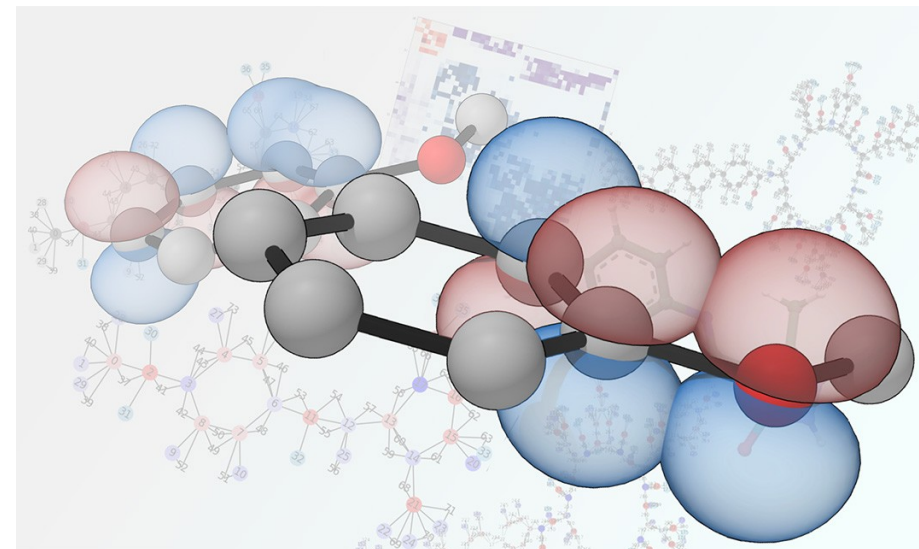


Aula 14 – Modelos Contínuos Polarizáveis (PCM)



Ref: Artigos Citados

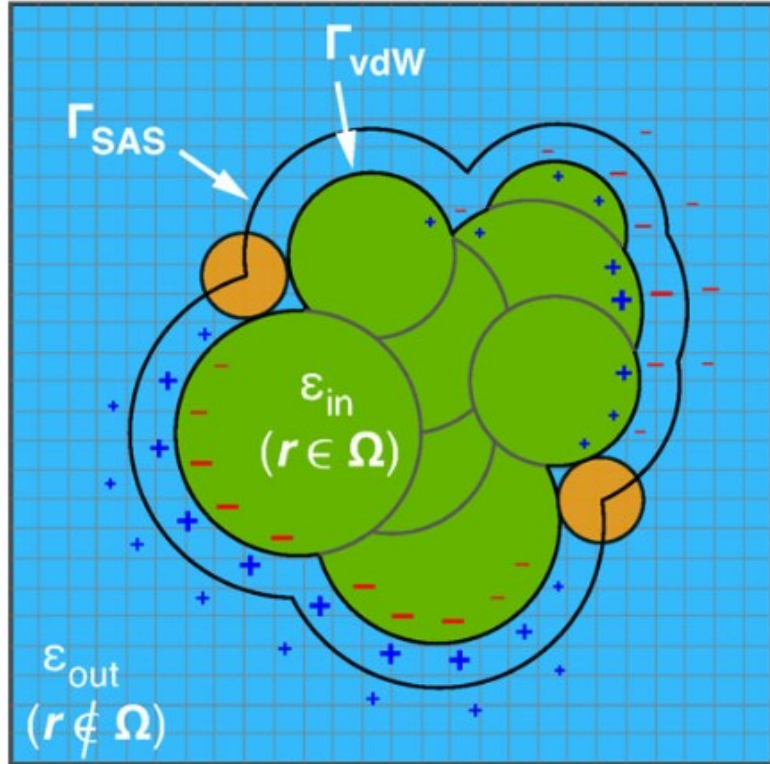
Prof. Elvis Soares
elvis@peq.coppe.ufrj.br

