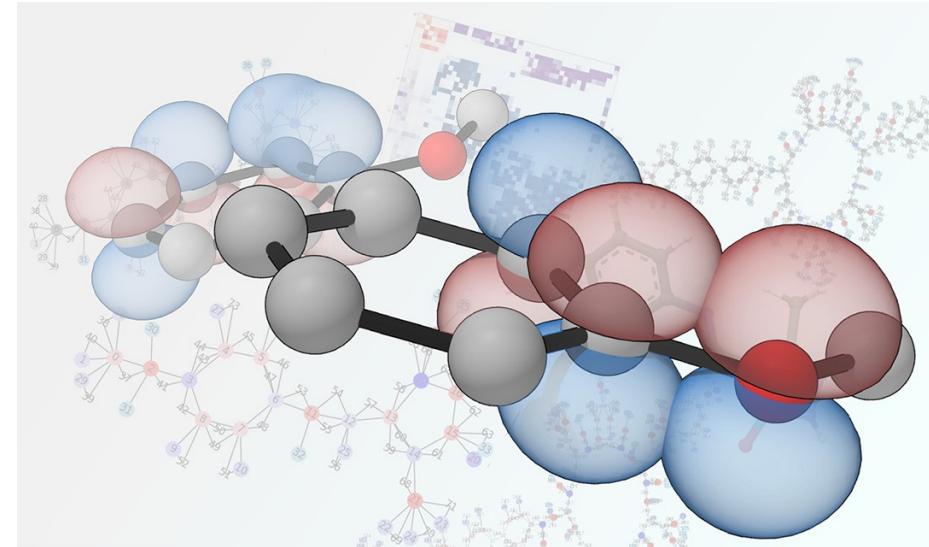


Aula 09 – Campo de Força Ab Initio

Ref: Cap 2 - Jensen

Prof. Elvis Soares
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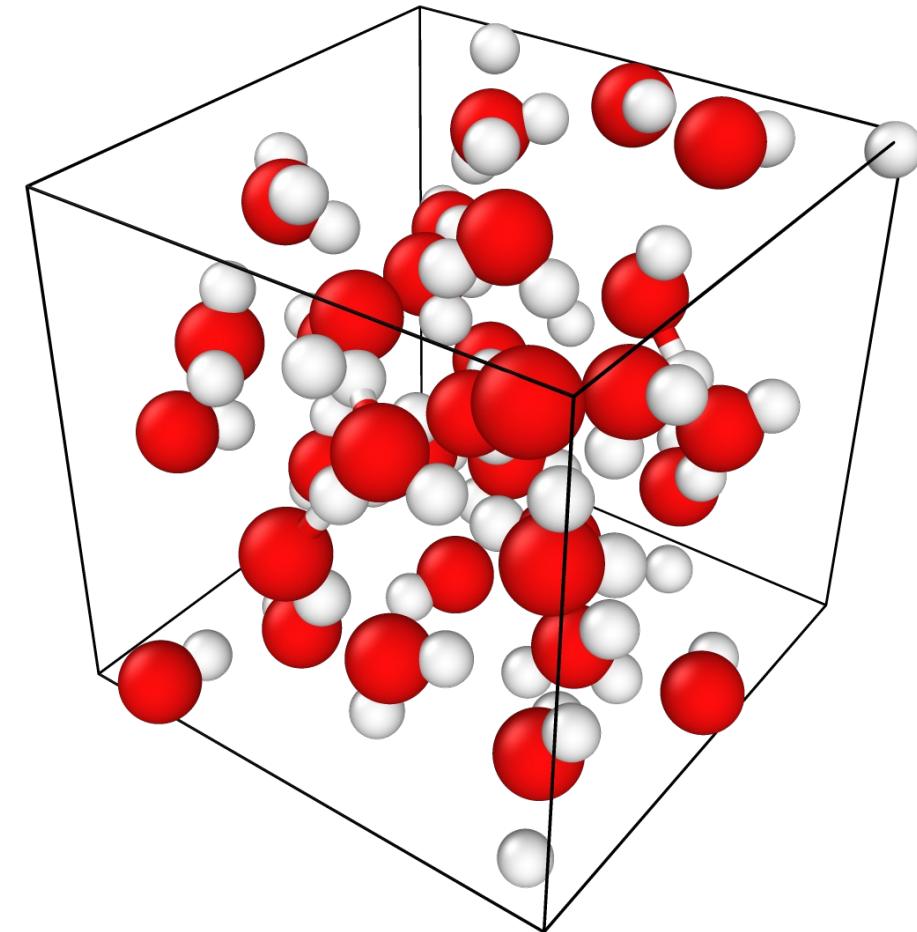


