

Moreau–Yosida Kohn–Sham inversion

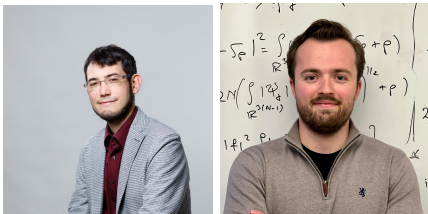
Numerical Methods in Quantum Chemistry Berlin June 18th, 2025

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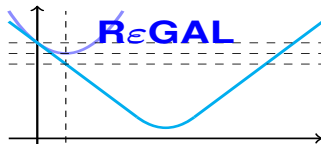
Acknowledgements

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Outline

1 Background

- Density-Functional Theory
- Kohn–Sham Problem
- Moreau–Yosida Regularisation

2 Inversion Scheme

- “KS” model Functional
- Exchange-Correlation Potential
- The Inversion Algorithm

3 Results

- Bulk Materials
- Error Bounds

4 Conclusions

5 References

Density-Functional Theory

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

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

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

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

The Kohn–Sham Approach

Interacting electrons

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

Non-interacting electrons (KS system)

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

ρ_{gs}

Exchange-correlation potential $v_{\text{xc}} \leftarrow$ unknown

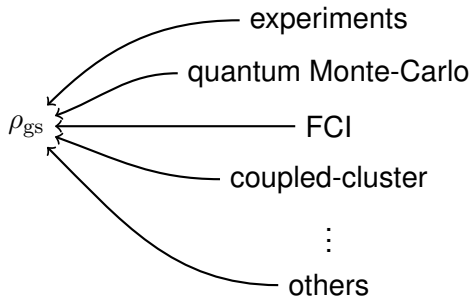
The forward problem:

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

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

Duality mapping $J_{\text{dual}} : \mathcal{D} \rightarrow \mathcal{V}$

Density space: $N\text{-rep} \subsetneq \mathcal{D} \ni \rho$

Potential space: $\mathcal{V} = \mathcal{D}^* \ni v$

Definition

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

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

Why? $F(\rho)$ in DFT is **everywhere** discontinuous (P. Lammert)
Introduced into DFT by Kvaal et. al

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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“KS” model Functional

Recall

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

Given ρ_{gs} , let

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

Minimise

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

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

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

The Exchange-Correlation Potential

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

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

Theorem. [1, 2] Exchange-correlation potential obtained from

$$v_{\text{xc}}(\mathbf{r}) = \lim_{\varepsilon \rightarrow 0^+} v_{\text{xc}}^\varepsilon = \lim_{\varepsilon \rightarrow 0^+} \frac{1}{\varepsilon} J_{\text{dual}}[\rho_{\text{gs}}^\varepsilon - \rho_{\text{gs}}](\mathbf{r})$$

The form of J_{dual} depends on the choice of $\mathcal{D}$:

Ex1. $\mathcal{D} = L^2 \implies J_{\text{dual}} = I$ (van Leeuwen & Baerends)

Ex2. $\mathcal{D} = \text{homogeneous Sobolev space} \implies J_{\text{dual}}(\rho) = v_{\text{H}}(\rho)$ (ZMP)

Sketch of proof: By assumption v_{KS} exists s.t. the KS system “gives” ρ_{gs} :

$$\min_{\rho} (T(\rho) + \langle v_{\text{KS}}, \rho \rangle) \iff \underline{\partial} T(\rho_{\text{gs}}) + v_{\text{KS}} \ni 0 \quad (2)$$

