Kohn–Sham Inversion with Mathematical Guarantees

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Motivation

Density-functional theory (DFT)
Indispensable tool in chemistry, materials science, and solid-state physics [1].
Key ingredients: density ρ & universal density functional $\mathcal{F}(\rho)$.
In practice $\mathcal{F}$ is approximated.
Significant efforts devoted to new approx.
$\rho_{\rm gs}$ = ground-state density

Kohn–Sham (KS) approach

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

Non-interacting electrons (KS system)
$-\frac{1}{2}\sum_j \nabla_j^2 + \sum_j [v_{\rm ext}(\mathbf{r}_j) + v_{\rm H}(\mathbf{r}_j) + v_{\rm xc}(\mathbf{r}_j)]$

$\rho_{\rm gs}$

Critical unknown: $v_{\rm xc}$
Typically from choice of an approximate $\mathcal{F}$

Inverse KS
Given $\rho_{\rm gs}$, what is the corresponding $v_{\rm xc}$?
Significantly less studied than KS.
Rigorous approach to understanding $\mathcal{F}$ and obtaining approximations [2].

Differentiability of $\mathcal{F}$
Standard formulation, the exact $\mathcal{F}$ is non-differentiable with respect to ρ [3].
Practical implementations often assume differentiability, e.g., $v_{\rm xc} = \delta E_{\rm xc}/\delta\rho$.
Regularising $\mathcal{F} \Rightarrow$ differentiable $\mathcal{F}$.

"Lossless" Moreau–Yosida Regularisation of DFT

Densities $\rho \in \mathcal{D}$ and potentials $v \in \mathcal{V}$.
$\mathcal{D}$ uniformly convex and $\mathcal{F}: \mathcal{D} \to \mathbb{R}$ convex & l.s.c.
The *Moreau–Yosida* (MY) *regularisation* of $\mathcal{F}$ at $\varepsilon > 0$: the infimal convolution

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

$\mathcal{F}$ relates to the regularised and exact ground-state energy as

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

i.e., MY regularisation is *lossless*. Consequence of inf-conv. and E(concave) $\leftrightarrow \mathcal{F}$(convex).

Obtaining the Exchange-Correlation Potential

Fix $\rho_{\rm gs}$ and guiding functional $\mathcal{F}(\rho) = T(\rho) + E_{\rm H}(\rho) + \int_\Omega v_{\rm ext}\rho$.
$T(\rho)$: kinetic contribution, $E_{\rm H}$: Hartree term, $v_{\rm ext}$: external potential.
$\mathcal{D} = H^{-1}_{\rm per}$ and $\mathcal{V} = H^1_{\rm per}$: periodic Sobolev spaces [4].
Crucial step: minimisation over $\rho \in \mathcal{D}$ of

$$\mathcal{E}(\rho\,;\rho_{\rm gs}) = \mathcal{F}(\rho) + \tfrac{1}{2\varepsilon}\|\rho - \rho_{\rm gs}\|_{\mathcal{D}}^2. \quad (3)$$

