

# HARTREE–FOCK LEVEL DENSITY-POTENTIAL INVERSION FOR PERIODIC SYSTEMS

Oliver M. Bohle<sup>1,\*,†,‡</sup>, Maryam Lotfigolian<sup>2,\*</sup>, Andre Laestadius<sup>1,2,\*,\*</sup> & Erik I. Tellgren<sup>1,\*</sup>

1 Hylleraas Centre for Quantum Molecular Sciences, Department of Chemistry, University of Oslo, 0315 Oslo, Norway

2 Department of Computer Science, Oslo Metropolitan University, 0130 Oslo, Norway

Supported under; \* Hylleraas Centre Grant No. 262695, \* ERC Starting Grant No. 101041487 REGAL, † CompSci

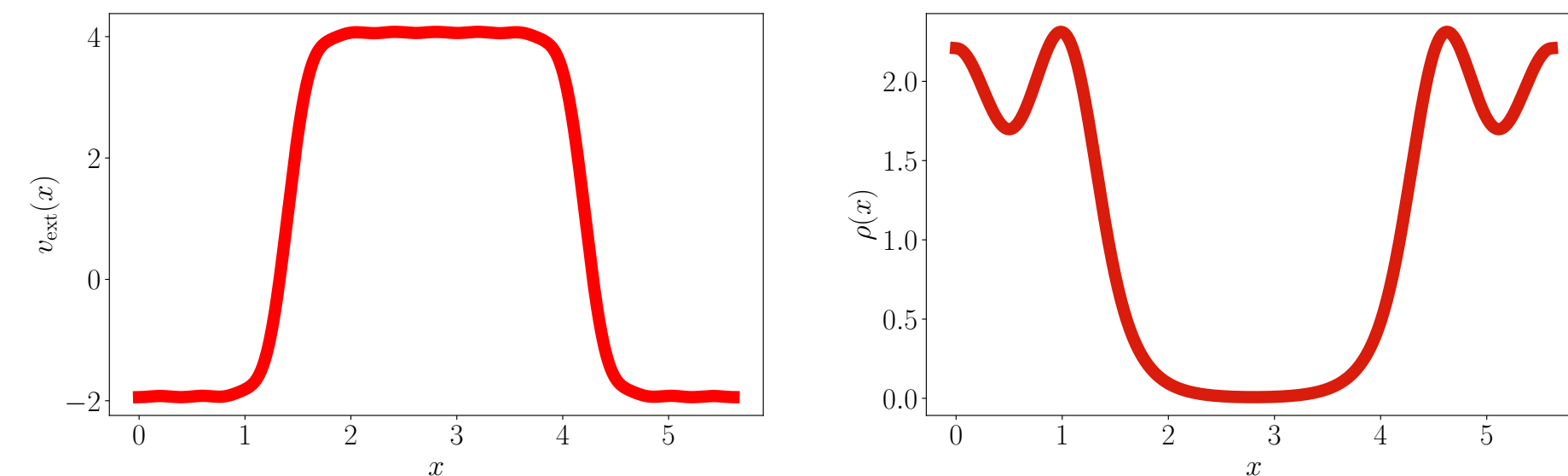
European Union's Horizon 2020 No. 945371, UNINETT Sigma2 Grant No. NN4654K

