Domain Decomposition Methods for the Poisson-Boltzmann Equations

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Joint work with B. Stamm (Universität Stuttgart, Stuttgart)

Outline

- Poisson-Boltzman (PB) Equation

$$-\nabla \cdot \left[\varepsilon(\mathbf{x})\nabla\tilde{\psi}(\mathbf{x})\right] = 4\pi\left(\rho^{\text{sol}}(\mathbf{x}) + \rho^{\text{ions}}(\mathbf{x})\right) \quad \text{in } \mathbb{R}^3$$

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

- Poisson-Boltzman (PB) Equation

$$-\nabla \cdot \left[\varepsilon(\mathbf{x})\nabla\tilde{\psi}(\mathbf{x})\right] = 4\pi\left(\rho^{\text{sol}}(\mathbf{x}) + \rho^{\text{ions}}(\mathbf{x})\right) \quad \text{in } \mathbb{R}^3$$

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

- $\rho^{\text{ions}}(\mathbf{x})$: Ionic charge 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: JCP, 151(22), 2019

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

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

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

[1] Stein, Herbert, Head-Gordon: JCP, 151(22), 2019

- For $1:1$ solution Poisson-Boltzman (PB) Equation

$$-\nabla \cdot \left[\varepsilon(\mathbf{x})\nabla\tilde{\psi}(\mathbf{x})\right] + 8\pi ec\lambda(\mathbf{x})\sinh\left(\frac{e\tilde{\psi}(\mathbf{x})}{K_B T}\right) = 4\pi\rho^{\text{sol}}(\mathbf{x}) \quad \text{in } \mathbb{R}^3$$

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- Dimensionless Poisson-Boltzman (PB) Equation

$$-\nabla \cdot [\varepsilon(\mathbf{x})\nabla\psi(\mathbf{x})] + \kappa^2\varepsilon_s\lambda(\mathbf{x}) \sinh(\psi(\mathbf{x})) = \frac{4\pi}{\beta}\rho^{\mathrm{sol}}(\mathbf{x}) \quad \text{in } \mathbb{R}^3$$

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$$-\nabla \cdot \left[\varepsilon(\mathbf{x})\nabla\tilde{\psi}(\mathbf{x})\right] + 8\pi ec\lambda(\mathbf{x})\sinh\left(\frac{e\tilde{\psi}(\mathbf{x})}{K_\mathrm{B}T}\right) = 4\pi\rho^{\mathrm{sol}}(\mathbf{x}) \quad \text{in } \mathbb{R}^3$$

- Dimensionless Poisson-Boltzman (PB) Equation

$$-\nabla \cdot \left[\varepsilon(\mathbf{x})\nabla\psi(\mathbf{x})\right] + \kappa^2\varepsilon_s\lambda(\mathbf{x})\sinh\left(\psi(\mathbf{x})\right) = \frac{4\pi}{\beta}\rho^{\mathrm{sol}}(\mathbf{x}) \quad \text{in } \mathbb{R}^3$$

  - $\psi(\mathbf{x}) : \tilde{\psi}(\mathbf{x})\beta$
  - κ : Debye Hückel Screening Constant
  - β : $e/K_\mathrm{B}T$

