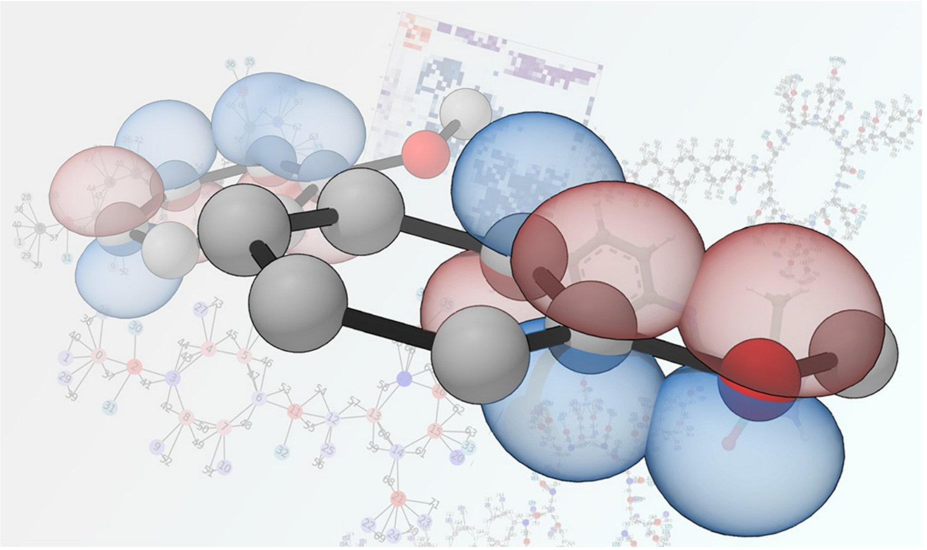
COQ878 – Química Quântica Computacional
2025/3

Aula 09 – Campo de Força Ab Initio



Ref: Cap 2 - Jensen

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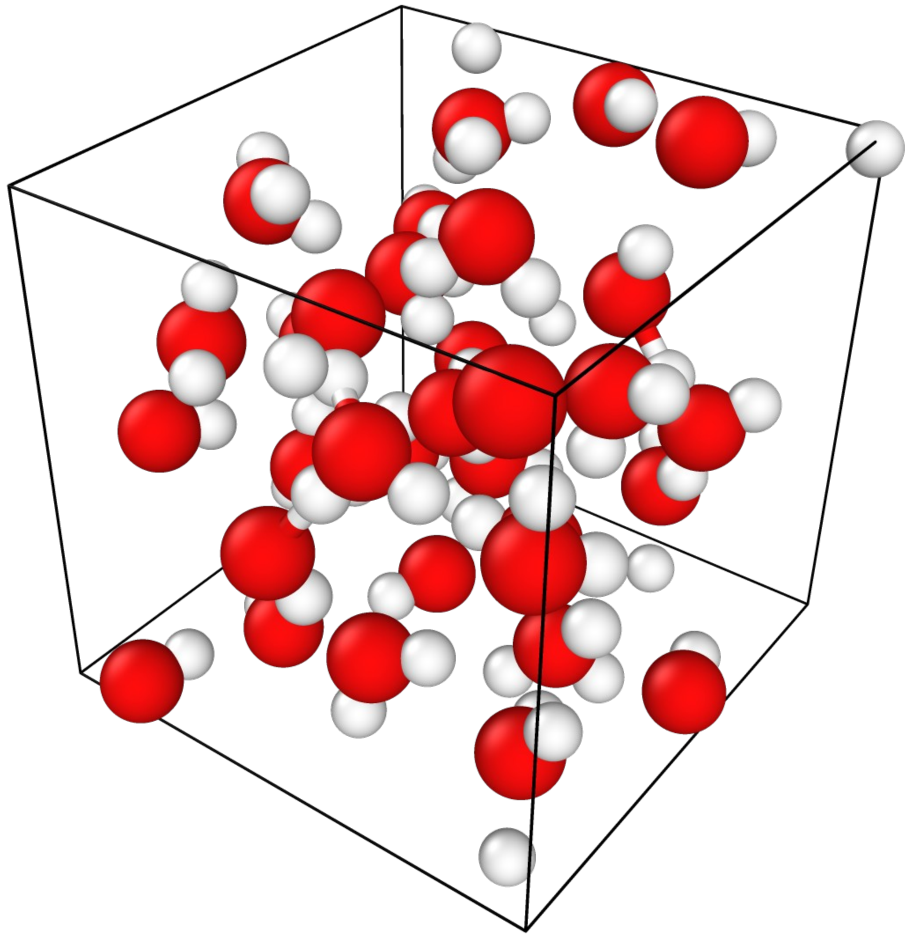
$$i\hbar\frac{\partial}{\partial t}|\Psi\rangle = \hat{H}|\Psi\rangle$$