‡ o.m.bohel@kjemi.uio.no

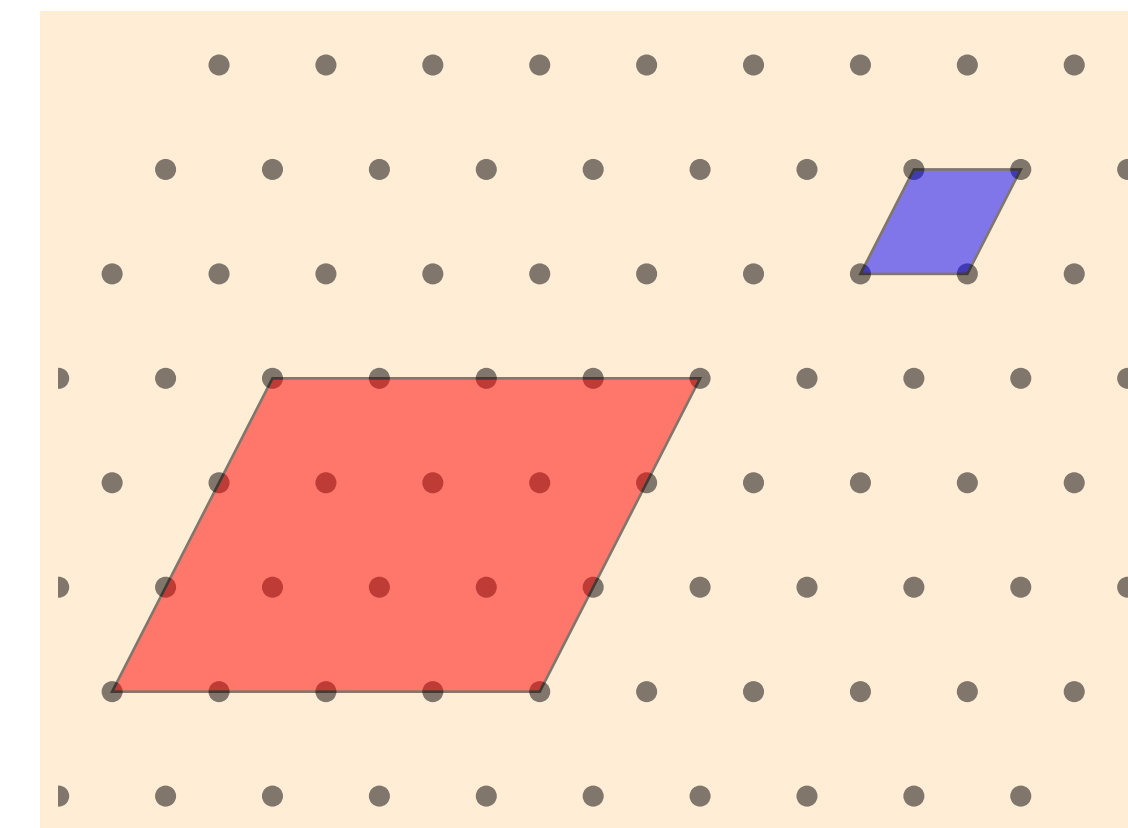
## Introduction

- The **Forward problem** in DFT is to calculate the groundstate density,  $\rho$ , from a potential,  $v$ .
- The **Inverse problem**, we start from a  $\rho$  and determine the potential  $v$  which reproduces  $\rho$ .

- We investigated the **Inversion problem** to obtain the local potential that describes Fock exchange using the Moreau–Yosida (MY) regularisation formulation of DFT using HF.



## Periodicity



- The theoretical framework is general for spatial domains  $\mathbb{R}^d$  of any dimension  $d$  and number of periodic directions  $p$ , such that  $p \leq d$ .

- Fig. case of  $p=d=2$ , blue shaded cell is the unit cell and the red shaded cell is the Born–von Kármán

- Results illustrates  $p = d = 1$

## Hamiltonian

- The wave function is periodic over the Born–von Kármán zone (BvK).
- The Hamiltonian is defined as,

$$H = -\frac{1}{2} \sum_{i=1}^M \frac{d^2}{dx_i^2} + \sum_{i=1}^M v_{\text{ext}}(x_i) + \lambda \sum_{i < j} w_{\text{per}}(x_i - x_j),$$

$$w_{\text{per}}(x) := \sum_m \frac{e^{-\gamma|x-m|}}{2\gamma},$$

where  $v_{\text{ext}}(x_i)$  is the external potential and  $M$  the number of electrons in the BvK

- Potentials and densities are periodic in the unit cell.
- The last term is the two-electron interaction, the Yukawa interaction.

## Duality mapping

- $\rho$ 's with finite Hartree/Yukawa self-energy form Sobolev space,  $X$ .

- $v$  lives in the dual space,  $X^*$ .

