Kohn–Sham Inversion with Mathematical Guarantees

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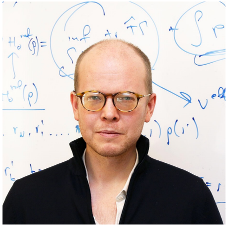
Acknowledgements

In collaboration with M. Herbst[1,2] and A. Laestadius.[3,4]



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Outline

The Kohn–Sham Approach

Interacting electrons

$$-\frac{1}{2}\sum_j \nabla_j^2 + \sum_{k<j} |\mathbf{r}_j - \mathbf{r}_k|^{-1} + \sum_j v_{\text{ext}}(\mathbf{r}_j)$$

ρ_{gs}

Non-interacting electrons (KS system)

$$-\frac{1}{2}\sum_j \nabla_j^2 + \sum_j [v_{\text{ext}}(\mathbf{r}_j) + v_{\text{H}}(\mathbf{r}_j) + v_{\text{xc}}(\mathbf{r}_j)]$$

the exchange correlation potential, $v_{\text{xc}} \longleftarrow$ unknown

The forward problem: given a v_{xc}, what is the ρ_{gs}?

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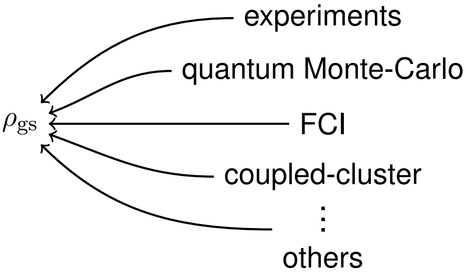
The Inverse Kohn–Sham Problem

The reverse problem:
Given a ρ_{gs}, what is the v_{xc}?



Approach to understanding the *universal density functional* $\mathcal{F}$

Road to new approximations of $\mathcal{F}$

Moreau–Yosida Regularisation

Moreau–Yosida Regularisation

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

Definition

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

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

An infimal convolution

A Lossless Regularisation

The regularised energy

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

Exact ground-state energy

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

The regularisation retains the ground state energy

Consequence of infimal convolution and E(concave) $\leftrightarrow$ $\mathcal{F}$(convex).

The Inversion Scheme

Periodic Systems

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

Periodic Sobolev spaces [1]

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

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

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

Fix $\rho_{\text{gs}} \in \mathcal{D}$ and

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

The Exchange-Correlation Potential

Minimise

$$\mathcal{E}(\rho\,;\rho_{\mathrm{gs}}) = \mathcal{F}(\rho) + \tfrac{1}{2\varepsilon}\|\rho - \rho_{\mathrm{gs}}\|_{\mathcal{D}}^2 \quad \text{over} \quad \rho \in \mathcal{D} \tag{1}$$

Proximal density

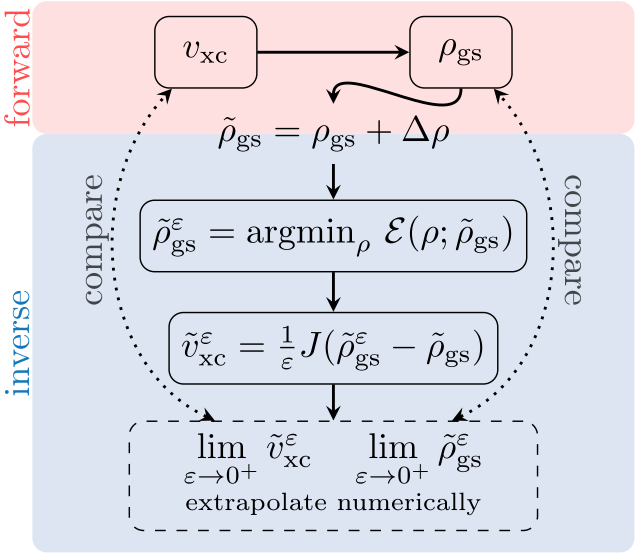
$$\rho_{\mathrm{gs}}^{\varepsilon} = \operatorname*{argmin}_{\rho} \mathcal{E}(\rho, \rho_{\mathrm{gs}})$$

is the unique minimser of $\mathcal{E}(\rho\,;\rho_{\mathrm{gs}})$ [2]

The exchange-correlation potential [3, 4]