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

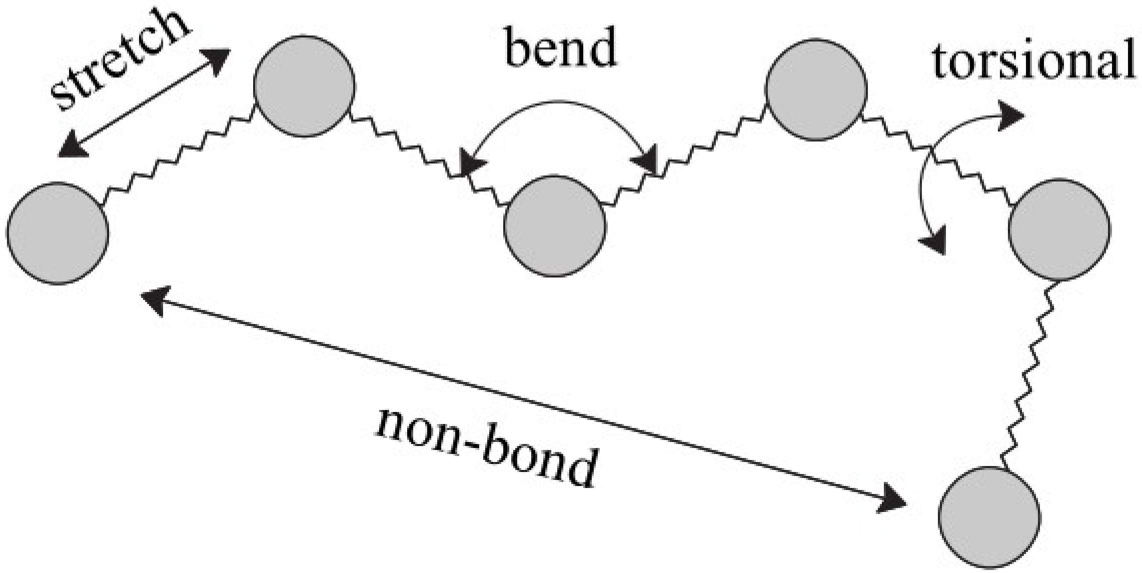
$$\hat{H}|\psi\rangle = E|\psi\rangle$$

Origem dos Campos de Força

- **Parametrizados**
  - <u>Empíricos:</u> OPLS, UFF, CHARMM, TraPPE
  - <u>Ab Initio:</u> ~COMPASS
- **Não-parametrizados**
  - Machine Learning FF



Campos de Força Parametrizáveis



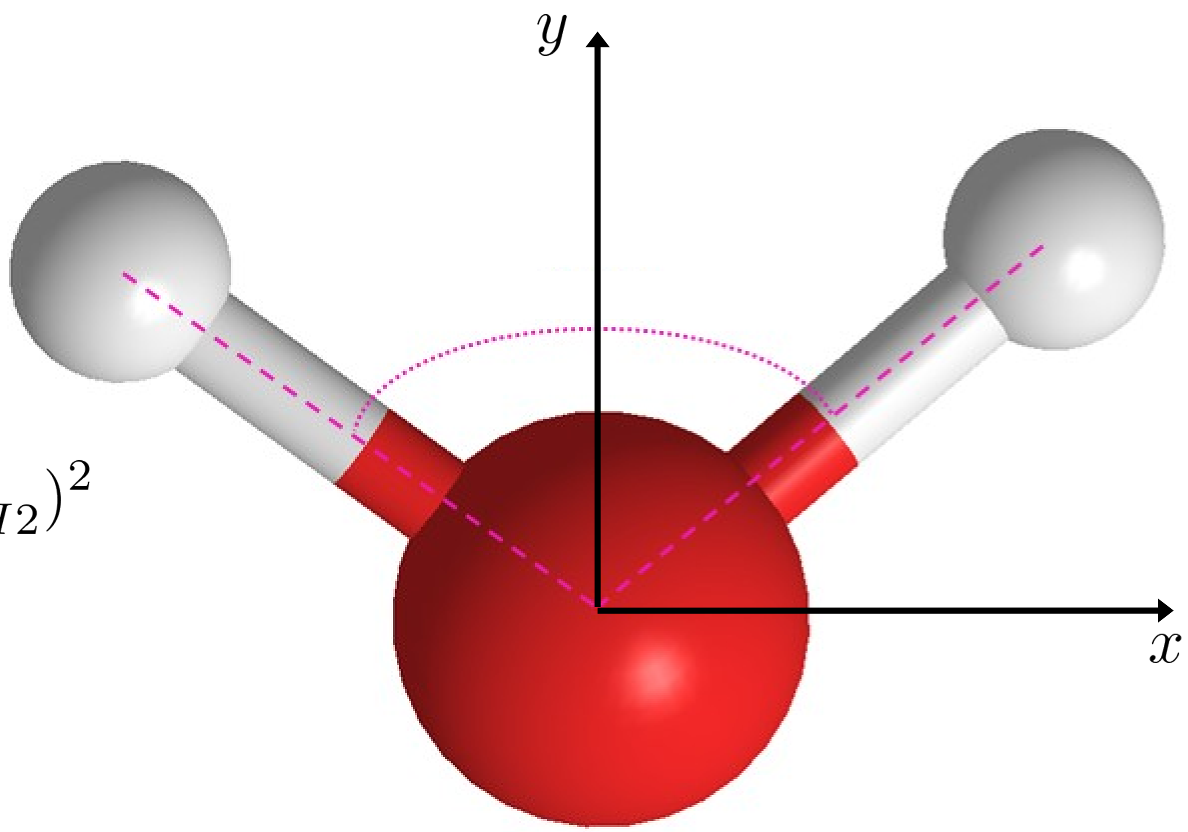
$$E_{\mathrm{FF}} = E_{\mathrm{str}} + E_{\mathrm{bend}} + E_{\mathrm{tors}} + E_{\mathrm{vdw}} + E_{\mathrm{ele}} + E_{\mathrm{cross}}$$

