Reliable Solution of the Poisson-Boltzmann Equation with Application to the SecYEG Membrane Channel

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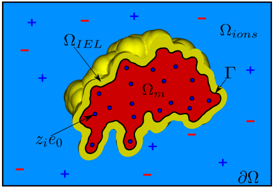
Outline

Poisson-Boltzmann equation of electrostatics

$\Omega \subset \mathbb{R}^3$ bounded Lipschitz domain,

$$\overline{\Omega} = \underbrace{\overline{\Omega}_m}_{\text{molecule}} \cup \underbrace{\overline{\Omega}_{IEL}}_{\text{ion exclusion layer}} \cup \underbrace{\overline{\Omega}_{ions}}_{\text{ions domain}},$$

$$\underbrace{\overline{\Omega}_s}_{\text{solvent}} = \overline{\Omega}_{IEL} \cup \overline{\Omega}_{ions}, \qquad \epsilon(x) = \begin{cases} \epsilon_m, & x \in \Omega_m, \\ \epsilon_s(x), & x \in \Omega_s. \end{cases}$$



The dimensionless potential ϕ satisfies

$$-\nabla \cdot (\epsilon \nabla \phi) + \overline{k}^2 \sinh(\phi) = \frac{4\pi e_0^2}{k_B T} \sum_{i=1}^{N_m} z_i \delta_{x_i} =: \mathcal{F} \quad \text{in } \Omega, \tag{1a}$$

$$\phi = g \quad \text{on } \partial\Omega. \tag{1b}$$

$$\overline{k}^2(x) = \begin{cases} 0, & x \in \Omega_m \cup \Omega_{IEL}, \\ \overline{k}_{ions}^2 = \frac{8\pi N_A e_0^2 I_s}{1000 k_B T}, & x \in \Omega_{ions}, \end{cases}$$

e_0 elementary charge, z_i valency of $i-th$ partial charge, N_{ions} number of ion species in the solvent, k_B Boltzmann constant, T absolute temperature, N_A Avogadro's number, I_s ionic strength

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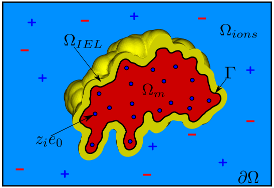

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Linearized PBE

If $\phi \ll 1$ the Poisson-Boltzmann equation (1a) can be linearized:

$$-\nabla \cdot (\epsilon \nabla \phi) + \overline{k}^2 \phi = \mathcal{F} \quad \text{in } \Omega. \qquad \text{(LPBE)}$$

For the subsequent analysis of the PBE and the Linearized PBE (LPBE):

$$G := \frac{e_0^2}{\epsilon_m k_B T} \sum_{i=1}^{N_m} \frac{z_i}{|x - x_i|}, \quad G \in \bigcap_{p < \frac{d}{d-1}} W^{1,p}(\Omega)$$

G describes the Coulomb part of the potential due to the partial charges $\{z_i e_0\}_{i=1}^{N_m}$ in a uniform dielectric medium with ϵ_m.

Formulation for G

It is well known that G is the distributional solution of the problem (ϵ_m is constant)

$$-\nabla \cdot (\epsilon_m \nabla G) = \mathcal{F} \quad \text{in } \mathbb{R}^3$$

i.e.,

$$-\int_{\mathbb{R}^3} \epsilon_m G \Delta v dx = \langle \mathcal{F}, v \rangle, \quad \text{for all } v \in C_0^\infty(\mathbb{R}^3).$$

Using integration by parts and Sobolev embeddings:

$$G \in \bigcap_{p < \frac{d}{d-1}} W^{1,p}(\Omega),$$

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Weak formulations for problems with measure data

Different ways to define a solution to a linear problem of the form

$$-\operatorname{div}(\boldsymbol{A}(x)\nabla u) = f \text{ in } \Omega,$$
$$u = 0 \text{ on } \partial\Omega,$$

Ω a bounded Lipschitz domain,
f a bounded Radon measure ($f(\Omega) < \infty$),

$$\boldsymbol{A} \in [L^\infty(\Omega)]^{d\times d}, \quad \exists\mu > 0 : \boldsymbol{A}(x)\xi\cdot\xi \geq \mu\,|\xi|^2 \text{ for a.e. } x \in \Omega \text{ and all } \xi \in \mathbb{R}^d.$$

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Existence and uniqueness for the LPBE

Notation:

Trace operator: $\gamma_p : W^{1,p}(\Omega) \to \; W^{1-1/p,p}(\partial\Omega)$,

$$W_g^{1,p}(\Omega) := \{v \in W^{1,p}(\Omega), \text{ such that } \gamma_p(v) = g \text{ on } \partial\Omega\}.$$

Definition 1 (Weak solution of the LPBE)

We call the measurable function ϕ a weak solution of (LPBE)

$$-\nabla \cdot (\epsilon \nabla \phi) + \overline{k}^2 \phi = \mathcal{F} \quad \text{in } \Omega, \; \phi = g \text{ on } \partial\Omega \qquad \text{(LPBE)}$$

if it satisfies

$$\phi \in \bigcap_{p < \frac{d}{d-1}} W_g^{1,p}(\Omega), \quad \int_\Omega \epsilon \nabla \phi \cdot \nabla v dx + \int_\Omega \overline{k}^2 \phi v dx = \langle \mathcal{F}, v \rangle, \forall v \in \bigcup_{q > d} W_0^{1,q}(\Omega) \qquad \text{(WLPBE)}$$

2- and 3-term splittings of ϕ

Idea: Separate the singular part of the potential due to the fixed charges in Ω_m.

