Some recent results on the inverse Kohn-Sham problem

using the proximal point of Moreau-Yosida regularization

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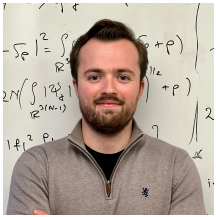
Acknowledgements

In collaboration with M. Herbst[1,2] and V. Bakkestuen.[3]



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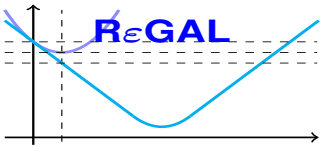

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Outline

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Density-Functional Theory

$$\widehat{H}(v) = \overbrace{-\frac{1}{2}\sum_j \nabla_j^2 + \frac{1}{2}\sum_{k\neq j}\frac{1}{|\mathbf{r}_j - \mathbf{r}_k|}}^{\widehat{H}_0} + \sum_j v(\mathbf{r}_j)$$

$$\psi : \mathbb{R}^{3N} \to \mathbb{C}, \qquad \rho_\psi = N\int_{\mathbb{R}^{3(N-1)}} |\psi|^2 \qquad \langle v,\, \rho\rangle = \int v\rho$$

$$\begin{aligned} E(v) &= \inf_\psi \langle\psi|\widehat{H}|\psi\rangle \\ &= \inf_\rho \{F(\rho) + \langle v,\, \rho\rangle\} \end{aligned}$$

$$\begin{aligned} F(\rho) &= \sup_v \{E(v) - \langle v,\, \rho\rangle\} \\ &= \inf_{\Gamma\mapsto\rho} \operatorname{Tr}\widehat{H}_0\Gamma \\ &= \inf_{\sum_j p_j\rho_{\psi_j}=\rho} \sum_j p_j \langle\psi_j|\widehat{H}_0|\psi_j\rangle \end{aligned}$$

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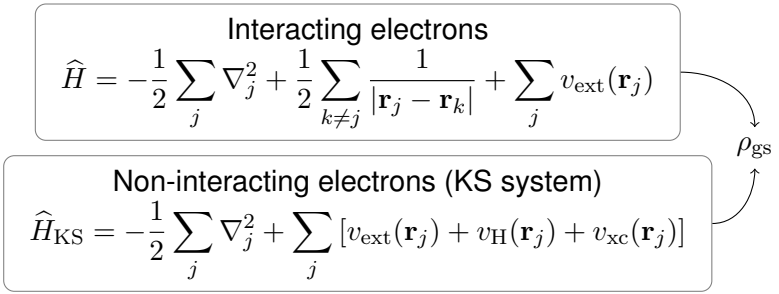
The Kohn–Sham Approach



Exchange correlation potential $v_{\mathrm{xc}} \longleftarrow$ unknown

The forward problem:
Given a v_{ext} and an approximate E_{xc}, i.e., v_{xc}, determine ρ_{gs}

Kohn–Sham DFA

GGA = Generalized Gradient Approximation

$$E_{\mathrm{xc}}(\rho) = \int e_{\mathrm{xc}}^{\mathrm{LDA}} \overbrace{f_{\mathrm{xc}}(\rho, \nabla\rho)}^{\text{enhancement factor}} \qquad s = \underbrace{\frac{|\nabla\rho|}{2k_{\mathrm{F}}\rho} = \frac{x}{2(3\pi^2)^{1/3}} = \frac{|\nabla\rho|}{\rho^{4/3}}}_{\text{reduced gradient}}$$

PBE (Perdew, Burke, Ernzerhof): parameters κ, μ

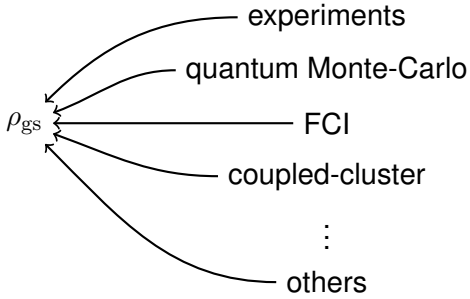
$$f_{\mathrm{x}}(s) = 1 + \kappa - \frac{\kappa}{1 + \mu s^2/\kappa} = 1 + \mu s^2 + \mathcal{O}(s^4) \tag{1}$$

$$E_{\mathrm{x}} = \int \underbrace{e_{\mathrm{x}}^{\mathrm{LDA}}}_{\sim\rho^{4/3}} f_{\mathrm{x}}(s), \quad E_{\mathrm{c}} = [\text{too complicated}]$$

$$E_{\mathrm{x}},\ E_{\mathrm{c}} \implies v_{\mathrm{xc}} = \frac{\delta}{\delta\rho} E_{\mathrm{xc}}(\rho)$$

The Inverse Kohn–Sham Problem

The reverse problem:
Given a ρ_{gs}, determine v_{xc}



Why?