Graus de Liberdade

$$\mathcal{L} = \frac{M}{2}\dot{\boldsymbol{R}}_O^2 + \frac{m}{2}(\dot{\boldsymbol{R}}_{H1}^2 + \dot{\boldsymbol{R}}_{H2}^2)$$

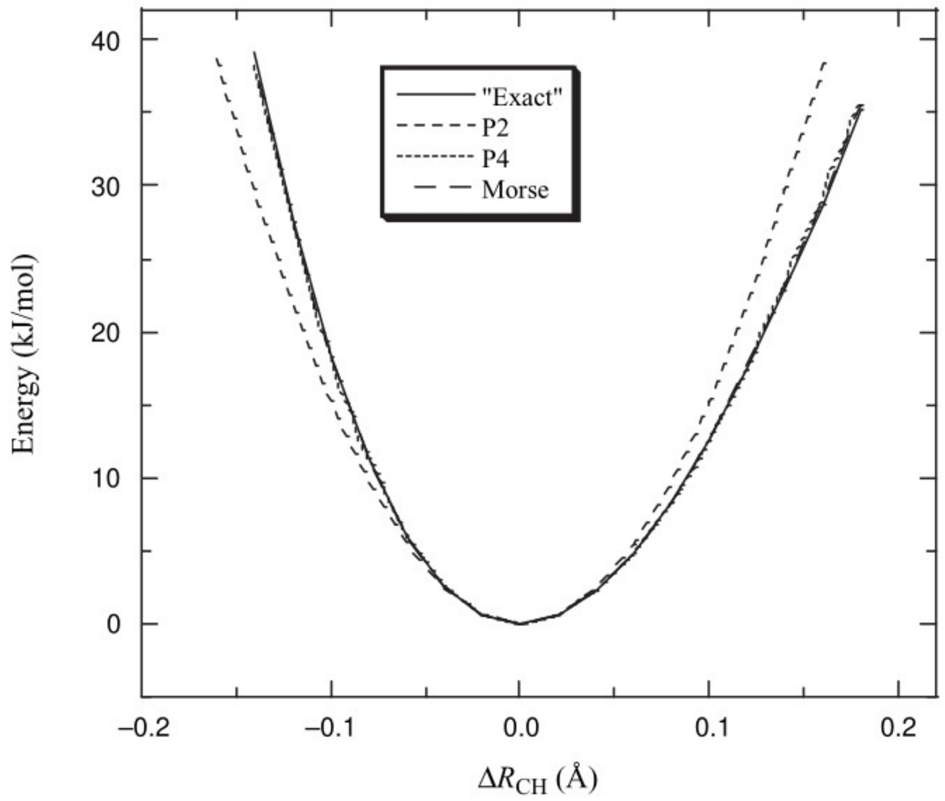
$$+\frac{k}{2}(\boldsymbol{R}_{OH1} - \boldsymbol{R}_{OH1}^{(0)})^2 + \frac{k}{2}(\boldsymbol{R}_{OH2} - \boldsymbol{R}_{OH2}^{(0)})^2$$

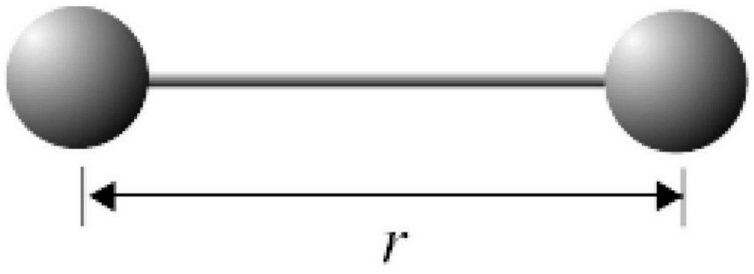
$$+\frac{k'}{2}(\boldsymbol{R}_{H1H2} - \boldsymbol{R}_{H1H2}^{(0)})^2$$