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

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

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

Modelos Contínuos Polarizáveis



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

reaction field

$$\phi(\mathbf{r}) = \phi^\rho(\mathbf{r}) + \phi_{\text{rxn}}(\mathbf{r})$$

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

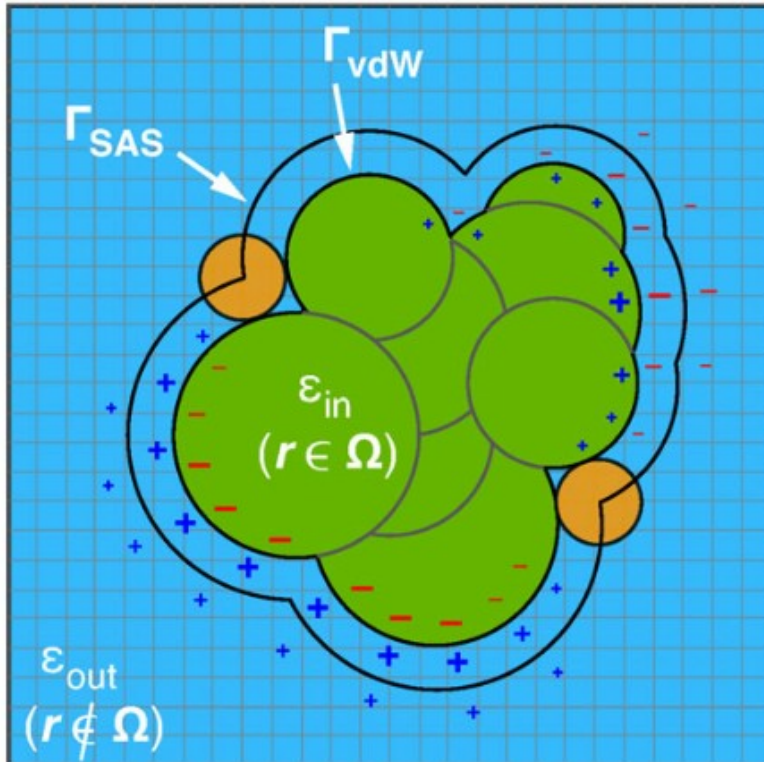
$$\mathcal{G}_{\text{elst}}[\epsilon(\mathbf{r}), \rho(\mathbf{r})] = \frac{1}{2} \int \rho(\mathbf{r}) \phi_{\text{rxn}}(\mathbf{r}) d\mathbf{r}$$

Energia total

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

Reaction Field e Cavidade

$$\phi^{\text{rxn}}(\mathbf{r}) = \phi^{\beta}(\mathbf{r}) + \phi^{\sigma}(\mathbf{r})$$



Termo volumétrico

$$\nabla^2 \phi^{\beta}(\mathbf{r}) = \begin{cases} 0, & \mathbf{r} \in \Omega \\ 4\pi(\epsilon_{\text{in}}^{-1} - \epsilon_{\text{out}}^{-1})\rho(\mathbf{r}), & \mathbf{r} \notin \Omega \end{cases}$$

Termo superficial

$$\phi^{\sigma}(\mathbf{r}) = \int_{s \in \Gamma} \frac{\sigma(s)}{\|\mathbf{s} - \mathbf{r}\|} d\mathbf{s}$$

VdW ou SAS: Superfícies geradas a partir de esferas centradas nos átomos com tamanhos definidos.

Raios das esferas da cavidade

$$R_A = \alpha_{\text{vdW}} R_{\text{vdW},A} + R_{\text{probe}}$$

Equação Principal do PCM

$$\sigma(\mathbf{s}) = \left(\frac{f_\epsilon}{2\pi} \right) \partial_{\mathbf{s}} [\phi^\rho(\mathbf{s}) + \phi^\beta(\mathbf{s}) + \phi^\sigma(\mathbf{s})]$$



$$\hat{S} \left[\hat{1} - \left(\frac{f_\epsilon}{2\pi} \right) \hat{D}^\dagger \right] \tilde{\sigma}(\mathbf{s}) = f_\epsilon \left[\frac{1}{2\pi} \hat{D} - \hat{1} \right] \phi^\rho(\mathbf{s})$$