$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle = \hat{H} |\Psi\rangle$$

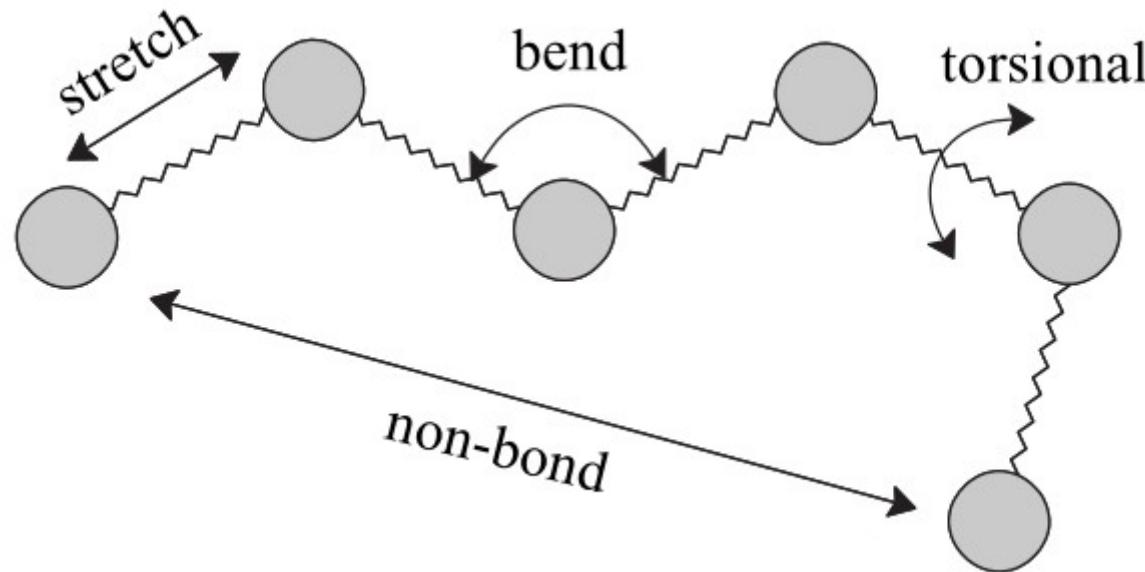
$$|\Psi\rangle = |\psi\rangle e^{-iEt/\hbar}$$
$$\hat{H} |\psi\rangle = E |\psi\rangle$$

