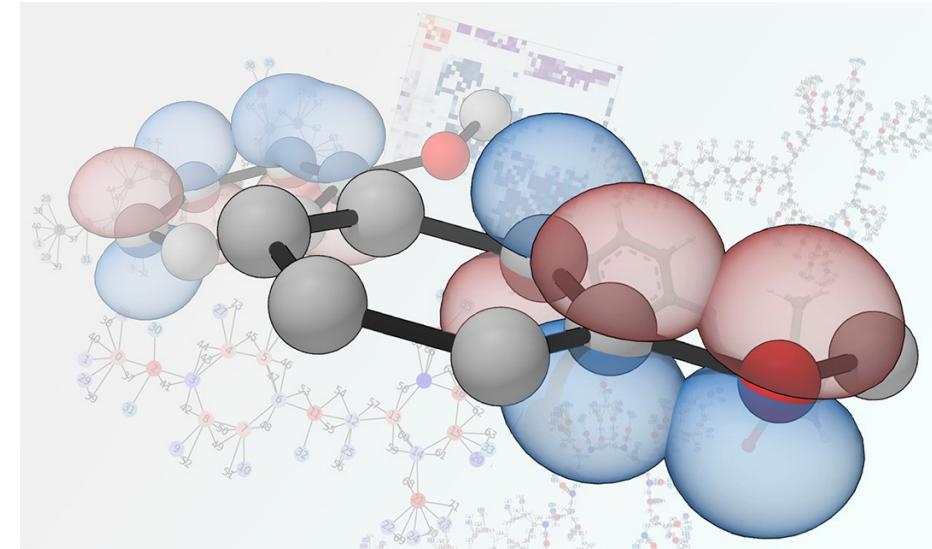


Aula 14 – Modelos Contínuos Polarizáveis (PCM)

Ref: Artigos Citados

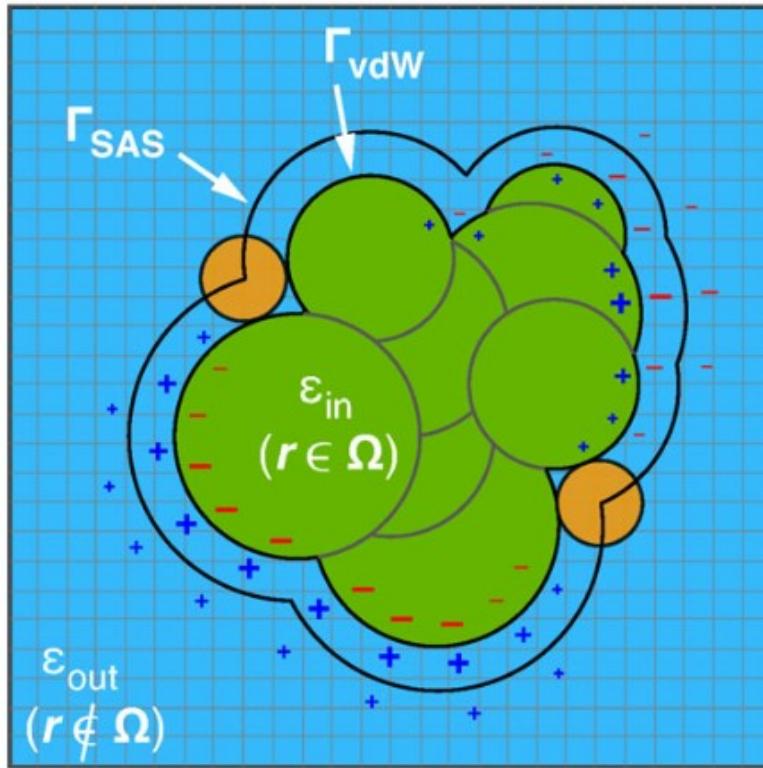
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$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle = \hat{H} |\Psi\rangle$$