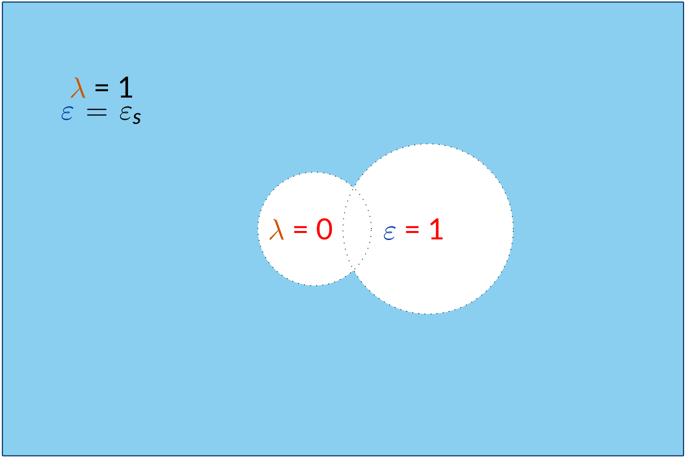
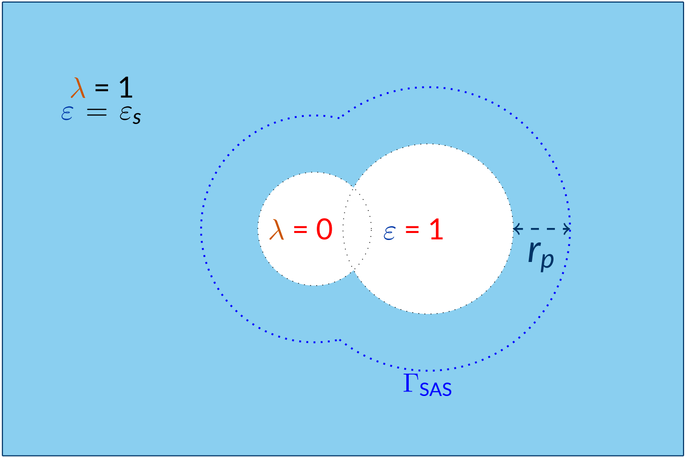


Figure 1: Solute probes and solute-solvent boundary for a molecule



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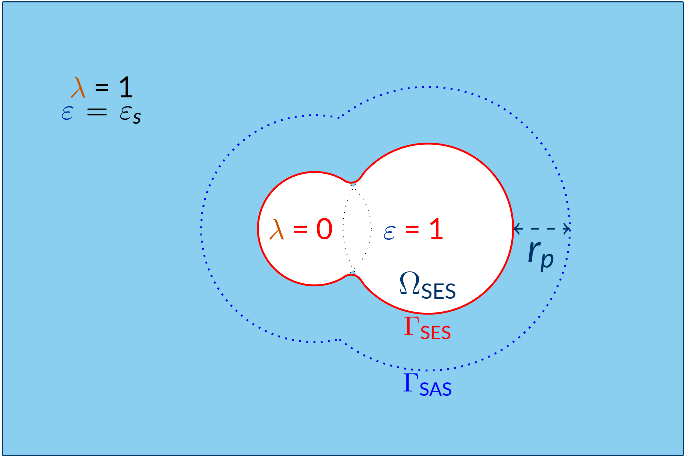

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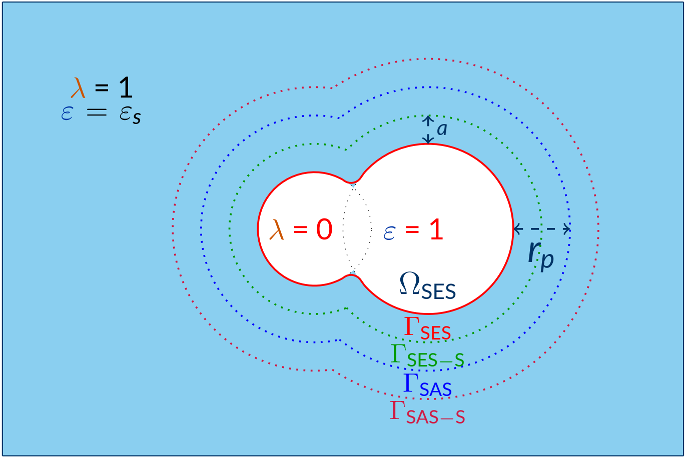
Solute Cavity



