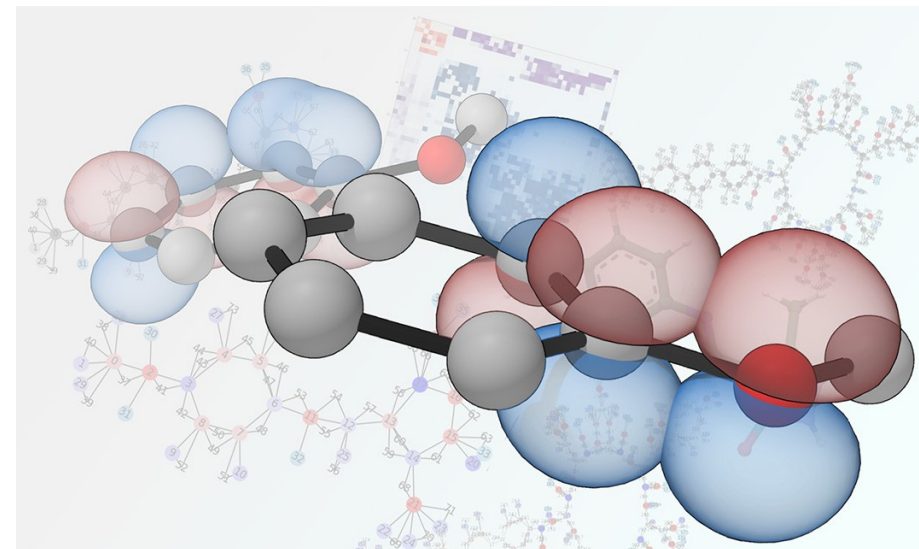# Aula 04 – Cálculos de Energia Livre

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

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

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

Qtds Termodinâmicas (Aula 03)

$$\frac{U}{N} = \boxed{\frac{3}{2}k_B T} + \boxed{\frac{d_{\mathrm{rot}}}{2}k_B T} + \boxed{\sum_{v=1}^{\mathrm{vibrações}} h\nu_v \left[\frac{1}{2} + \frac{e^{-\beta h\nu_v}}{(1 - e^{-\beta h\nu_v})}\right]} + \boxed{E_{\mathrm{DFT}}}$$

trans   rot

vib

elec

Em baixas temperaturas

$$\lim_{T \to 0} \frac{U}{N} = \boxed{\sum_{v=1}^{\mathrm{vibrações}} \frac{1}{2}h\nu_v} + \boxed{E_{\mathrm{DFT}}}$$

Energia do estado
fundamental eletrônico
da molécula

ZVPE
(**Z**ero **V**ibrational **P**oint **E**nergy)
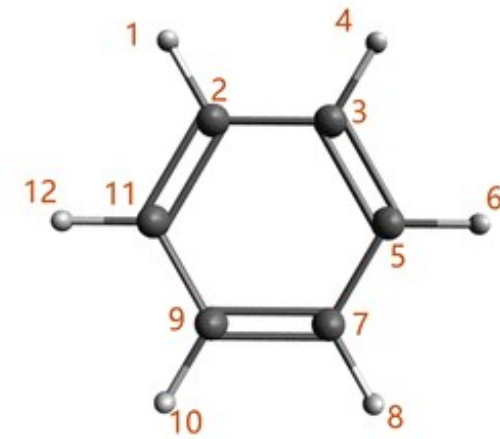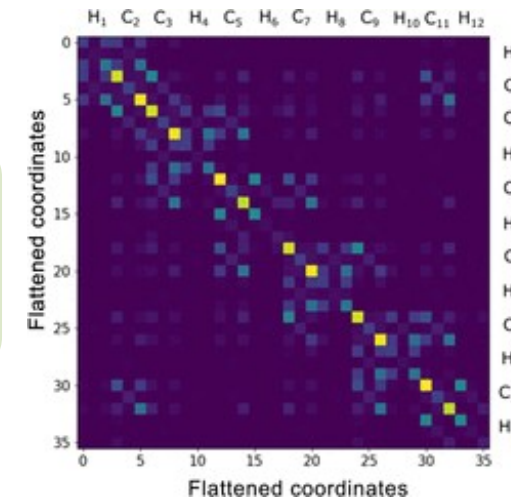
Modos vibracionais e Hessiana (Aula 02)

- 3 modos de translação

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

- 3M-6 modos de vibração (3M-5 para moléculas linerares e 0 para molécula pontual)

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

3M

3M

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

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.