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

Modelos Contínuos Polarizáveis



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

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

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

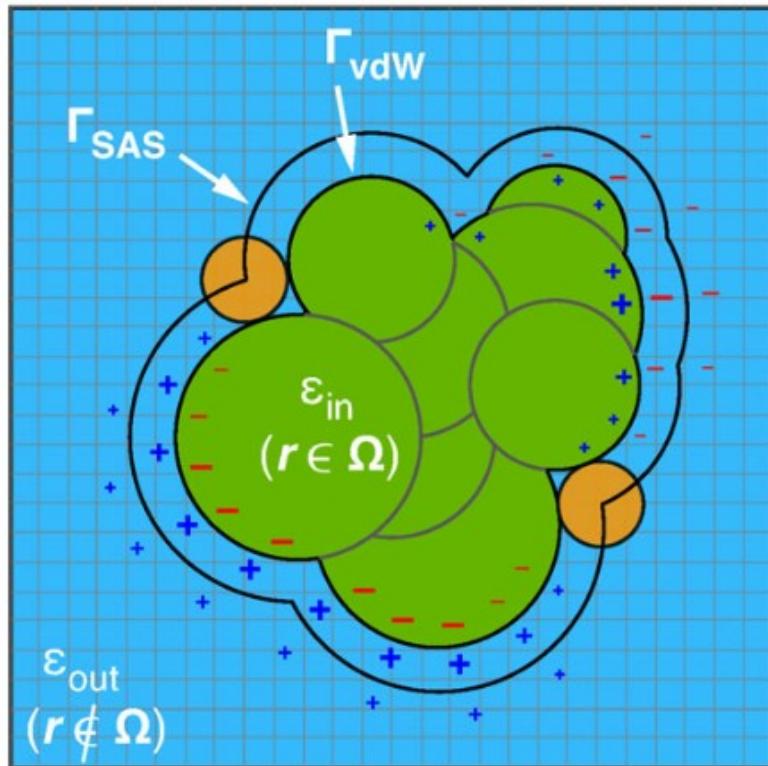
$$\mathcal{G}_{elst}[\epsilon(\mathbf{r}), \rho(\mathbf{r})] = \frac{1}{2} \int \rho(\mathbf{r}) \phi_{rxn}(\mathbf{r}) d\mathbf{r}$$

Energia total

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

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

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

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

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



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

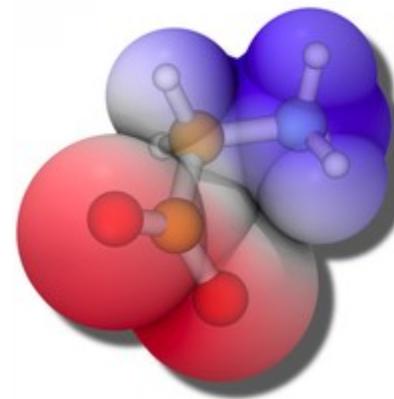


Discretização da
superfície da cavidade

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

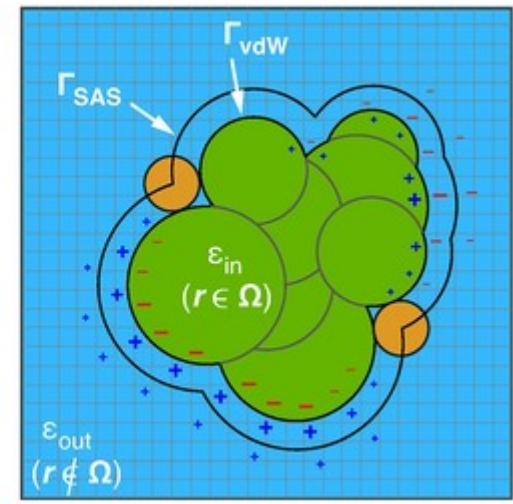


(a)