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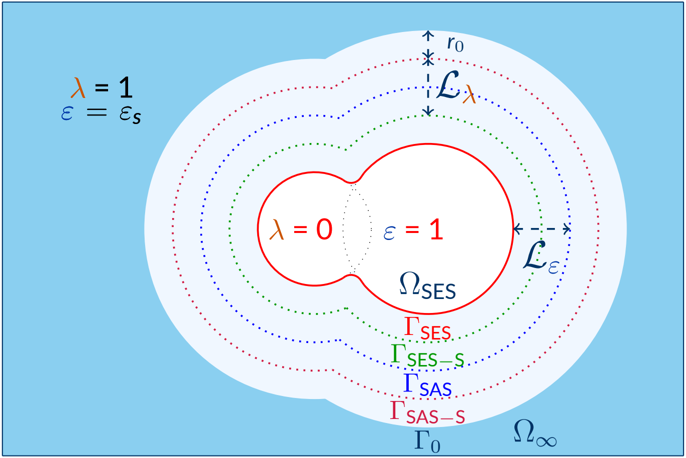

Figure 1: Solute probes and solute-solvent boundary for a molecule

- Dielectric Permittivity Function[1]

$$\varepsilon(\mathbf{x}) = \begin{cases} 1 & \mathbf{x} \in \Omega_{\mathrm{SES}}, \\ 1 + (\varepsilon_s - 1)\xi\left(\dfrac{f_{\mathrm{SAS-S}}(\mathbf{x}) + r_p}{r_0 + r_p + a}\right) & \mathbf{x} \in \mathcal{L}_\varepsilon, \\ \varepsilon_s & \text{else}, \end{cases}$$

[1] Quan, Stamm: JCP, 322, 760-782, 2016

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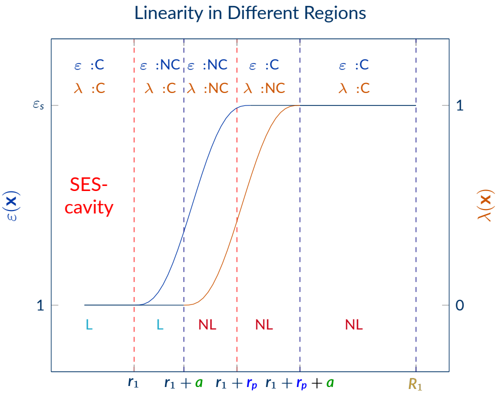
- Ion-Exclusion Function

$$\lambda(\mathbf{x}) = \begin{cases} 0 & \mathbf{x} \in \Omega_{\mathsf{SES-S}}, \\ \xi\left(\dfrac{f_{\mathsf{SAS-S}}(\mathbf{x}) + r_p}{r_0 + r_p + a}\right) & \mathbf{x} \in \mathcal{L}_\lambda, \\ 1 & \text{else,} \end{cases}$$

[1] Quan, Stamm: JCP, 322, 760-782, 2016



- R_1: $r_1 + r_p + a + r_0$
- C: Constant, NC: Non-Constant
- L: Linear, NL: Non-Linear

- The PB equation can be written in two equations

$$\begin{aligned} -\nabla\cdot[\varepsilon(\mathbf{x})\nabla\psi(\mathbf{x})] + \kappa^2\varepsilon_s\lambda(\mathbf{x})\sinh(\psi(\mathbf{x})) &= \frac{4\pi}{\beta}\rho^{\mathrm{sol}}(\mathbf{x}) \quad &\text{in } \Omega_0,\\ -\Delta\psi(\mathbf{x}) + \kappa^2\psi(\mathbf{x}) &= 0 \quad &\text{in } \Omega_\infty, \end{aligned}$$

with

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

- Using Potential Theory the final equations are

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

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$$-\nabla \cdot [\varepsilon(\mathbf{x})\nabla\psi_r(\mathbf{x})] + \kappa^2\varepsilon_s\lambda(\mathbf{x})\mathcal{F}(\psi_r + \psi_0)(\psi_r + \psi_0)(\mathbf{x}) = \nabla \cdot [(\varepsilon(\mathbf{x}) - 1)\nabla\psi_0(\mathbf{x})] \quad \text{in } \Omega_0 \qquad \text{[GSP]}$$

