Domain Decomposition Method for Poisson Boltzmann Equation

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GANIT Seminar
4^{th} November 2024

Joint work with: Prof. Dr. Benjamin Stamm, Universität Stuttgart

Outline

Why Study Computational Chemistry?

	Web of Science	MathSciNet	
Navier Stokes Equations	43737		
Density Functional Theory			

- As of 30^{th} October 2024.

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Navier Stokes Equations	43737	18481	42.23%
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- As of 30^{th} October 2024.

Why Study Computational Chemistry?

	Web of Science	MathSciNet	
Navier Stokes Equations	43737	18481	42.23%
Density Functional Theory	257888	480	0.19%

- As of 30^{th} October 2024.

Solvation Models

- Ionic Solvation Models [1]
  - Explicit Solvation Models
    - Adopts molecular representation of both solute and solvent
    - Accurate results
    - Computationally expensive

[1] Zhang et. al.: *Journal of Chemical Theory and Computation*, 13 (**3**), 1034-1043, 2017

[2] Cances, Mennucci, Tomasi: *The Journal of Chemical Physics*, 107 (**8**), 3032-3041, 1997

[3] Honig, Nicholls: *Science*, 268 (**5214**), 1144-1149, 1995

Solvation Models

- Ionic Solvation Models [1]
  - Explicit Solvation Models
    - Adopts molecular representation of both solute and solvent
    - Accurate results
    - Computationally expensive
  - Implicit Solvation Models [2,3]
    - Microscopic treatment of solute
    - Macroscopic treatment of solvent using physical properties
    - Less computational cost

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Model Problem

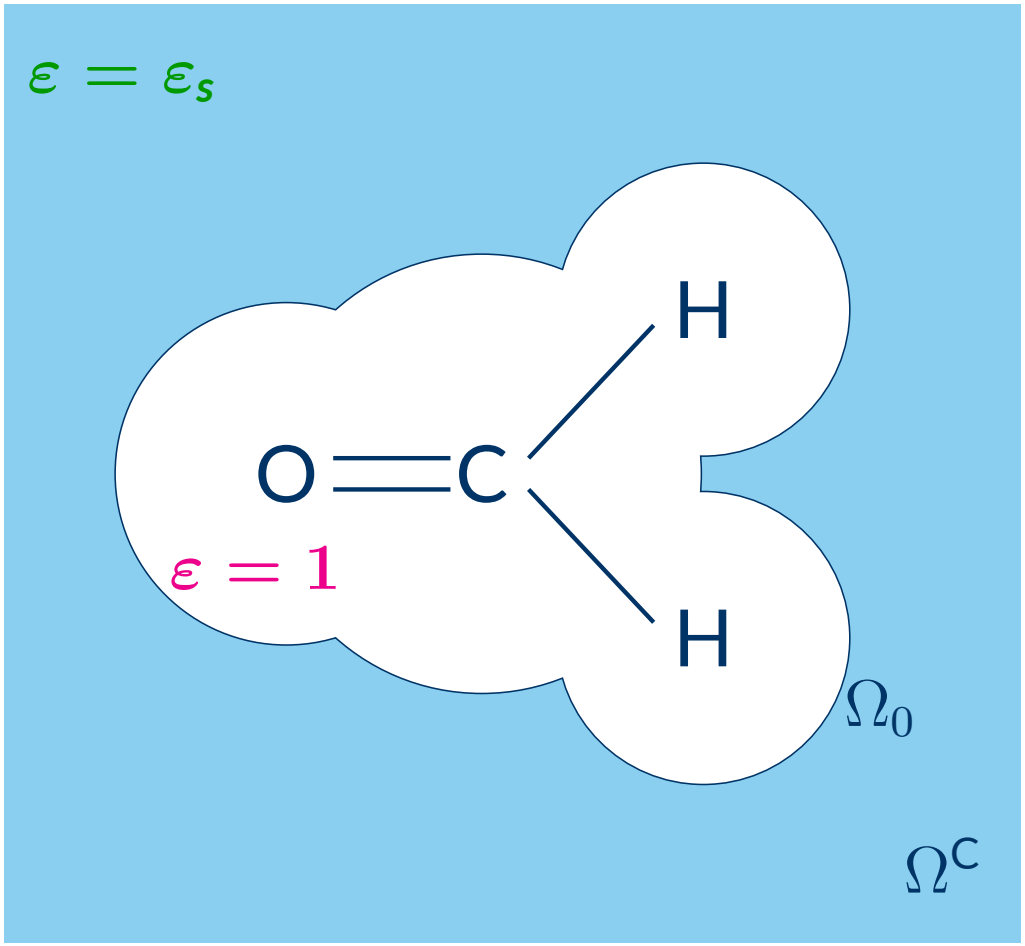

Figure 1: Formaldehyde Molecule

Model Problem

- Poisson-Boltzman (PB) Equation [1,2]

$$-\nabla \cdot \left[\varepsilon_{\text{abs}}\varepsilon(\mathbf{x})\nabla\tilde{\psi}(\mathbf{x})\right] = \rho^{\text{sol}}(\mathbf{x}) + \rho^{\text{ions}}(\mathbf{x}) \quad \text{in } \mathbb{R}^3$$

  - $\tilde{\psi}(\mathbf{x})$: Electrostatic potential

[1] Gouy: *Journal of Physics: Theories and Applications*, 9 (**1**), 457-468, 1910

[2] Chapman: *Journal of Science*, 25 (**1**), 475-481, 1913

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  - $\varepsilon(\mathbf{x})$: Relative space-dependent dielectric permittivity

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  - $\tilde{\psi}(\mathbf{x})$: Electrostatic potential
  - $\varepsilon(\mathbf{x})$: Relative space-dependent dielectric permittivity
  - $\rho^{\text{sol}}(\mathbf{x})$: Solute charge distribution

$$\rho^{\text{sol}}(x) = \sum_{i=1}^{M} q_i \delta(\mathbf{x} - \mathbf{x}_i)$$

  - M : Number of solute atoms
  - q_i : Total charge on the i^{th} atom

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Model Problem

- $\rho^{\text{ions}}(\mathbf{x})$: Ionic charge distribution (Boltzmann distribution)

$$\rho^{\text{ions}}(\mathbf{x}) = \sum_{i=1}^{N_{\text{ions}}} z_i e \lambda(\mathbf{x}) c_i^{\infty} \exp\left(\frac{-z_i e \tilde{\psi}(\mathbf{x})}{K_B T}\right)$$

[1] Stein, Herbert, Head-Gordon: *The Journal of Chemical Physics*, 151 (**22**), 224111, 2019

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- For $1:1$ ionic solution[1]

$$\rho^{\text{ions}}(\mathbf{x}) = -2ce\lambda(\mathbf{x}) \sinh\left(\frac{e\tilde{\psi}(\mathbf{x})}{K_B T}\right)$$

  - $\lambda(\mathbf{x})$: Ion-exclusion function

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- Dimensionless Poisson-Boltzman (PB) Equation

$$-\nabla \cdot [\varepsilon(\mathbf{x})\nabla\psi(\mathbf{x})] + \kappa^2\varepsilon_s\lambda(\mathbf{x})\sinh(\psi(\mathbf{x})) = \frac{1}{\beta\varepsilon_{\text{abs}}}\rho^{\text{sol}}(\mathbf{x}) \quad \text{in } \mathbb{R}^3$$

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  - $\psi(\mathbf{x}) : \tilde{\psi}(\mathbf{x})\beta$
  - κ : Debye Hückel Screening Constant [1]
  - $\beta : e/K_B T$