Energia de alongamento da ligação

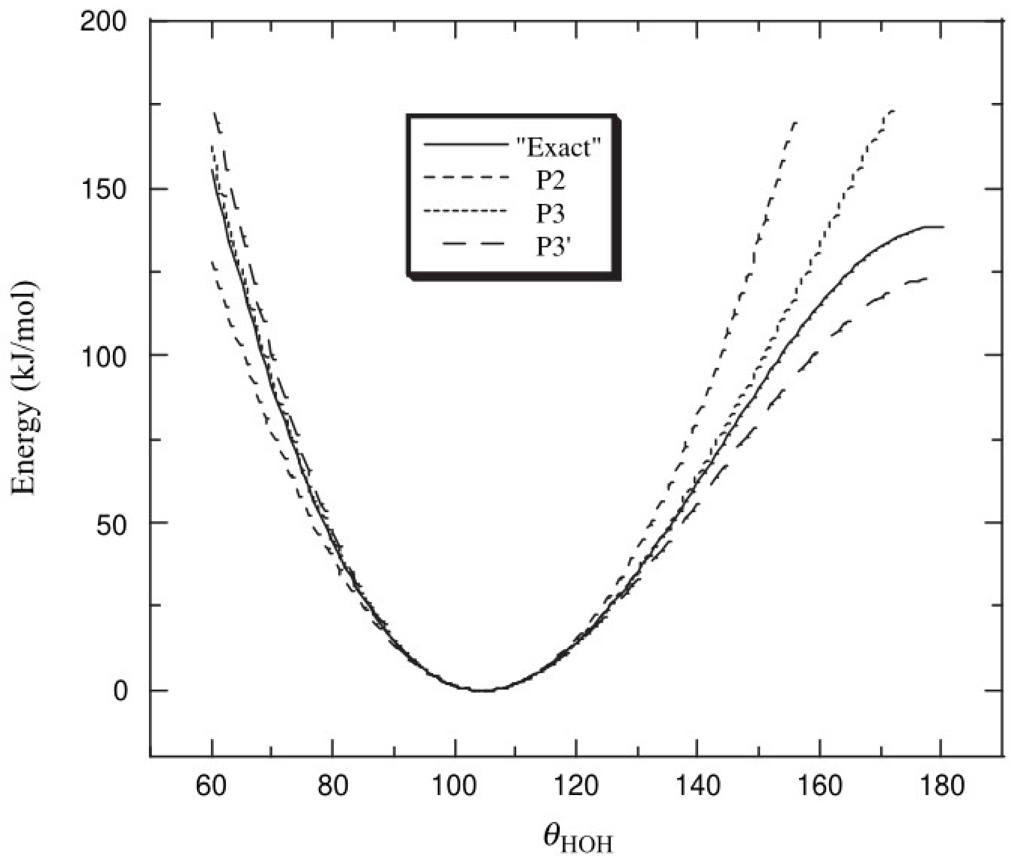
$$E_{\mathrm{str}}(R_{AB}) = E(R_{AB}^{(0)}) + \frac{\partial E}{\partial R_{AB}}(R_{AB} - R_{AB}^{(0)}) + \frac{1}{2}\frac{\partial^2 E}{\partial R_{AB}^2}(R_{AB} - R_{AB}^{(0)})^2 + \ldots$$