- The duality map from density to potentials,

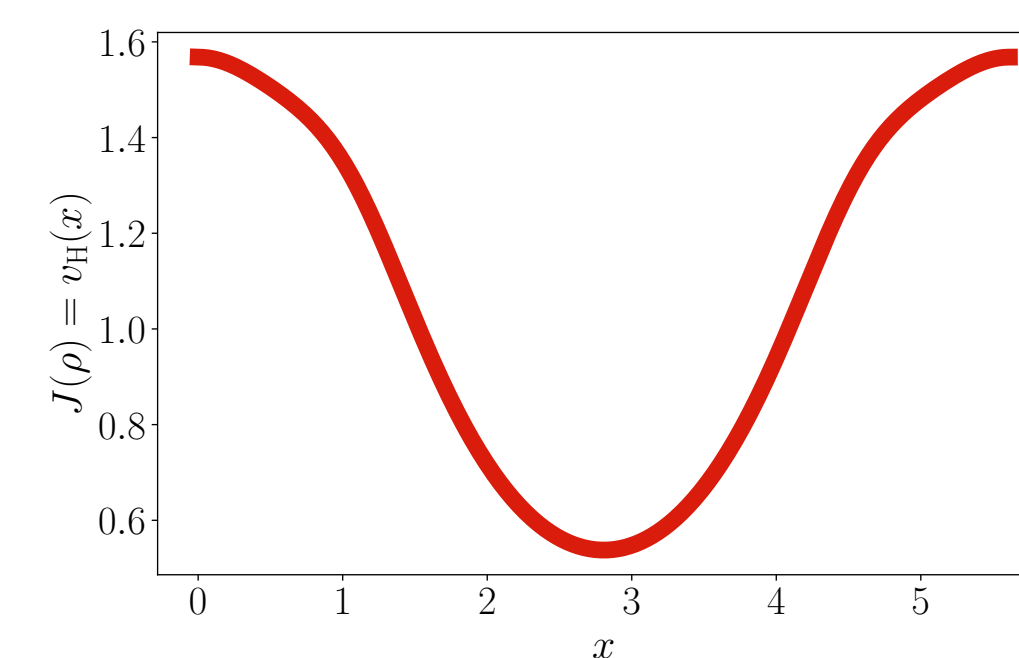
$$v = J(\rho) = \sum_{G \in \mathcal{RL}} \frac{\tilde{\rho}(G)}{\gamma^2 + G^2} e^{iGx}, \quad v^\varepsilon = \frac{1}{\varepsilon} J(\rho^\varepsilon - \rho_{\text{ref}}),$$

- and from potentials to density

$$\rho = J^{-1}(v) = \sum_{G \in \mathcal{RL}} (\gamma^2 + G^2) \tilde{v}(G) e^{iGx}.$$

- The duality map satisfies

$$\text{Hartree energy} = \frac{1}{2} \|\rho\|_X^2 = \frac{1}{2} \|v\|_{X^*}^2 = \frac{1}{2} \langle J(\rho), \rho \rangle$$



## Moreau–Yosida regularisation

- We define the Moreau–Yosida regularisation of  $f$  at  $\rho \in X$  as,

$$f^\varepsilon(\rho) = \inf_{\rho' \in X} \left\{ f(\rho') + \frac{1}{2\varepsilon} \|\rho' - \rho\|_X^2 \right\} = f(\rho^\varepsilon) + \frac{1}{2\varepsilon} \|\rho^\varepsilon - \rho\|_X^2,$$

where  $\varepsilon > 0$  is the regularisation parameter.

- $\rho^\varepsilon$  the proximal point.
- $\frac{1}{2\varepsilon} \|\rho - \rho'\|_X^2$  penalty term  $\implies \rho^\varepsilon \rightarrow \rho$  as  $\varepsilon \rightarrow 0+$ .

## Regularised Hartree–Fock

- The Hartree–Fock energy is given by,

$$\mathcal{E}(\mathcal{D}) = \text{tr}(\mathcal{D}h) + \frac{\lambda}{2} \langle J(\rho_{\mathcal{D}}), \rho_{\mathcal{D}} \rangle - \mu \mathcal{X}(\mathcal{D}),$$

where  $\mathcal{D}$  is the 1-PRDM,  $h$  the core Hamiltonian,  $\langle J(\rho), \rho \rangle$  the direct Hartree energy and,  $\mathcal{X}$  the exchange energy.

- We are interested in finding the exchange potential,  $v_X$ , from a reference density,  $\rho_{\text{ref}}$ , hence,  $\mu = 0$  in the inversion calculation.
- To determine  $v_X$  arising from  $\rho_{\text{ref}}$ , we include a penalty term to the HF energy,

$$\frac{1}{2\varepsilon} \langle J(\rho_{\mathcal{D}} - \rho_{\text{ref}}), \rho_{\mathcal{D}} - \rho_{\text{ref}} \rangle$$

where,  $\rho_{\text{ref}}$  is the target density.

- The penalty term guides the proximal point to the reference density as  $\varepsilon \rightarrow 0+$ .