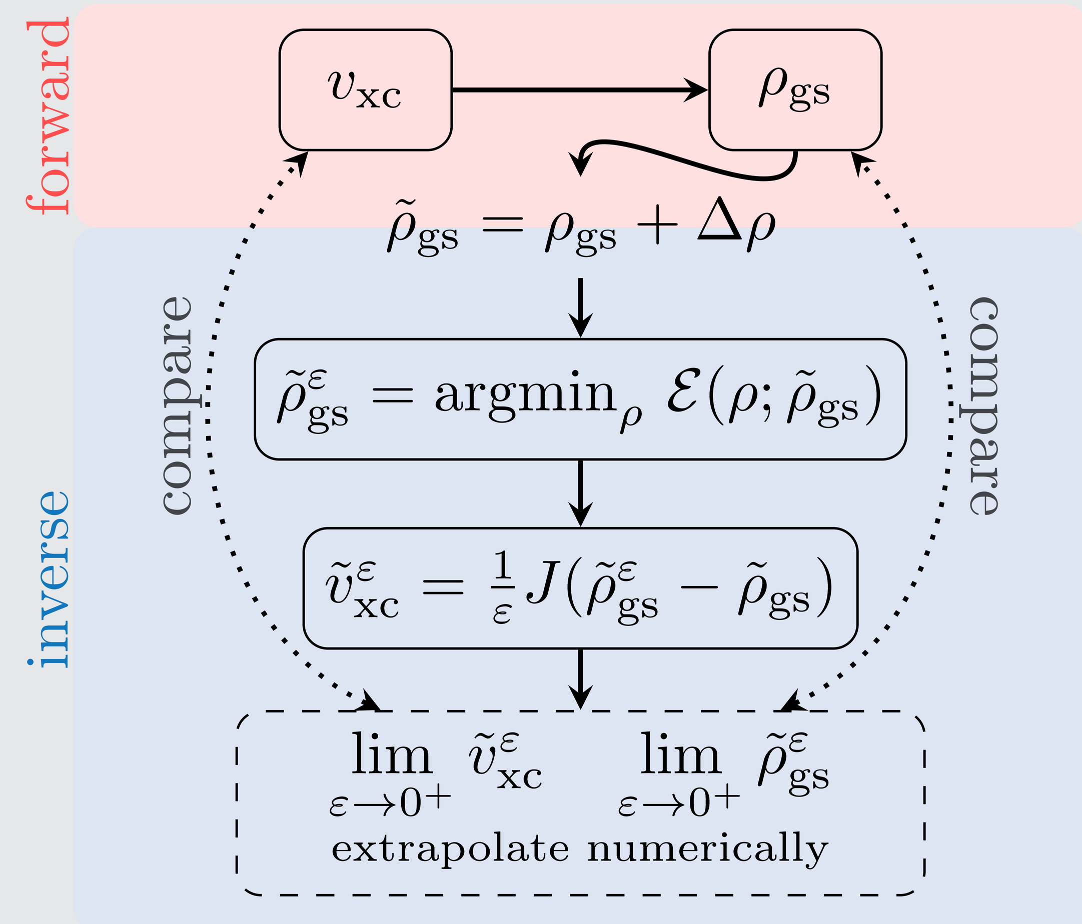
Minimum of $\mathcal{E}$, the *proximal density* $\rho^\varepsilon_{\rm gs} = \mathrm{argmin}_\rho\, \mathcal{E}(\rho, \rho_{\rm gs})$ attained uniquely [5].
Duality mapping $J: \mathcal{D} \to \mathcal{V}$

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

The xc potential is [6, 7]

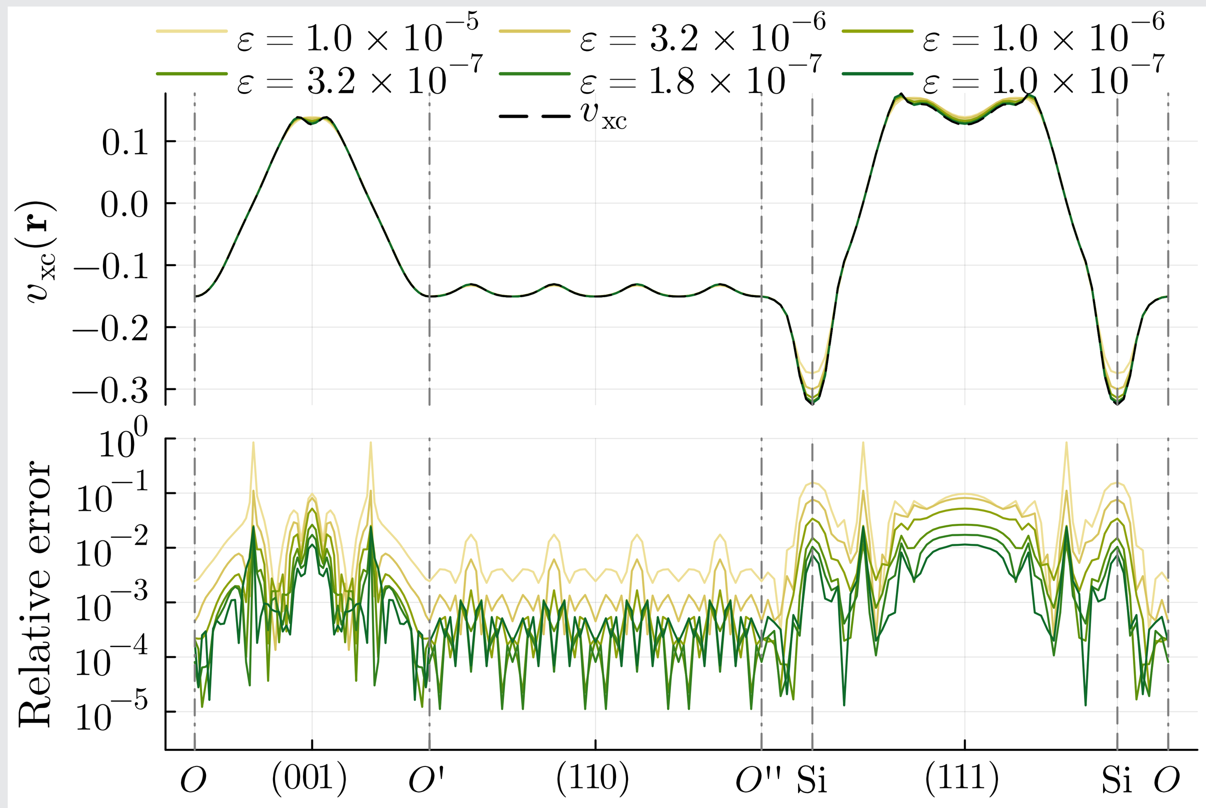
$$v_{\rm xc}(\mathbf{r}) = \lim_{\varepsilon\to 0^+} \frac{1}{\varepsilon} \int_{\mathbb{R}^3} \frac{\rho^\varepsilon_{\rm gs}(\mathbf{r}') - \rho_{\rm gs}(\mathbf{r}')}{4\pi|\mathbf{r}-\mathbf{r}'|} e^{-|\mathbf{r}-\mathbf{r}'|}\, {\rm d}^3 r'. \quad (5)$$