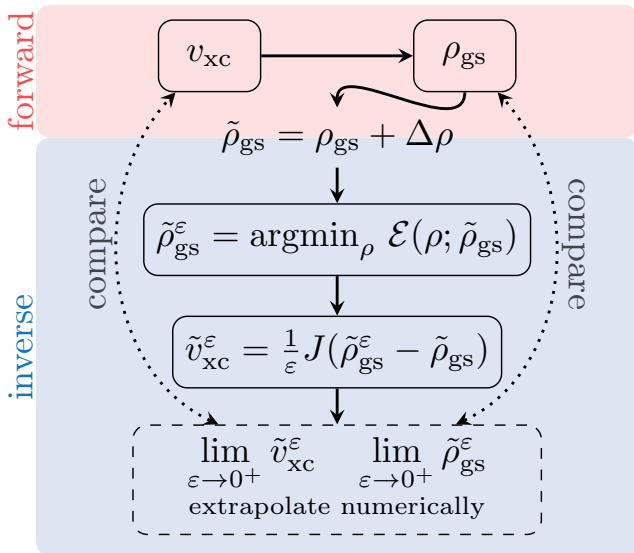
$$\min_{\rho} (\mathcal{F}(\rho) + \langle v_{\text{xc}}, \rho \rangle) \iff \underbrace{\underline{\partial} \mathcal{F}(\rho_{\text{gs}}) + v_{\text{xc}} \ni 0}_{(*)} \quad (3)$$

Moreau-Yosida:

$$\min_{\rho} \left\{ \mathcal{F}(\rho) + \frac{1}{2\varepsilon} \|\rho - \rho_{\text{gs}}\|_{\mathcal{D}}^2 \right\} \iff \underbrace{\underline{\partial} \mathcal{F}(\rho_{\text{gs}}^{\varepsilon}) + \frac{1}{\varepsilon} J_{\text{dual}}(\rho_{\text{gs}}^{\varepsilon} - \rho_{\text{gs}}) \ni 0}_{(**)} \quad (4)$$

$$(*), (**) \text{ and } \rho_{\text{gs}}^{\varepsilon} \rightarrow \rho_{\text{gs}} \text{ as } \varepsilon \rightarrow 0+ \implies v_{\text{xc}} = \lim_{\varepsilon \rightarrow 0+} \frac{1}{\varepsilon} J_{\text{dual}}(\rho_{\text{gs}}^{\varepsilon} - \rho_{\text{gs}})$$

The Inversion Algorithm with error $\Delta\rho$



Implementation: Periodic Systems

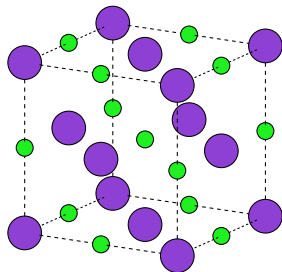
$$\mathcal{D} = H_{\text{per}}^{-1}(\Omega, \mathbb{C}) \quad \mathcal{V} = \mathcal{D}^* = H_{\text{per}}^1(\Omega, \mathbb{C})$$

Periodic Sobolev spaces [3]

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

The *duality mapping* $J_{\text{dual}} : \mathcal{D} \rightarrow \mathcal{V}$,

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



Numerical details

KS-DFT implementation: parametrize $\rho_{\text{gs}}^\varepsilon$ in terms of orthonormal orbitals

$$\Phi = (\psi_1, \dots, \psi_{N_b}), \int_{\Omega} \psi_i^* \psi_j = \delta_{ij}$$

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

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

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

PsP approximation for v_{ext}

Numerical details

Direct minimization in terms of orbitals (Stiefel manifold):

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

enabling to rewrite the minimization of

$$\begin{aligned} \mathcal{E}(\Phi, \rho_{\text{gs}}) = & \sum_{i=1} f_i \int_{\Omega} |\nabla \psi_i|^2 + E_{\text{H}}(\rho_{\Phi}) \\ & + \int_{\Omega} v_{\text{ext}} \rho_{\Phi} + \frac{1}{2\varepsilon} \|\rho_{\Phi} - \rho_{\text{gs}}\|_{\mathcal{D}}^2 \end{aligned} \tag{5}$$

with respect to the orbitals Φ . (Spin-unpolarized $f_i \in \{0, 2\}$)