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

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with

$$\psi_0 + \psi_r = \psi_e \quad \text{on } \Gamma,$$
$$\psi_e = S_\kappa \sigma_e \quad \text{on } \Gamma$$

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

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with

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

where

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

$$-\Delta\psi_0 = \frac{4\pi}{\beta}\rho_{\mathsf{M}}$$

- 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
- $\mathcal{F}(\Phi) = \dfrac{\sinh(\Phi)}{\Phi}$

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Problem Transformation

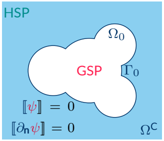
- ψ_e : Extended potential from Ω^C to Ω^0
- $\mathcal{F}(\Phi) = \dfrac{\sinh(\Phi)}{\Phi}$
- σ_e : Charge density generating ψ_e satisfying

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

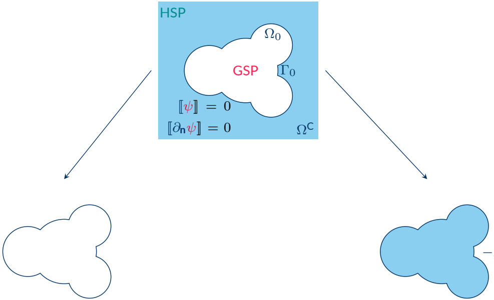
- S_κ : Invertible single-layer potential operator [1]

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

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


HSP
Ω_0
GSP
Γ_0
$[\![\psi]\!] = 0$
$[\![\partial_n \psi]\!] = 0$
Ω^C

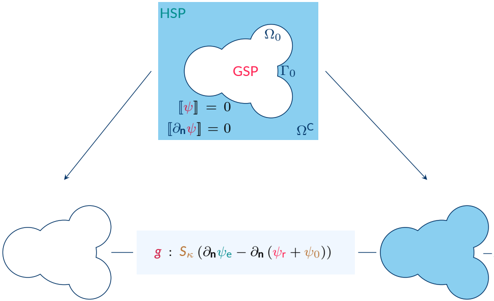
ddPB-Method



GSP on Ω_0
$\psi_r + \psi_0 = g$ on Γ_0

$-\Delta\psi_e + \kappa^2\psi_e = 0$ in Ω_0
$\psi_e = g$ on Γ_0

GSP on Ω_0
$\psi_r + \psi_0 = g$ on Γ_0



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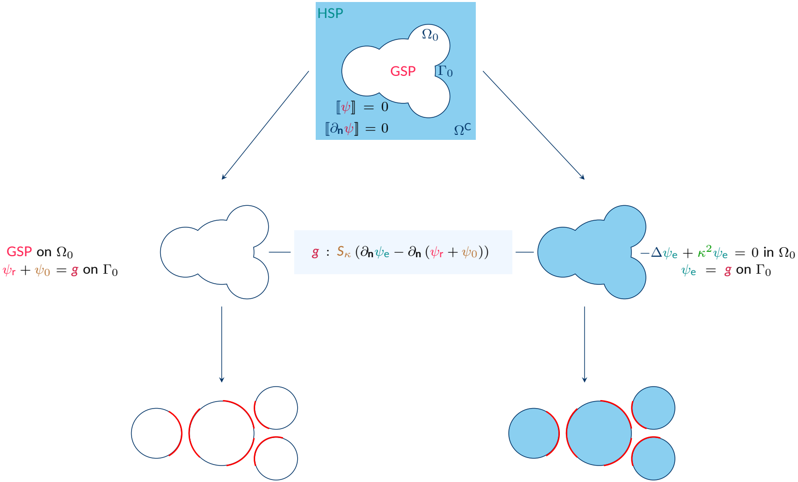