The Inversion Scheme



Initiating forward scheme:
Find a reference $\rho_{\rm gs}$.
Origin e.g., experimental data, FCI, coupled-cluster, and quantum MC calculations.
Errors: $\Delta\rho$ introduced
$\Rightarrow$ inexact reference $\tilde\rho_{\rm gs}$.
Origins e.g., experimental errors, basis truncations, and numerical inaccuracies.
Inversion scheme given $\tilde\rho_{\rm gs}$:
(1) obtain the proximal density $\tilde\rho^\varepsilon_{\rm gs}$ by minimising eq. (3).
(2) obtain $\tilde v^\varepsilon_{\rm xc}$ by application of the duality mapping, eq. (4).
(3) repeat (1) & (2) for a decreasing sequence in ε.
(4) $\tilde v_{\rm xc}$ and corresponding $\tilde\rho_{\rm gs}$ are obtained by extrapolating $\varepsilon \to 0^+$.
The extrapolated $\tilde\rho^\varepsilon_{\rm gs}$ (and $\tilde v^\varepsilon_{\rm xc}$) is compared to the reference ρ_{gs} (and $v_{\rm xc}$, if known).

Numerical Example: Bulk Silicone



Forward:
From a $v_{\rm xc}$, $\rho_{\rm gs}$ found by solving forward KS SCF problem with PBE xc functional.
Errors:
$\Delta\rho$ from interpolation of $\rho_{\rm gs}$ on smaller basis $\to \tilde\rho_{\rm gs}$.
Inverse:
For exponentially decreasing sequence in ε, expect: $v^\varepsilon_{\rm xc} \to v_{\rm xc}$ and $\tilde\rho^\varepsilon_{\rm gs} \to \tilde\rho_{\rm gs}$.
To match the forward KS, use a parametrisation of $\tilde\rho^\varepsilon_{\rm gs}$ in terms of orthonormal orbitals and minimise $\mathcal{E}$ using a BFGS-based quasi-Newton scheme.
Details, code, and data on GitHub [8].

Inverse crime [2]:
Same quantum-chemical model and discretisation basis for both forward and inverse.
To highlight the strict mathematical results: (1) Knowledge of ref. $v_{\rm xc}$ necessary. (2) Direct comparison of ref. $\tilde\rho_{\rm gs}$ and $\tilde\rho^\varepsilon_{\rm gs}$ beneficial. (3) Adding controlled perturbations $\Delta\rho$.