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Teoria de Perturbação em DFT (DFTPT)

Funcional de Energia Livre

$$E[\rho(\boldsymbol{r})] = E_{HK}[\rho(\boldsymbol{r})] + \int V_{\text{ext}}(\boldsymbol{r})\rho(\boldsymbol{r})\mathrm{d}\boldsymbol{r}$$

Densidade eletrônica

$$\rho(\boldsymbol{r}) = \sum_{i=1}^{N} |\psi_i(\boldsymbol{r})|^2$$

Teoria de Perturbação (TP)

$$V_{\text{ext}}(\boldsymbol{r};\lambda) = V_{\text{ext}}(\boldsymbol{r}) + \lambda\frac{\partial V_{\text{ext}}(\boldsymbol{r})}{\partial \lambda} + \frac{\lambda^2}{2!}\frac{\partial^2 V_{\text{ext}}(\boldsymbol{r})}{\partial \lambda^2} + \ldots$$

Potencial Externo

$$V_{\text{ext}}(\boldsymbol{r}) = -\sum_{A=1}^{M}\frac{Z_A}{|\boldsymbol{r} - \boldsymbol{R}_A|}$$

$$\rho(\boldsymbol{r};\lambda) = \rho(\boldsymbol{r}) + \lambda\frac{\partial \rho(\boldsymbol{r})}{\partial \lambda} + \frac{\lambda^2}{2!}\frac{\partial^2 \rho(\boldsymbol{r})}{\partial \lambda^2} + \ldots$$

$$E(\lambda) = E(0) + \lambda\frac{\partial E}{\partial \lambda} + \frac{\lambda^2}{2!}\frac{\partial^2 E}{\partial \lambda^2} + \ldots$$

TP 1ª ordem

$$\frac{\partial E}{\partial \lambda} = \int \rho(\boldsymbol{r})\frac{\partial V_{\text{ext}}(\boldsymbol{r})}{\partial \lambda}\,\mathrm{d}\boldsymbol{r}$$

Teoria de Perturbação em DFT (DFTPT)

TP 2ª ordem

$$\frac{\partial^2 E}{\partial\lambda\partial\mu} = \int \boxed{\frac{\partial\rho(\boldsymbol{r})}{\partial\mu}}\frac{\partial V_{\text{ext}}(\boldsymbol{r})}{\partial\lambda}\,\mathrm{d}\boldsymbol{r} + \int \rho(\boldsymbol{r})\frac{\partial^2 V_{\text{ext}}(\boldsymbol{r})}{\partial\lambda\partial\mu}\,\mathrm{d}\boldsymbol{r}$$

2ª derivada de E depende da 1ª
derivada de ρ **(teorema 2n+1)**

$$\left[-\frac{1}{2}\nabla^2 + V_{KS}(\boldsymbol{r})\right]\psi_i(\boldsymbol{r}) = \epsilon_i\psi_i(\boldsymbol{r})$$

$$\frac{\partial}{\partial\lambda}$$

Equação de KS perturbada

$$\left[\epsilon_i - \hat{H}_{KS}(\boldsymbol{r})\right]\frac{\partial\psi_i(\boldsymbol{r})}{\partial\lambda} = \frac{\partial\hat{V}_{KS}(\boldsymbol{r})}{\partial\lambda}\psi_i(\boldsymbol{r})$$

$$\frac{\partial\rho(\boldsymbol{r})}{\partial\lambda} = \sum_{i=1}^{N}\frac{\partial\psi_i^*(\boldsymbol{r})}{\partial\lambda}\psi_i(\boldsymbol{r}) + \psi_i^*(\boldsymbol{r})\frac{\partial\psi_i(\boldsymbol{r})}{\partial\lambda}$$

Cálculo de Hessiana no VASP

Cálculo de DFTPT

- **IBRION**=5 finite differences without symmetry
- **IBRION**=6 finite differences with symmetry
- **IBRION**=7 perturbation theory without symmetry
- **IBRION**=8 perturbation theory with symmetry

Usam DFTPT

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

3M

3M
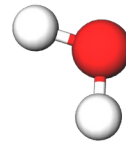
Tutorial:
- **Passo 1:** Otimização da Geometria da Molécula
- **Passo 2:** Cálculo de DFTPT para Hessiana
- **Passo 3:** Cálculo das frequências de vibração a partir da Hessiana
- **Passo 4 (opcional):** Exporta os arquivos de trajetória dos modos vibracionais