The irregular distribution $\mathcal{F}$ is transformed to another irregular distribution which this time is bounded in $H_0^1(\Omega)$.

- 2-term splitting: $\phi = G + u$
- 3-term splitting (usefull when $\epsilon_m \ll \epsilon_s$):
$\phi = G + u^H + u$, where $u^H \in H^1(\Omega)$, u^H harmonic in Ω_m and $u^H = -G$ in $\Omega_s = \Omega \setminus \Omega_m$

Find $u \in \bigcap_{p<\frac{d}{d-1}} W_{\overline{g}}^{1,p}(\Omega)$ such that

$$\int_{\Omega} \epsilon \nabla u \cdot \nabla v dx + \int_{\Omega_{ions}} \overline{k}^2 (u+w) v dx = \int_{\Omega} \boldsymbol{f} \cdot \nabla v dx, \ \forall v \in \bigcup_{q>d} W_0^{1,q}(\Omega)$$

where $w \in L^\infty(\Omega_{ions})$, $\boldsymbol{f} \in [L^s(\Omega)]^d$ with $s > d$.

Theorem 2 (Existence and uniqueness for the LPBE)

There exists a weak solution ϕ of equation (LPBE) satisfying (WLPBE). A particular ϕ satisfying (WLPBE) can be given in the form $\phi = G + u$ or $\phi = G + u^H + u$, where $u \in H^1_{\overline{g}}(\Omega)$ is the unique solution of the problem

$$\int_{\Omega} \epsilon \nabla u \cdot \nabla v dx + \int_{\Omega_{ions}} \overline{k}^2 (u+w) v dx = \int_{\Omega} \boldsymbol{f} \cdot \nabla v dx \ \text{ for all } v \in H_0^1(\Omega). \quad (2)$$

If we assume in addition that $\Gamma \in C^1$, then ϕ is unique (using Elschner, Rehberg & Schmidt 2007).

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Existence for the (nonlinear) PBE

$$-\nabla\cdot(\epsilon\nabla\phi)\underbrace{\overline{k}^2(x)\sinh(\phi)}_{:=b(x,\phi)}=\mathcal{F}\quad\text{in }\Omega,\ \phi=g\text{ on }\partial\Omega. \tag{PBE}$$

A natural way to extend the weak formulation for the LPBE is:

Definition 3 (Weak solution of the PBE)

We call ϕ a weak solution of problem (PBE) if $\phi\in\bigcap_{p<\frac{d}{d-1}}W_g^{1,p}(\Omega)$ is such that $b(x,\phi)v\in L^1(\Omega)$ for all $v\in\bigcup_{q>d}W_0^{1,q}(\Omega)$ and

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In both 2-term ($\phi = G + u$) and 3-term ($\phi = G + u^H + u$) splittings, the "standard" weak formulation defining a particular u can be written in the general form

$$\text{Find } u \in H^1_{\overline{g}}(\Omega) \text{ such that } b(x, u + w)v \in L^1(\Omega) \text{ for all } v \in V \text{ and}$$
$$a(u, v) + \int_\Omega b(x, u + w)v dx = \int_\Omega \boldsymbol{f} \cdot \nabla v dx, \text{ for all } v \in V, \tag{4}$$

where $V = H^1_0(\Omega)$, $a(u, v) := \int_\Omega \epsilon \nabla u \cdot \nabla v dx$, $w \in L^\infty(\Omega_{ions})$, $\boldsymbol{f} \in [L^s(\Omega)]^d$ with $s > d$, and $\overline{g}$ specifies the Dirichlet boundary condition on $\partial\Omega$.

