Kohn–Sham Inversion with Strict Error Bounds

Michael F. Herbst,[1,2] Vebjørn H. Bakkestuen,[3,*] and Andre Laestadius[3,4,*]

[1]Mathematics for Materials Modelling, Institute of Mathematics & Institute of Materials, École Polytechnique Fédérale de Lausanne
[2]National Centre for Computational Design and Discovery of Novel Materials (MARVEL), École Polytechnique Fédérale de Lausanne
[3]Mathematical Modelling Group, Department of Computer Science, Oslo Metropolitan University
[4]Hylleraas Centre for Quantum Molecular Sciences, University of Oslo
*Supported under ERC Starting Grant No. 101041487 REGAL

Motivation

Kohn–Sham (KS) approach

Interacting electrons

$$\hat{H} = -\frac{1}{2}\sum_j \nabla_j^2 + \frac{1}{2}\sum_{k\neq j}\frac{1}{|\mathbf{r}_j - \mathbf{r}_k|} + \sum_j v_{\text{ext}}(\mathbf{r}_j) \longrightarrow \rho_{\text{gs}}$$

Non-interacting electrons (KS system)

$$\hat{H}_{\text{KS}} = -\frac{1}{2}\sum_j \nabla_j^2 + \sum_j \left[v_{\text{ext}}(\mathbf{r}_j) + v_{\text{H}}(\mathbf{r}_j) + v_{\text{xc}}(\mathbf{r}_j)\right] \longrightarrow \rho_{\text{gs}}$$

Critical unknown: $v_{\text{xc}} \longleftarrow \frac{\delta \tilde{F}(\rho)}{\delta\rho}$

Forward KS problem: Given an $\tilde{F}$, obtain ρ_{gs}

Inverse KS problem: Given ρ_{gs}, find v_{xc}

The Inversion Scheme

forward: $v_{\text{xc}} \longrightarrow \rho_{\text{gs}}$

inverse:

$$\tilde{\rho}_{\text{gs}} = \rho_{\text{gs}} + \Delta\rho$$
$$\downarrow$$
$$\tilde{\rho}^{\varepsilon}_{\text{gs}} = \operatorname{argmin}_{\rho}\, \mathcal{E}(\rho; \tilde{\rho}_{\text{gs}})$$
$$\downarrow$$
$$\tilde{v}^{\varepsilon}_{\text{xc}} = \tfrac{1}{\varepsilon} J(\tilde{\rho}^{\varepsilon}_{\text{gs}} - \tilde{\rho}_{\text{gs}})$$
$$\downarrow$$
$$\lim_{\varepsilon\to 0^+} \tilde{v}^{\varepsilon}_{\text{xc}} \qquad \lim_{\varepsilon\to 0^+} \tilde{\rho}^{\varepsilon}_{\text{gs}}$$

extrapolate numerically

compare | compare

Implementation:

$$\Phi = (\psi_1, \psi_2, \ldots, \psi_{N_b})$$

$$\int_\Omega \psi_i^* \psi_j = \delta_{ij}$$

$$\rho_\Phi(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2$$

Minimise $\mathcal{E}(\rho_\Phi, \rho_{\text{gs}})$

DFTK

Moreau–Yosida Regularisation

$\rho \in \mathcal{D}$ uniformly convex, $\quad v \in \mathcal{V} = \mathcal{D}^*, \quad F : \mathcal{D} \to \mathbb{R}$ convex & l.s.c.

Moreau–Yosida regularisation at $\varepsilon > 0$:

$$F^{\varepsilon}(\rho) = \inf_{\sigma\in\mathcal{D}} \left\{ F(\sigma) + \tfrac{1}{2\varepsilon}\|\sigma - \rho\|^2_{\mathcal{D}} \right\} \tag{1}$$

$$E^{\varepsilon}(v) = \inf_{\rho\in\mathcal{D}} \left\{ F^{\varepsilon}(\rho) + \langle v, \rho\rangle \right\} \quad \Longrightarrow \quad E(v) = E^{\varepsilon}(v) + \frac{\varepsilon}{2}\|v\|^2_{\mathcal{V}}$$