Vide **notebook_Aula04.ipynb**

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Cálculo de ZVPE

Tutorial:
- **Passo 1:** Calcula as energias vibracionais a partir das frequências de vibração
- **Passo 2:** Calcula o ZPVE

$$ZPVE = \sum_{v=1}^{\text{modos de vibração}} \frac{1}{2} h\nu_v$$

Modo de Vibração	Frequência (cm^{-1})	Energia (eV)
1		
2		
3		

Vide **notebook_Aula04.ipynb**

ZPVE =   eV

Cálculo de Qtds Termodinâmicas

$$\frac{H(T)}{N} = E_{\mathrm{DFT}} + E_{\mathrm{ZPE}} + \int_0^T \frac{C_P}{N} \, \mathrm{d}T$$

$$C_P = R + C_V$$

$$\int_0^T \frac{C_V^{\mathrm{trans}}}{N} \, \mathrm{d}T = \frac{3}{2} k_B T$$

$$\int_0^T \frac{C_V^{\mathrm{rot}}}{N} \, \mathrm{d}T = \frac{d_{\mathrm{rot}}}{2} k_B T$$

$$\int_0^T \frac{C_V^{\mathrm{vib}}}{N} \mathrm{d}T = \sum_{v=1}^{\mathrm{vibrações}} h\nu_v \frac{e^{-\beta h\nu_v}}{(1 - e^{-\beta h\nu_v})} - \sum_{v=1}^{\mathrm{vibrações}} h\nu_v$$

$\int C_V/N \, dT$	eV
trans	
rot	
vib	

H(300K) =   eV

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Cálculo de Qtds Termodinâmicas

$$G(T) = H(T) - TS$$

$$\frac{S_{\text{trans}}}{Nk_B} = \ln\left[\left(\frac{2\pi Mk_BT}{h^2}\right)^{3/2}\frac{k_BT}{P}\right] + \frac{3}{2}$$

$$\frac{S_{\text{rot}}}{Nk_B} = \ln\left[\pi^{1/2}\left(\frac{8\pi^2 k_BT(I_AI_BI_C)^{1/3}}{h^2\sigma}\right)^{3/2}\right] + \frac{d_{\text{rot}}}{2}$$

$$\frac{S_{\text{vib}}}{Nk_B} = \sum_{v=1}^{\text{vibrações}}\left[\frac{1}{T}\frac{h\nu_v e^{-\beta h\nu_v}}{(1-e^{-\beta h\nu_v})} - \ln(1-e^{-\beta h\nu_v})\right]$$

$$\frac{S_{\text{ele}}}{Nk_B} = \ln(2s+1)$$

Vide **notebook_Aula04.ipynb**

Simetria da molécula sob rotação

Depende da geometria da molécula (linear ou não-linear)

T.S	eV
trans	
rot	
vib	
ele	

G(300K, 1bar) =   eV

Point Group

Table 10.1 Rotational symmetry numbers for molecular point groups

Point Group[a]	σ
C_1	1
C_i	1
C_s	1
$C_{\infty v}$	1
$D_{\infty h}$	2
$S_n, n = 2, 4, 6, \ldots$	$n/2$
$C_n, n = 2, 3, 4, \ldots$	n
$C_{nh}, n = 2, 3, 4, \ldots$	n
$C_{nv}, n = 2, 3, 4, \ldots$	n
$D_n, n = 2, 3, 4, \ldots$	$2n$
$D_{nh}, n = 2, 3, 4, \ldots$	$2n$
$D_{nd}, n = 2, 3, 4, \ldots$	$2n$
T	12
T_d	12
O_h	24
I_h	60

[a] See Appendix B for explanations of point groups.

Table 10.1 and Appendix B of C. Cramer "Essentials of Computational Chemistry", 2nd Ed

only one rotational axis = C_2

two σ_v but no σ_h mirror planes means point group is C_{2v}

The point group of the water molecule is C_{2v}
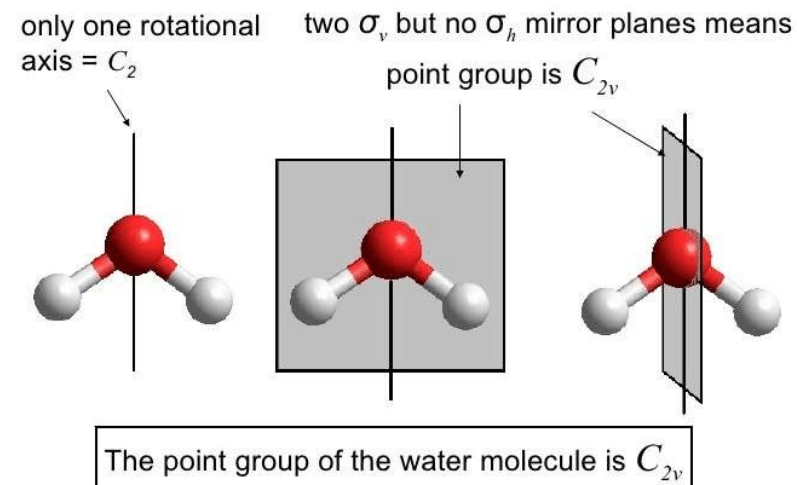
a) Carbon dioxide monomer CO_2

$D_{\infty h}$ point group

one ∞-fold improper rotation axis (reflection & rotation)

infinite vertical symmetry planes (only one shown)

infinite 2-fold proper symmetry axes (only one shown)

one ∞-fold proper rotation axis

inversion center