However, one can consder the following 3 cases:

$$V = H^1_0(\Omega) \supset V = H^1_0(\Omega) \cap L^\infty(\Omega) \supset V = C^\infty_0(\Omega).$$

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$$(P) \qquad \text{Find } u_{\min} \in H^1_{\frac{}{g}}(\Omega) \text{ such that } J(u_{\min}) = \min_{v \in H^1_{\frac{}{g}}(\Omega)} J(v),$$

where $J : H^1_{\frac{}{g}}(\Omega) \to \mathbb{R} \cup \{+\infty\}$

$$J(v) := \begin{cases} \frac{1}{2} a(v,v) + \int_\Omega B(x, v+w)dx - \int_\Omega \boldsymbol{f} \cdot \nabla v dx, & \text{if } B(x, v+w) \in L^1(\Omega), \\ +\infty, & \text{if } B(x, v+w) \notin L^1(\Omega). \end{cases}$$

$B(x,\cdot)$ an antiderivative of $b(x,\cdot)$: $B(x,s) := \overline{k}^2(x)\cosh(s) \geq 0$

Theorem 4 (Existence, uniqueness, and boundedness)

There exists a unique solution of the variational problem (P) which also gives the unique solution of the problem

$$\begin{aligned} &\textit{Find } u \in H^1_{\frac{}{g}}(\Omega) \textit{ such that } b(x, u+w)v \in L^1(\Omega) \textit{ for all } v \in V \textit{ and} \\ &a(u,v) + \int_\Omega b(x, u+w) v dx = \int_\Omega \boldsymbol{f} \cdot \nabla v dx, \textit{ for all } v \in V \end{aligned} \tag{4}$$

with

$$V = H^1_0(\Omega) \supset V = H^1_0(\Omega) \cap L^\infty(\Omega) \supset V = C^\infty_0(\Omega).$$

Moreover, $u \in L^\infty(\Omega)$.

Abstract framework

Notation: V, Y reflexive Banach spaces, V^*, Y^* dual spaces, $\langle v^*, v\rangle$ duality product of v^* and v in $V^* \times V$, (y^*, y) duality product of y^* and y in $Y^* \times Y$.
$\Lambda : V \to Y$ bounded linear operator, $\Lambda^* : Y^* \to V^*$ adjoint of Λ defined by

$$\langle \Lambda^* y^*, v\rangle = (y^*, \Lambda v), \forall v \in V, \forall y^* \in Y^*.$$

$F : V \to \mathbb{R} \cup \{+\infty\}$, $G : Y \to \mathbb{R} \cup \{+\infty\}$ are convex, proper and lower semi-continuous functionals, $J(v) = G(\Lambda v) + F(v)$ is coercive and $J(0_V) < +\infty$, G continuous at $\Lambda 0_Y = 0_V$.

Find $u \in V$ such that

$$(P) \quad J(u) = \inf_{v \in V} J(v),$$

Find $p^* \in Y^*$ such that

$$(P^*) \quad I^*(p^*) = \sup_{y^* \in Y^*} I^*(y^*), \text{ where } I^*(p^*) = -G^*(y^*) - F^*(-\Lambda^* y^*).$$

Strong duality holds (Fenchel-Rockafellar, e.g. see Ekeland & Temam 1978)

$$J(u) = \inf_{v \in V} J(v) = \sup_{y^* \in Y^*} I^*(y^*) = I^*(p^*), \quad \Lambda u \in \partial G^*(p^*), \quad p^* \in \partial G(\Lambda u).$$

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See Repin 1999, Repin 2000

$$D_G(\Lambda v, y^*) := G(\Lambda v) + G^*(y^*) - (y^*, \Lambda v) \geq 0$$

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Linear elliptic problem

$V = H^1_0(\Omega)$, $V^* = H^{-1}(\Omega)$, $Y = [L^2(\Omega)]^d = Y^*$,
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$$\begin{cases} -\operatorname{div}(\boldsymbol{A}\nabla u) + u = f_0 \text{ in } \Omega, \\ u = 0 \text{ on } \partial\Omega. \end{cases}$$

$$|||\nabla(v-u)|||^2 + \|v-u\|^2_{L^2(\Omega)} + |||y^* - p^*|||^2_* + \|\operatorname{div}(y^* - p^*)\|^2_{L^2(\Omega)}$$

$$= |||\boldsymbol{A}\nabla v - y^*|||^2_* + \|v - \operatorname{div} y^* - f_0\|^2_{L^2(\Omega)} = 2M^2_\oplus(v, y^*),$$

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$G(\Lambda v) = G(\nabla v) = \int_\Omega \frac{1}{2} \boldsymbol{A}\nabla v \cdot \nabla v dx$ and $F(v) = \int_\Omega \left(\frac{1}{2} v^2 - f_0 v\right) dx$

$$\begin{cases} -\operatorname{div}(\boldsymbol{A}\nabla u) + u = f_0 \text{ in } \Omega, \\ u = 0 \text{ on } \partial\Omega. \end{cases}$$

$$|||\nabla(v-u)|||^2 + \|v-u\|^2_{L^2(\Omega)} + |||y^* - p^*|||^2_* + \|\operatorname{div}(y^* - p^*)\|^2_{L^2(\Omega)}$$
$$= |||A\nabla v - y^*|||^2_* + \|v - \operatorname{div} y^* - f_0\|^2_{L^2(\Omega)} = 2M^2_\oplus(v, y^*),$$

$$\text{where } |||\boldsymbol{q}|||^2 = \int_\Omega \boldsymbol{A}\boldsymbol{q}\cdot\boldsymbol{q}dx,\ |||\boldsymbol{q}|||^2_* = \int_\Omega \boldsymbol{A}^{-1}\boldsymbol{q}\cdot\boldsymbol{q}dx.$$