Origem dos Campos de Força

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



Campos de Força Parametrizáveis



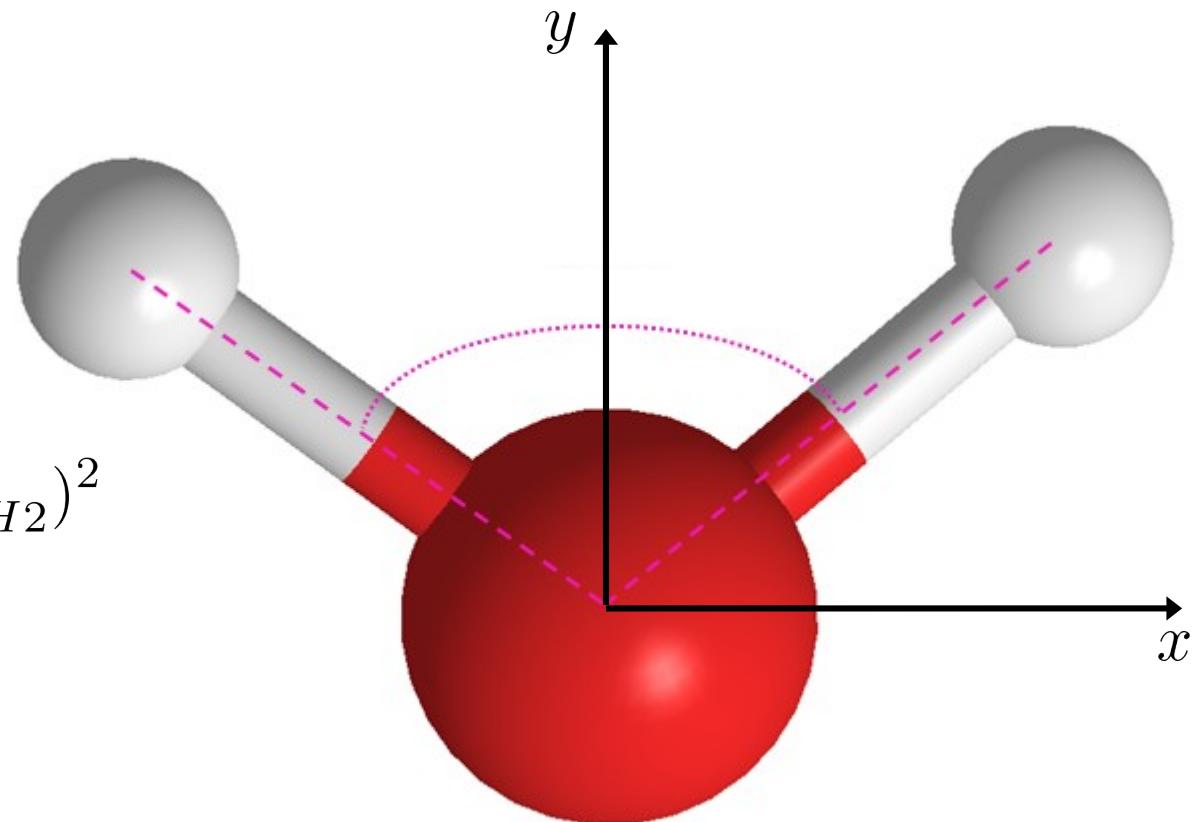
$$E_{\text{FF}} = E_{\text{str}} + E_{\text{bend}} + E_{\text{tors}} + E_{\text{vdw}} + E_{\text{ele}} + E_{\text{cross}}$$