Error Bounds: Analytical & Numerical

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

$$\|\rho^\varepsilon - \tilde\rho^\varepsilon\|_{\mathcal{D}} \le \|\rho - \tilde\rho\|_{\mathcal{D}}, \quad \forall \rho, \tilde\rho \in \mathcal{D}. \quad (6)$$

The *total* error

$$\|v_{\rm xc} - \tilde v^\varepsilon_{\rm xc}\|_{\mathcal{V}} \le \underbrace{\|v_{\rm xc} - v^\varepsilon_{\rm xc}\|_{\mathcal{V}}}_{\text{terminating at finite }\varepsilon} + \underbrace{\|v^\varepsilon_{\rm xc} - \tilde v^\varepsilon_{\rm xc}\|_{\mathcal{V}}}_{\text{using inexact }\rho_{\rm gs}}. \quad (7)$$

Error bounds for the second term,

$$\|\tilde v^\varepsilon_{\rm xc} - v^\varepsilon_{\rm xc}\|_{\mathcal{V}} \le \frac{1 + Q_\varepsilon(\Delta\rho)}{\varepsilon}\|\Delta\rho\|_{\mathcal{D}}, \quad (8)$$

$$\left\|v^\varepsilon_{\rm xc} - \tilde v^\varepsilon_{\rm xc} - \tfrac{1}{\varepsilon}J(\Delta\rho)\right\|_{\mathcal{V}} \le \frac{1}{\varepsilon} Q_\varepsilon(\Delta\rho)\|\Delta\rho\|_{\mathcal{D}}, \quad (9)$$

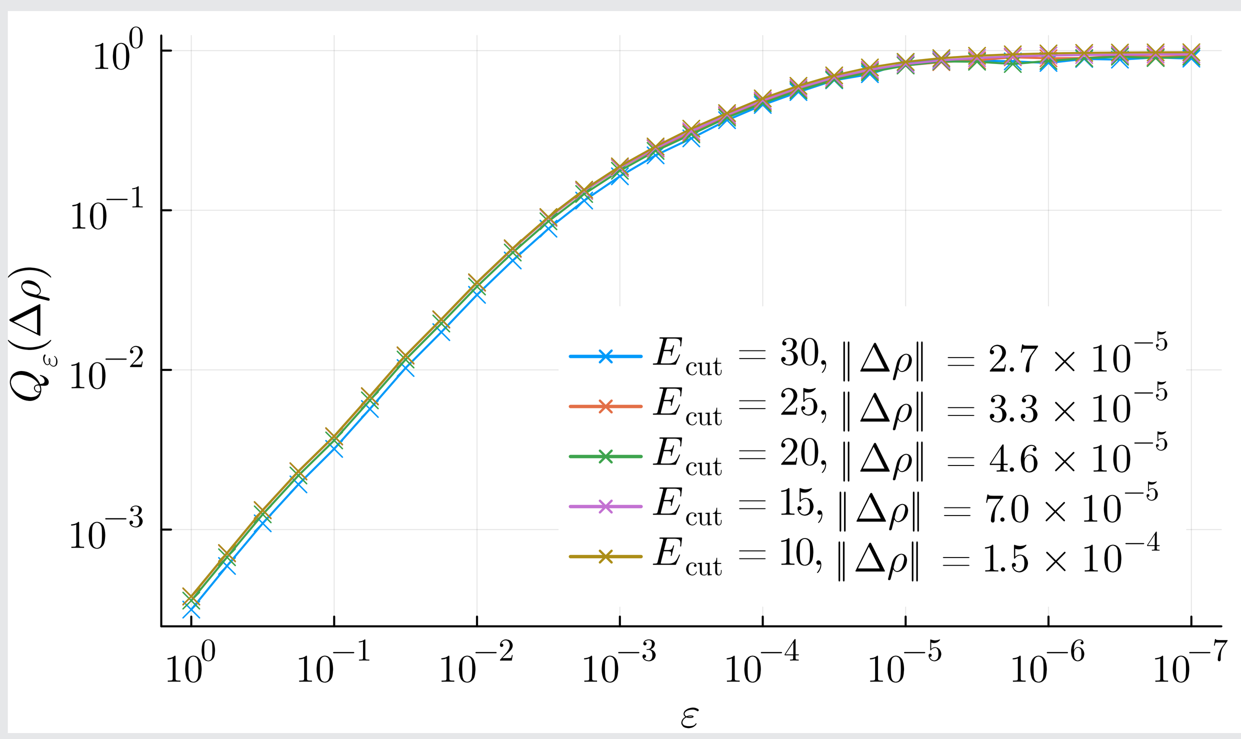
where

$$Q_\varepsilon(\Delta\rho) := \frac{\|\rho^\varepsilon_{\rm gs} - \tilde\rho^\varepsilon_{\rm gs}\|_{\mathcal{D}}}{\|\rho_{\rm gs} - \tilde\rho_{\rm gs}\|_{\mathcal{D}}} = \frac{\|\rho^\varepsilon_{\rm gs} - \tilde\rho^\varepsilon_{\rm gs}\|_{\mathcal{D}}}{\|\Delta\rho_{\rm gs}\|_{\mathcal{D}}}.$$