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

(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	$-f_\varepsilon \mathbf{1}$	$(\varepsilon - 1) / (\varepsilon + 1/2)$
C-PCM	934, 57	S	$-f_\varepsilon \mathbf{1}$	$(\varepsilon - 1) / \varepsilon$
IEF-PCM	174, 137	$\mathbf{S} - (f_\varepsilon / 2\pi) \mathbf{DAS}$	$-f_\varepsilon \left(\mathbf{1} - \frac{1}{2\pi} \mathbf{DA} \right)$	$(\varepsilon - 1) / (\varepsilon + 1)$
SS(V)PE	174, 172	$\mathbf{S} - (f_\varepsilon / 4\pi) (\mathbf{DAS} + \mathbf{SAD}^\dagger)$	$-f_\varepsilon \left(\mathbf{1} - \frac{1}{2\pi} \mathbf{DA} \right)$	$(\varepsilon - 1) / (\varepsilon + 1)$

Alguns Resultados

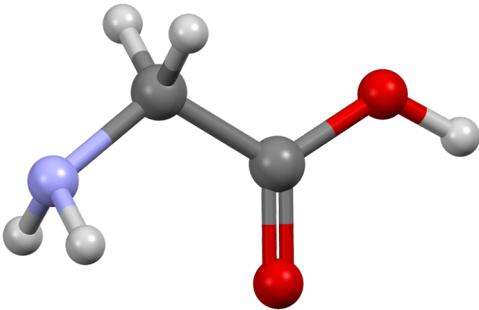
$$\mathcal{G}_{\text{elst}}[\epsilon(\mathbf{r}), \rho(\mathbf{r})] = \frac{1}{2} \int \rho(\mathbf{r}) \phi_{\text{rxn}}(\mathbf{r}) \, d\mathbf{r}$$

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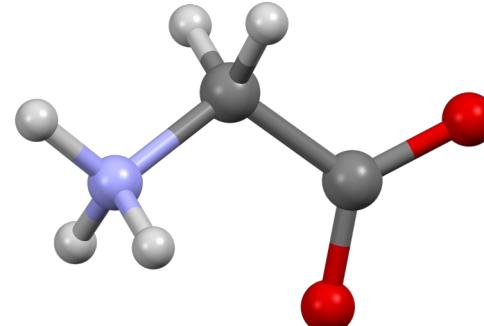
Solute	ε_s	$\mathcal{G}_{\text{elst}}$ (kcal/mol)					
		SVPE	SS(V)PE	SPE	C-PCM ^b		Q_{out} (a.u.) ^c
		$\zeta = 0$	$\zeta = 1/2$				
H ₂ O	2.4	-3.9	-3.9	-4.0	-4.8	-3.9	
CH ₃ CONH ₂	2.4	-5.3	-5.0	-5.2	-5.9	-4.8	
NO ⁺	2.4	-52.2	-52.2	-55.3	-52.5	-43.4	
CN ⁻	2.4	-39.4	-39.4	-35.0	-39.4	-32.5	
H ₂ O	78.3	-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 ($\varepsilon_s = 2.4$) and in water ($\varepsilon_s = 78.3$), computed with various approaches.^a