Graus de Liberdade

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

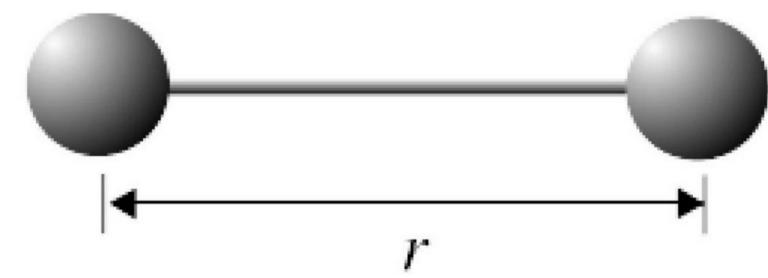
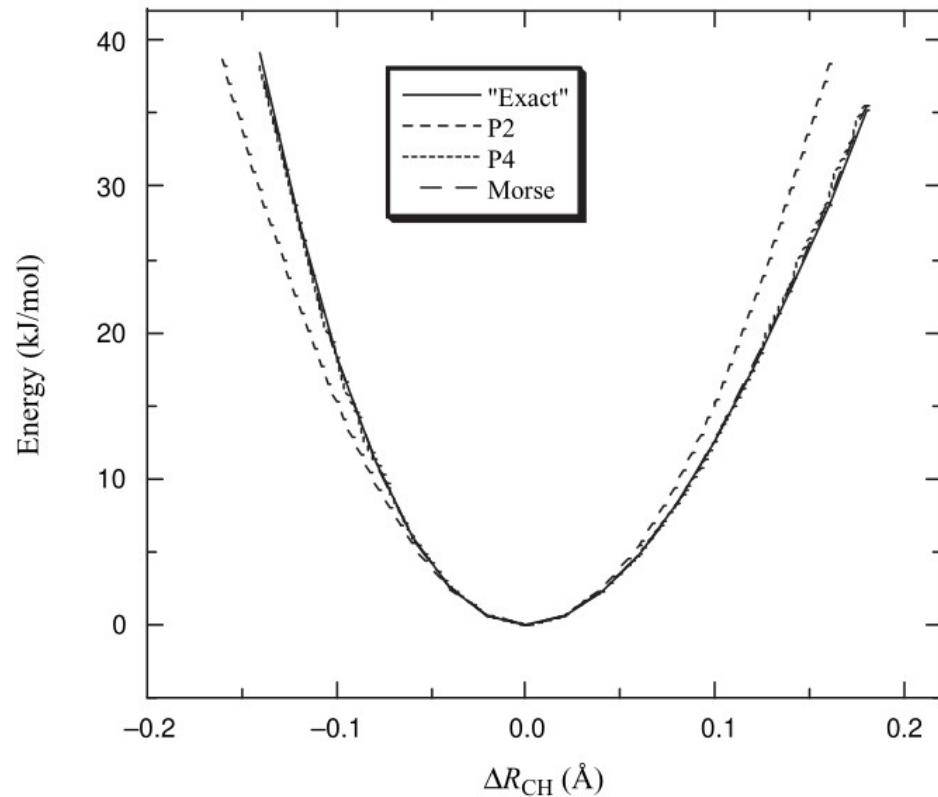
$$+ \frac{k}{2} (\mathbf{R}_{OH1} - \mathbf{R}_{OH1}^{(0)})^2 + \frac{k}{2} (\mathbf{R}_{OH2} - \mathbf{R}_{OH2}^{(0)})^2$$

