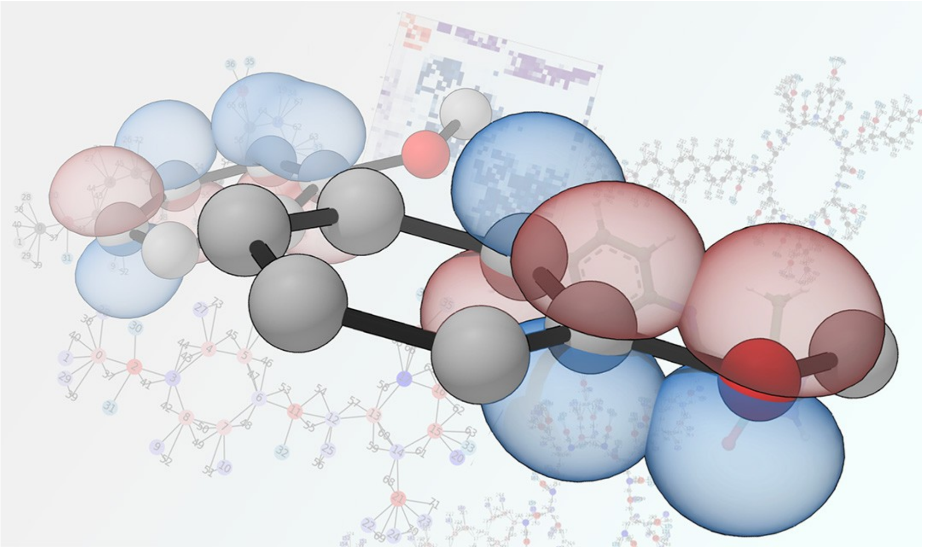
Aula 13 – Modelos de Solventes Contínuos



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

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

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

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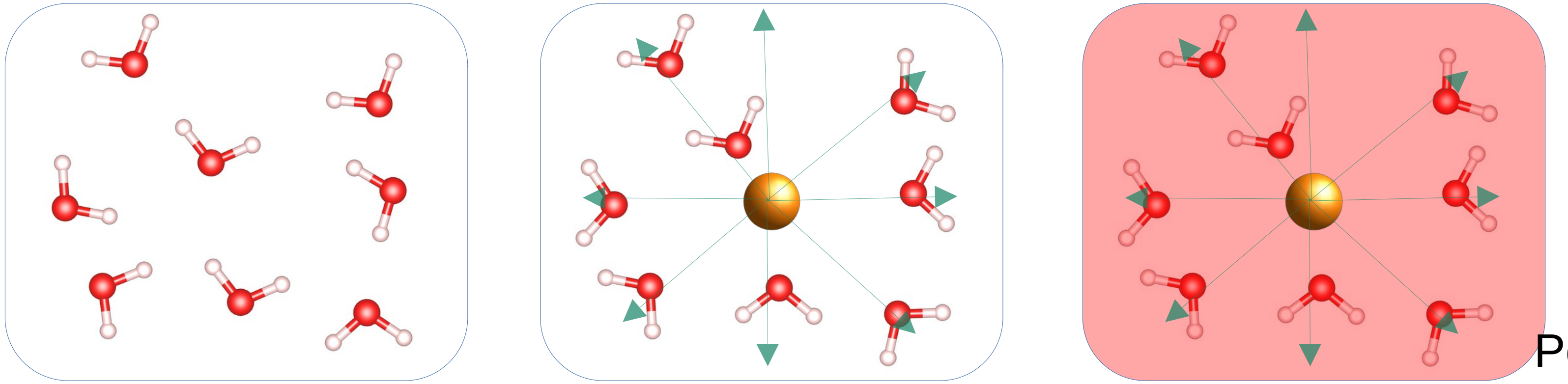
Polarização de um meio

Momento de dipólo por unidade de volume $\boldsymbol{P} = \frac{d\boldsymbol{p}}{dV}$