For the particular choices of density- and potential spaces

$$\begin{aligned} v_{xc} &= \lim_{\varepsilon \rightarrow 0^+} \frac{1}{\varepsilon} \int_{\mathbb{R}^3} \frac{\rho_{gs}^\varepsilon(\mathbf{x}) - \rho_{gs}(\mathbf{x})}{4\pi|\mathbf{r} - \mathbf{x}|} e^{-|\mathbf{r} - \mathbf{x}|} d\mathbf{x} \\ &= \lim_{\varepsilon \rightarrow 0^+} \frac{1}{\varepsilon} \sum_{\mathbf{G} \neq 0} \frac{(\widehat{\rho}_{gs}^\varepsilon)_{\mathbf{G}} - (\widehat{\rho}_{gs})_{\mathbf{G}}}{1 + |\mathbf{G}|^2} e_{\mathbf{G}}(\mathbf{r}) \end{aligned}$$

In practice: Fourier space cutoff, $|\mathbf{G}|^2 \leq 2E_{\text{cut}}$

Results

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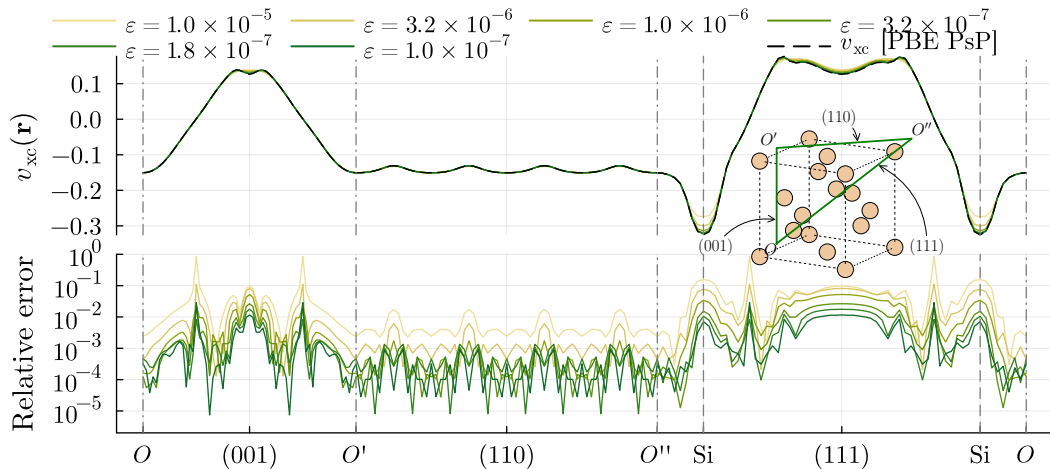
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Bulk Silicon



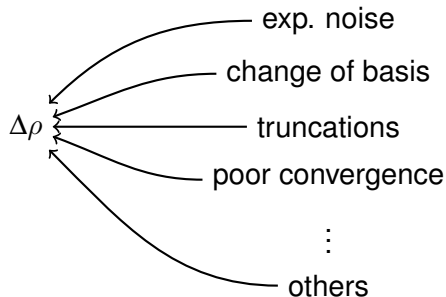
Implementation on github.com/mfherbst/supporting-my-inversion

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Error Bounds

Inexact density:

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



The *total error*

$$\|v_{\text{xc}} - \tilde{v}_{\text{xc}}^{\varepsilon}\|_{\mathcal{V}} \leq \underbrace{\|v_{\text{xc}} - v_{\text{xc}}^{\varepsilon}\|_{\mathcal{V}}}_{\text{terminating at finite } \varepsilon} + \underbrace{\|v_{\text{xc}}^{\varepsilon} - \tilde{v}_{\text{xc}}^{\varepsilon}\|_{\mathcal{V}}}_{\text{using inexact } \rho_{\text{gs}}} \quad (6)$$