Better understanding of $F(\rho)$
Additional constraints for $F(\rho)$ to use when designing approximations

Moreau–Yosida Regularisation

Densities: $\rho \in \mathcal{D}$ Potentials: $v \in \mathcal{V} = \mathcal{D}^*$

Definition

Let $\mathcal{D}$ be uniformly convex and $F : \mathcal{D} \to \mathbb{R} \cup \{+\infty\}$ convex and lower semicontinous functional. For some $\varepsilon > 0$, the *Moreau–Yosida regularisation* of F is

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

An infimal convolution

A Lossless Regularisation

$$E^{\varepsilon}(v) = \inf_{\rho \in \mathcal{D}} \{F^{\varepsilon}(\rho) + \langle v, \rho \rangle\}$$

$$E^{\varepsilon}(v) = E(v) - \frac{\varepsilon}{2}\|v\|_{\mathcal{V}}^2.$$

The regularisation retains the ground state energy

Consequence of infimal convolution and (F, E) being a convex-concave ("conjugate") pair

Inversion Scheme

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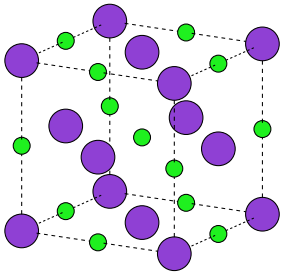
Periodic Systems

$$\mathcal{D} = H^{-1}_{\mathrm{per}}(\Omega, \mathbb{C}) \qquad \mathcal{V} = \mathcal{D}^* = H^{1}_{\mathrm{per}}(\Omega, \mathbb{C})$$



Periodic Sobolev spaces [1]

$$\|u\|^2_{H^s_{\mathrm{per}}} = \sum_{\mathbf{G}} (1 + |\mathbf{G}|^2)^s |\widehat{u}_{\mathbf{G}}|^2$$

The *duality mapping* $J : \mathcal{D} \to \mathcal{V}$,

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

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Model Functional

Recall

$$\widehat{H}_{\mathrm{KS}} = -\frac{1}{2}\sum_j \nabla_j^2 + \sum_j \overbrace{\left[v_{\mathrm{ext}}(\mathbf{r}_j) + v_{\mathrm{H}}(\mathbf{r}_j) + v_{\mathrm{xc}}(\mathbf{r}_j)\right]}^{v_{\mathrm{KS}}}$$

Given $\rho_{\mathrm{gs}} \in \mathcal{D}$, let

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

Minimise

$$\mathcal{E}(\rho\,;\rho_{\mathrm{gs}}) = \underbrace{\mathcal{F}(\rho)}_{\text{no xc}} + \underbrace{\tfrac{1}{2\varepsilon}\|\rho-\rho_{\mathrm{gs}}\|_{\mathcal{D}}^2}_{\text{targets xc as } \varepsilon\to 0+} \quad \text{over} \quad \rho\in\mathcal{D} \tag{2}$$

Proximal density, unique minimiser of $\mathcal{E}$:

$$\rho_{\mathrm{gs}}^{\varepsilon} = \operatorname*{argmin}_{\rho\in\mathcal{D}} \mathcal{E}(\rho,\rho_{\mathrm{gs}})$$

The Exchange-Correlation Potential

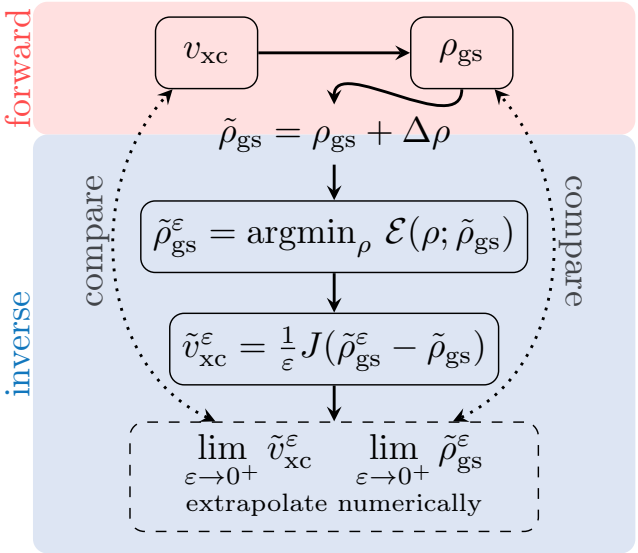
Since $\mathcal{F}^\varepsilon(\rho)$ is differentiable,