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Solute Cavity

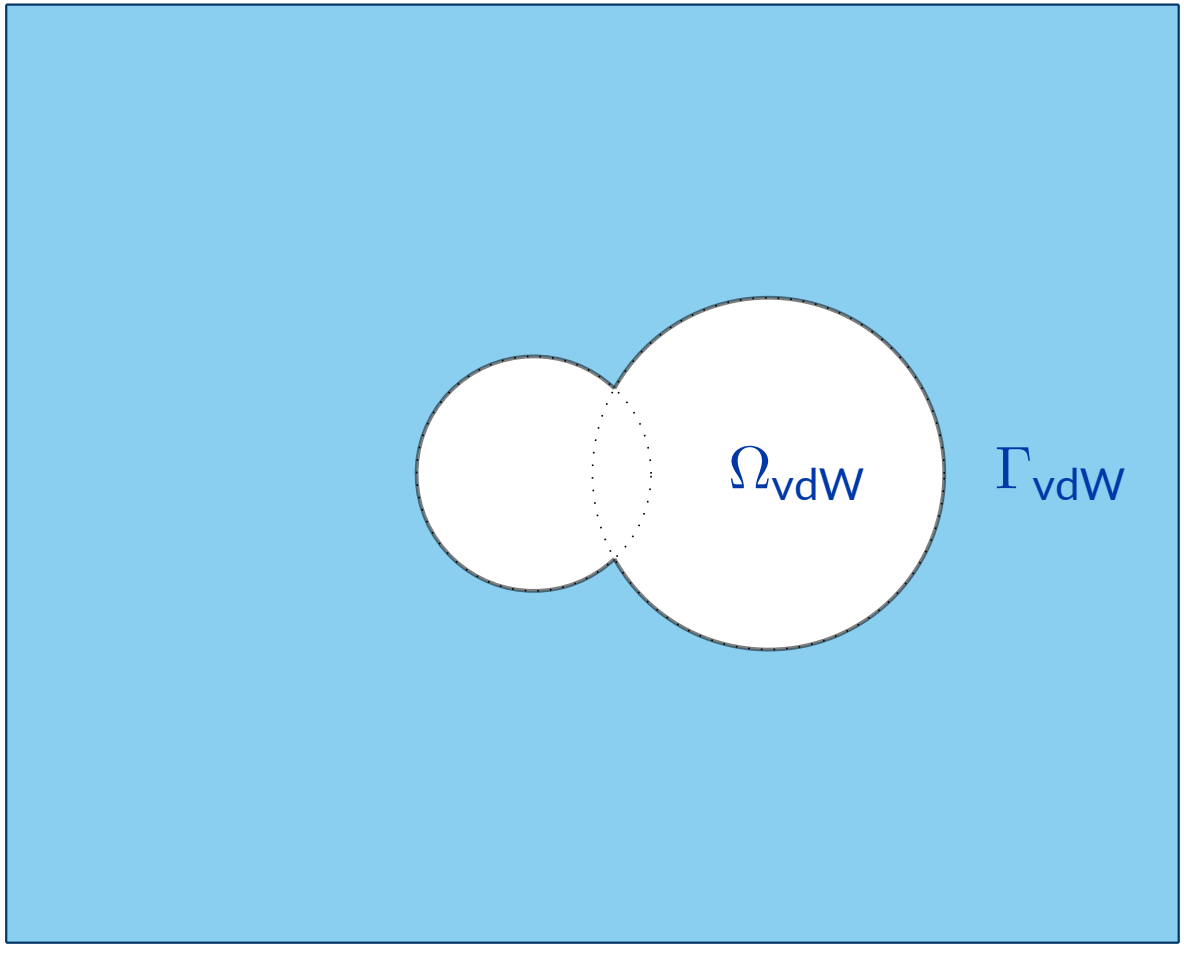
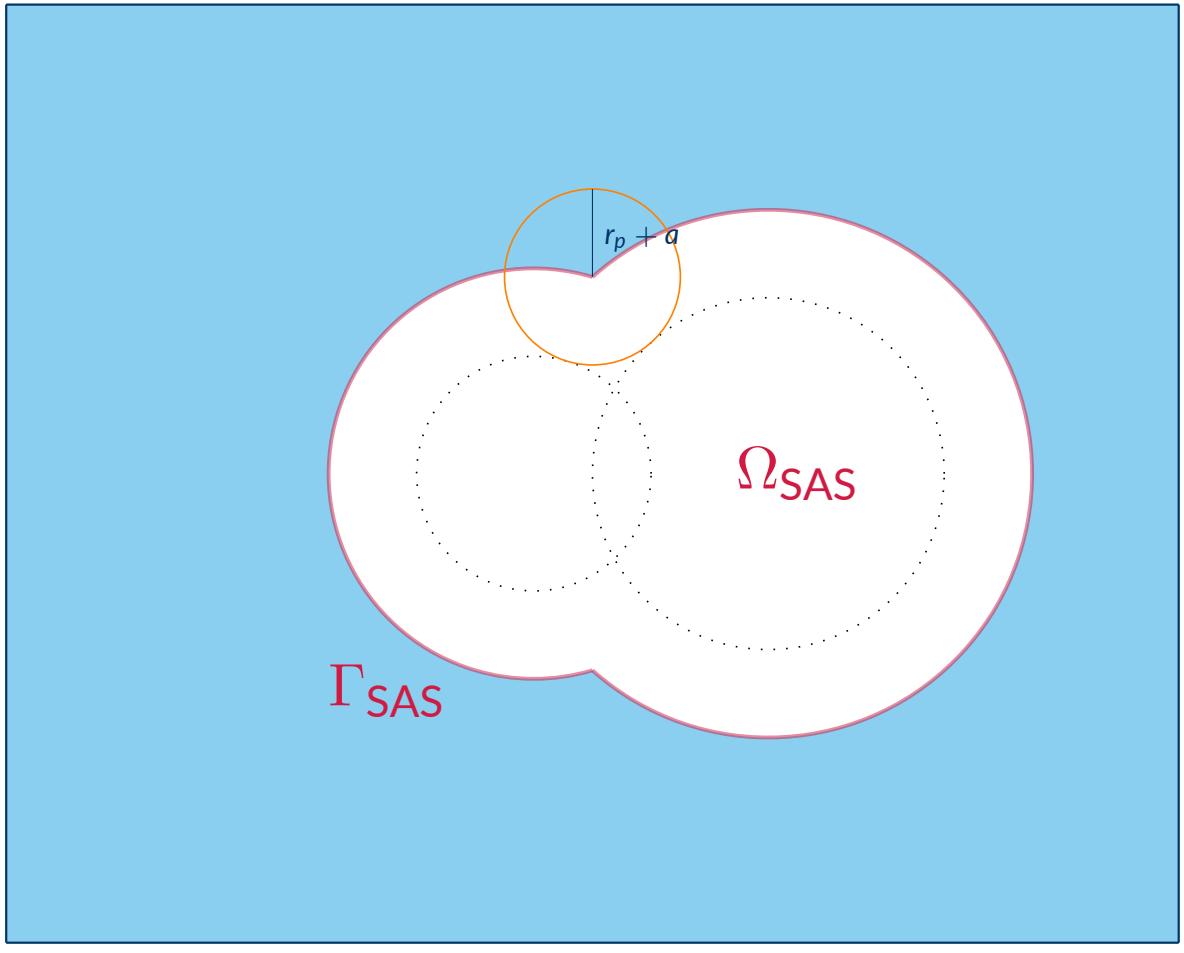


Figure 2: Solute probes and solute-solvent boundary for a diatmoic molecule.

- vdW: vad-der Waal's Surface

Solute Cavity



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- SAS: Solvent Accessible Surface

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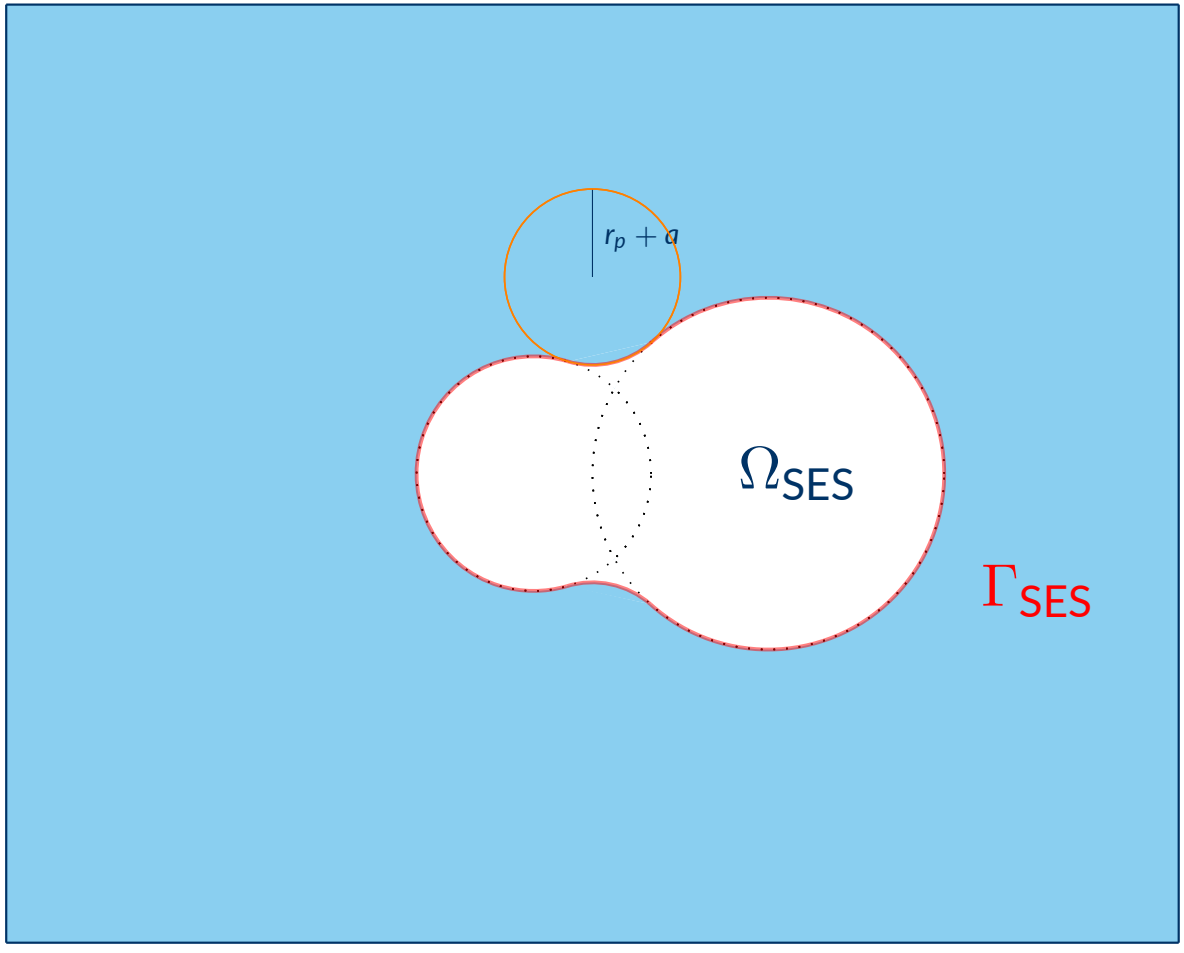

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- SES: Solvent Excluded Surface