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



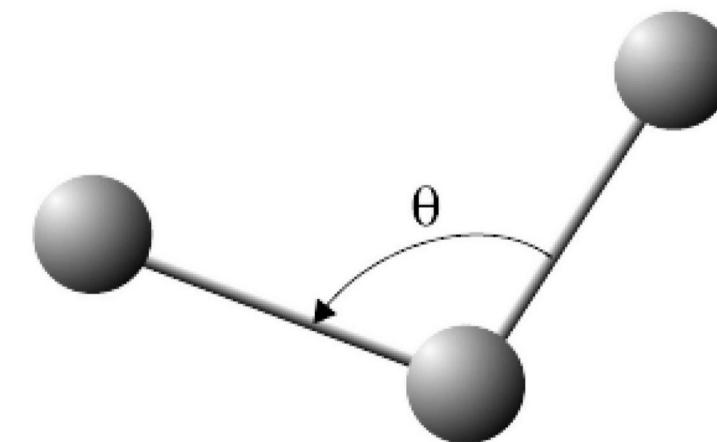
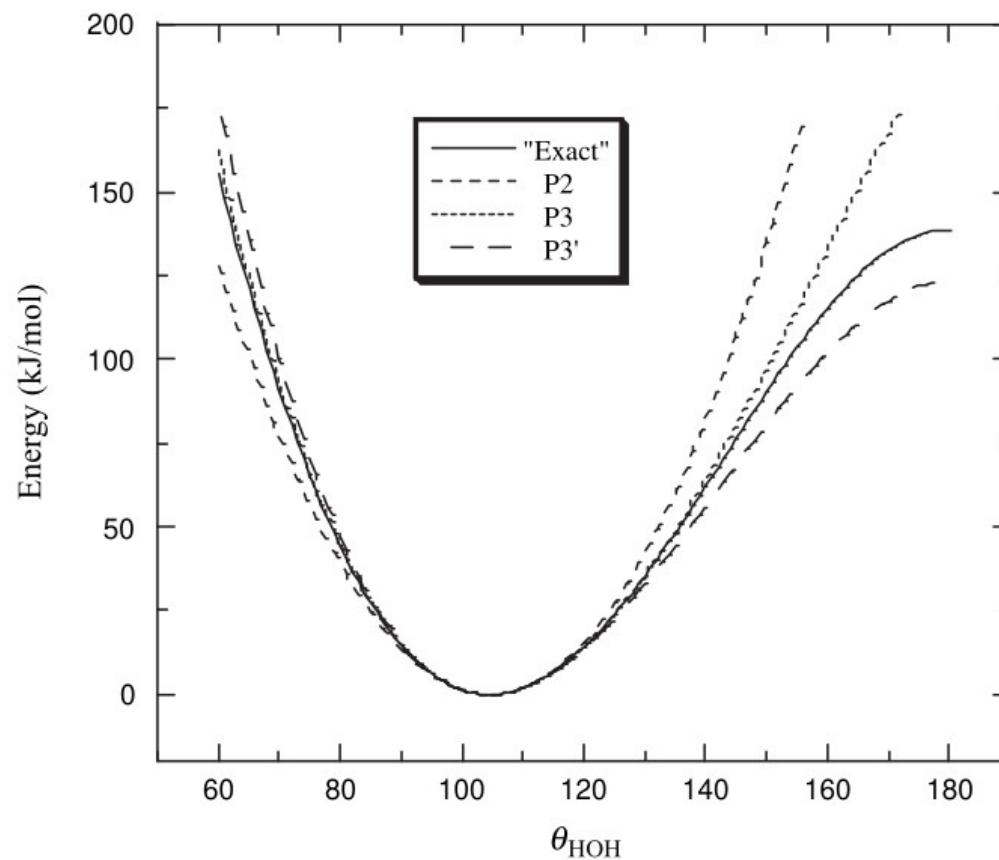
Energia de alongamento da ligação