Suscetibilidade elétrica

Polarização $\boldsymbol{P} = \epsilon_0 \chi \boldsymbol{E}$

Unidades gaussianas

$4\pi\epsilon_0 = 1$

$\rho_t = \rho + \rho_{\text{pol}}$ cargas ligadas - induzidas

Campo Elétrico no meio $\boldsymbol{D} = \boldsymbol{E} + \boldsymbol{P}$

Equações de Maxwell (meio)

$$\nabla \cdot \boldsymbol{D} = 4\pi\rho$$

$$\nabla \times \boldsymbol{D} = 0$$

Equações de Maxwell (vácuo)

$$\nabla \cdot \boldsymbol{E} = 4\pi\rho_t$$

$$\nabla \times \boldsymbol{E} = 0$$

$\epsilon = (1 + \chi_e)$ Permissividade elétrica ou constante dielétrica

Potencial Eletrostático num meio dielétrico

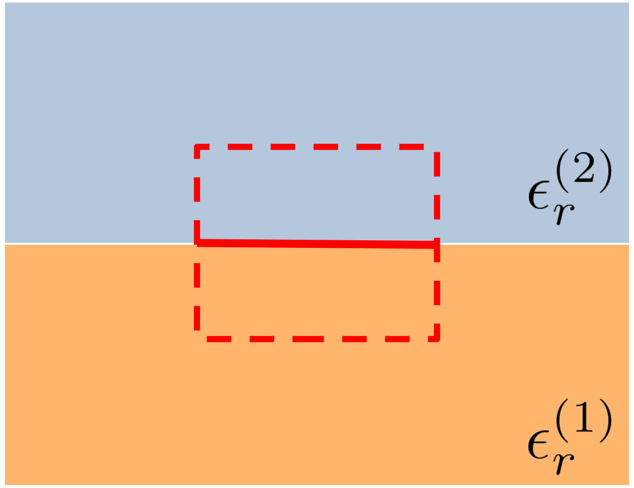
$$\boldsymbol{D}(\boldsymbol{r}) = \epsilon(\boldsymbol{r})\boldsymbol{E}(\boldsymbol{r}) \Rightarrow \nabla \cdot \boldsymbol{D} = 4\pi\rho \Rightarrow$$

$$\boldsymbol{E} = -\nabla\phi \Rightarrow$$

Potencial Eletrostático

$$\nabla \cdot [\epsilon(\boldsymbol{r})\nabla\phi(\boldsymbol{r})] = -4\pi\rho$$

$$\Downarrow$$

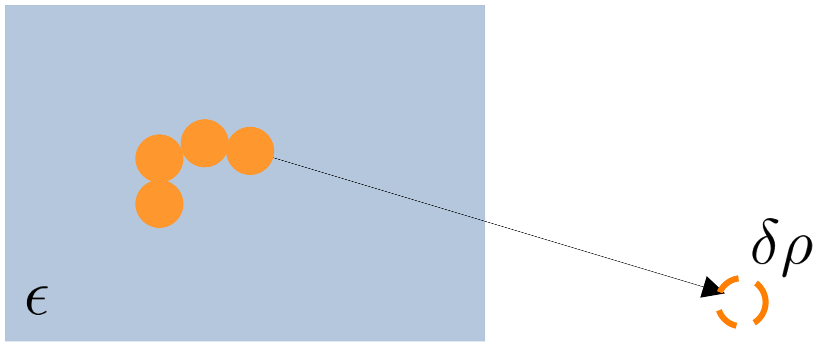


Condições de contorno

$$\left[\epsilon_r^{(1)}\nabla\phi_1 - \epsilon_r^{(2)}\nabla\phi_2\right]\hat{\boldsymbol{n}} = 4\pi\sigma$$