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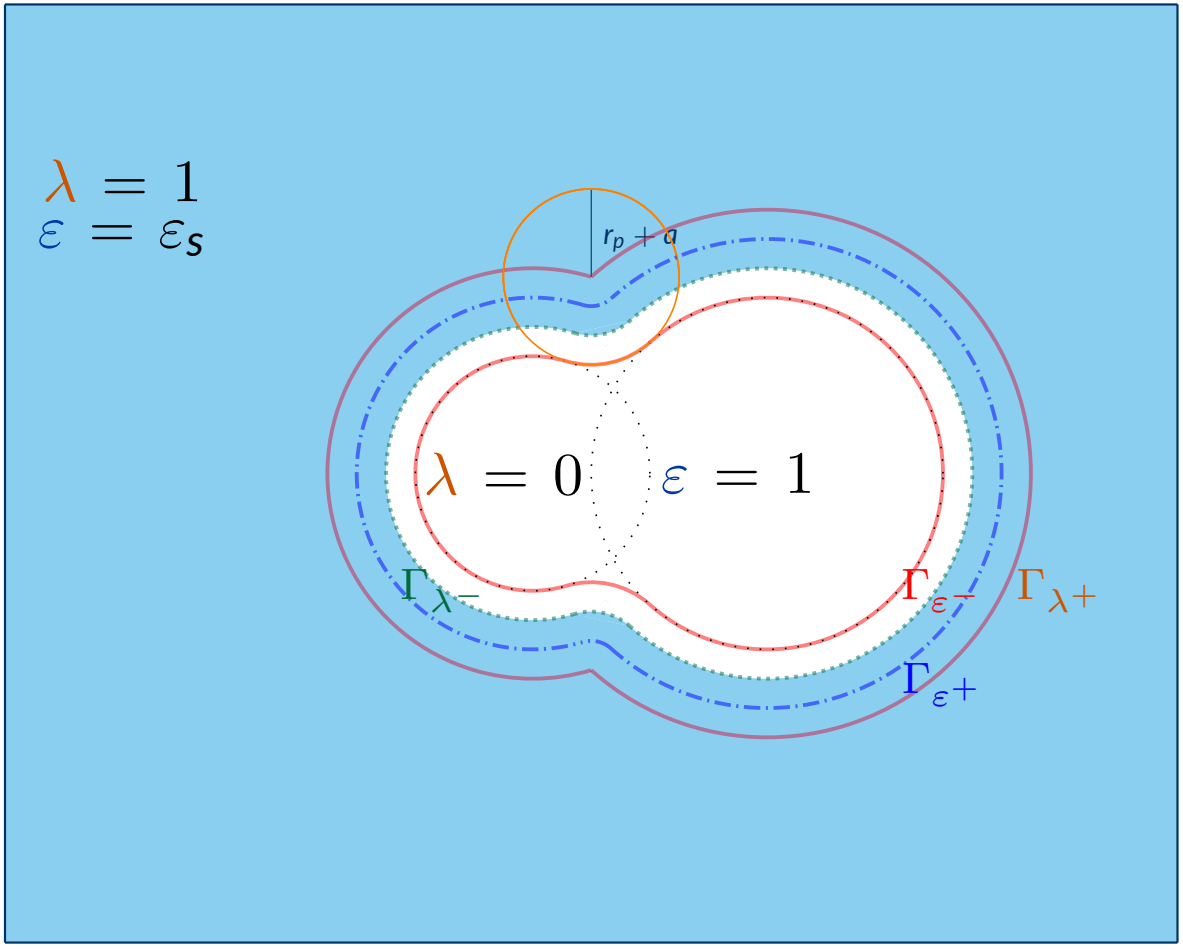

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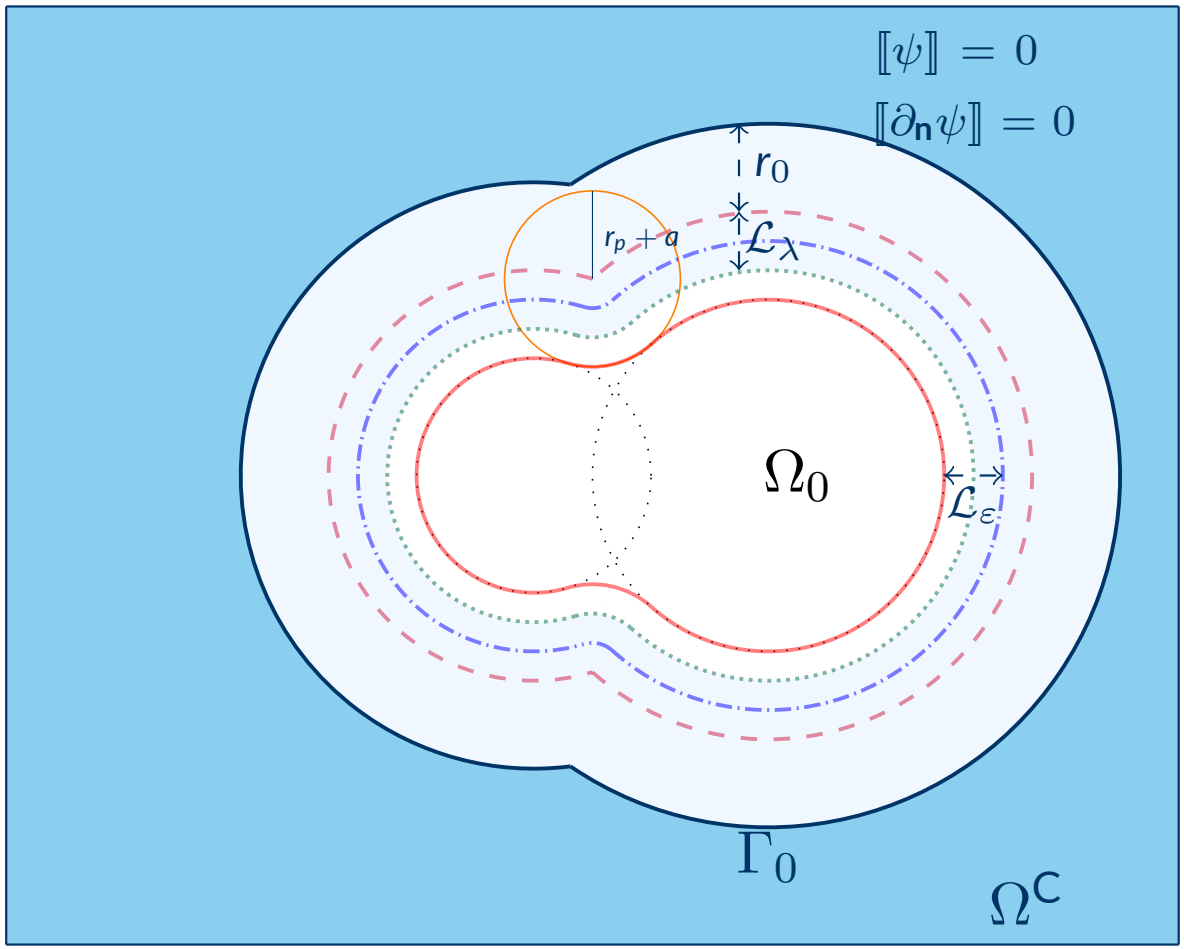

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Permittivity and Ion-Exclusion Function

- Dielectric Permittivity Function[1]

$$\varepsilon(\mathbf{x}) = \begin{cases} 1 & \mathbf{x} \in \Omega_{\text{SES}}, \\ 1 + (\varepsilon_s - 1)\xi\left(\dfrac{f_{\text{SAS}}(\mathbf{x}) + r_p + a}{r_p}\right) & \mathbf{x} \in \mathcal{L}_\varepsilon, \\ \varepsilon_s & \text{else}, \end{cases}$$

[1] Quan, Stamm: *Journal of Computational Physics*, 322 (**1**), 760-782, 2016

[2] Stern: *Zeitschrift für Elektrochemie*, 30 (**508**), 21-22, 1924

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- Ion-Exclusion Function[2]

$$\lambda(\mathbf{x}) = \begin{cases} 0 & \mathbf{x} \in \Omega_{\lambda^-}, \\ \xi\left(\dfrac{f_{\text{SAS}}(\mathbf{x}) + r_p}{r_p}\right) & \mathbf{x} \in \mathcal{L}_\lambda, \\ 1 & \text{else}, \end{cases}$$

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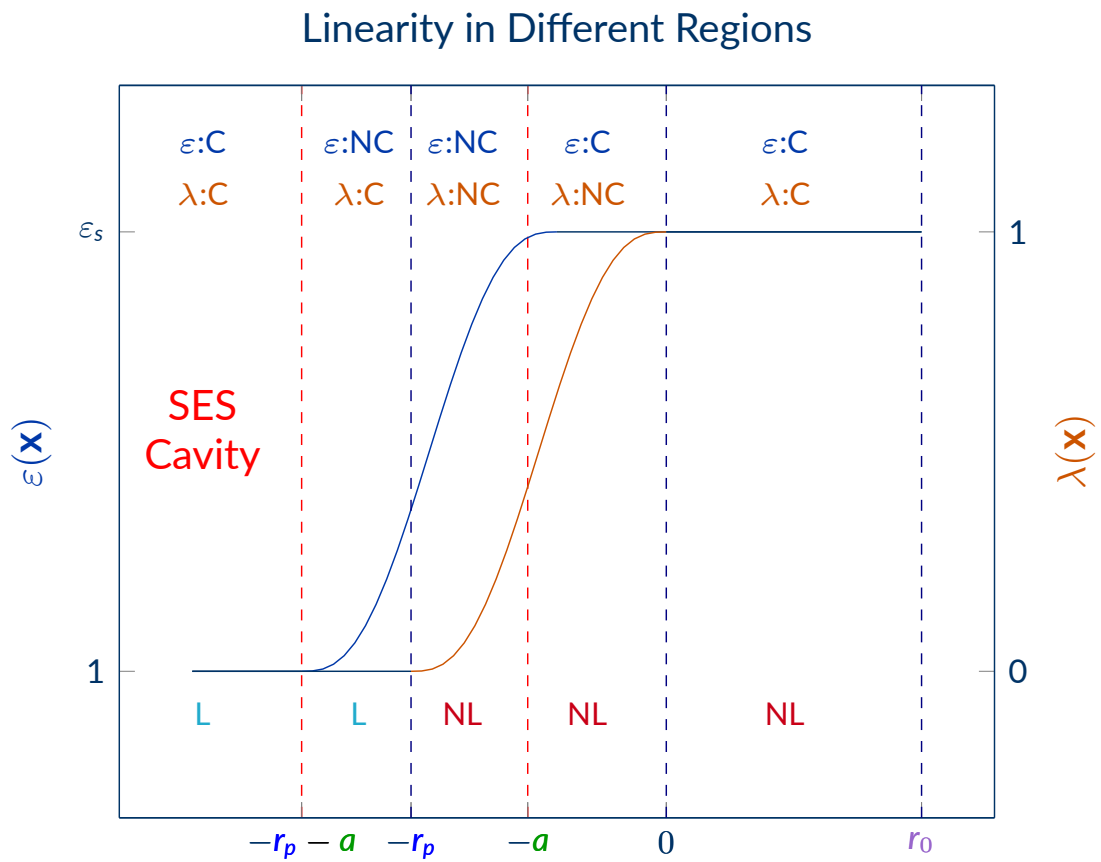
Permittivity and Ion-Exclusion Function