Explicit form of the error identity for the PBE

$$(P) \qquad \text{Find } u_{\min} \in H^1_{\frac{1}{g}}(\Omega) \text{ such that } J(u_{\min}) = \min_{v \in H^1_{\frac{1}{g}}(\Omega)} J(v),$$

$$J(v) := \underbrace{\frac{1}{2}a(v,v)}_{G(\Lambda v)} + \underbrace{\int_\Omega B(x, v+w)dx - \int_\Omega \boldsymbol{f} \cdot \nabla v dx}_{F(v)},$$

Homogeneous Dirichlet BC

Take $V = H_0^1(\Omega)$, $V^* = H^{-1}(\Omega)$, $Y = Y^* = \left[L^2(\Omega)\right]^d$, $\Lambda = \nabla$, $\Lambda^* = -\operatorname{div}$.

From $\Lambda u \in \partial G^*(\boldsymbol{p}^*)$ or $\boldsymbol{p}^* \in \partial G(\Lambda u) \Rightarrow \boldsymbol{p}^* = \epsilon \nabla u$

Fenchel conjugate of G

$$G^*(\boldsymbol{y}^*) = \int_\Omega \frac{1}{2\epsilon} |\boldsymbol{y}^*|^2 \, dx.$$

Fenchel conjugate of F

- Observe that $\boldsymbol{p}^* = \epsilon \nabla u \in \left[L^2(\Omega)\right]^d$ can be represented in the form

$$\boldsymbol{p}^* = \boldsymbol{f} + \boldsymbol{p}_0^*, \quad \text{where } \boldsymbol{p}_0^* \in H(\operatorname{div};\Omega).$$

- Enough to consider $\boldsymbol{y}^* \in \left[L^2(\Omega)\right]^d$ of the form

$$\boldsymbol{y}^* = \boldsymbol{f} + \boldsymbol{y}_0^* \quad \text{for some } \boldsymbol{y}_0^* \in H(\operatorname{div};\Omega).$$

Proposition 5

For any $\boldsymbol{y}^* = \boldsymbol{f} + \boldsymbol{y}_0^*$ *with* $\boldsymbol{y}_0^* \in H(\operatorname{div};\Omega)$ *and* $\operatorname{div} \boldsymbol{y}_0^* = 0$ *in* $\Omega_m \cup \Omega_{IEL}$ *(the region where* $\overline{k} \equiv 0$*) we can explicitly compute* $F^*(-\Lambda^* \boldsymbol{y}^*)$.

$$D_F(v, -\Lambda^* \boldsymbol{y}^*) = F(v) + F^*(-\Lambda^* \boldsymbol{y}^*) + \langle \Lambda^* \boldsymbol{y}^*, v \rangle \quad \checkmark$$

For $C_1\left(\delta_1, \|u\|_{L^\infty(\Omega)}\right)$ and $C_2\left(\delta_2, \|\operatorname{div} \boldsymbol{p}_0^*\|_{L^\infty(\Omega_2)}\right)$ it holds:

$$\int_{\Omega_{ions}} \frac{k^2}{2}(v-u)^2 dx \le D_F(v, -\Lambda^* \boldsymbol{p}^*) \le C_1 \int_{\Omega_{ions}} \frac{k^2}{2}(v-u)^2 dx$$

$$C_2 \int_{\Omega_{ions}} \frac{1}{2k^2}\left(\operatorname{div}(\boldsymbol{y}_0^* - \boldsymbol{p}_0^*)\right)^2 dx \le D_F(u, -\Lambda^* \boldsymbol{y}^*) \le \int_{\Omega_{ions}} \frac{1}{2k^2}\left(\operatorname{div}(\boldsymbol{y}_0^* - \boldsymbol{p}_0^*)\right)^2 dx.$$

Proposition 5

For any $\boldsymbol{y}^* = \boldsymbol{f} + \boldsymbol{y}_0^*$ *with* $\boldsymbol{y}_0^* \in H(\mathrm{div};\Omega)$ *and* $\mathrm{div}\, \boldsymbol{y}_0^* = 0$ *in* $\Omega_m \cup \Omega_{IEL}$ *(the region where* $\overline{k} \equiv 0$*) we can explicitly compute* $F^*(-\Lambda^* \boldsymbol{y}^*)$*.*

$$D_F(v, -\Lambda^* \boldsymbol{y}^*) = F(v) + F^*(-\Lambda^* \boldsymbol{y}^*) + \langle \Lambda^* \boldsymbol{y}^*, v \rangle \quad \checkmark$$