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



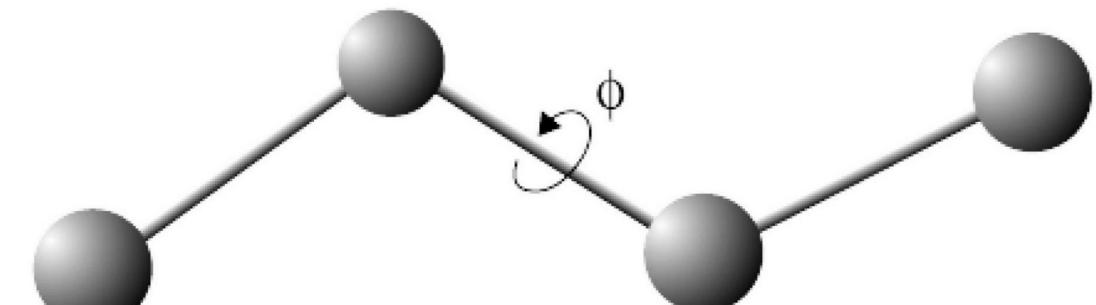
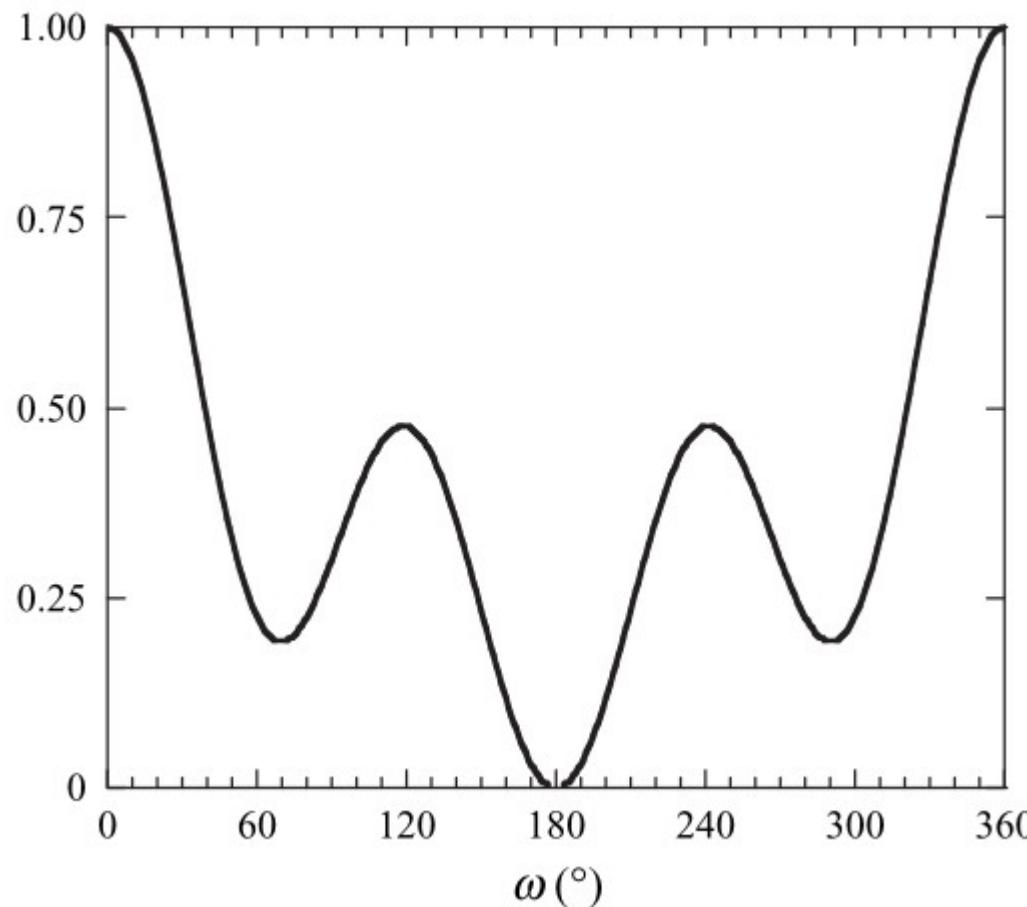
Energia de ângulo de ligação