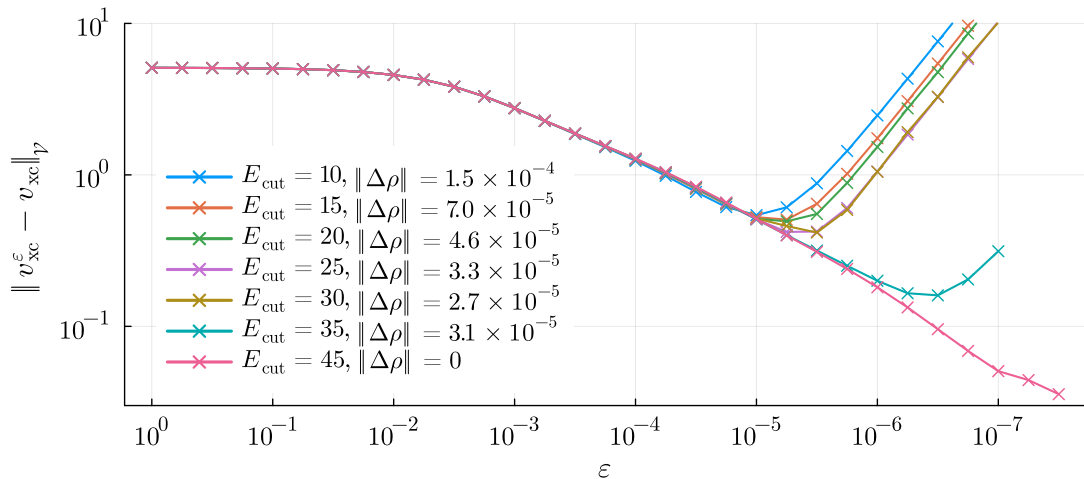
Energy error splitting

Kim, Sim and Burke: Density-driven error

$$\begin{aligned}\Delta E &= E(\rho_{\text{gs}}) - E_{\text{appr}}(\rho_{\text{gs}} + \Delta\rho) \\ &= \underbrace{(E(\rho_{\text{gs}}) - E_{\text{appr}}(\rho_{\text{gs}}))}_{\text{error from functional}} + \underbrace{(E_{\text{appr}}(\rho_{\text{gs}}) - E_{\text{appr}}(\rho_{\text{gs}} + \Delta\rho))}_{\text{error from density}}\end{aligned}\quad (7)$$

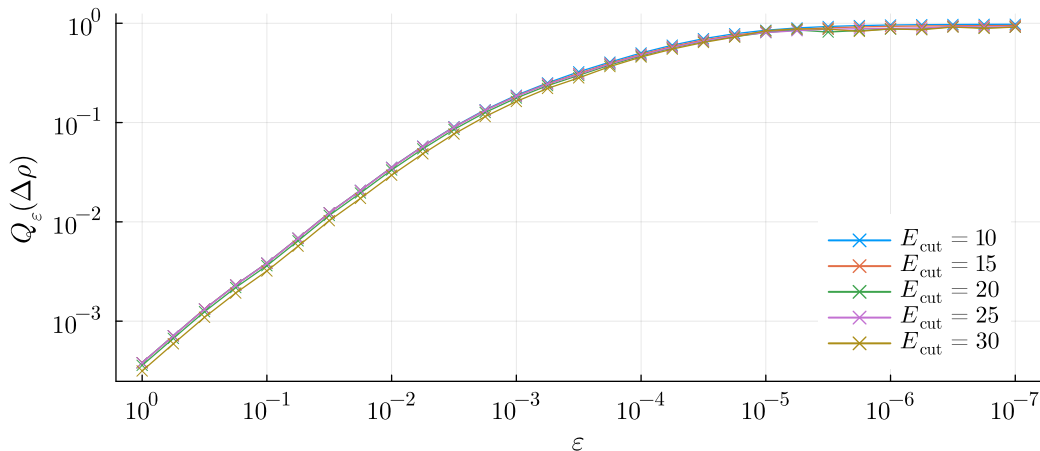
We borrow the term “density-driven” when we speak of errors in the potentials caused by inexact densities.

Convergence: Bulk Silicon



Non-Expansiveness of $\rho \mapsto \rho^\varepsilon$

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



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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]



DFTK

Outlook

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

References I

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2. **Herbst *et al.*, M. F.** Kohn-Sham inversion with mathematical guarantees. *Phys. Rev. B* **111**, 205143 (2025).
3. **Cancès, E., Chakir, R. & Maday, Y.** Numerical analysis of the planewave discretization of some orbital-free and Kohn-Sham models. en. *ESAIM: M2AN* **46**, 341–388 (2012).
4. [. github.com/mfherbst/supporting-my-inversion](https://github.com/mfherbst/supporting-my-inversion).



Thank you for your attention!

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