- C: Constant, NC: Non-Constant
- L: Linear, NL: Non-Linear

- The PB equation can be written in two equations

$$
\begin{aligned}
-\nabla \cdot [\varepsilon(\mathbf{x}) \nabla \psi(\mathbf{x})] + \kappa^2 \varepsilon_s \lambda(\mathbf{x}) \sinh(\psi(\mathbf{x})) &= \frac{1}{\beta \varepsilon_{\text{abs}}} \rho^{\text{sol}}(\mathbf{x}) && \text{in } \Omega_0, \\
-\Delta \psi(\mathbf{x}) + \kappa^2 \psi(\mathbf{x}) &= 0 && \text{in } \Omega^{\mathsf{C}},
\end{aligned}
$$

with

$$
\begin{aligned}
[\![\psi]\!] &= 0, \\
[\![\partial_{\mathbf{n}} \psi]\!] &= 0 \quad \text{on} \quad \Gamma_0 := \partial\Omega_0,
\end{aligned}
$$

Problem Transformation

- Using Potential Theory the final equations are

$$-\nabla \cdot [\varepsilon(\mathbf{x})\nabla\psi_{\mathsf{r}}(\mathbf{x})] + \kappa^2\varepsilon_{\mathsf{s}}\lambda(\mathbf{x})\mathcal{F}\left(\psi_{\mathsf{r}}+\psi_0\right)\left(\psi_{\mathsf{r}}+\psi_0\right)(\mathbf{x})$$
$$= \nabla \cdot \left[\left(\varepsilon(\mathbf{x})-1\right)\nabla\psi_0(\mathbf{x})\right] \qquad \text{in } \Omega_0 \qquad [\text{GSP}]$$

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-\nabla \cdot [\varepsilon(\mathbf{x}) \nabla \psi_{\mathsf{r}}(\mathbf{x})] + \kappa^2 \varepsilon_{\mathsf{s}} \lambda(\mathbf{x}) \mathcal{F}\left(\psi_{\mathsf{r}} + \psi_0\right)\left(\psi_{\mathsf{r}} + \psi_0\right)(\mathbf{x}) \\
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\end{aligned}
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$$
-\Delta \psi_{\mathsf{e}}(\mathbf{x}) + \kappa^2 \psi_{\mathsf{e}}(\mathbf{x}) = 0 \qquad \text{in } \Omega_0 \qquad \text{[HSP]}
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with

$$
\begin{aligned}
\psi_0 + \psi_{\mathsf{r}} &= \psi_{\mathsf{e}} \quad \text{on } \Gamma_0, \\
\psi_{\mathsf{e}} &= S_\kappa \sigma_{\mathsf{e}} \quad \text{on } \Gamma_0
\end{aligned}
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$$-\nabla \cdot [\varepsilon(\mathbf{x})\nabla\psi_{\mathsf{r}}(\mathbf{x})] + \kappa^2\varepsilon_{\mathsf{s}}\lambda(\mathbf{x})\mathcal{F}\left(\psi_{\mathsf{r}}+\psi_0\right)\left(\psi_{\mathsf{r}}+\psi_0\right)(\mathbf{x})$$
$$= \nabla \cdot [(\varepsilon(\mathbf{x})-1)\nabla\psi_0(\mathbf{x})] \quad \text{in } \Omega_0 \quad \text{[GSP]}$$

$$-\Delta\psi_{\mathsf{e}}(\mathbf{x}) + \kappa^2\psi_{\mathsf{e}}(\mathbf{x}) = 0 \quad \text{in } \Omega_0 \quad \text{[HSP]}$$

with

$$\psi_0 + \psi_{\mathsf{r}} = \psi_{\mathsf{e}} \quad \text{on } \Gamma_0,$$
$$\psi_{\mathsf{e}} = S_\kappa \sigma_{\mathsf{e}} \quad \text{on } \Gamma_0$$

where

- ψ_{r} : Reaction potential in Ω
- ψ_0 : Potential generated by ρ_{M} satisfying,

$$-\Delta\psi_0 = \frac{1}{\beta\varepsilon_{\mathsf{abs}}}\rho_{\mathsf{M}}$$

Problem Transformation

- ψ_e : Extended potential from Ω^C to Ω_0

[1] Sauter, Schwab, Springer, Berlin-2011, 101-181

Problem Transformation

- ψ_e : Extended potential from Ω^C to Ω_0
- $\mathcal{F}(\Phi) = \dfrac{\sinh(\Phi)}{\Phi}$

[1] Sauter, Schwab, Springer, Berlin-2011, 101-181

Problem Transformation

- ψ_e : Extended potential from Ω^C to Ω_0
- $\mathcal{F}(\Phi) = \dfrac{\sinh(\Phi)}{\Phi}$
- σ_e : Charge density generating ψ_e satisfying

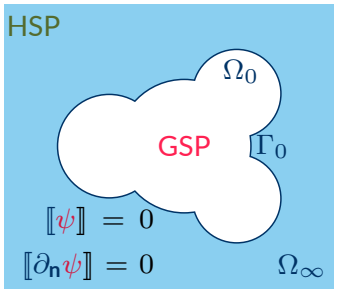
$$S_\kappa \sigma_e(\mathbf{x}) = \int_{\Gamma_0} \frac{\exp\left(-\kappa|\mathbf{x}-\mathbf{y}|\right)\sigma_e(\mathbf{y})}{4\pi|\mathbf{x}-\mathbf{y}|} = \psi_e \quad \forall\, \mathbf{x} \in \Gamma_0$$

- S_κ : Invertible single-layer potential operator [1]

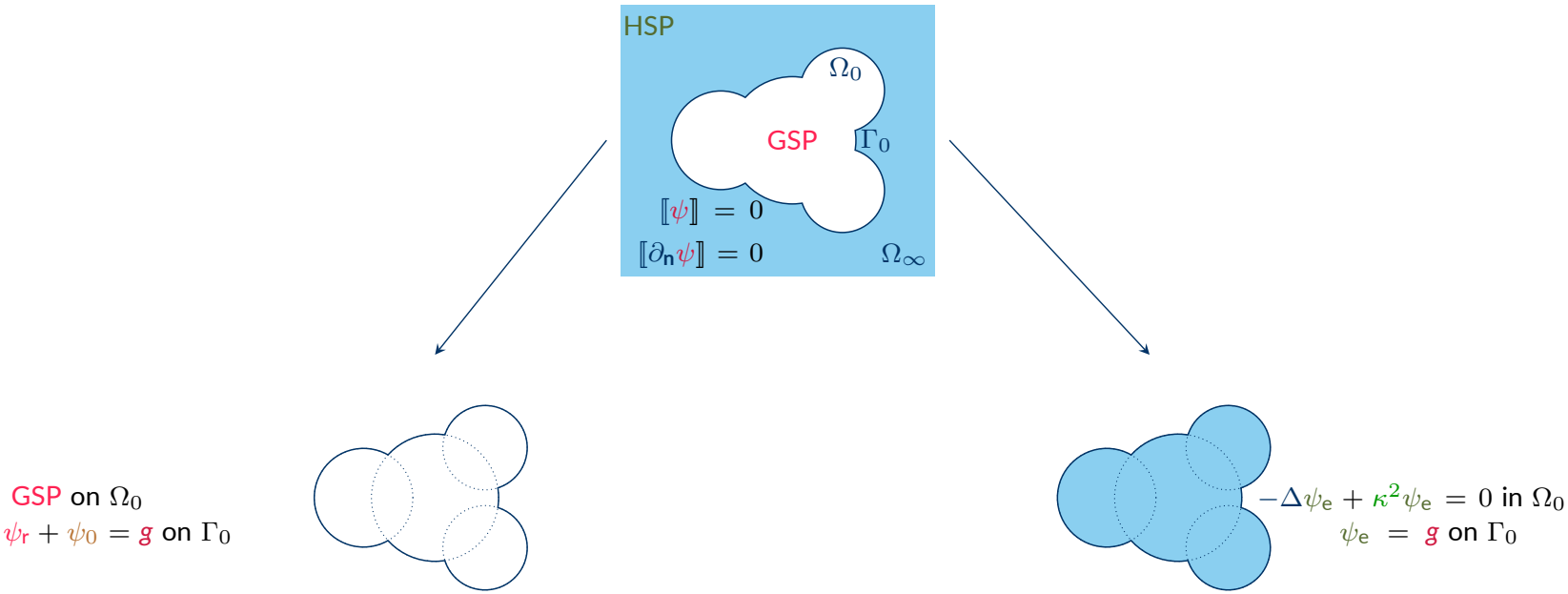
$$S_\kappa : H^{-1/2}(\Gamma_0) \to H^{1/2}(\Gamma_0)$$