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



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

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

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

Like charges repel



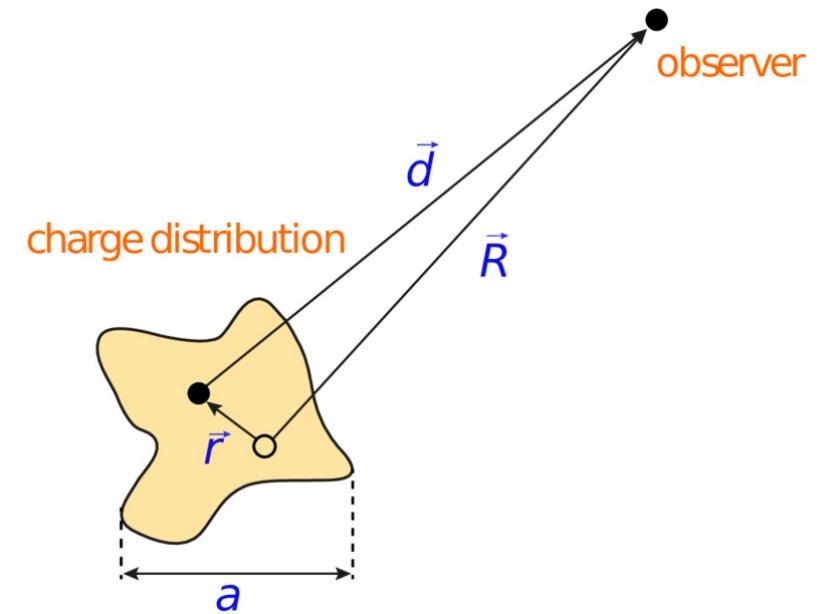
Opposite charges attract



Expansão em Multipólos

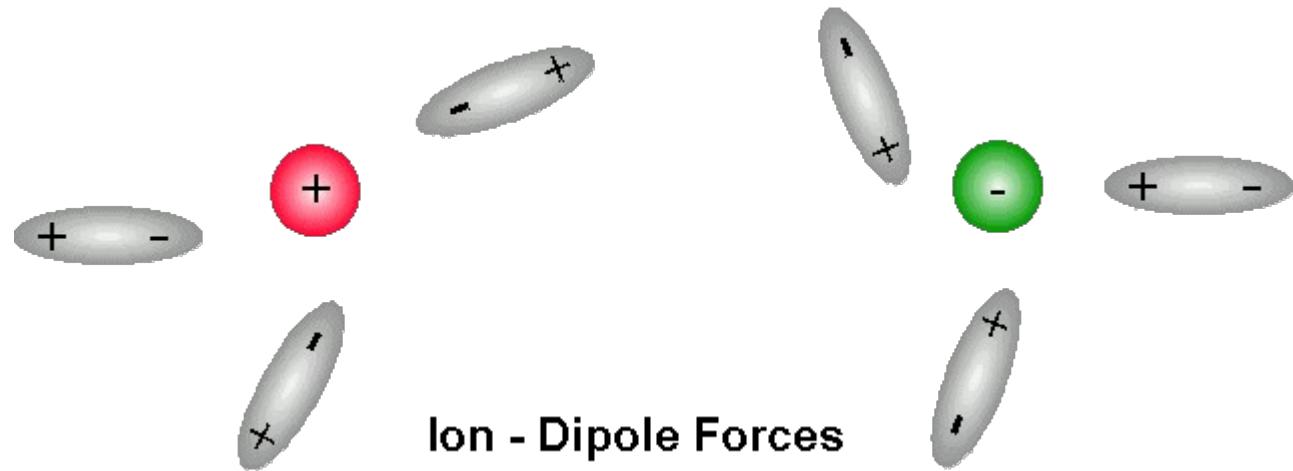
Potencial eletrostático produzido por uma molécula

$$V(\mathbf{R}) = \sum_A \frac{Q_A}{(4\pi\epsilon_0)|\mathbf{R} - \mathbf{R}_A|}$$