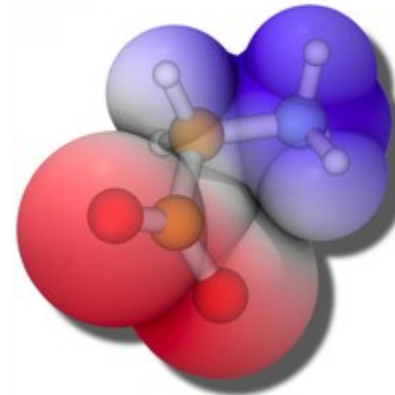


Discretização da
superfície da cavidade

$$\hat{K} \tilde{\sigma}(\mathbf{s}) = \hat{R} \phi^\rho(\mathbf{s})$$

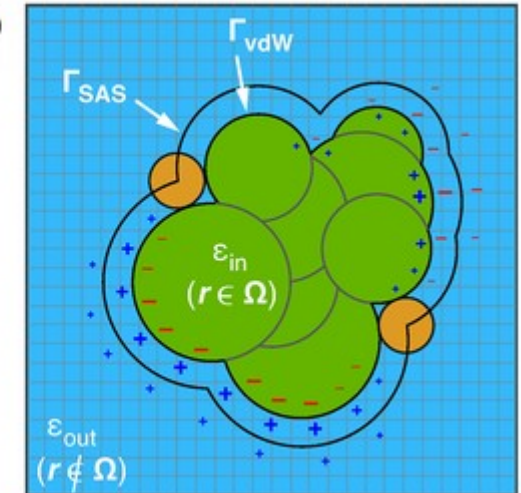


(a)



Potencial Eletrostático
na sup. da cavidade $\phi^\rho(\mathbf{s})$

(b)



Cargas induzidas e
definição da cavidade

Equação Principal do PCM

$$Kq = Rv$$

Modelos Diversos

Equação Principal do PCM

$$Kq = Rv$$

Model	Literature Refs.	Matrix K	Matrix R	Scalar f_ϵ
COSMO	477	S	$-f_\epsilon \mathbf{1}$	$(\epsilon - 1) / (\epsilon + 1/2)$
C-PCM	934, 57	S	$-f_\epsilon \mathbf{1}$	$(\epsilon - 1) / \epsilon$
IEF-PCM	174, 137	$\mathbf{S} - (f_\epsilon / 2\pi) \mathbf{DAS}$	$-f_\epsilon \left(\mathbf{1} - \frac{1}{2\pi} \mathbf{DA} \right)$	$(\epsilon - 1) / (\epsilon + 1)$
SS(V)PE	174, 172	$\mathbf{S} - (f_\epsilon / 4\pi) (\mathbf{DAS} + \mathbf{SAD}^\dagger)$	$-f_\epsilon \left(\mathbf{1} - \frac{1}{2\pi} \mathbf{DA} \right)$	$(\epsilon - 1) / (\epsilon + 1)$

Alguns Resultados

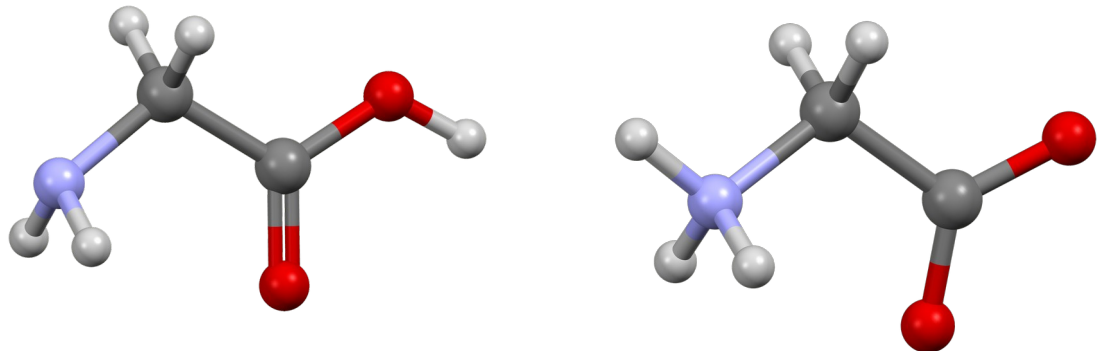
$$\mathcal{G}_{\text{elst}}[\epsilon(\boldsymbol{r}), \rho(\boldsymbol{r})] = \frac{1}{2} \int \rho(\boldsymbol{r}) \phi_{\text{rxn}}(\boldsymbol{r}) \, d\boldsymbol{r}$$