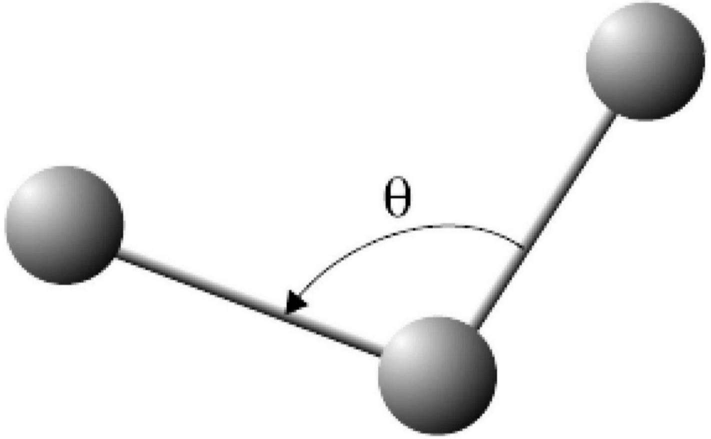




Energia de ângulo de ligação

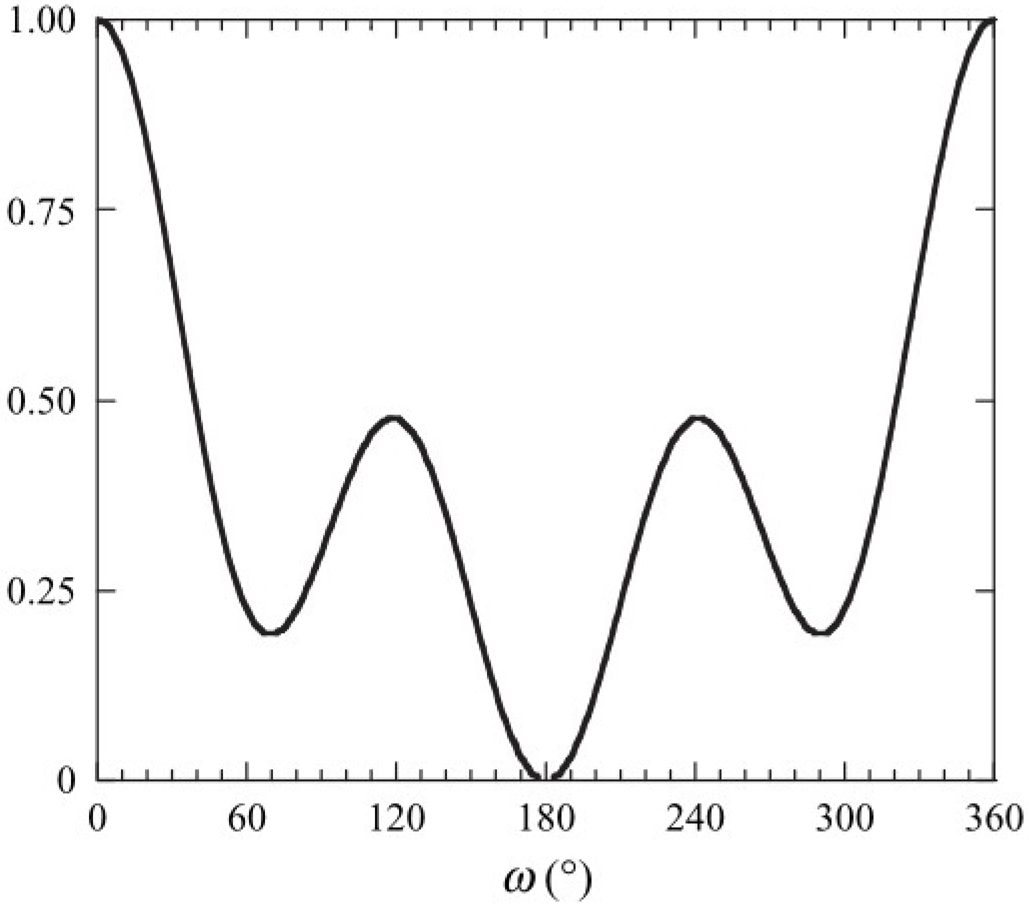
$$E_{\text{bend}}(\theta_{ABC}) = E(\theta_{ABC}^{(0)}) + \overbrace{\frac{\partial E}{\partial \theta_{ABC}}}^{=\,0}(\theta_{ABC} - \theta_{ABC}^{(0)}) + \frac{1}{2}\frac{\partial^2 E}{\partial \theta_{ABC}^2}(\theta_{ABC} - \theta_{ABC}^{(0)})^2 + \ldots$$

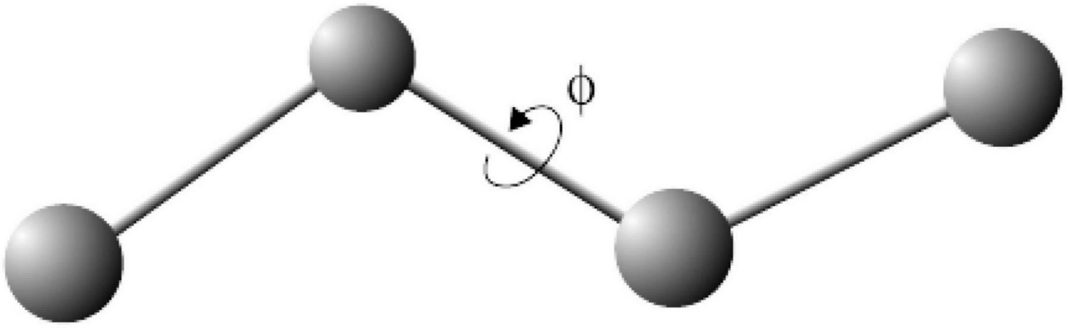




Energia de torção de ligação

$$E_{\text{tors}}(\phi_{ABCD}) = \frac{1}{2}k_1(1 - \cos(\phi_{ABCD})) + \frac{1}{2}k_2(1 - \cos(2\phi_{ABCD})) + \frac{1}{2}(1 - k_3\cos(3\phi_{ABCD}))$$

