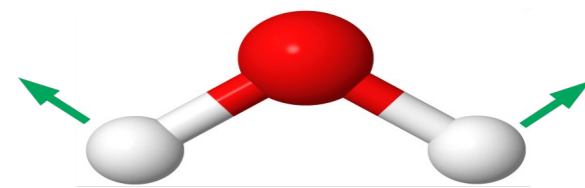
symmetric stretching

3652 cm^{-1}



asymmetric stretching

3756 cm^{-1}



bending

1595 cm^{-1}