$$v_{\mathrm{xc}}^\varepsilon = -\frac{\delta \mathcal{F}^\varepsilon}{\delta \rho}(\rho_{\mathrm{gs}}^\varepsilon) = \frac{1}{\varepsilon} J[\rho_{\mathrm{gs}}^\varepsilon - \rho_{\mathrm{gs}}]$$

Exchange-correlation potential [2, 3]

$$\begin{aligned} v_{\mathrm{xc}}(\mathbf{r}) &= \lim_{\varepsilon \to 0^+} v_{\mathrm{xc}}^\varepsilon \\ &= \lim_{\varepsilon \to 0^+} \frac{1}{\varepsilon} J\left[\rho_{\mathrm{gs}}^\varepsilon - \rho_{\mathrm{gs}}\right](\mathbf{r}) \\ &= \lim_{\varepsilon \to 0^+} \frac{1}{\varepsilon} \int_{\mathbb{R}^3} \frac{\rho_{\mathrm{gs}}^\varepsilon(\mathbf{x}) - \rho_{\mathrm{gs}}(\mathbf{x})}{4\pi|\mathbf{r}-\mathbf{x}|} e^{-|\mathbf{r}-\mathbf{x}|}\, \mathrm{d}\mathbf{x} \end{aligned}$$

The Inversion Algorithm with error $\Delta\rho$



Numerical details

KS-DFT implementation: parametrize $\rho_{\mathrm{gs}}^{\varepsilon}$ in terms of orthonormal orbitals $\mathbf{\Phi} = (\psi_1, \ldots, \psi_{N_b})$, $\int_\Omega \psi_i^* \psi_j = \delta_{ij}$

Planewaves (PW) $e_{\mathbf{G}}(\mathbf{r}) = |\Omega|^{-1/2} e^{i\mathbf{G}\cdot\mathbf{r}}$

Fourier space cutoff: $|\mathbf{G}|^2 \leq 2E_{\mathrm{cut}}$

Coulomb energy replaced by: $E_{\mathrm{H}}(\rho) = \sum_{\mathbf{G}\neq 0} \frac{|\widehat{\rho}_{\mathbf{G}}|^2}{|\mathbf{G}|^2}$

PsP approximation for v_{ext}

Numerical details

Direct minimization in terms of orbitals (Stiefel manifold):

$$\rho_\Phi(\mathbf{r}) = 2\sum_{i=1}^{N_b} |\psi_i(\mathbf{r})|^2$$

enabling to rewrite the minimization of

$$\begin{aligned}\mathcal{E}(\Phi, \rho_{\mathrm{gs}}) = \sum_{i=1}^{N_b} \int_\Omega |\nabla\psi_i|^2 + E_{\mathrm{H}}(\rho_\Phi) \\ + \int_\Omega v_{\mathrm{ext}}\rho_\Phi + \frac{1}{2\varepsilon}\|\rho_\Phi - \rho_{\mathrm{gs}}\|_{\mathcal{D}}^2\end{aligned} \tag{3}$$

with respect to the orbitals Φ.

Results

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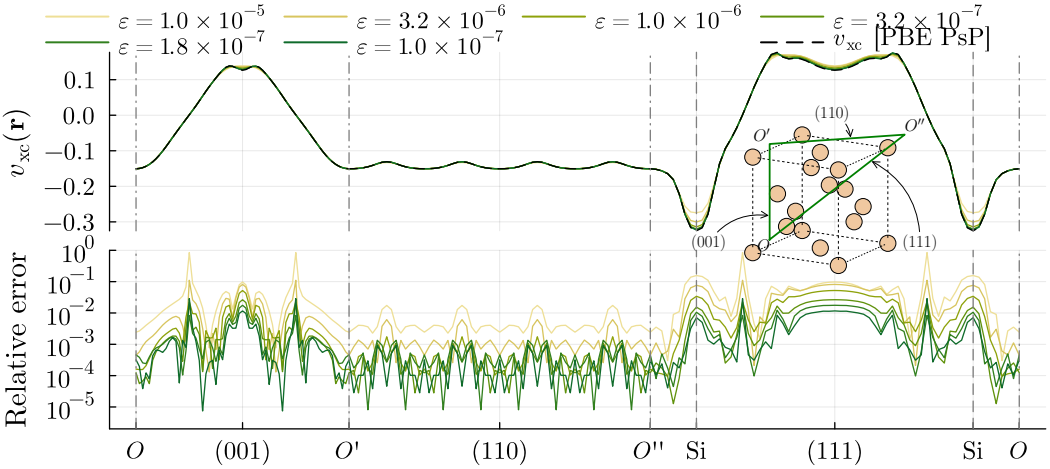
Bulk Silicon