HSP
Ω_0
GSP
Γ_0
$[\![\psi]\!] = 0$
$[\![\partial_n \psi]\!] = 0$
Ω^C
GSP on Ω_0
$\psi_r + \psi_0 = g$ on Γ_0
$g : S_\kappa \left(\partial_n \psi_e - \partial_n (\psi_r + \psi_0)\right)$
$-\Delta\psi_e + \kappa^2\psi_e = 0$ in Ω_0
$\psi_e = g$ on Γ_0

- GSP equation in unit ball

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

- GSP equation in unit ball

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

- Transformation to Homogeneous Problem

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

Single Domain Solvers

- GSP equation in unit ball

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

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

- GSP equation in unit ball

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

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

- GSP equation in unit ball

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

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  - $\psi_{\mathrm{r}}(\mathbf{x})$ is harmonic in $B_{r_j}(\mathbf{x}_j)$

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  - $\hat{u}_1(\mathbf{x})$: Laplace solution satisfying the boundary condition
- $B_{r_j}(\mathbf{x}_j) \subset \Omega_j$
  - $\psi_{\mathrm{r}}(\mathbf{x})$ is harmonic in $B_{r_j}(\mathbf{x}_j)$
  - $w(\mathbf{x})$ is harmonic in $B_\delta(\mathbf{0})$ where

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

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

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

Single Domain Solvers

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

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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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- Using Galerkin discretisation

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

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

- System of Equation

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

where

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

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

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

- HSP equation in unit ball [1]

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

- 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: SISC, 41(2), B320-B350, 2019

Single Domain Solvers

- HSP equation in unit ball [1]

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

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

[1] Quan, Stamm, Maday: SISC, 41(2), B320-B350, 2019

- Numerical Integration[1,2]

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

[2] Parter: JSC, 14, 347-355, 1999

- Numerical Integration[1,2]

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

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[2] Parter: JSC, 14, 347-355, 1999

- Energy Computation[1]

$$E_s = \frac{1}{2}\int_{\mathbb{R}} \left(\rho^{\text{sol}}(\mathbf{x})\psi_r(\mathbf{x}) - \rho^{\text{ions}}(\mathbf{x})\psi_r(\mathbf{x}) - 2\Delta\Pi\right) d\mathbf{x}$$

  - $\Delta\Pi$: Osmotic Pressure

[1] Stein, Herbert, Head-Gordon: JCP, 151(22), 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: JCP, 151(22), 2019

Numerical Studies

- Energy Computation[1]

$$E_s = \frac{1}{2}\int_{\mathbb{R}} \left(\rho^{\text{sol}}(\mathbf{x})\psi_{\text{r}}(\mathbf{x}) - \rho^{\text{ions}}(\mathbf{x})\psi_{\text{r}}(\mathbf{x}) - 2\Delta\Pi\right) d\mathbf{x}$$