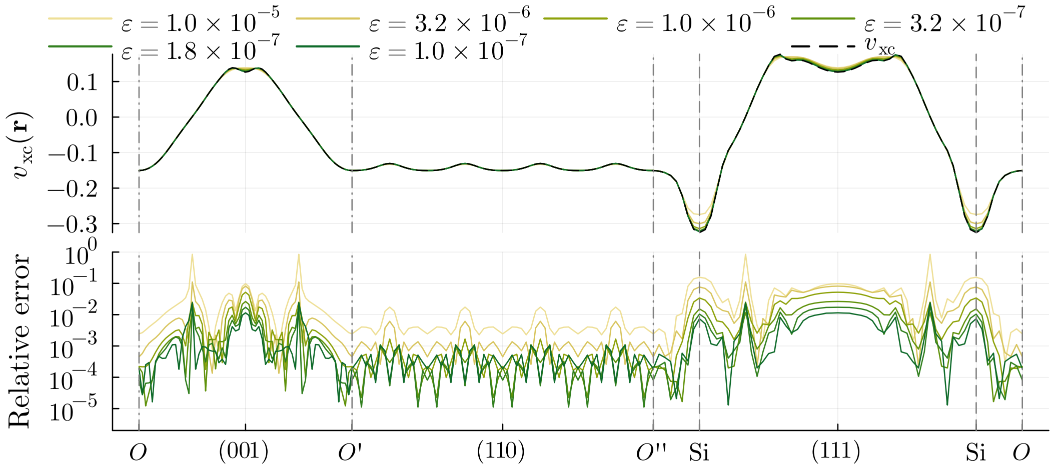
$$\begin{aligned} v_{\mathrm{xc}}(\mathbf{r}) &= \lim_{\varepsilon\to 0^+} \frac{1}{\varepsilon} J\left[\rho_{\mathrm{gs}}^{\varepsilon} - \rho_{\mathrm{gs}}\right](\mathbf{r}) \\ &= \lim_{\varepsilon\to 0^+} \frac{1}{\varepsilon} \int_{\mathbb{R}^3} \frac{\rho_{\mathrm{gs}}^{\varepsilon}(\mathbf{x})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

The Inversion Algorithm



Results

Bulk Silicone



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

Error Bounds

The proximal mapping $\rho \mapsto \rho^\varepsilon$ is non-expansive,

$$\|\rho^\varepsilon - \widetilde{\rho}^\varepsilon\|_{\mathcal{D}} \leq \|\rho - \widetilde{\rho}\|_{\mathcal{D}}, \quad \forall \rho, \widetilde{\rho} \in \mathcal{D} \tag{2}$$

Consider inexact references:

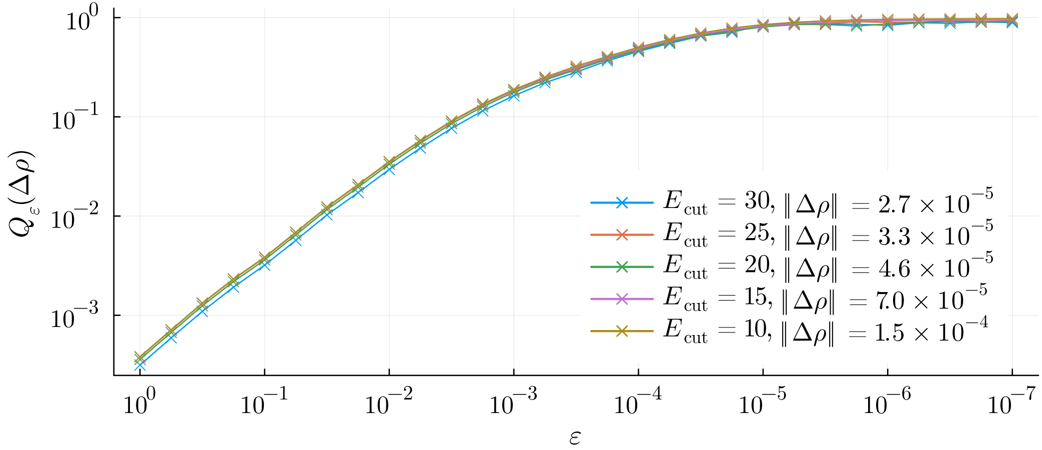
$$\widetilde{\rho}_{\mathrm{gs}} = \rho_{\mathrm{gs}} + \Delta\rho$$

The *total error*

$$\|v_{\mathrm{xc}} - \widetilde{v}^\varepsilon_{\mathrm{xc}}\|_{\mathcal{V}} \leq \underbrace{\|v_{\mathrm{xc}} - v^\varepsilon_{\mathrm{xc}}\|_{\mathcal{V}}}_{\text{terminating at finite } \varepsilon} + \underbrace{\|v^\varepsilon_{\mathrm{xc}} - \widetilde{v}^\varepsilon_{\mathrm{xc}}\|_{\mathcal{V}}}_{\text{using inexact } \rho_{\mathrm{gs}}} \tag{3}$$