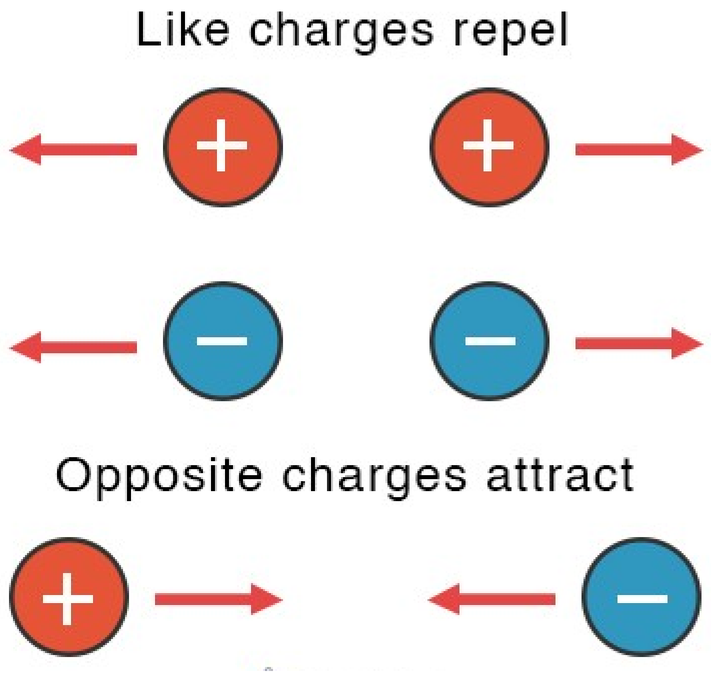




Energia eletrostática

$$E_{\mathrm{ele}}(R_{AB}) = \frac{Q_A Q_B}{4\pi\epsilon R_{AB}}$$

- Cargas obtidas a partir da superfície de potencial eletrostático;
- **Origem de interações intermoleculares!**



Interação Intermolecular

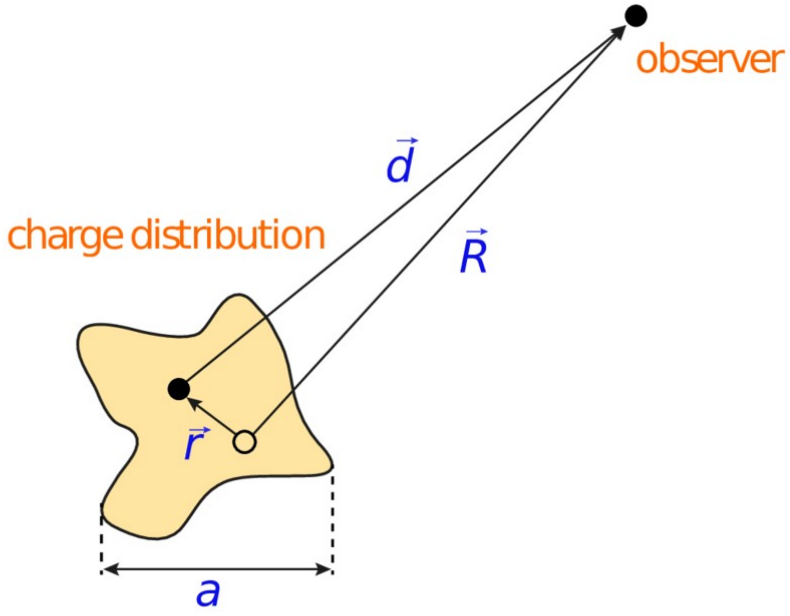
Interação eletrostática entre duas moléculas

$$E_{\text{ele}} = \sum_A \sum_B \frac{Q_A Q_B}{(4\pi\epsilon)|\boldsymbol{R}_B - \boldsymbol{R}_A|}$$

Expansão em multipólos do potencial eletrostático produzido pela molécula A

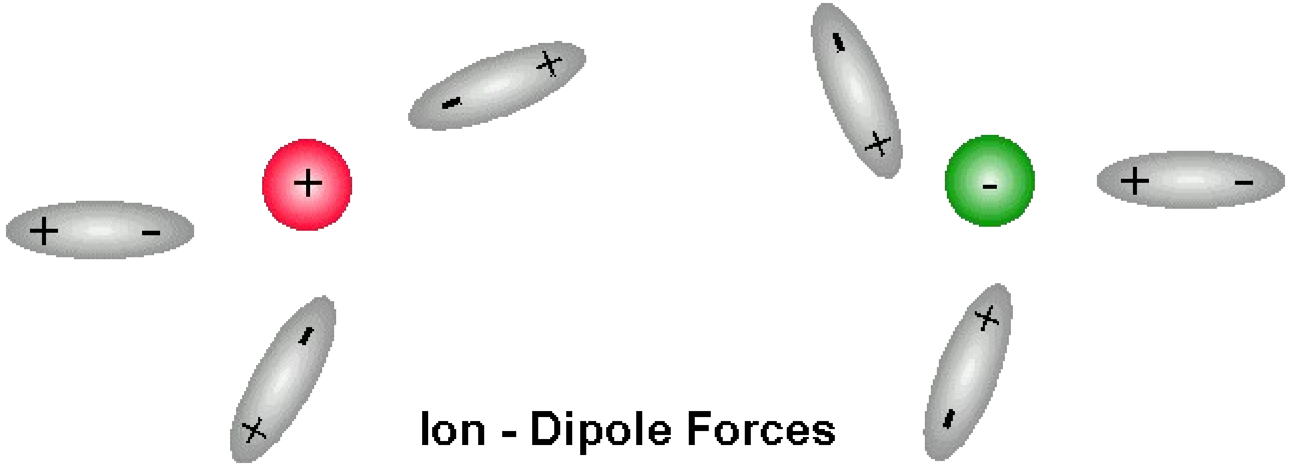
$$V(\boldsymbol{R}) = \sum_A \frac{Q_A}{(4\pi\epsilon)|\boldsymbol{R} - \boldsymbol{R}_A|}$$