[1] Sauter, Schwab, Springer, Berlin-2011, 101-181

ddPB-Method


HSP
Ω_0
GSP
Γ_0
$[\![\psi]\!] = 0$
$[\![\partial_{\mathbf{n}}\psi]\!] = 0$
Ω_∞

ddPB-Method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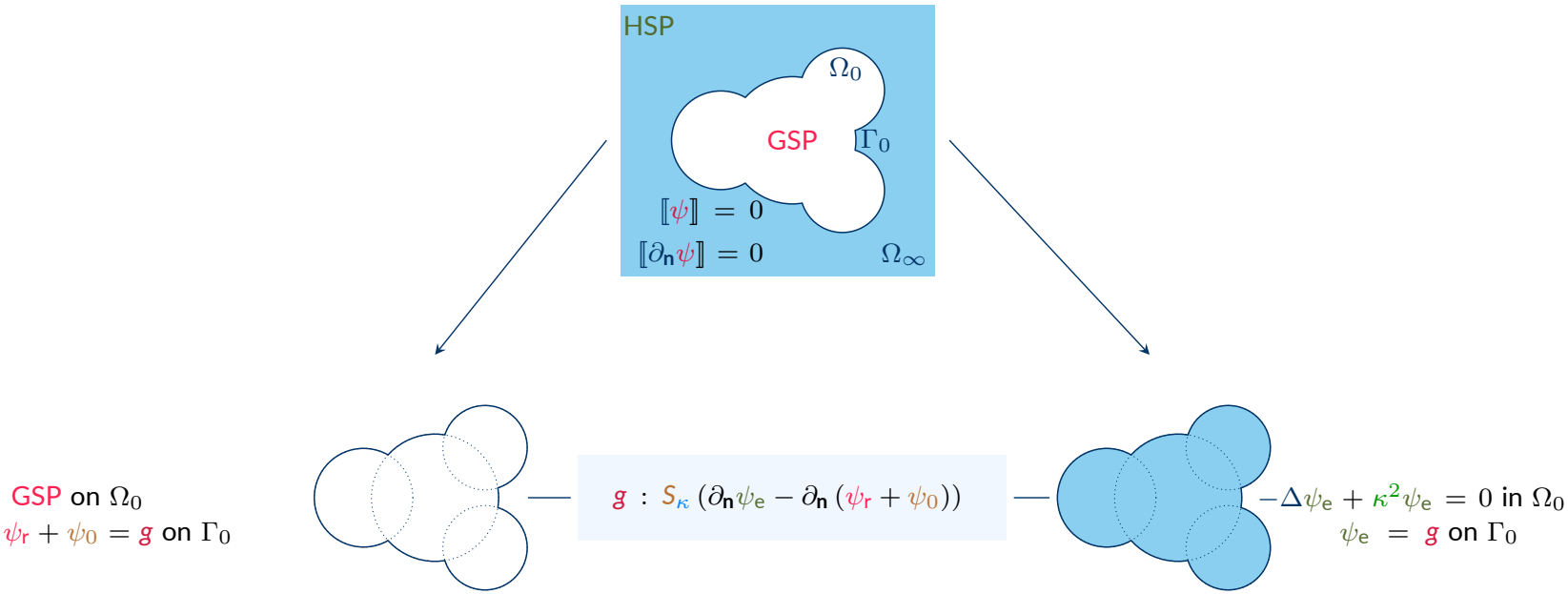
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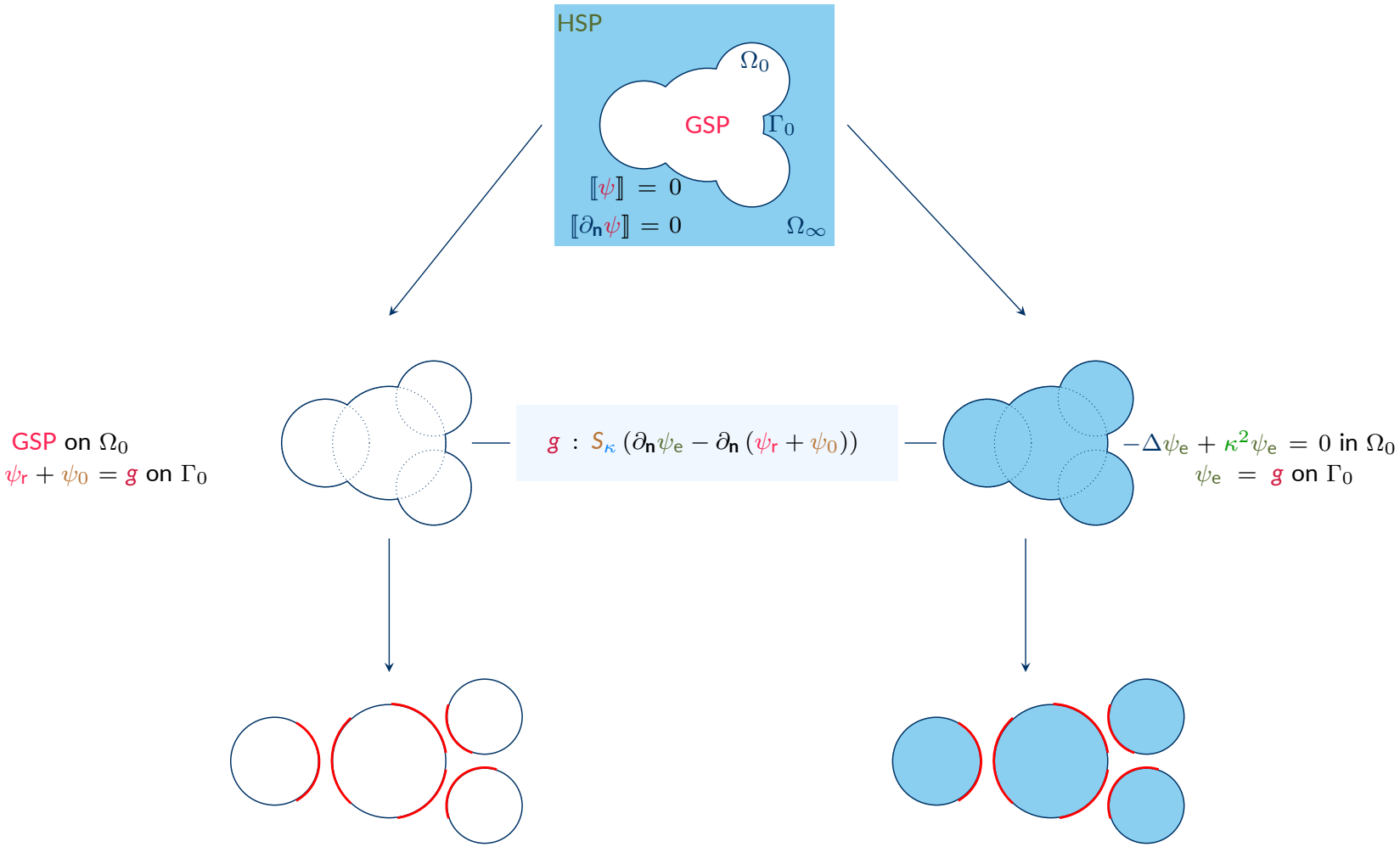
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ddPB-Method

- We can decompose Ω_0

$$\Omega_0 = \bigcup_{j=1}^{M} \Omega_j, \qquad \Omega_j = B_{R_j}(\mathbf{x}_j)$$

  - $R_j = r_j + a + r_0 + r_p$

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- History of dd-methods
  - ddCOSMO: COnductor-like Screening MOdel[1,2,3] $(\kappa \to \infty)$

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  - ddPCM: Polarizable Continuum Model[4,5] $(\kappa \to 0)$
  - ddLPB: Linear Poisson-Boltzmann[6,7] $(\|\psi\| \ll 1)$

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[1] Cances, Maday, Stamm: *The Journal of Chemical Physics*, 139 (**5**), 054111, 2013

[2] Lipparini, Stamm, Cances, Maday, Mennucci: *Journal of Chemical Theory and Computation*, 9 (**8**), 3637-3648 , 2013

[3] Lipparini, et.al. : *The Journal of Physical Chemistry Letters*, 5 (**4**), 953-958, 2014

[4] Stamm, Cances, Lipparini, Maday: *The Journal of Chemical Physics*, 144 (**1**), 054101, 2016

[5] Gatto, Lipparini, Stamm: *The Journal of Chemical Physics*, 147 (**1**), 224108, 2017

[6] Quan, Stamm, Maday: *SIAM Journal on Scientific Computing*, 41 (**2**), B320-B350, 2019

[7] J., Nottoli, Mikhalev, Quan, Stamm: *The Journal of Chemical Physics*, 158 (**1**), 104105, 2023

[8] Nottoli, Herbst, J., Lipparini, Mikhalev, Stamm: *WIREs Computational Molecular Science*, 14 (**4**), e1726, 2024

ddPB-Method

- We can decompose Ω_0

$$\Omega_0 = \bigcup_{j=1}^{M} \Omega_j, \qquad \Omega_j = B_{R_j}(\mathbf{x}_j)$$

  - $R_j = r_j + a + r_0 + r_p$
- History of dd-methods
  - ddCOSMO: COnductor-like Screening MOdel[1,2,3] $(\kappa \to \infty)$
  - ddPCM: Polarizable Continuum Model[4,5] $(\kappa \to 0)$
  - ddLPB: Linear Poisson-Boltzmann[6,7] $(\|\psi\| \ll 1)$
  - ddX[8]

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[1] Cances, Maday, Stamm: *The Journal of Chemical Physics*, 139 (**5**), 054111, 2013

[2] Lipparini, Stamm, Cances, Maday, Mennucci: *Journal of Chemical Theory and Computation*, 9 (**8**), 3637-3648 , 2013

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Single Domain Solvers

- GSP equation in unit ball

$$
\begin{aligned}
-\nabla \cdot [\tilde{\varepsilon}(\mathbf{x}) \nabla u(\mathbf{x})] + \tilde{\lambda}(\mathbf{x}) \tilde{\mathcal{F}}\left(\overline{u}(\mathbf{x})\right) u(\mathbf{x}) &= f(\mathbf{x}) \quad \text{in} \quad B_1(\mathbf{0}), \\
u(\mathbf{x}) &= \phi_r(\mathbf{x}) \quad \text{on} \quad \partial B_1(\mathbf{0})
\end{aligned}
$$

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- Transformation to Homogeneous Problem

$$\begin{aligned} -\nabla \cdot [\tilde{\varepsilon}(\mathbf{x}) \nabla w(\mathbf{x})] + \tilde{\lambda}(\mathbf{x}) \tilde{\mathcal{F}}\left(\left(\overline{w + \hat{u}_1}\right)(\mathbf{x})\right) w(\mathbf{x}) &= \tilde{f}(\mathbf{x}) \quad \text{in} \quad B_1(\mathbf{0}), \\ w(\mathbf{x}) &= 0 \quad \text{on} \quad \partial B_1(\mathbf{0}) \end{aligned}$$

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  - $\tilde{f}(\mathbf{x}) = f(\mathbf{x}) + \nabla \cdot [\tilde{\varepsilon}(\mathbf{x}) \nabla \hat{u}_1(\mathbf{x})] - \tilde{\lambda}(\mathbf{x}) \tilde{\mathcal{F}}\left(\left(\overline{w + \hat{u}_1}\right)(\mathbf{x})\right) \hat{u}_1(\mathbf{x})$

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  - $\hat{u}_1(\mathbf{x})$: Laplace solution satisfying the boundary condition

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- $B_{r_j}(\mathbf{x}_j) \subset \Omega_j$

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  - $\psi_r(\mathbf{x})$ is harmonic in $B_{r_j}(\mathbf{x}_j)$

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- $B_{r_j}(\mathbf{x}_j) \subset \Omega_j$
  - $\psi_r(\mathbf{x})$ is harmonic in $B_{r_j}(\mathbf{x}_j)$
  - $w(\mathbf{x})$ is harmonic in $B_\delta(\mathbf{0})$ where

$$\delta = \frac{r_j}{r_j + r_0 + r_p + a} \in (0, 1)$$

Single Domain Solvers

- Find $w \in H^1_{0,\delta}(\mathcal{D})$ such that

$$\int_{\mathcal{D}} \tilde{\varepsilon}(\mathbf{x}) \nabla w(\mathbf{x}) \nabla \tilde{w}(\mathbf{x}) \quad + \quad \int_{\mathcal{D}} \tilde{\lambda}(\mathbf{x}) \tilde{\mathcal{F}}\left(\overline{w}(\mathbf{x})\right) w(\mathbf{x}) \tilde{w}(\mathbf{x})$$

$$+ \int_{\partial B_\delta(\mathbf{0})} (\mathcal{T} w)\, \tilde{w}(\mathbf{x}) = \int_{\mathcal{D}} \tilde{f}(\mathbf{x}) \tilde{w}(\mathbf{x}) \quad \forall \ \tilde{w} \in H^1_{0,\delta}(\mathcal{D}),$$