To investigate eqs. (8) and (9), define

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

$$S_\varepsilon(\Delta\rho) := \varepsilon \frac{\left\|v^\varepsilon_{\rm xc} - \tilde v^\varepsilon_{\rm xc} - \frac{1}{\varepsilon}J(\Delta\rho)\right\|_{\mathcal{V}}}{\|\Delta\rho\|_{\mathcal{D}}}.$$



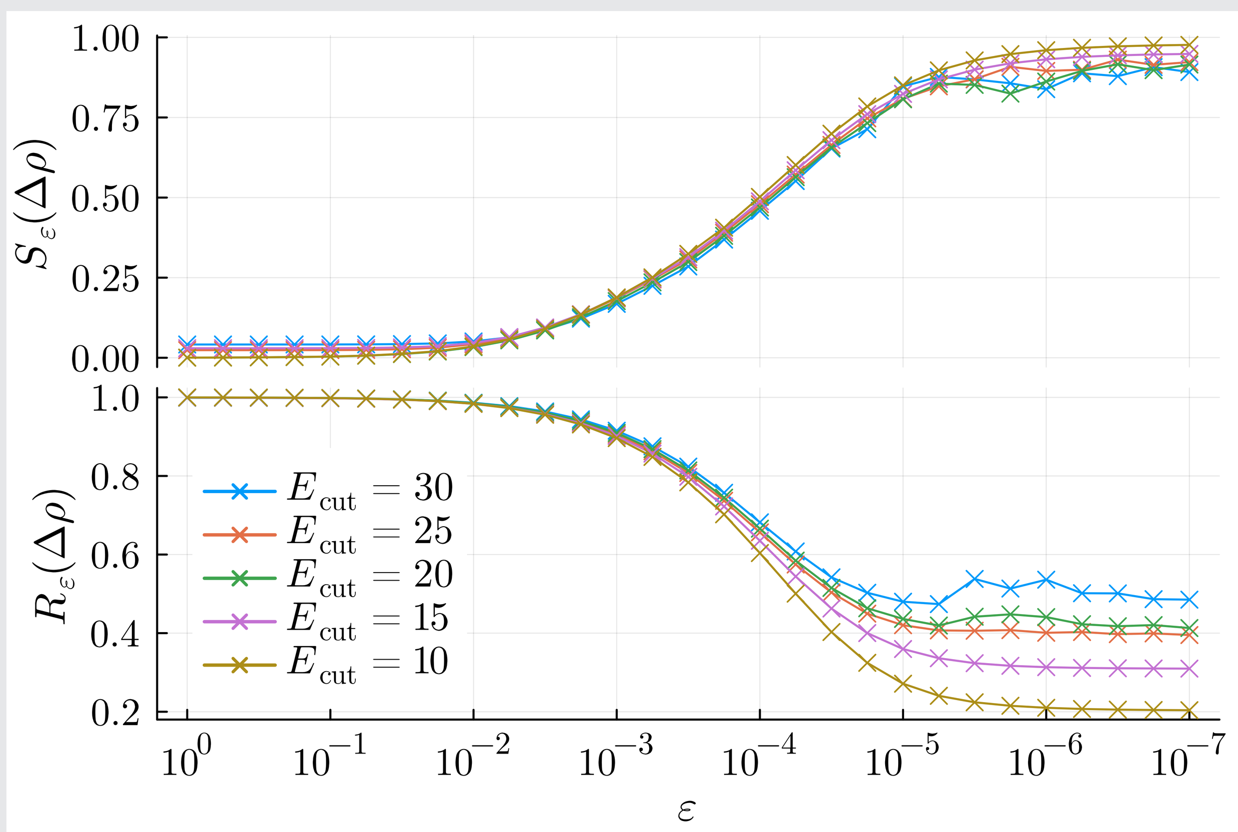
The ratios theoretically satisfies $\forall\, \Delta\rho \in \mathcal{D}$

$$0 \le Q_\varepsilon(\Delta\rho) \le 1,$$

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

$$0 \le S_\varepsilon(\Delta\rho) \le Q_\varepsilon(\Delta\rho) \le 1.$$

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



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[8] `github.com/mfherbst/supporting-my-inversion`.

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