$$= \frac{Q}{(4\pi\epsilon)R} + \frac{\boldsymbol{\mu}\cdot\hat{\boldsymbol{R}}}{(4\pi\epsilon)R^2} + \frac{1}{2}\frac{\hat{\boldsymbol{R}}\cdot\boldsymbol{\Theta}\cdot\hat{\boldsymbol{R}}}{(4\pi\epsilon)R^4} + \dots$$



Interação Carga- Dipólo

$$E_{\mathrm{ele}}(R_{AB},\theta) = -\frac{Q_A\mu_B\cos\theta}{4\pi\epsilon R_{AB}^2}$$



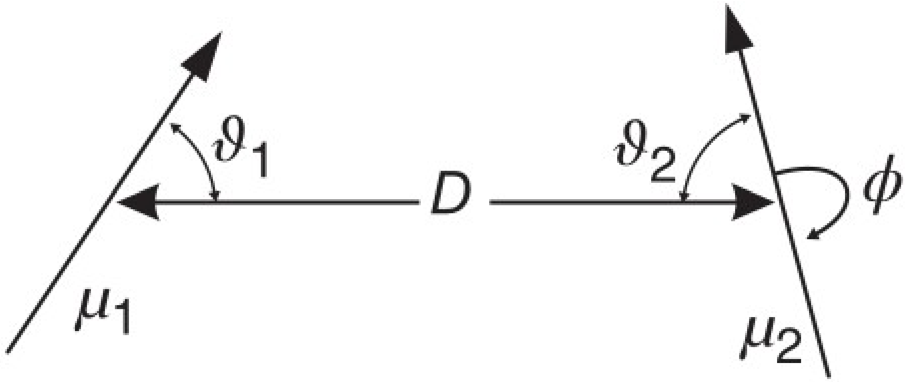
Média de orientações do dipolos

$$\langle E_{\mathrm{ele}}(R_{AB})\rangle = \frac{1}{Z}\int_0^{\pi} E_{\mathrm{ele}}(R_{AB},\theta)e^{-E_{\mathrm{ele}}(R_{AB},\theta)/k_BT}\sin\theta\ \mathrm{d}\theta$$

$$\langle E_{\mathrm{ele}}(R_{AB})\rangle = -\frac{Q_A^2\mu_B^2}{6(4\pi\epsilon)^2k_BTR_{AB}^4}$$

Interação Dipólo – Dipólo

$$E_{\text{ele}}(R_{AB},\theta_A,\theta_B,\phi) = \frac{\mu_A\mu_B}{(4\pi\epsilon)^2 R_{AB}^3}(2\cos\theta_A\cos\theta_B - \sin\theta_A\sin\theta_B\cos\phi)$$



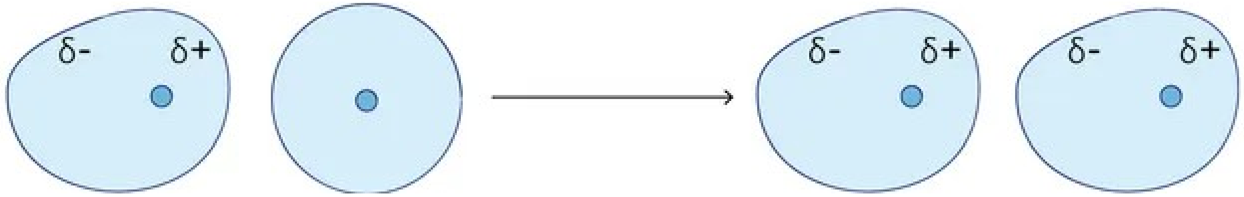
Média de orientações do dipolos

$$\langle E_{\text{ele}}(R_{AB})\rangle = \frac{1}{Z}\int E_{\text{ele}}(R_{AB},\theta)e^{-E_{\text{ele}}(R_{AB},\theta)/k_BT}\mathrm{d}\Omega$$

$$\langle E_{\text{ele}}(R_{AB})\rangle = -\frac{\mu_A^2\mu_B^2}{3(4\pi\epsilon)^2 k_B T R_{AB}^6} = -\frac{C_{\text{orient}}}{R_{AB}^6}$$