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  - $\mathcal{D} = B_1(\mathbf{0}) \setminus B_\delta(\mathbf{0})$
  - $H^1_{0,\delta}(\mathcal{D}) = \left\{ w \in H^1(\mathcal{D}) : w|_{\partial B_1(\mathbf{0})} = 0 \right\}$

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  - $H^1_{0,\delta}(\mathcal{D}) = \left\{ w \in H^1(\mathcal{D}) : w|_{\partial B_1(\mathbf{0})} = 0 \right\}$
- Using Galerkin discretisation

$$w_{\mathcal{B}}(r, \theta, \varphi) = \sum_{i=0}^{N} \sum_{\ell=0}^{\ell_{\max}} \sum_{m=-\ell}^{\ell} [\phi_r]^m_{i\ell}\, \varrho_i(r) Y^m_\ell(\theta, \varphi) \quad \forall\ \delta \le r \le 1; \quad 0 \le \theta \le \pi; \quad 0 \le \varphi \le 2\pi,$$

  - ϱ_i : Legendre polynomial of order i
  - N : Maximum degree of Legendre polynomial of order ϱ_i
  - Y^m_ℓ : Spherical Harmonic Basis
  - $\ell_{\max}$: Maximum degree of Y^m_ℓ

- System of Equation

$$\mathbf{A}X_r = \mathbf{F}$$

where

- $k(:= N\left(\ell^2 + m + 1\right) + i \in \{1, 2, \ldots, N\left(\ell_{\max} + 1\right)^2\}), k'$ entry

$$\begin{aligned}[\mathbf{A}]_{k,k'} &= \int_{\mathcal{D}} \tilde{\varepsilon}(\mathbf{x}) \nabla \left(\varrho_i Y_\ell^m\right) \cdot \nabla \left(\varrho_j Y_{\ell'}^{m'}\right) \\ &\quad + \int_{\mathcal{D}} \tilde{\lambda}(\mathbf{x}) \tilde{\mathcal{F}} \left(\overline{\tilde{w}}(\mathbf{x})\right) \varrho_i Y_\ell^m \varrho_j Y_{\ell'}^{m'} \\ &\quad + \frac{\ell}{\delta} \int_{\partial B_\delta(\mathbf{0})} \varrho_i Y_\ell^m \varrho_j Y_{\ell'}^{m'},\end{aligned}$$

-

$$[\mathbf{F}]_k = \int_{\mathcal{D}} \tilde{f} \varrho_j Y_{\ell'}^{m'} \quad \forall \; k \in \{1, \ldots, N(\ell_{\max} + 1)^2\}.$$

Single Domain Solvers

- HSP equation in unit ball [1]

$$\begin{aligned} -\Delta u_e + \kappa^2 u_e^2 &= 0 \quad \text{in } B_1(\mathbf{0}), \\ u_e &= \phi_e \quad \text{on } \mathbb{S}^2 \end{aligned}$$

- u_e can be numerically approximated by $\tilde{u}_e$

$$\tilde{u}_e(r,\theta,\varphi) = \sum_{\ell=0}^{\ell_{\max}} \sum_{m=-\ell}^{\ell} \left[\tilde{\phi}_e\right]_\ell^m \frac{i_\ell(r)}{i_\ell(1)} Y_\ell^m(\theta,\varphi)$$

for $0 \le r \le 1,\ 0 \le \theta \le \pi,\ 0 \le \varphi < 2\pi$

[1] Quan, Stamm, Maday: *SIAM Journal on Scientific Computing*, 41 (**2**), B320-B350, 2019

[2] Lebedev: *USSR Computational Mathematics and Mathematical Physics*, 16 (**2**), 293-306, 1976

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for $0 \le r \le 1,\ 0 \le \theta \le \pi,\ 0 \le \varphi < 2\pi$

  - $\left[\tilde{\phi}_e\right]_\ell^m$: Numerical approximation of $[\phi_e]_\ell^m$ [2]

$$\left[\tilde{\phi}_e\right]_\ell^m = \sum_{n=1}^{N_{\text{leb}}} \omega_n^{\text{leb}} \phi_e(s_n) Y_\ell^m(s_n)$$

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Numerical Studies

- Numerical Integration[1,2]

[1] Haxton: *J.Phy.B*, 40 (**1**), 4443, 2007

[2] Parter: *Journal of Scientific Computing*, 14 (**1**), 347-355, 1999

- Numerical Integration[1,2]

$$\begin{aligned}\int_{\mathcal{D}} h(\mathbf{x})d\mathbf{x} &= \int_{\delta}^{1} r^2 \int_{\mathbb{S}^2} h(r,\mathbf{s})d\mathbf{s}dr \\ &\approx \frac{1-\delta}{2}\sum_{m=1}^{N_{\text{lgl}}}\sum_{n=1}^{N_{\text{leb}}} \omega_m^{\text{lgl}}\omega_n^{\text{leb}}\left(\frac{1-\delta}{2}(x_m+1)+\delta\right)^2 \\ &\quad \times h\left(\frac{1-\delta}{2}(x_m+1)+\delta, \mathbf{s}_n\right).\end{aligned}$$

[1] Haxton: *J.Phy.B*, 40 (**1**), 4443, 2007

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Numerical Studies

- Energy Computation[1]

$$E_s = \frac{\beta}{2}\int_\Omega \rho^{\text{sol}}(\mathbf{x})\psi_{\text{r}}(\mathbf{x}) + \frac{\beta^2\kappa^2\varepsilon_s}{8\pi}\int_\Omega \lambda(\mathbf{x})\left(\psi_{\text{r}}(\mathbf{x})\sinh\left(\psi_{\text{r}}(\mathbf{x})\right) - 2\cosh\left(\psi_{\text{r}}(\mathbf{x})\right)\right)$$

[1] Stein, Herbert, Head-Gordon: *The Journal of Chemical Physics*, 151 (**22**), 224111, 2019

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- Stopping Criteria
  - Global Iterative Process

$$|E_s^{\,k} - E_s^{\,k-1}|/|E_s^{\,k}| \leq \text{tol}$$

[1] Stein, Herbert, Head-Gordon: *The Journal of Chemical Physics*, 151 (**22**), 224111, 2019

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- Stopping Criteria
  - Global Iterative Process

$$|E_s^{\,k} - E_s^{\,k-1}|/|E_s^{\,k}| \leq \text{tol}$$

  - DD loop

$$\frac{\|X_r^{\,k} - X_r^{\,k-1}\|_{\ell^2}}{\|X_r^{\,k}\|_{\ell^2}} \leq 10 \times \text{tol}$$

[1] Stein, Herbert, Head-Gordon: *The Journal of Chemical Physics*, 151 (**22**), 224111, 2019

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  - Matrix loop

$$\frac{\|X_{\text{r},i}{}^{\text{k}} - X_{\text{r},i}{}^{\text{k}-1}\|_{\ell^2}}{\|X_{\text{r},i}{}^{\text{k}}\|_{\ell^2}} \leq 100 \times \text{tol}$$

[1] Stein, Herbert, Head-Gordon: *The Journal of Chemical Physics*, 151 (**22**), 224111, 2019

Numerical Studies

- Constants in the model

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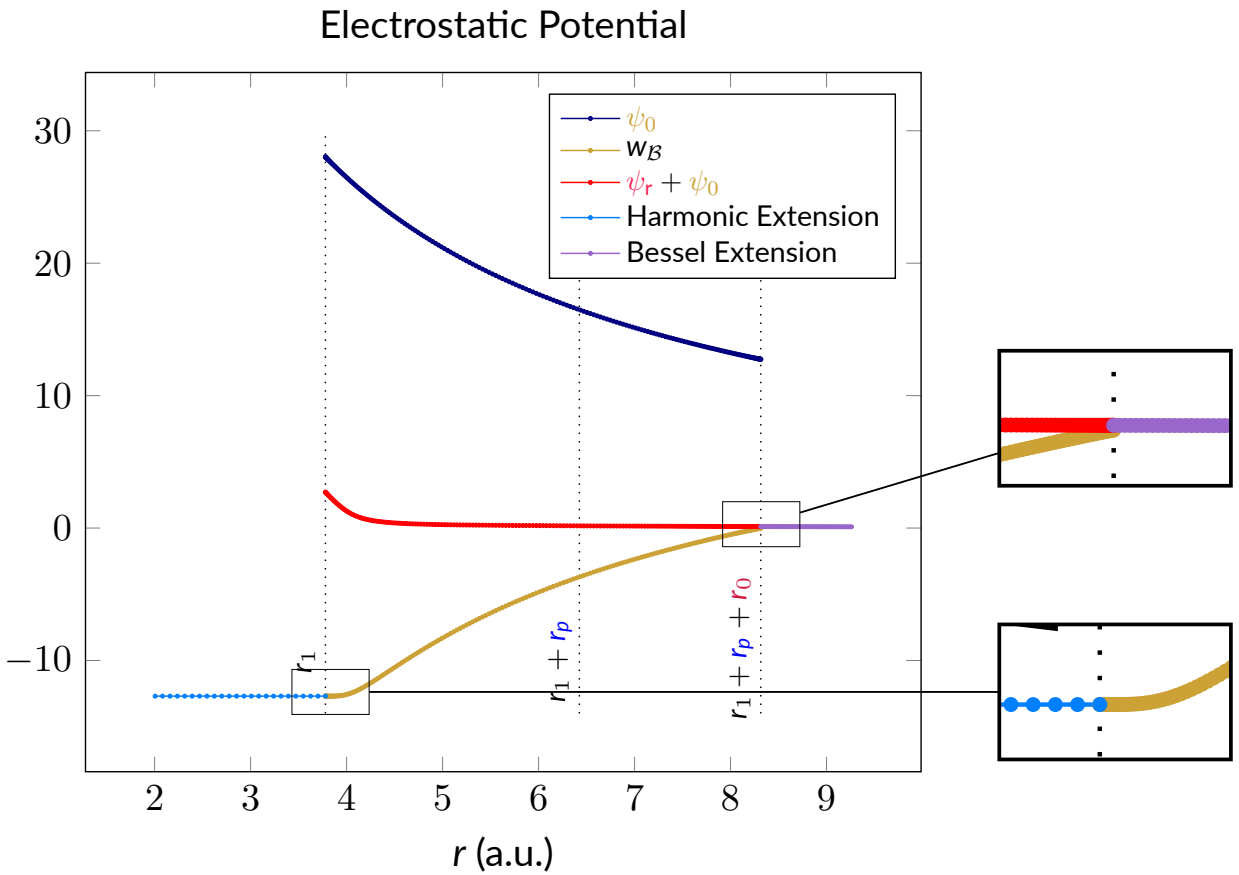
  - ε_s: 78.54
  - κ: 0.104 Å^{-1}
  - r_p: 1.4 Å
  - T: 298.15 K
  - tol: 10^{-7}