$$\phi_2 - \phi_1 = 0$$

Energia de Interação Carga e Dielétrico



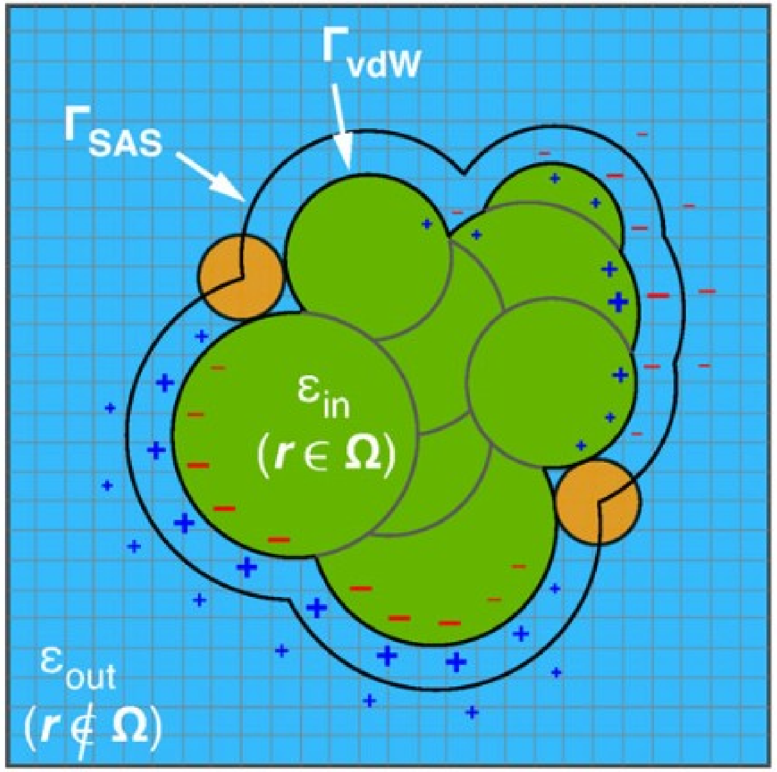
$$\delta W = \frac{1}{4\pi}\int_V \delta\rho(\boldsymbol{r})\phi(\boldsymbol{r})\ \mathrm{d}\boldsymbol{r}$$

$$\delta W = \delta\left[\frac{1}{2}\frac{1}{4\pi}\int_V \boldsymbol{D}\cdot\boldsymbol{E}\ \mathrm{d}\boldsymbol{r}\right]$$

Trabalho total feito para colocar cargas no dielétrico

$$W = \frac{1}{8\pi}\int_V \boldsymbol{D}\cdot\boldsymbol{E}\ \mathrm{d}\boldsymbol{r}$$

Molécula em solvente



$$\nabla \cdot [\epsilon(\boldsymbol{r}) \nabla \phi(\boldsymbol{r})] = -4\pi\rho$$

reaction field

$$\phi(\boldsymbol{r}) = \phi^{\rho}(\boldsymbol{r}) + \phi_{\mathrm{rxn}}(\boldsymbol{r})$$

$$\phi^{\rho}(\boldsymbol{r}) = \int \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \, \mathrm{d}\boldsymbol{r}'$$

$$\mathcal{G}_{\mathrm{elst}}[\epsilon(\boldsymbol{r}), \rho(\boldsymbol{r})] = \frac{1}{2} \int \rho(\boldsymbol{r}) \phi_{\mathrm{rxn}}(\boldsymbol{r}) \, \mathrm{d}\boldsymbol{r}$$

Energia total

$$\begin{aligned} \mathcal{G}_0[\Psi] &= \langle \Psi | \hat{H}_{\mathrm{vac}} | \Psi \rangle + \mathcal{G}_{\mathrm{elst}} \\ &= \langle \Psi | \hat{H}_{\mathrm{vac}} + \tfrac{1}{2} \mathcal{R}_0 | \Psi \rangle \end{aligned}$$

Herbert, J. M. (2021). Wiley Interdisciplinary Reviews: Computational Molecular Science, 11(4), e1519.