Model	Literature Refs.	Matrix K	Matrix R	Scalar f_ϵ
COSMO	477	S	$-f_\epsilon \mathbf{1}$	$(\epsilon - 1) / (\epsilon + 1/2)$
C-PCM	934, 57	S	$-f_\epsilon \mathbf{1}$	$(\epsilon - 1) / \epsilon$
IEF-PCM	174, 137	$\mathbf{S} - (f_\epsilon / 2\pi) \mathbf{DAS}$	$-f_\epsilon \left(\mathbf{1} - \frac{1}{2\pi} \mathbf{DA} \right)$	$(\epsilon - 1) / (\epsilon + 1)$
SS(V)PE	174, 172	$\mathbf{S} - (f_\epsilon / 4\pi) (\mathbf{DAS} + \mathbf{SAD}^\dagger)$	$-f_\epsilon \left(\mathbf{1} - \frac{1}{2\pi} \mathbf{DA} \right)$	$(\epsilon - 1) / (\epsilon + 1)$

Solute	ϵ_s	$\mathcal{G}_{\text{elst}}$ (kcal/mol)					Q_{out} (a.u.) ^c
		SVPE	SS(V)PE	SPE	C-PCM ^b		
					$\zeta = 0$	$\zeta = 1/2$	
H ₂ O	2.4	−3.9	−3.9	−4.0	−4.8	−3.9	
CH ₃ CONH ₂	2.4	−5.3	−5.0	−5.2	−5.9	−4.8	
NO ⁺	2.4	−52.2	−52.2	−55.3	−52.5	−43.4	
CN [−]	2.4	−39.4	−39.4	−35.0	−39.4	−32.5	
H ₂ O	78.3	−8.6	−8.6	−8.7	−8.6	−8.6	−0.06
CH ₃ CONH ₂	78.3	−10.9	−10.8	−11.1	−10.9	−10.8	−0.15
NO ⁺	78.3	−89.5	−89.5	−94.7	−89.5	−88.9	−0.07
CN−	78.3	−67.4	−67.3	−56.8	−67.3	−66.9	−0.17

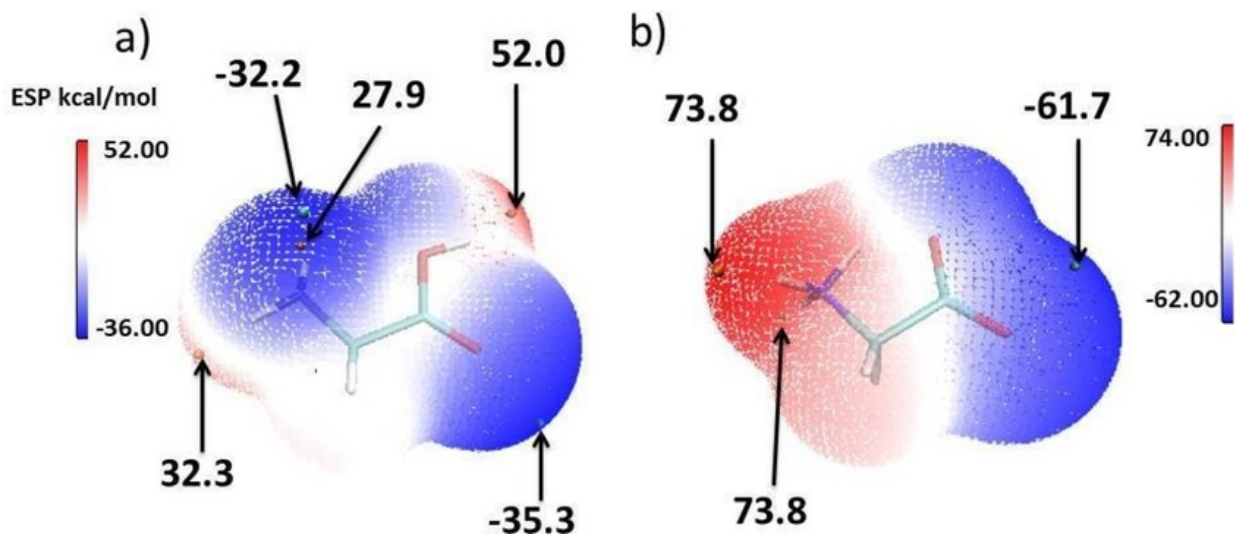
TABLE 1 Electrostatic solvation energies in toluene ($\epsilon_s = 2.4$) and in water ($\epsilon_s = 78.3$), computed with various approaches.^a