Obtaining the Exchange-Correlation Potential

$$\mathcal{F}(\rho) = T(\rho) + E_{\text{H}}(\rho) + \int_\Omega v_{\text{ext}}\rho$$

Periodic Sobolev spaces [1]: $\rho \in \mathcal{D} = H^{-1}_{\text{per}}(\Omega), \qquad v \in \mathcal{V} = H^{1}_{\text{per}}(\Omega)$

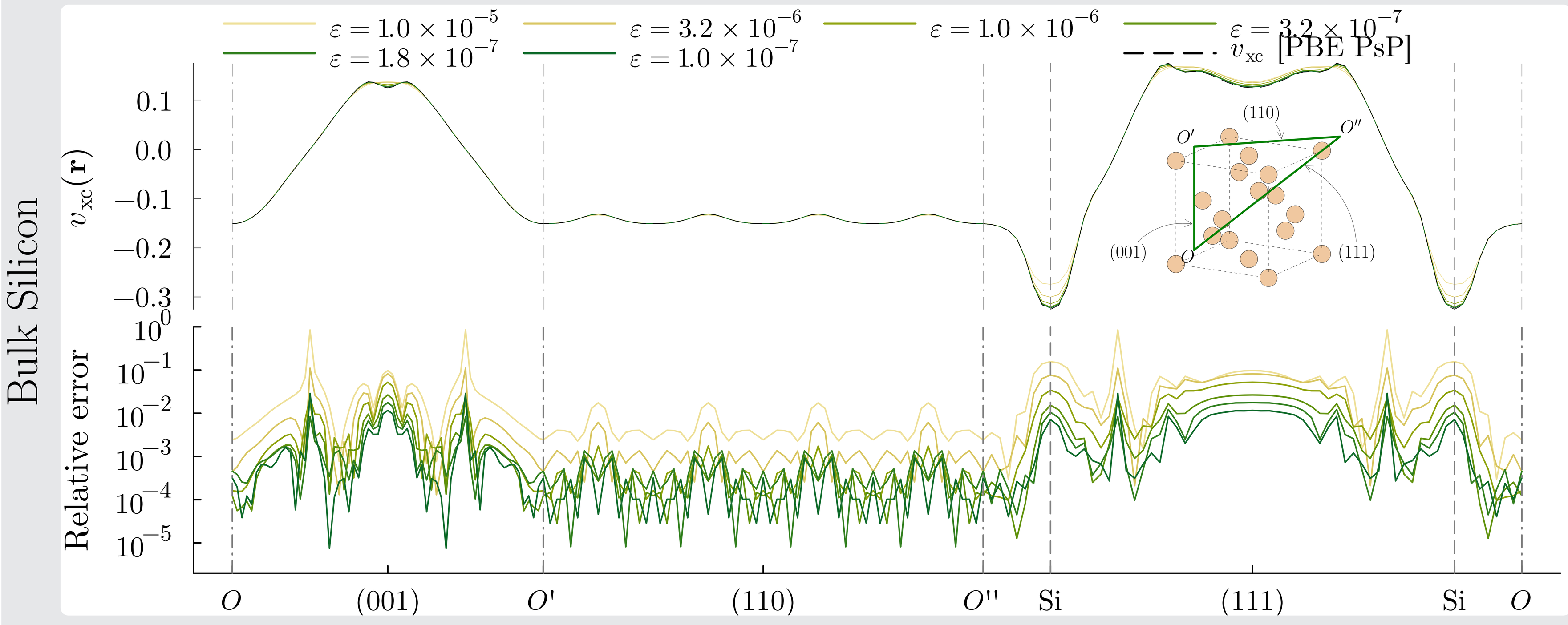
minimise $\quad \mathcal{E}(\rho\,; \rho_{\text{gs}}) = \mathcal{F}(\rho) + \tfrac{1}{2\varepsilon}\|\rho - \rho_{\text{gs}}\|^2_{\mathcal{D}} \qquad (\rho_{\text{gs}}$ fixed$) \qquad (2)$