For $C_1\left(\delta_1, \|u\|_{L^\infty(\Omega)}\right)$ and $C_2\left(\delta_2, \|\mathrm{div}\, \boldsymbol{p}_0^*\|_{L^\infty(\Omega_2)}\right)$ it holds:

$$\int_{\Omega_{ions}} \frac{k^2}{2}(v-u)^2 dx \leq D_F(v, -\Lambda^* \boldsymbol{p}^*) \leq C_1 \int_{\Omega_{ions}} \frac{k^2}{2}(v-u)^2 dx$$

$$C_2 \int_{\Omega_{ions}} \frac{1}{2k^2} \left(\mathrm{div}(\boldsymbol{y}_0^* - \boldsymbol{p}_0^*)\right)^2 dx \leq D_F(u, -\Lambda^* \boldsymbol{y}^*) \leq \int_{\Omega_{ions}} \frac{1}{2k^2} \left(\mathrm{div}(\boldsymbol{y}_0^* - \boldsymbol{p}_0^*)\right)^2 dx.$$

Near best approximation result

$$\frac{1}{2}|||\nabla(v-u)|||^2 + \frac{1}{2}|||\boldsymbol{y}^* - \boldsymbol{p}^*|||_*^2 + D_F(v, -\Lambda^*\boldsymbol{p}^*) + D_F(u, -\Lambda^*\boldsymbol{y}^*) = M_\oplus^2(v, \boldsymbol{y}^*)$$

$$2M_\oplus^2(v, \boldsymbol{y}^*) = |||\epsilon\nabla v - \boldsymbol{y}^*|||_*^2 + 2D_F(v, -\Lambda^*\boldsymbol{y}^*) = \int_\Omega 2\eta^2 dx,$$

$\|\sqrt{2}\eta\|_{L^2(K)}$ error indicator

Proposition 6

Let $V_h \subset L^\infty(\Omega)$ be a closed subspace of $H_0^1(\Omega)$ and $u_h \in V_h$ be the Galerkin approximation of u defined by

Find $u_h \in V_h$ such that

$$a(u_h, v) + \int_\Omega b(x, u_h + w)v dx = \int_\Omega \boldsymbol{f} \cdot \nabla v dx, \quad \text{for all } v \in V_h. \qquad \text{(GF)}$$

Then

$$|||\nabla(u_h - u)|||^2 \le \inf_{v \in V_h} \left\{ |||\nabla(v-u)|||^2 + \int_{\Omega_{ions}} k^2(\sinh(v+w) - \sinh(u+w))^2 dx \right\}.$$

How to obtain a good $\boldsymbol{y}^*$? (Flux reconstruction)

- Recall that $\boldsymbol{p}_0^* = \underbrace{\epsilon\nabla u}_{\boldsymbol{p}^*} - \boldsymbol{f} \in H(\mathrm{div};\Omega)$

- $\boldsymbol{q} := \epsilon\nabla u_h - \boldsymbol{f}$.

- Define $\boldsymbol{y}_0^* \in RT_0$ as the patchwise equilibrated flux reconstruction of $\Pi_{L_h}(\boldsymbol{q}) \in L_h$ from Braess & Schöberl 2008 (orthogonal L^2 projection onto piecewise constants).

- Since $\overline{k} = 0$ in $\Omega_m \cup \Omega_{IEL}$, the obtained $\boldsymbol{y}_0^*$ satisfies the relation $\mathrm{div}\,\boldsymbol{y}_0^* = 0$ in $\Omega_m \cup \Omega_{IEL}$ exactly.

PBE overall error estimation

2-term splitting $\phi = G + u$: Just solve for u.

3-term splitting $\phi = G + u^H + u$:

- Find a conforming approximation $\tilde{u}^H$ of $u^H \in H^1_{-G}(\Omega_m)$ by solving

$$\int_{\Omega_m} \nabla u^H \cdot \nabla v dx = 0, \ \forall v \in H^1_0(\Omega_m).$$

- Find $\tilde{u} \in H^1_0(\Omega)$ such that for all $v \in H^1_0(\Omega)$

$$\int_{\Omega} \epsilon \nabla \tilde{u} \cdot \nabla v dx + \int_{\Omega} \overline{k}^2 \sinh(\tilde{u}) v dx = \int_{\Omega} \tilde{\mathbf{f}} \cdot \nabla v dx, \qquad (\widetilde{\text{WF}})$$

where $\tilde{\mathbf{f}} := -\chi_{\Omega_m} \epsilon_m T\left(\nabla \tilde{u}^H\right) + \chi_{\Omega_s} \epsilon_m \nabla G$ and T is an operator which maps the numerical flux into a subspace of $H(\text{div}; \Omega_m)$.

- Find an approximation $\tilde{u}_h \in H^1_0(\Omega)$ of $\tilde{u}$.

GOAL: Estimate $|||\nabla(\tilde{u}_h - u)|||$.