Numerical Studies

- Constants in the model
  - ε_s: 78.54
  - κ: 0.104 Å^{-1}
  - r_p: 1.4 Å
  - T: 298.15 K
  - tol: 10^{-7}
  - Conversion to atomic units

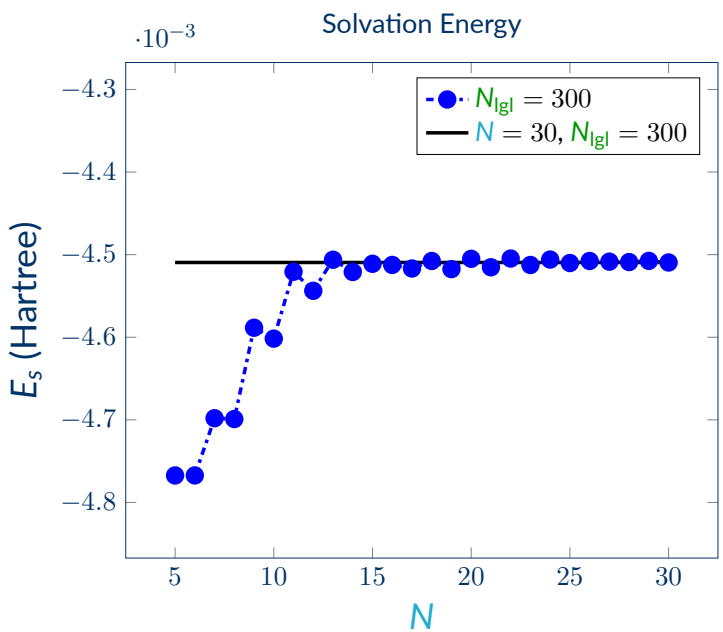
Potential for One Sphere

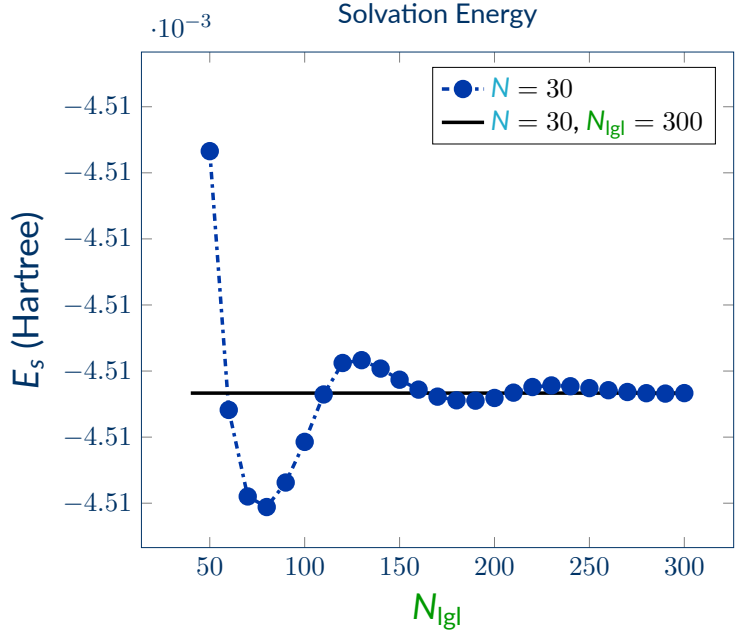
- One Sphere
- Discretisation Parameters: $N = 20$, $N_{\text{lgl}} = 200$
- Geometric Parameters: $r_1 = 2$ Å, $r_0 = 1$ Å, $a = 0$ Å



Effect of Discretisation Parameters

- Discretisation Parameters: $N = 30$, $N_{\text{lgl}} = 300$
- Geometric Parameters: $r_1 = 2$ Å, $r_0 = 5$ Å, $a = 0$ Å

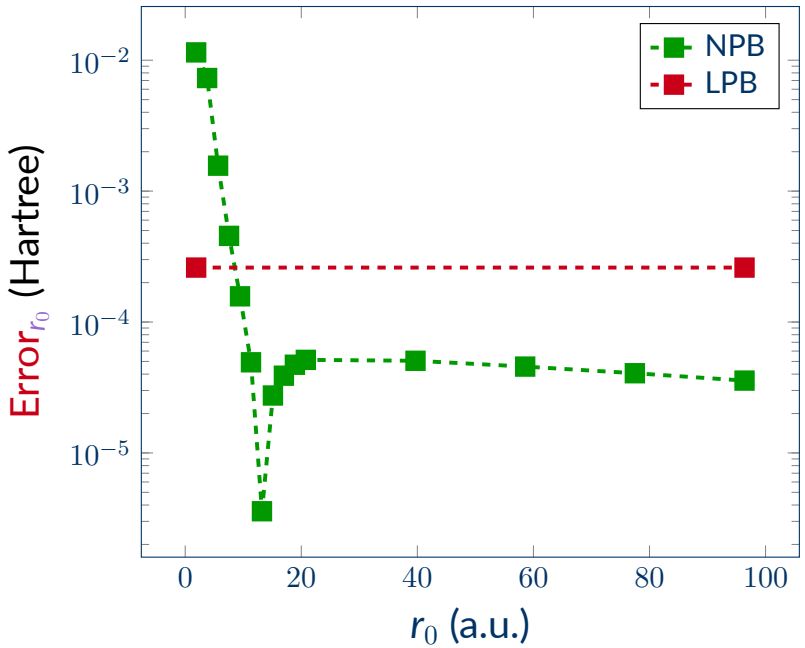




- Similar observations for spherical discretisation

Variation of ψ_r

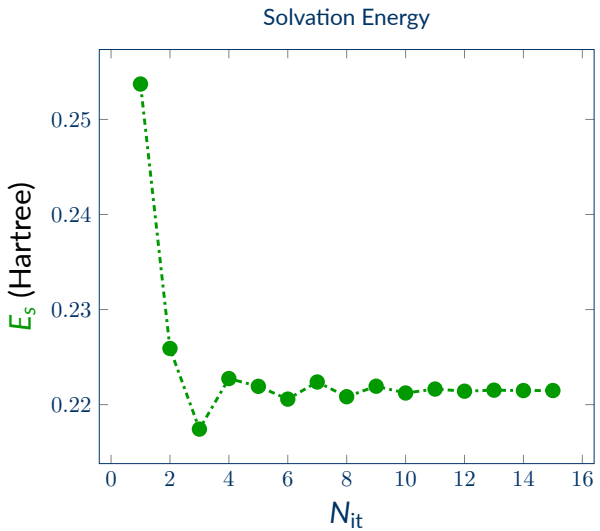
- Hydrogen Fluoride Molecule
- Discretisation Parameters: $N = 40$, $N_{\text{lgl}} = 500$, $\ell_{\text{max}} = 7$, $N_{\text{leb}} = 86$
- Geometric Parameters: $a = 1$ Å, ${r_0}^{\text{max}} = 91$ Å

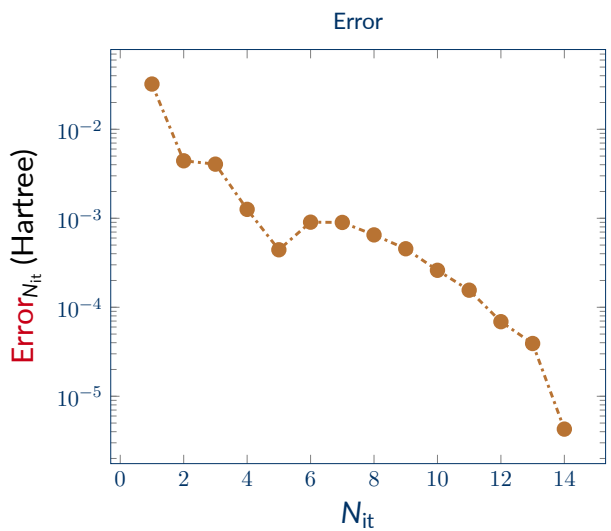


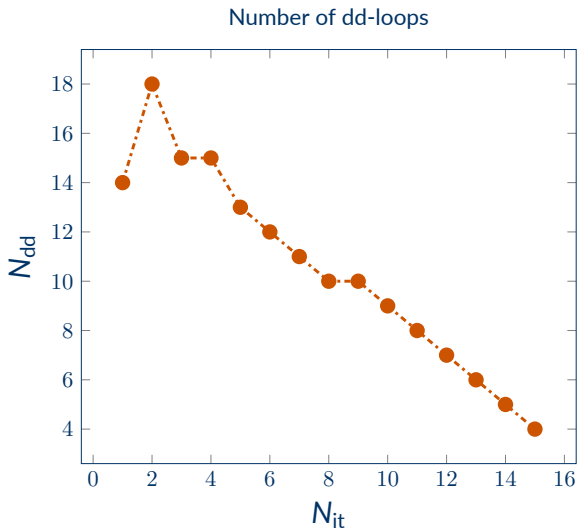
- $\text{Error}_{r_0} := |E_s(r_0) - E_s({r_0}^{\text{max}})|$