Implementation on github.com/mfherbst/supporting-my-inversion

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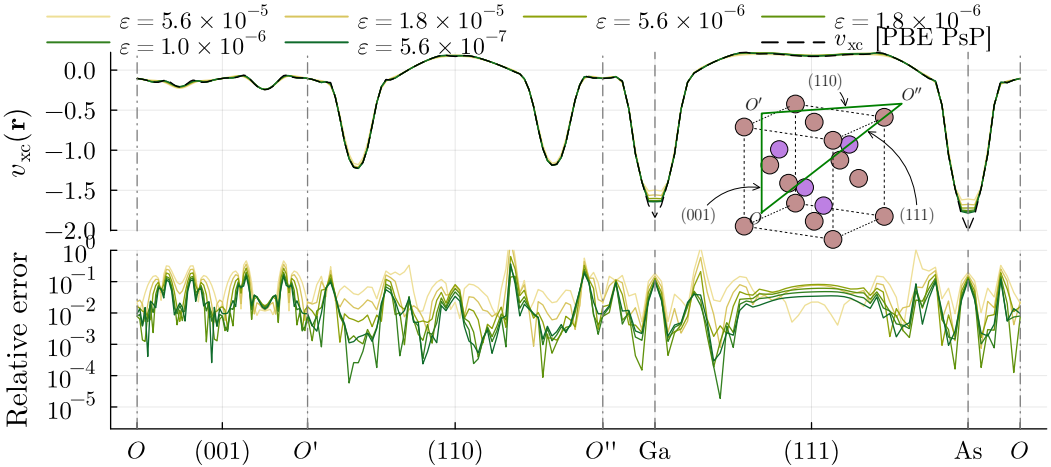
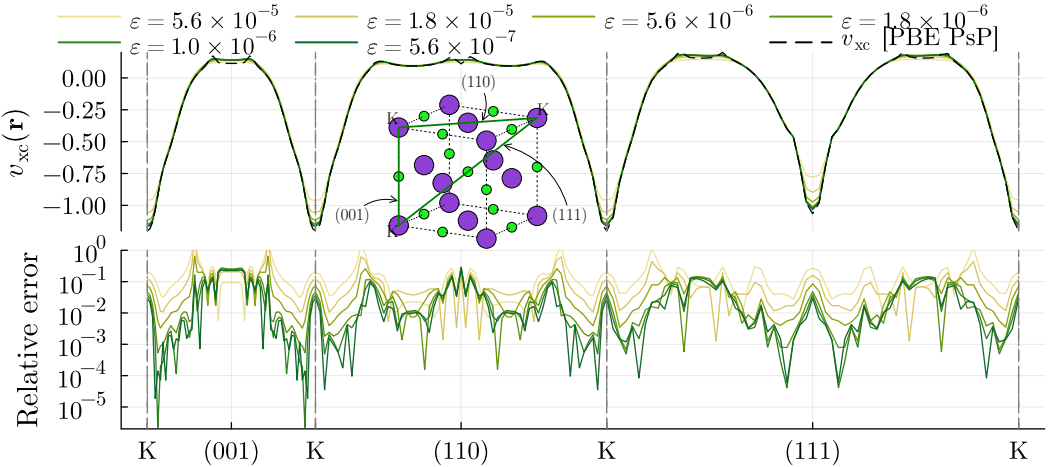
Gallium Arsenide