PBE overall error estimation

2-term splitting $\phi = G + u$: Just solve for u.
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- Find a conforming approximation $\tilde{u}^H$ of $u^H \in H^1_{-G}(\Omega_m)$ by solving

$$\int_{\Omega_m} \nabla u^H \cdot \nabla v dx = 0, \ \forall v \in H^1_0(\Omega_m).$$

- Find $\tilde{u} \in H^1_0(\Omega)$ such that for all $v \in H^1_0(\Omega)$

$$\int_\Omega \epsilon \nabla \tilde{u} \cdot \nabla v dx + \int_\Omega \overline{k}^2 \sinh(\tilde{u}) v dx = \int_\Omega \tilde{\boldsymbol{f}} \cdot \nabla v dx, \qquad (\widetilde{\text{WF}})$$

where $\tilde{\boldsymbol{f}} := -\chi_{\Omega_m} \epsilon_m T\left(\nabla \tilde{u}^H\right) + \chi_{\Omega_s} \epsilon_m \nabla G$ and T is an operator which maps the numerical flux into a subspace of $H(\text{div}; \Omega_m)$.

- Find an approximation $\tilde{u}_h \in H^1_0(\Omega)$ of $\tilde{u}$.

GOAL: Estimate $|||\nabla(\tilde{u}_h - u)|||$.

A posteriori estimate for u^H and $\tilde{u}$

$T\left(\nabla \tilde{u}^H\right) \in RT_0$ is the patchwise flux reconstruction based on Braess & Schöberl

$$\|\nabla u^H - T\left(\nabla \tilde{u}^H\right)\|_{L^2(\Omega_m)} \leq M_{\oplus,H}\left(\tilde{u}^H, T\left(\nabla \tilde{u}^H\right)\right)$$

Note: When $T\left(\nabla \tilde{u}^H\right)$ is exactly equilibrated, i.e., $\operatorname{div}\left(T\left(\nabla \tilde{u}^H\right)\right) = 0$, then also

$$\|\nabla(\tilde{u}^H - u^H)\|_{L^2(\Omega_m)} \leq M_{\oplus,H}\left(\tilde{u}^H, T\left(\nabla \tilde{u}^H\right)\right).$$

• For a conforming approximation $\tilde{u}_h$ of $\tilde{u} \in H^1_g(\Omega)$ and for any $\tilde{\boldsymbol{y}}^* = \tilde{\boldsymbol{f}} + \tilde{\boldsymbol{y}}_0^*$ with $\tilde{\boldsymbol{y}}_0^* \in H(\operatorname{div};\Omega)$ and $\operatorname{div} \tilde{\boldsymbol{y}}_0^* = 0$ in $\Omega_m \cup \Omega_{IEL}$ it holds

$$|\!|\!|\nabla(\tilde{u}_h - \tilde{u})|\!|\!| \leq \sqrt{2} M_{\oplus}(\tilde{u}_h, \tilde{\boldsymbol{y}}^*)$$

Overall error estimate

Proposition 7

Let $\tilde{u}^H$ be a conforming approximation of u^H, $T\left(\nabla \tilde{u}^H\right) \in H(\mathrm{div}; \Omega_m)$ a reconstruction of the numerical flux $\nabla \tilde{u}^H$, $\tilde{u}_h \in H^1_g(\Omega)$ a conforming approximation of the solution $\tilde{u}$ of $(\widetilde{\mathrm{WF}})$.

Then, for any $\tilde{\boldsymbol{y}}^*$ of the form $\tilde{\boldsymbol{y}}^* = \tilde{\boldsymbol{f}} + \tilde{\boldsymbol{y}}_0^*$ with $\tilde{\boldsymbol{y}}_0^* \in H(\mathrm{div}; \Omega)$ and $\mathrm{div}\, \tilde{\boldsymbol{y}}_0^* = 0$ in $\Omega_m \cup \Omega_{IEL}$ the following guaranteed error estimate holds:

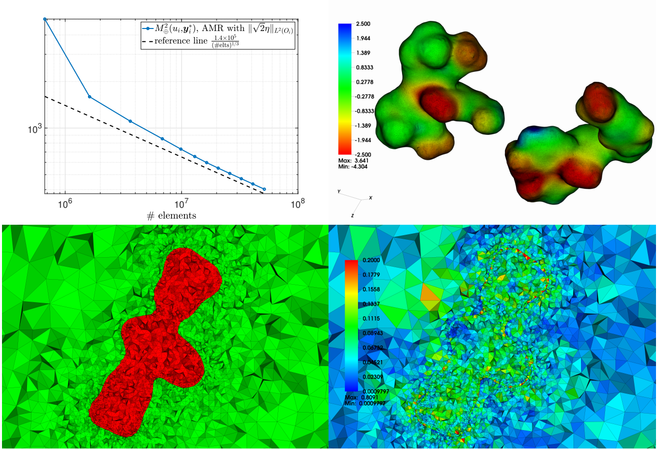
$$|||\nabla\left(\tilde{u}_h - u\right)||| \leq \sqrt{\epsilon_m} M_{\oplus,H}\left(\tilde{u}^H, T\left(\nabla \tilde{u}^H\right)\right) + \sqrt{2} M_{\oplus}\left(\tilde{u}_h, \tilde{\boldsymbol{y}}^*\right).$$