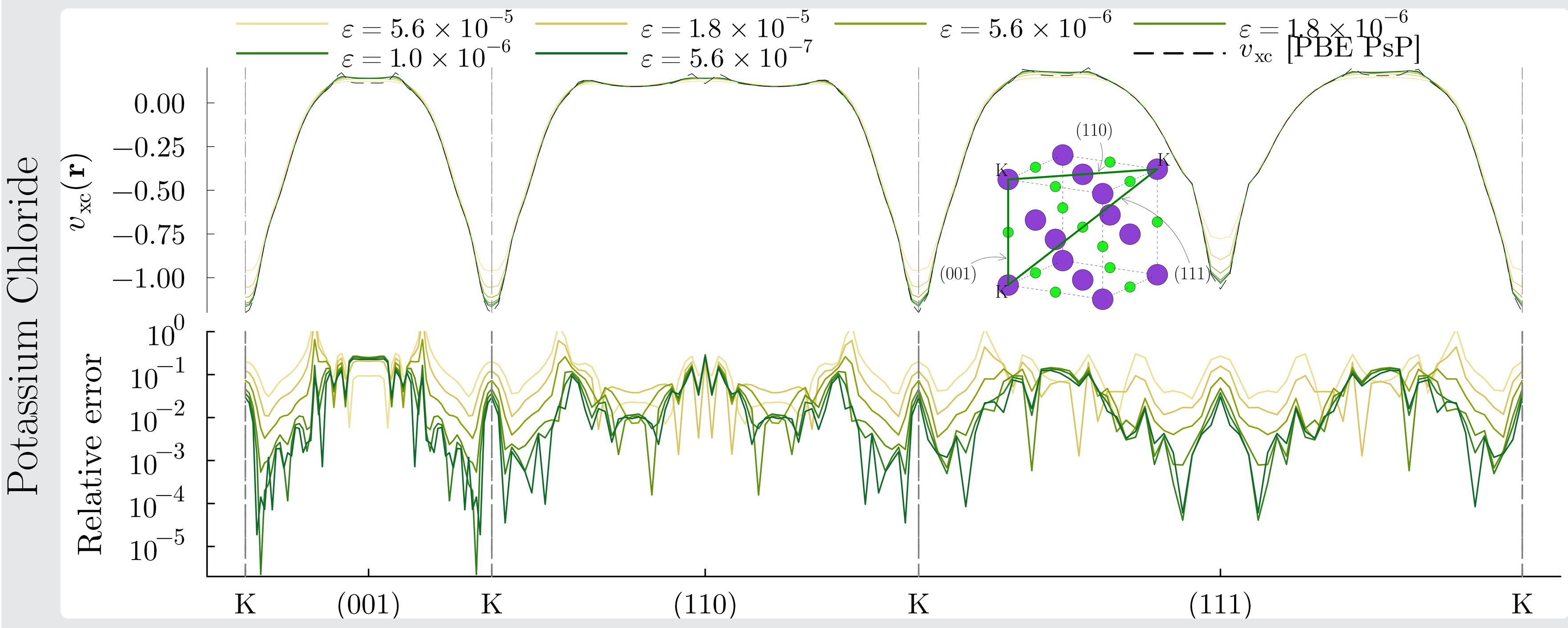
$$\rho^{\varepsilon}_{\text{gs}} = \operatorname*{argmin}_{\rho\in\mathcal{D}} \mathcal{E}(\rho, \rho_{\text{gs}}) \qquad \text{(unique element [2])}$$

Duality mapping: $\quad J[\rho](\mathbf{r}) = [\Phi * \rho](\mathbf{r}) = \int_{\mathbb{R}^3} \frac{\rho(\mathbf{r}')}{4\pi|\mathbf{r} - \mathbf{r}'|} e^{-|\mathbf{r}-\mathbf{r}'|}\, \mathrm{d}\mathbf{r}' \quad (3)$

xc potential [3, 4]: $\quad v_{\text{xc}}(\mathbf{r}) = \lim_{\varepsilon\to 0^+} \frac{1}{\varepsilon} \int_{\mathbb{R}^3} \frac{\rho^{\varepsilon}_{\text{gs}}(\mathbf{r}') - \rho_{\text{gs}}(\mathbf{r}')}{4\pi|\mathbf{r} - \mathbf{r}'|} e^{-|\mathbf{r}-\mathbf{r}'|}\, \mathrm{d}\mathbf{r}' \quad (4)$