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  - DD loop

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

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

  - Matrix loop

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

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- Constants in the model

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  - ε_s: 78.54
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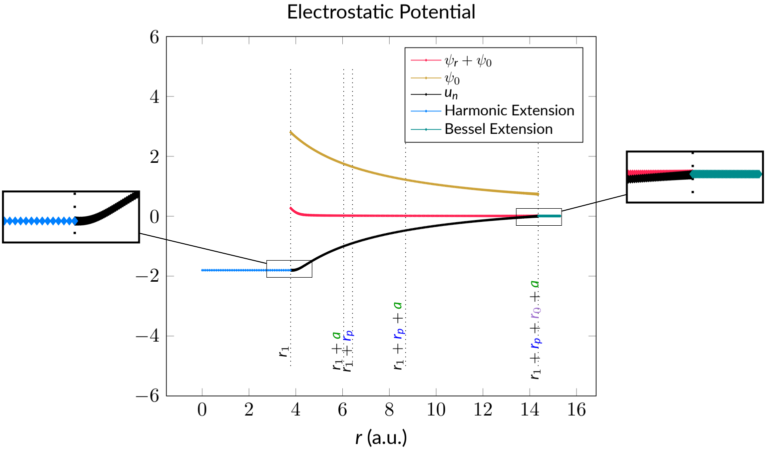
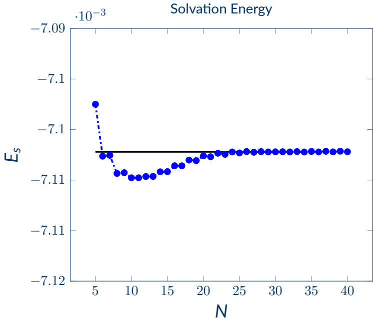
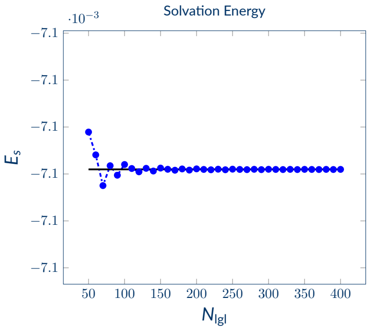
- Discretisation Parameters: $N = 20$, $N_{lgl} = 300$
- Geometric Parameters: $r_1 = 2$ Å, $r_0 = 3$ Å, $r_p = 1.4$ Å, $a = 1.2$ Å

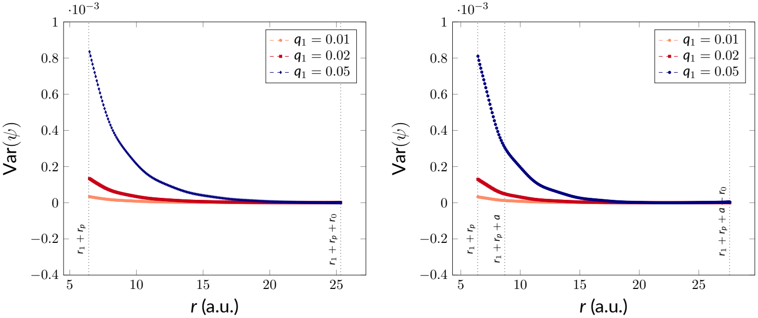


- Discretisation Parameters: $N = 40$, $N_{\text{lgl}} = 400$
- Geometric Parameters: $r_1 = 2$ Å, $r_0 = 10$ Å, $r_p = 1.4$ Å, $a = 1.2$ Å



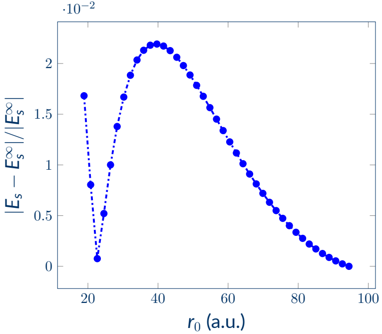


- Discretisation Parameters: $N = 20$, $N_{\text{lgl}} = 200$
- Geometric Parameters: $r_1 = 2$ Å, $r_0 = 10$ Å, $r_p = 1.4$ Å, $a = 0$ Å (left) , and $a = 1.2$ Å (right)

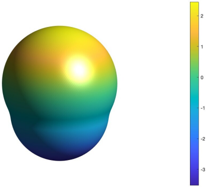


- Var(ψ)=$|\sinh(\psi)/\psi - 1|$

- Discretisation Parameters: $N = 20$, $N_{\mathrm{lgl}} = 500$
- Geometric Parameters: $r_1 = 2$ Å, $r_0 = 50$ Å, $r_p = 1.4$ Å, $a = 1.2$ Å



- Discretisation Parameters: $N = 15$, $N_{\text{lgl}} = 50$, $\ell_{\text{max}} = 11$, $N_{\text{leb}} = 1202$
- Geometric Parameters: Hydrogen Fluoride Molecule, $r_0 = 30$ Å, $r_p = 1.4$ Å, $a = 1.2$ Å



- Conclusions
  - Formulation of domain decomposition method for PB equations

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Thank You!

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