Models with Alexa 488 and Alexa 594 molecules

2-term splitting

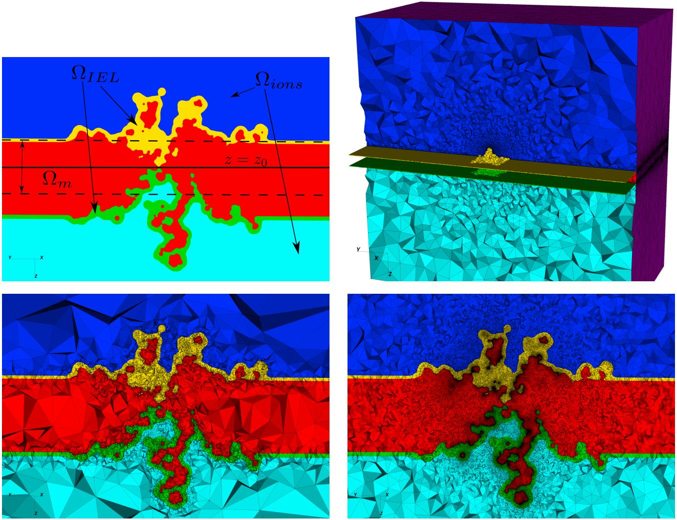
Example 2. Here $\frac{|||\nabla(u_i - u)|||}{|||\nabla u|||} \leq \frac{\sqrt{2}M_{\oplus}(u_i, \mathbf{y}_i^*)}{|||\nabla u_i||| - \sqrt{2}M_{\oplus}(u_i, \mathbf{y}_i^*)} =: \text{REN}^{\text{Up}}$.

Alexa 488 and Alexa 594: $\overline{k}^2_{ions} = 10\,\text{Å}^{-2}$, $\epsilon_m = 2$, $\epsilon_s = 80$						
level i	#elements	$\|u_i\|_0$	$\|\|\|\nabla u_i\|\|\|$	$\sqrt{2}M_{\ominus}(u_i, u_{\bar{p}})$	$\sqrt{2}M_{\oplus}(u_i, \mathbf{y}_i^*)$	REN$^{\text{Up}}$ [%]
0	667 008	64847.173	16446.255	3867.60	5067.89	44.539
1	1 619 690	64853.944	16282.891	1384.92	1594.16	10.852
2	3 624 678	64855.019	16278.101	933.867	1107.65	7.3014
3	6 830 130	64855.176	16283.830	681.347	853.001	5.5279
4	9 861 226	64855.249	16284.985	559.190	731.163	4.7008
5	12 982 453	64855.305	16285.379	476.068	654.706	4.1886
6	16 420 992	64855.346	16285.807	409.548	598.027	3.8120
7	20 636 057	64855.370	16286.127	349.061	550.920	3.5011
8	25 937 013	64855.382	16286.388	289.230	508.983	3.2260
9	32 602 138	64855.404	16286.599	226.473	470.673	2.9759
10	40 972 275	64855.430	16286.773	153.787	435.316	2.7462
11	51 409 492	64855.446	16286.923	-	402.703	2.5352



On the left: cross section of the mesh at level $i = 1$ in the mesh refinement procedure for finding the component $\tilde{u}$ with the **3-term splitting**. The molecule region Ω_m is marked red (Alexa 594). On the right: error indicator as a piecewise constant function.

SecYEG membrane channel

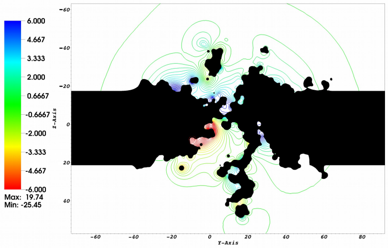


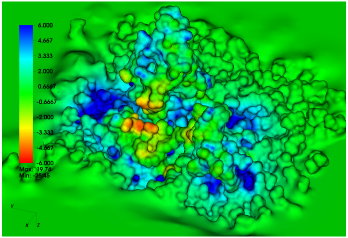
SecYEG: $I_s = 0.1\,M,\ \overline{k}^2_{ions} = 0.843\,Å^{-2},\ T = 300\,K,\ \epsilon_m = 4,\ \epsilon_s = 80$				
level i	# elements	$\lVert\nabla\tilde{u}_i^H\rVert_{L^2(\Omega_m)}$	$M_{\oplus,H}\left(\tilde{u}_i^H, T\left(\nabla\tilde{u}_i^H\right)\right)$	$\frac{M_{\oplus,H}\left(\tilde{u}_i^H, T\left(\nabla\tilde{u}_i^H\right)\right)}{\lVert\nabla\tilde{u}_i^H\rVert_{L^2(\Omega_m)}}$ [%]
0	4 113 729	1662.3557	544.81	32.77
1	9 859 418	1644.8591	264.61	16.08
2	19 497 424	1642.8727	185.06	11.26
3	33 167 516	1642.0064	150.29	9.153
4	48 298 685	1641.4157	130.73	7.964
5	65 604 295	1641.0111	116.98	7.128