Convergence of Global Strategy

- Caffeine Molecule
- Discretisation Parameters: $N = 15$, $N_{\text{lgl}} = 50$, $\ell_{\text{max}} = 9$, $N_{\text{leb}} = 350$
- Geometric Parameters: $r_0 = 5$ Å, $a = 1$ Å



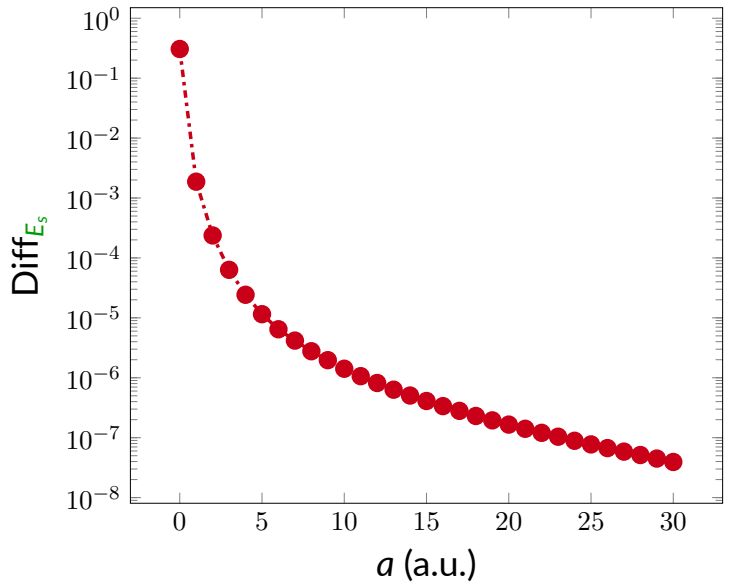




- $\text{Error}_{N_{\text{it}}} := |E_s^{\infty} - E_s^{N_{\text{it}}}|$
  - E_s^{∞}: 15 Outer Iterations

Effect of Stern layer

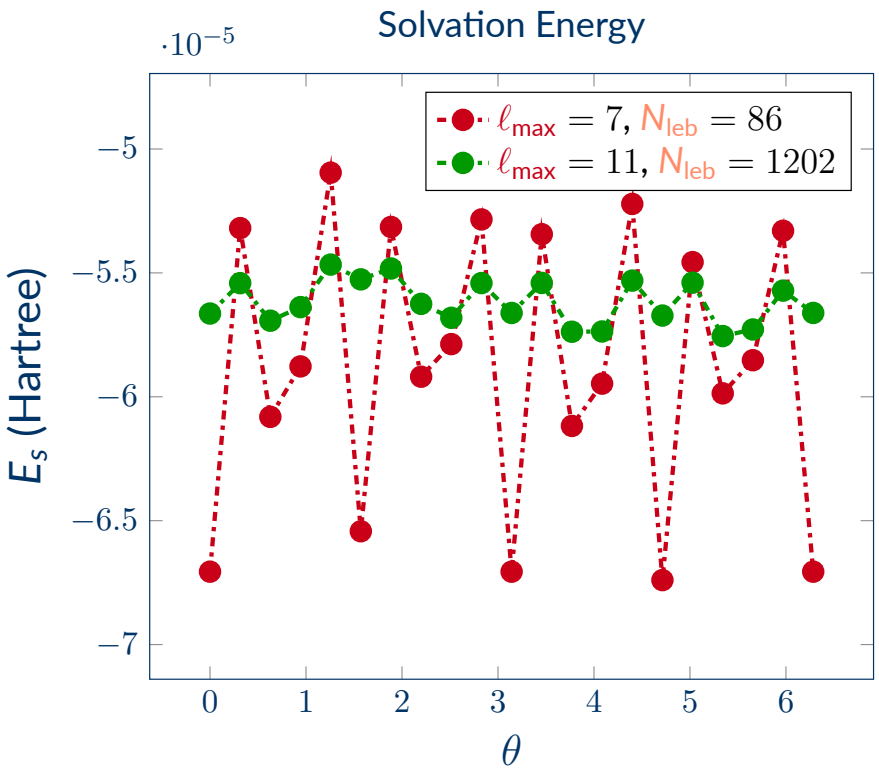
- Hydrogen Fluoride Molecule
- Discretisation Parameters: $N = 15$, $N_{\text{lgl}} = 50$, $\ell_{\text{max}} = 9$, $N_{\text{leb}} = 350$
- Geometric Parameters: $r_0 = 2$ Å



- $\text{Diff}_{E_s} = \left| \frac{\beta^2 \kappa^2 \varepsilon_s}{8\pi} \int_{\Omega_0} \lambda(\mathbf{x}) \left[\psi_r(\mathbf{x}) \sinh(\psi_r(\mathbf{x})) - 2\{\cosh(\psi_r(\mathbf{x})) - 1\} \right] \right|,$

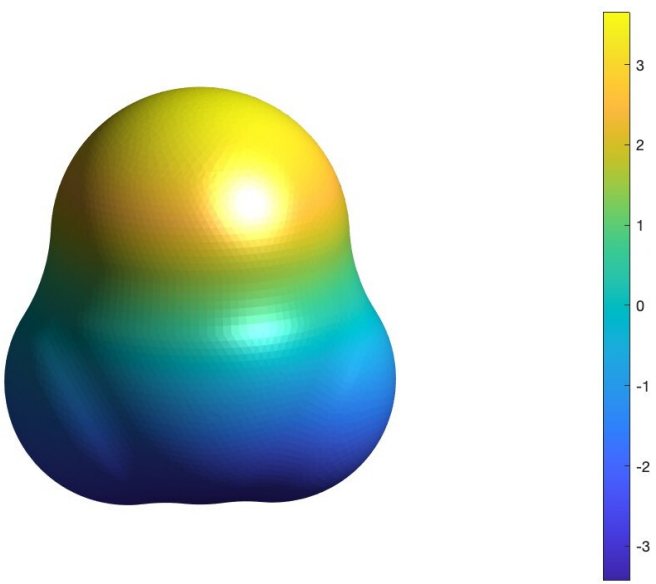
Rotational Symmetry

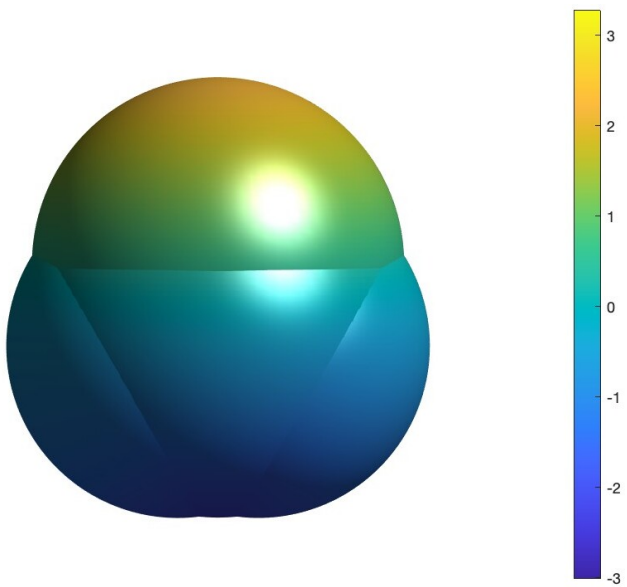
- Hydrogen Fluoride Molecule
- Discretisation Parameters: $N = 15$, $N_{\text{lgl}} = 50$
- Geometric Parameters: $r_0 = 3$ Å, $a = 5$ Å



Visualisation of Potential

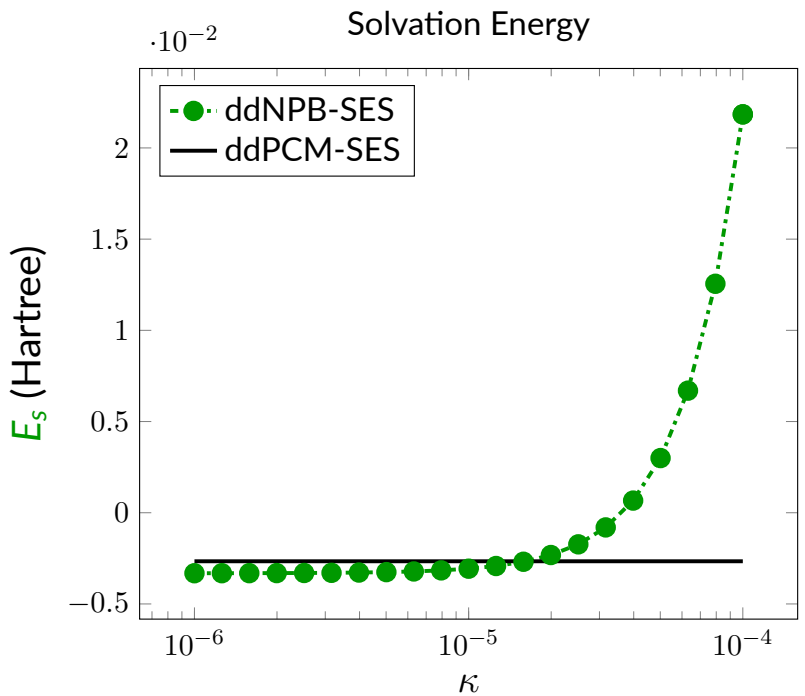
- Visualisation of ψ_r
- Discretisation Parameters: $N = 15$, $N_{lgl} = 50$, $\ell_{max} = 11$, $N_{leb} = 1202$
- Geometric Parameters: $r_0 = 3$ Å, $a = 1$ Å





Effect of κ

- Hydrogen Fluoride Molecule
- Variation of κ
- Discretisation Parameters: $N = 15$, $N_{\text{lgl}} = 30$, $\ell_{\text{max}} = 7$, $N_{\text{leb}} = 86$
- Geometric Parameters: $r_0 = 0$ Å, $a = 0$ Å



Conclusions and Outlook

- Conclusions[1]
  - Formulation of domain decomposition method for PB equations

[1] J., Stamm: arXiv:2309.06862, 2023

[2] Nottoli, Herbst, J., Lipparini, Mikhalev, Stamm: *WIREs Computational Molecular Science*, 14 (**4**), e1726, 2024

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  - Acceleration techniques

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[2] Nottoli, Herbst, J., Lipparini, Mikhalev, Stamm: *WIREs Computational Molecular Science*, 14 (**4**), e1726, 2024

Thank You!

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