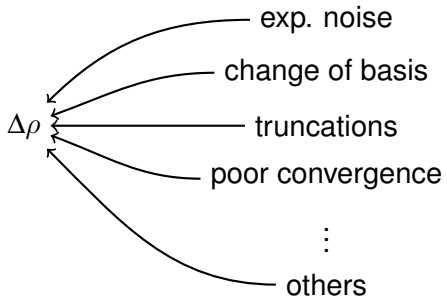
Potassium Chloride



Error Bounds

Inexact density:

$$\widetilde{\rho}_{\mathrm{gs}} = \rho_{\mathrm{gs}} + \Delta\rho$$



The *total error*

$$\|v_{\mathrm{xc}} - \widetilde{v}^{\varepsilon}_{\mathrm{xc}}\|_{\mathcal{V}} \leq \underbrace{\|v_{\mathrm{xc}} - v^{\varepsilon}_{\mathrm{xc}}\|_{\mathcal{V}}}_{\text{terminating at finite } \varepsilon} + \underbrace{\|v^{\varepsilon}_{\mathrm{xc}} - \widetilde{v}^{\varepsilon}_{\mathrm{xc}}\|_{\mathcal{V}}}_{\text{using inexact } \rho_{\mathrm{gs}}} \tag{4}$$

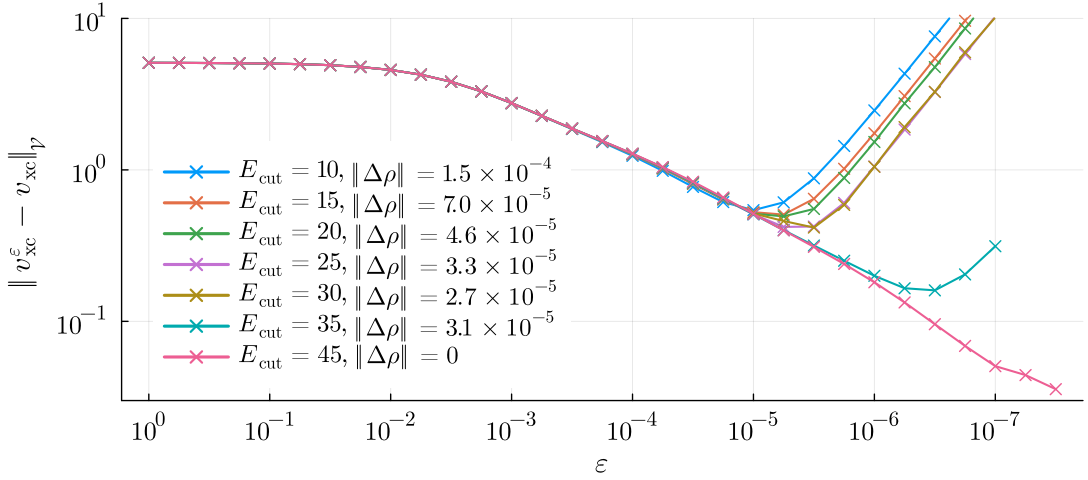
Energy error splitting

Kim, Sim and Burke: Density-driven error

$$\begin{aligned}\Delta E &= E(\rho_{\mathrm{gs}}) - E_{\mathrm{appr}}(\rho_{\mathrm{gs}} + \Delta\rho) \\ &= \underbrace{\big(E(\rho_{\mathrm{gs}}) - E_{\mathrm{appr}}(\rho_{\mathrm{gs}})\big)}_{\text{error from functional}} + \underbrace{\big(E_{\mathrm{appr}}(\rho_{\mathrm{gs}}) - E_{\mathrm{appr}}(\rho_{\mathrm{gs}} + \Delta\rho)\big)}_{\text{error from density}}\end{aligned} \tag{5}$$

We borrow the term “density-driven” when we speak of errors in the potentials caused by inexact densities.

Convergence: Bulk Silicon



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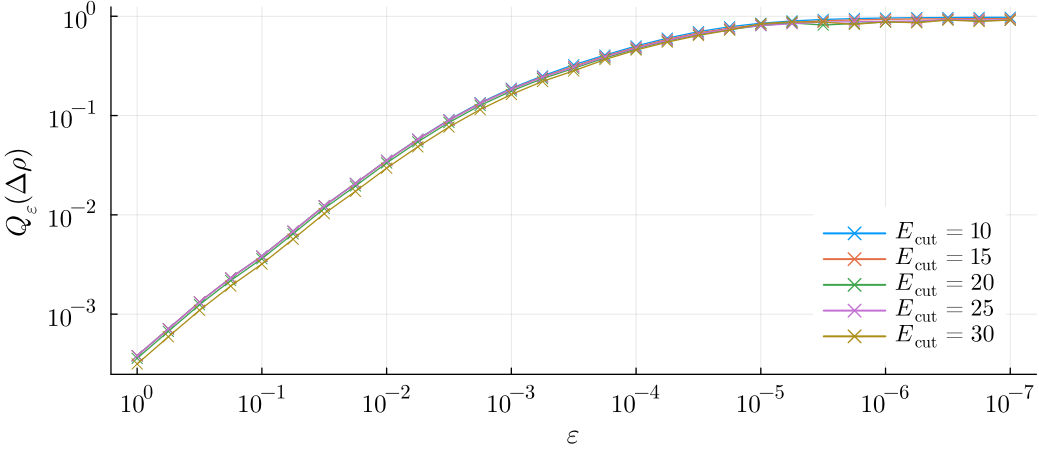
Non-Expansiveness of $\rho \longmapsto \rho^{\varepsilon}$