Non-Expansiveness

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



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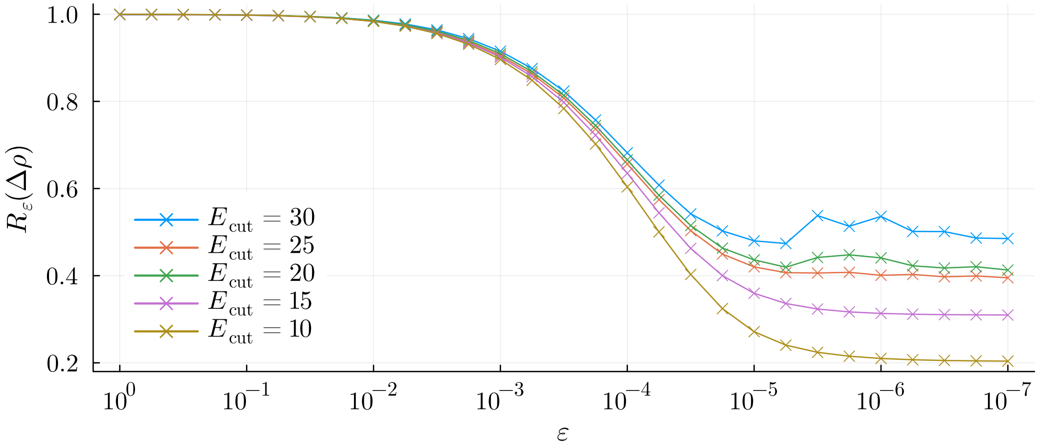
Error Bounds: Inexact Densities

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



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Conclusions

- Mathematically rigorous inversion scheme
- Rigorous error estimates
- Practical use case of Moreau–Yosida regularisation
- First system studied: bulk silicone
- Implemented using `DFTK.jl` [5]

Outlook

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

References I

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Thank you for your attention!

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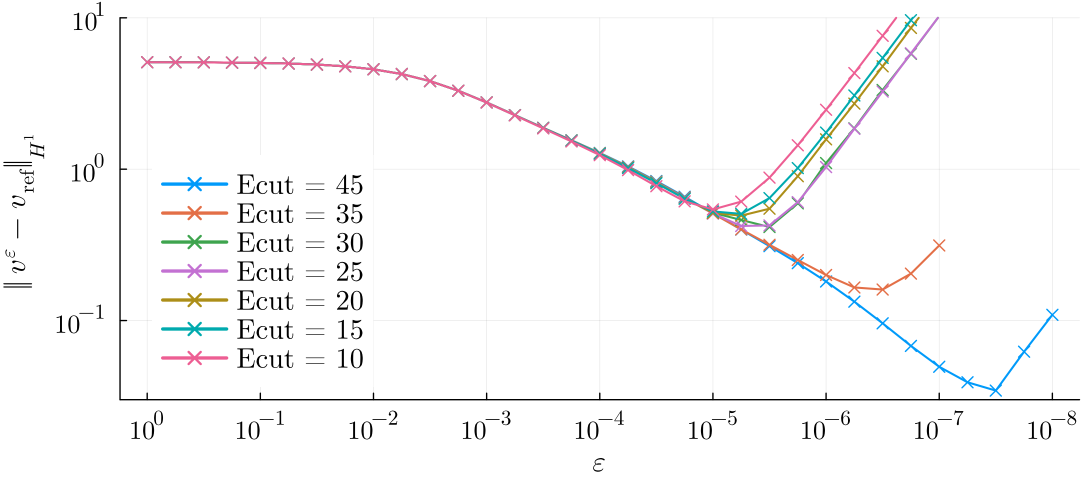
Motivation: The Differentiability of $\mathcal{F}$

- The exact universal functional $\mathcal{F}$ is non-differentiable with respect to ρ [6].
- Practical implementations often assume differentiability, e.g., $v_{\mathrm{xc}} = \delta E_{\mathrm{xc}}/\delta\rho$.
- Regularisation of $\mathcal{F}$ to ensure differentiability.

Convergence: Bulk Silicone



Analytic Error Bounds

Theoretically, the ratios satisfies $\forall\,\Delta\rho \in \mathcal{D}$

$$0 \leq Q_\varepsilon(\Delta\rho) \leq 1$$

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

$$0 \leq S_\varepsilon(\Delta\rho) \leq Q_\varepsilon(\Delta\rho) \leq 1$$

$$\lim_{\varepsilon \to 0^+} Q_\varepsilon(\Delta\rho) = 1 \quad \text{and} \quad \lim_{\varepsilon \to 0^+} S_\varepsilon(\Delta\rho) \leq 1$$

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Error Bounds: Inexact Densities

$$\left\| v_{\mathrm{xc}}^{\varepsilon} - \widetilde{v}_{\mathrm{xc}}^{\varepsilon} - \tfrac{1}{\varepsilon} J\left(\Delta\rho\right) \right\|_{\mathcal{V}} \leq \frac{1}{\varepsilon} Q_{\varepsilon}(\Delta\rho) \|\Delta\rho\|_{\mathcal{D}} \qquad S_{\varepsilon}(\Delta\rho) = \varepsilon \frac{\left\| v_{\mathrm{xc}}^{\varepsilon} - \widetilde{v}_{\mathrm{xc}}^{\varepsilon} - \tfrac{1}{\varepsilon} J\left(\Delta\rho\right) \right\|_{\mathcal{V}}}{\|\Delta\rho\|_{\mathcal{D}}}$$