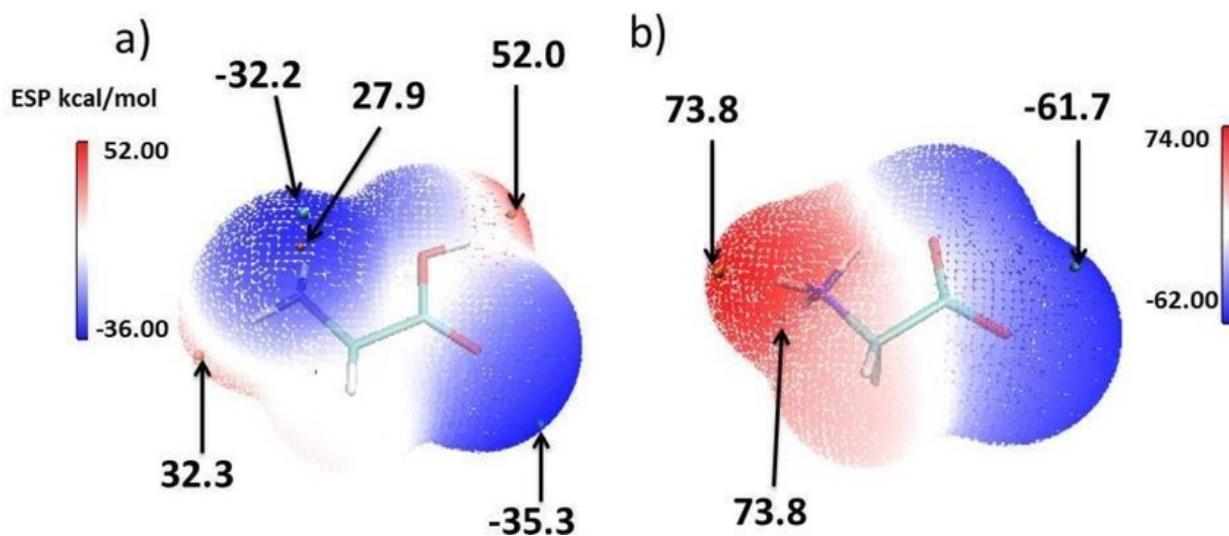
Exemplo: Tautômeros de Glicina



aminoácido



zwitterion



Cavity	α_{vdW}	R_{probe} (Å)	G_{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

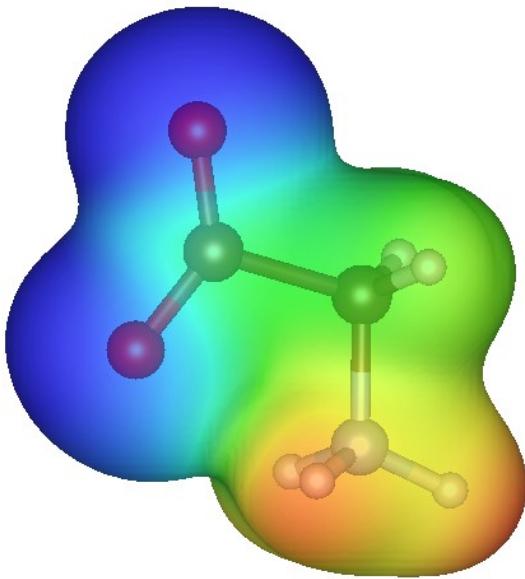
Note: Electronic structure calculations were performed at the B3LYP/6-31+G* level.

^aUsing $R_{\text{vdW}} = 1.10 \text{ \AA}$ (H), 1.70 \AA (C), 1.55 \AA (N), and 1.52 \AA (O), discretized using SwiG with 302 points per atom.

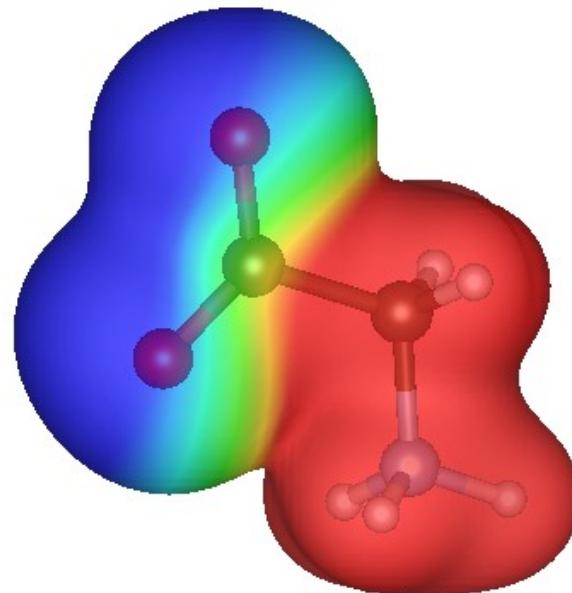
^bUsing an isocontour $\rho_0 = 0.001 \text{ a.u.}$ and 1202 grid points.

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

Zwitterion de glicina



vácuo



Em água

Resultado no PySCF

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

$$G_{\text{elst}}^* = -25.72 \text{ kcal/mol}$$

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;