Exemplo: Tautômeros de Glicina



aminoácido

zwitterion

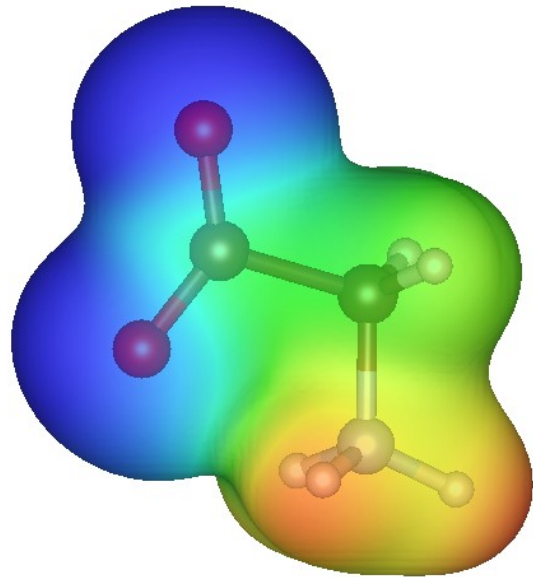


Cavity	α_{vdW}	R_{probe} (Å)	$\mathcal{G}_{\text{elst}}$ (kcal/mol)	
			Amino acid	Zwitterion
vdW ^a	1.0	0.0	-26.1	-68.2
vdW ^a	1.1	0.0	-20.2	-56.0
vdW ^a	1.2	0.0	-16.1	-46.8
vdW ^a	1.3	0.0	-12.9	-39.0
vdW ^a	1.4	0.0	-10.6	-32.6
SAS ^a	1.0	0.2	-18.0	-51.4
SAS ^a	1.0	1.4	-4.3	-13.9
Isodensity ^b			-16.4	-48.1

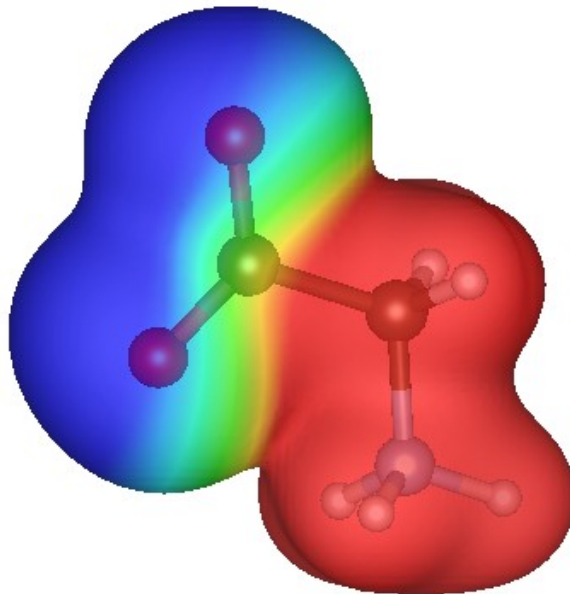
Note: Electronic structure calculations were performed at the B3LYP/6-31+G* level.
^aUsing R_{vdW} = 1.10 Å (H), 1.70 Å (C), 1.55 Å (N), and 1.52 Å (O), discretized using SwiG with 302 points per atom.
^bUsing an isocontour ρ_0 = 0.001 a.u. and 1202 grid points.

Isodensity: Superfícies geradas a partir de um dado *treshold* de densidade eletrônica.

Zwitterion de glicina



vácuo



Em água

Resultado no PySCF

- SS(V)PE
- $\epsilon = 78.3553$

$$\mathcal{G}_{\text{elst}}^* = -25.72 \text{ kcal/mol}$$

Vide [notebook_Aula14.ipynb](#)

*A geometria foi otimizada também na presença do solvente.

Energia de Solvatação

Energia de solvatação

$$\mathcal{G} = \mathcal{G}_{\text{elst}} + \mathcal{G}_{\text{nonelst}}$$

Tipos de energia não-eletrostáticas:

- **cavitação:** energia necessária para criar um buraco no solvente contínuo;
- **repulsão de Pauli:** interações repulsivas de curto-alcance com as moléculas do solvente;
- **dispersão:** interação atrativa;
- **ligação de hidrogênio** entre soluto e solvente;