Numerical Examples





Details, code, and data on GitHub [5]

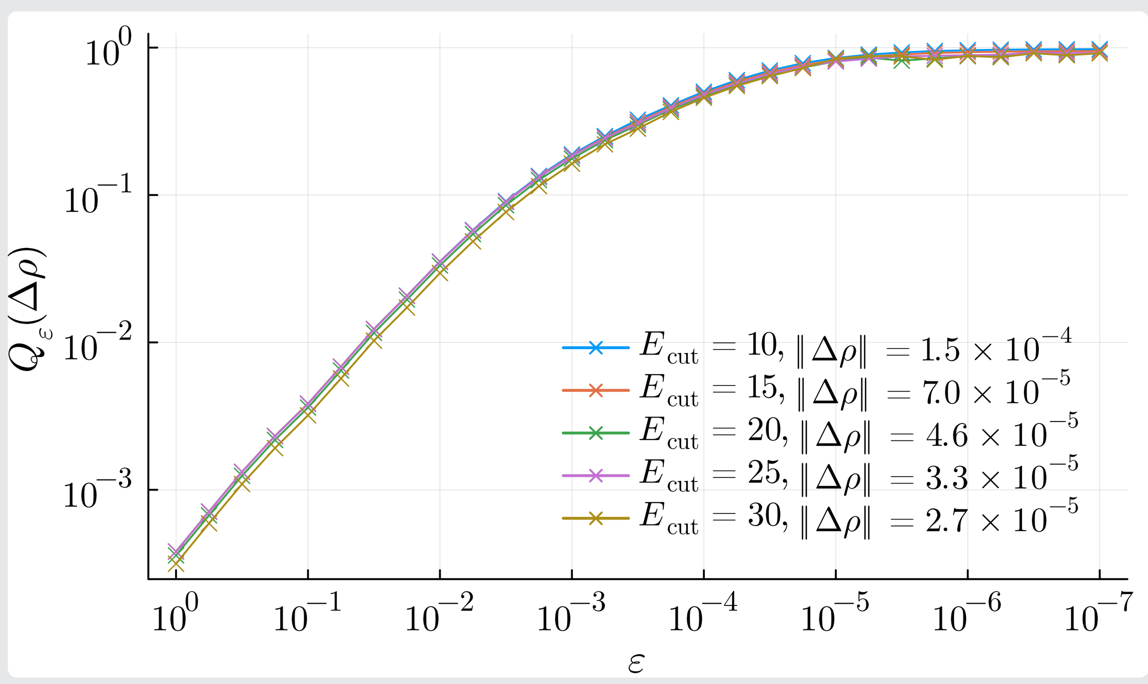
Error Bounds: Analytical & Numerical

Non-expansiveness

$$\|\rho^{\varepsilon} - \tilde{\rho}^{\varepsilon}\|_{\mathcal{D}} \leq \|\rho - \tilde{\rho}\|_{\mathcal{D}} \quad \forall \rho, \tilde{\rho} \in \mathcal{D} \tag{5}$$

Perturbations: $\tilde{\rho}_{\text{gs}} = \rho_{\text{gs}} + \Delta\rho$

$$Q_{\varepsilon}(\Delta\rho) = \frac{\|\rho^{\varepsilon}_{\text{gs}} - \tilde{\rho}^{\varepsilon}_{\text{gs}}\|_{\mathcal{D}}}{\|\Delta\rho_{\text{gs}}\|_{\mathcal{D}}} \leq 1$$



Total error

$$\|v_{\text{xc}} - \tilde{v}^{\varepsilon}_{\text{xc}}\|_{\mathcal{V}} \leq \underbrace{\|v_{\text{xc}} - v^{\varepsilon}_{\text{xc}}\|_{\mathcal{V}}}_{\text{term. at } \varepsilon > 0} + \underbrace{\|v^{\varepsilon}_{\text{xc}} - \tilde{v}^{\varepsilon}_{\text{xc}}\|_{\mathcal{V}}}_{\text{inexact } \rho_{\text{gs}}}$$