Interação Dipólo - Carga

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



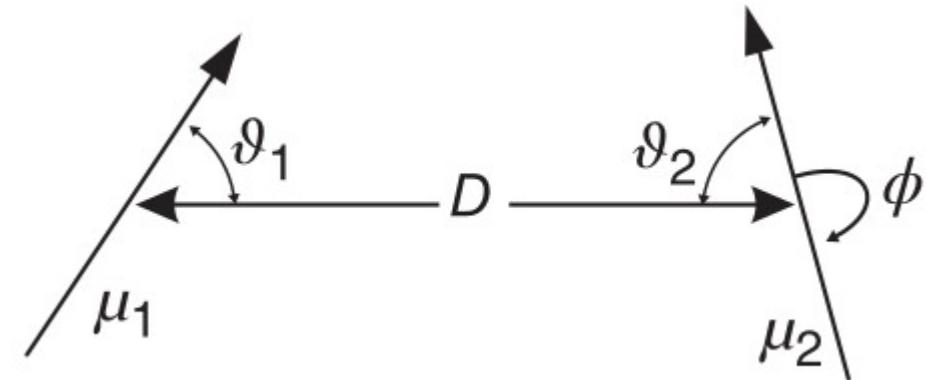
Média de orientações do dipolos

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

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

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

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

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

Interação Dipólo – Dipólo Induzido

$$\mu_{\text{ind}} = \alpha E$$

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



Média de orientações do dipolos

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

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

Energia de van der Waals

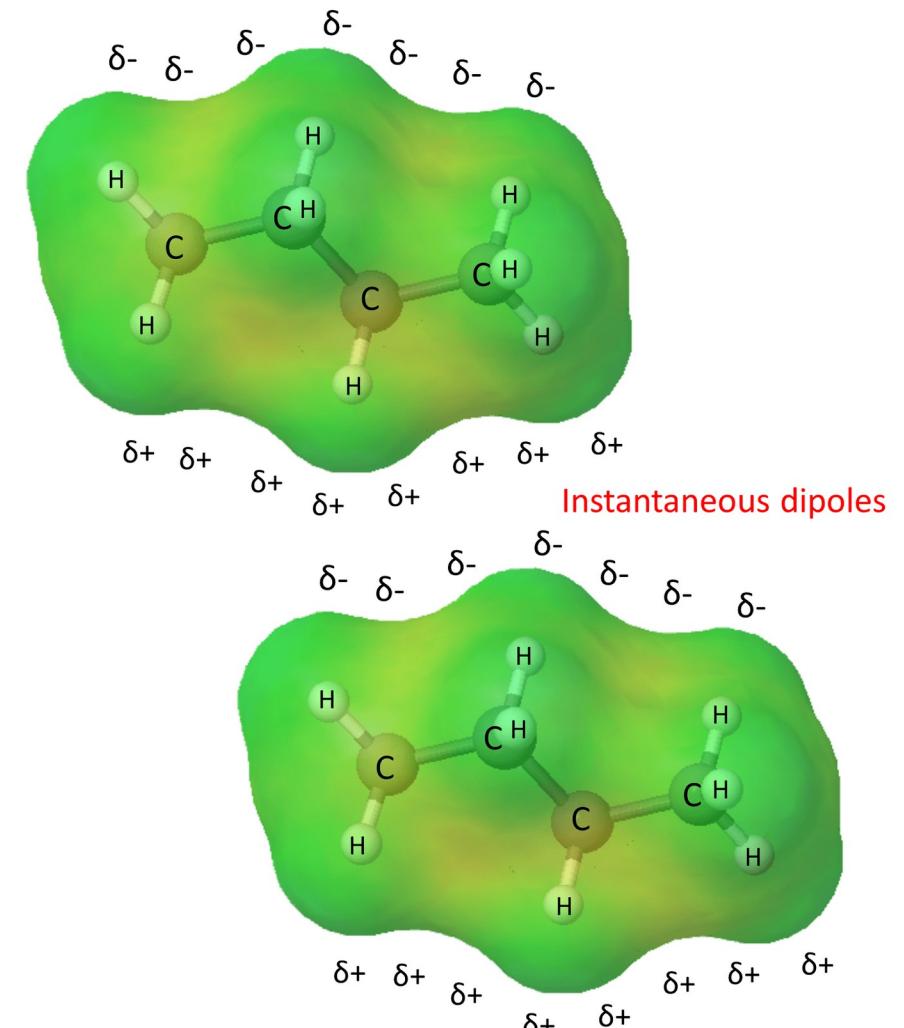
Interação de London – dipólo induzido – dipólo induzido

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

Interação de van der Waals

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

Interações
dispersivas
de London



Procedimento do COMPASS