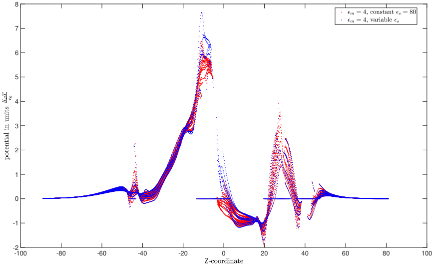
SecYEG: $I_s = 0.1\,M,\ \overline{k}^2_{ions} = 0.843\,Å^{-2},\ T = 300\,K,\ \epsilon_m = 4,\ \epsilon_s = 80$ with $\tilde{u}_5^H$					
level i	# elements	$\lVert\nabla\tilde{u}_i\rVert$	$\sqrt{2}M_{\ominus}(\tilde{u}_i, \tilde{u}_{\bar{p}})$	$\sqrt{2}M_{\oplus}(\tilde{u}_i, \tilde{\mathbf{y}}_i^*)$	$\frac{\sqrt{2}M_{\oplus}(\tilde{u}_i, \tilde{\mathbf{y}}_i^*)}{\lVert\nabla\tilde{u}_i\rVert}$ [%]
0	10 287 866	1462.18	446.41	996.39	68.14
1	18 713 711	1514.89	191.40	466.35	30.78
2	43 525 735	1524.72	80.102	293.41	19.24
3	79 867 368	1526.84	-	245.72	16.09

$$|||\nabla(u - \tilde{u}_3)||| \leq \sqrt{\epsilon_m} M_{\oplus,H}\left(\tilde{u}^H, T\left(\nabla\tilde{u}^H\right)\right) + \sqrt{2}M_{\oplus}(\tilde{u}_3, \tilde{\mathbf{y}}_3^*)$$

$$= \sqrt{4} \times 116.98 + 245.72 = 479.68$$


6.000
4.667
3.333
2.000
0.6667
-0.6667
-2.000
-3.333
-4.667
-6.000
Max: 19.74
Min: -25.45
Z-Axis
Y-Axis


6.000
4.667
3.333
2.000
0.6667
-0.6667
-2.000
-3.333
-4.667
-6.000
Max: 19.74
Min: -25.45


$\epsilon_m = 4$, constant $\epsilon_s = 80$
$\epsilon_m = 4$, variable ϵ_s
potential in units $\frac{K_B T}{e_0}$
Z-coordinate

Conclusion

- Solution theory
  - ⋆ Existence of a weak solution to the LPBE and PBE through a 2- or 3-term splitting
  - ⋆ Uniqueness for the LPBE
- Functional type a posteriori error estimates for the regular component u of ϕ
  - ⋆ Lead to guaranteed and fully computable bounds on the energy norm of the error
  - ⋆ Valid for any conforming approximation v of u
  - ⋆ No global or local, mesh dependent, constants
  - ⋆ Two–sided error estimates whith which we can guarantee efficiency index close to 2-3 without knowledge of the exact solution.
  - ⋆ Near best approximation result
  - ⋆ Efficient construction of $\boldsymbol{y}^*$
- Applications

Thank you for listening!

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Main ingredient for the proof of boundedness and uniqueness:

Theorem 8 (H. Brezis and F. Browder, 1978)

Let Ω be a domain in $\mathbb{R}^d$, $T \in H^{-1}(\Omega) \cap L^1_{loc}(\Omega)$, and $v \in H^1_0(\Omega)$. If there exists a function $f \in L^1(\Omega)$ such that $T(x)v(x) \geq f(x)$, a.e in Ω, then $Tv \in L^1(\Omega)$ and the duality product $\langle T, v\rangle$ in $H^{-1}(\Omega) \times H^1_0(\Omega)$ coincides with $\int_\Omega Tvdx$.

Remark 9

In other words, we have the following situation: a locally summable function $b \in L^1_{loc}(\Omega)$ defines a bounded linear functional T_b over the dense subspace $D(\Omega) \equiv C_0^\infty(\Omega)$ of $H^1_0(\Omega)$ through the integral formula $\langle T_b, \varphi\rangle = \int_\Omega b\varphi dx$. It is clear that the functional T_b is uniquely extendable by continuity to a bounded linear functional $\overline{T}_b$ over the whole space $H^1_0(\Omega)$. Now the question is whether this extension is still representable by the same integral formula for any $v \in H^1_0(\Omega)$ (if the integral makes sense at all). If $v \in H^1_0(\Omega)$ is a fixed element, Theorem 8 gives a sufficient condition for bv to be summable and for the extension $\overline{T}_b$ evaluated at v to be representable with the same integral formula as above, i.e $\langle \overline{T}_b, v\rangle = \int_\Omega bvdx$.