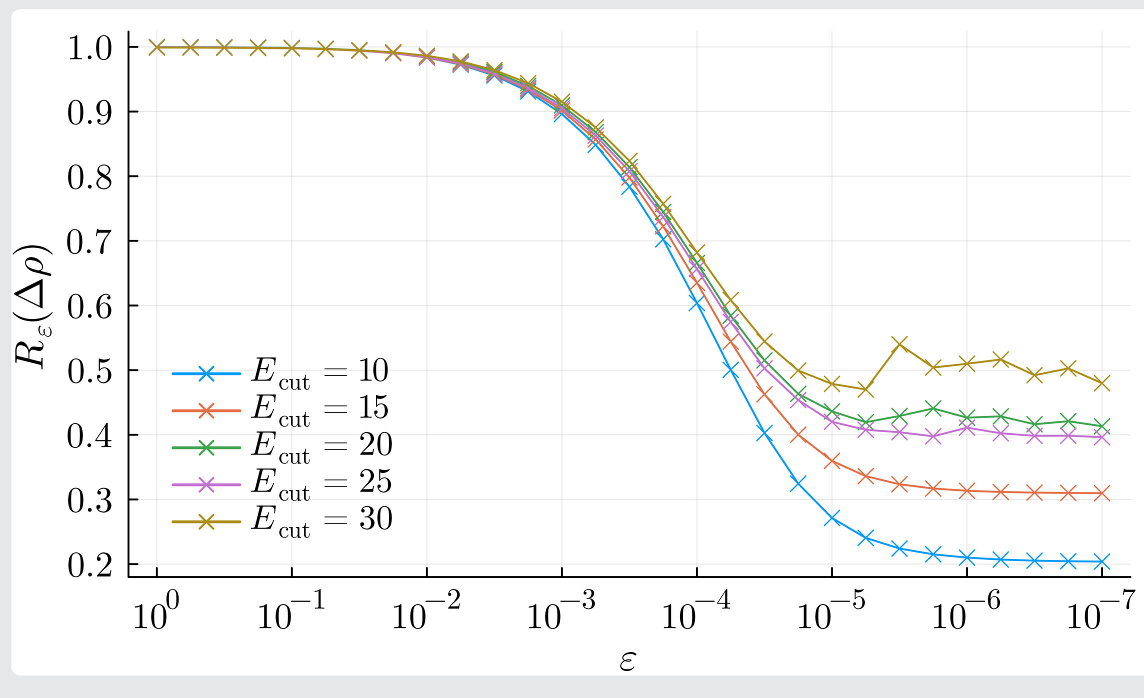
$$\lim_{\varepsilon\to 0^+} \|v_{\text{xc}} - v^{\varepsilon}_{\text{xc}}\|_{\mathcal{V}} = 0$$

Error from inexact density

$$\|\tilde{v}^{\varepsilon}_{\text{xc}} - v^{\varepsilon}_{\text{xc}}\|_{\mathcal{V}} \leq \frac{1 + Q_{\varepsilon}(\Delta\rho)}{\varepsilon}\|\Delta\rho\|_{\mathcal{D}} \tag{6}$$

$$R_{\varepsilon}(\Delta\rho) = \varepsilon\frac{\|\tilde{v}^{\varepsilon}_{\text{xc}} - v^{\varepsilon}_{\text{xc}}\|_{\mathcal{V}}}{\|\Delta\rho\|_{\mathcal{D}}}$$

$$0 \leq 1 - Q_{\varepsilon}(\Delta\rho) \leq R_{\varepsilon}(\Delta\rho) \leq 1 + Q_{\varepsilon}(\Delta\rho) \leq 2$$



[1] E. Cancès *et al.*, ESAIM:M2AN **46**, 341 (2012).
[2] V. Barbu and T. Precupanu, *Convexity and Opt.*..., 4th ed. (2012).
[3] M. Penz *et al.*, Electron. Struct. **5**, 014009 (2023).
[4] M. F. Herbst *et al.*, Phys. Rev. B **111**, 205143 (2025).
[5] `github.com/mfherbst/supporting-my-inversion`.

: *Phys. Rev. B* 111, 205143 (2025)

: `vebjorn.bakkestuen@oslomet.no`