Interação Dipólo – Dipólo Induzido

$$\boldsymbol{\mu}_{\text{ind}} = \alpha \boldsymbol{E}$$



$$E_{\text{ele}}(R_{AB}, \theta) = \frac{\mu_A^2 \alpha}{2(4\pi\epsilon)^2 R_{AB}^6}(1 + 3\cos^2\theta)$$

Média de orientações do dipolos

$$\langle E_{\text{ele}}(R_{AB}) \rangle = \frac{1}{Z} \int E_{\text{ele}}(R_{AB}, \theta) e^{-E_{\text{ele}}(R_{AB},\theta)/k_B T} \mathrm{d}\Omega$$

$$\langle E_{\text{ele}}(R_{AB}) \rangle = -\frac{\mu_A^2 \alpha}{(4\pi\epsilon)^2 R_{AB}^6} = -\frac{C_{\text{ind}}}{R_{AB}^6}$$

Energia de van der Waals

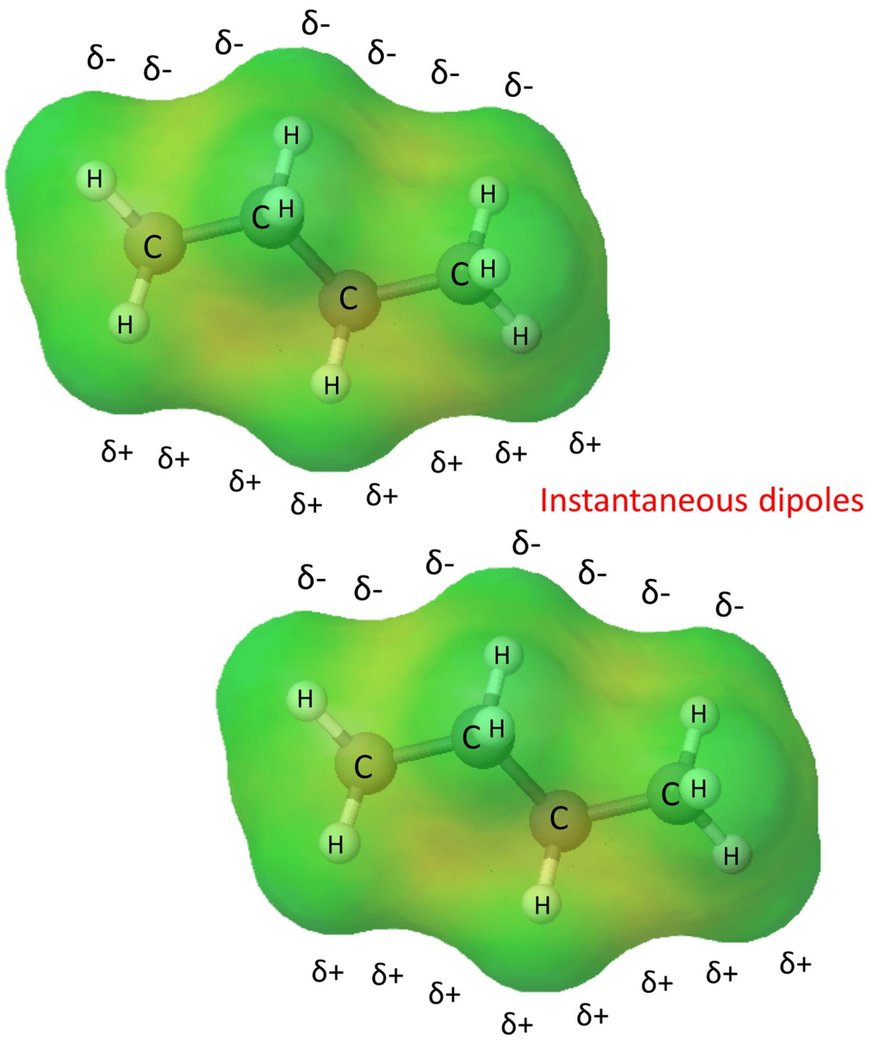
Interação de London – dipólo induzido – dipólo induzido

$$\langle E_{\text{ele}}(R_{AB})\rangle = -\frac{3}{2}\frac{\alpha_A\alpha_B}{(4\pi\epsilon)^2 R_{AB}^6}\frac{h\nu_A\nu_B}{\nu_A+\nu_B} = -\frac{C_{\text{disp}}}{R_{AB}^6}$$

$$C_{AB} = C_{\text{orien}} + C_{\text{ind}} + C_{\text{vdw}}$$

Interação de van der Waals

$$E_{\text{vdw}}(R_{AB}) = E_{\text{rep}}(R_{AB}) - \frac{C_{AB}}{R_{AB}^6}$$



Procedimento do COMPASS