$$\left\|\rho^{\varepsilon}_{\mathrm{gs}} - \widetilde{\rho}^{\varepsilon}_{\mathrm{gs}}\right\|_{\mathcal{D}} \leq \|\rho_{\mathrm{gs}} - \widetilde{\rho}_{\mathrm{gs}}\|_{\mathcal{D}} = \|\Delta\rho\|_{\mathcal{D}} \qquad Q_{\varepsilon}(\Delta\rho) = \frac{\left\|\rho^{\varepsilon}_{\mathrm{gs}} - \widetilde{\rho}^{\varepsilon}_{\mathrm{gs}}\right\|_{\mathcal{D}}}{\|\Delta\rho\|_{\mathcal{D}}}$$



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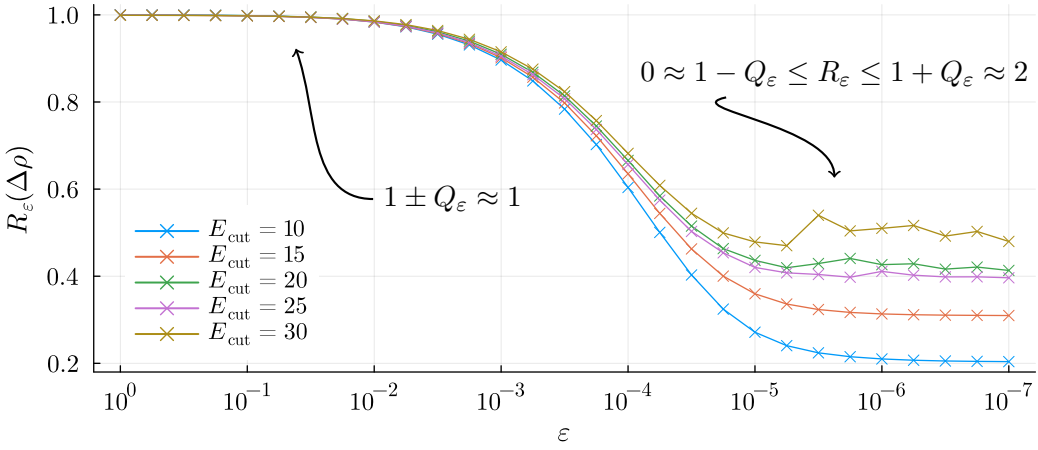
Error Bounds: Inexact Densities

$$\|\widetilde{v}_{\mathrm{xc}}^{\varepsilon} - v_{\mathrm{xc}}^{\varepsilon}\|_{\mathcal{V}} \leq \frac{1 + Q_{\varepsilon}(\Delta\rho)}{\varepsilon}\|\Delta\rho\|_{\mathcal{D}} \qquad R_{\varepsilon}(\Delta\rho) = \varepsilon\frac{\|\widetilde{v}_{\mathrm{xc}}^{\varepsilon} - v_{\mathrm{xc}}^{\varepsilon}\|_{\mathcal{V}}}{\|\Delta\rho\|_{\mathcal{D}}}$$



Conclusions

- Mathematically rigorous inversion scheme
- Rigorous error estimates
- Practical use case of Moreau–Yosida regularisation
- First systems studied: Si, GaAs, KCl
- Implemented using `DFTK.jl` [4]

Outlook

- More complicated systems
- Reference densities from other sources
- Further error analysis
- Investigate proximal point algorithms

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References I

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2. **Penz, M., Csirik, M. A. & Laestadius, A.** Density-potential inversion from Moreau–Yosida regularization. *Electron. Struct.* **5,** 014009 (2023).
3. **Herbst, M. F., Bakkestuen, V. H. & Laestadius, A.** *Kohn–Sham Inversion with Mathematical Guarantees.* 2025. arXiv: 2409.04372.
4. **.** github.com/mfherbst/supporting-my-inversion.

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Thank you for your attention!

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