- When expanding the penalty term we get an extra  $1/\varepsilon$  worth of direct Hartree energy added to  $\mathcal{E}^\varepsilon(\mathcal{D})$ ,

$$\mathcal{E}^\varepsilon(\mathcal{D}) = \mathcal{E}(\mathcal{D}) + \frac{1}{\varepsilon} \langle J(\rho_{\mathcal{D}}), \rho_{\mathcal{D}} \rangle - \frac{2}{\varepsilon} \langle J(\rho_{\mathcal{D}}), \rho_{\text{ref}} \rangle + \frac{1}{\varepsilon} \langle J(\rho_{\text{ref}}), \rho_{\text{ref}} \rangle.$$

## Determining the exchange potential

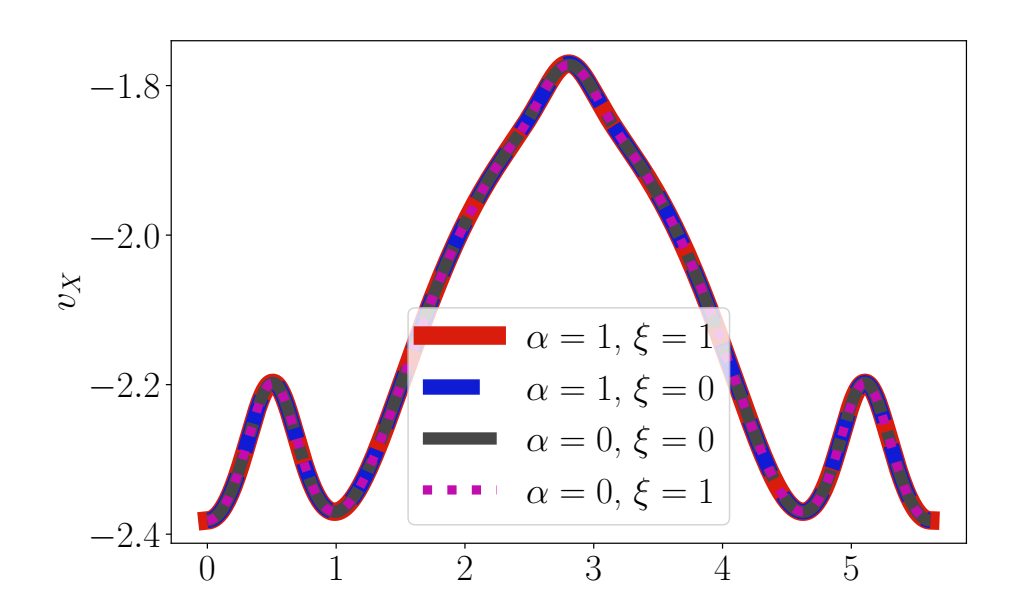
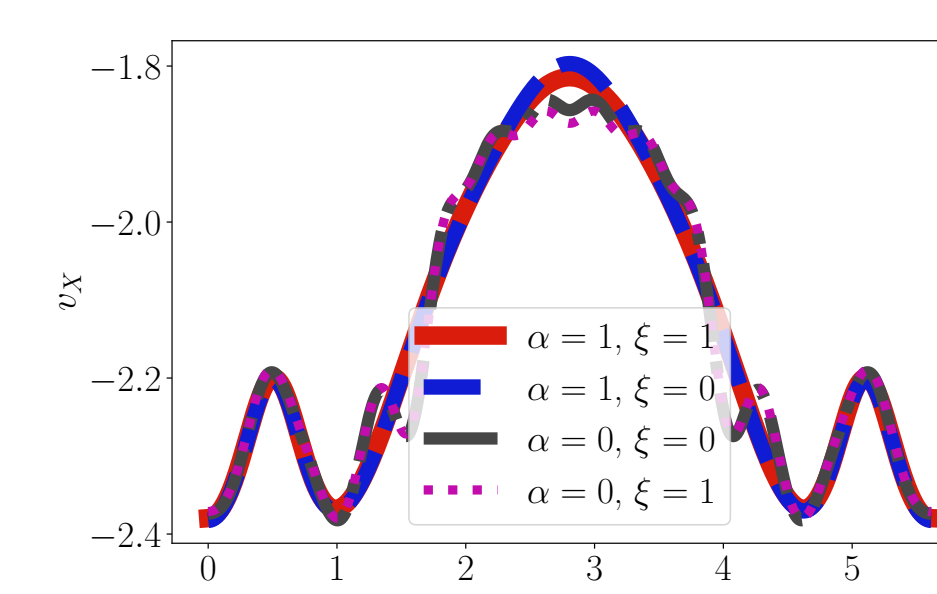
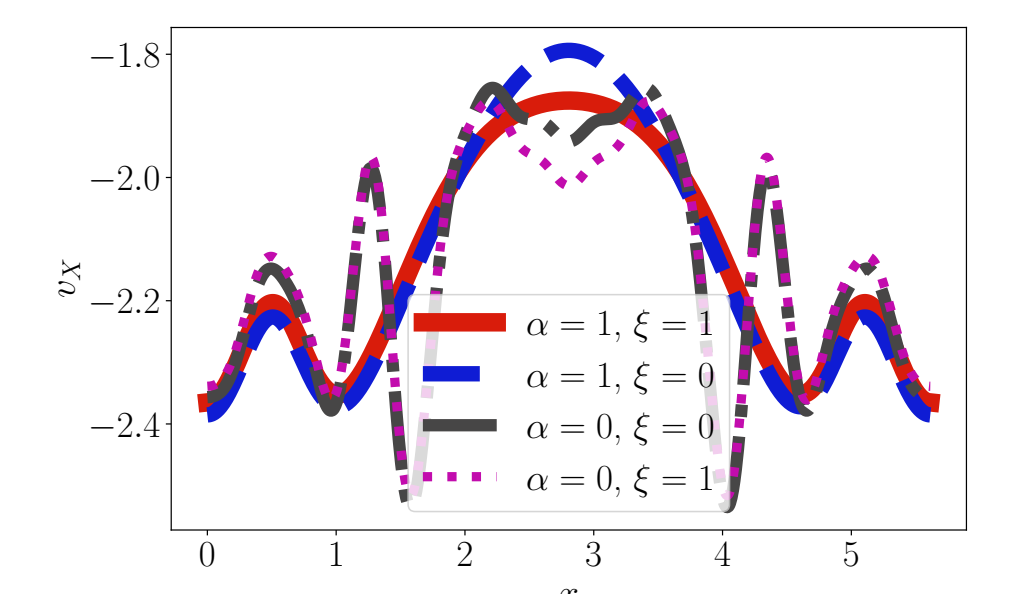
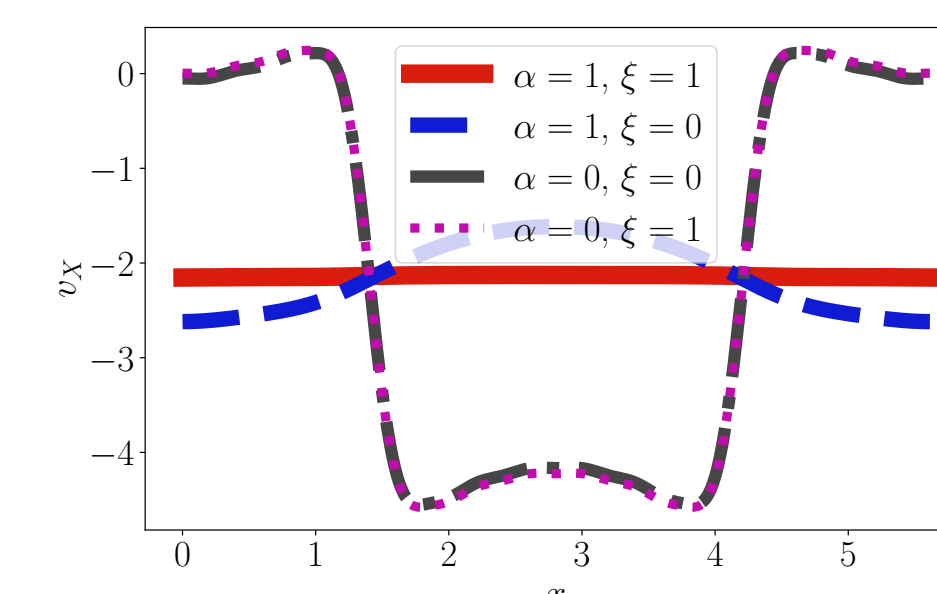
- We have four different methods to determine the exchange potential,

$$F_{\alpha,\xi}(\rho) = T(\rho) + \alpha \langle v_{\text{ext}}, \rho \rangle + \xi \langle J(\rho), \rho \rangle,$$

$$v_X = (\alpha - 1)v_{\text{ext}} + (\xi + \sigma)J(\rho_{\mathcal{D}}) - (\sigma + 1)J(\rho_{\text{ref}}),$$

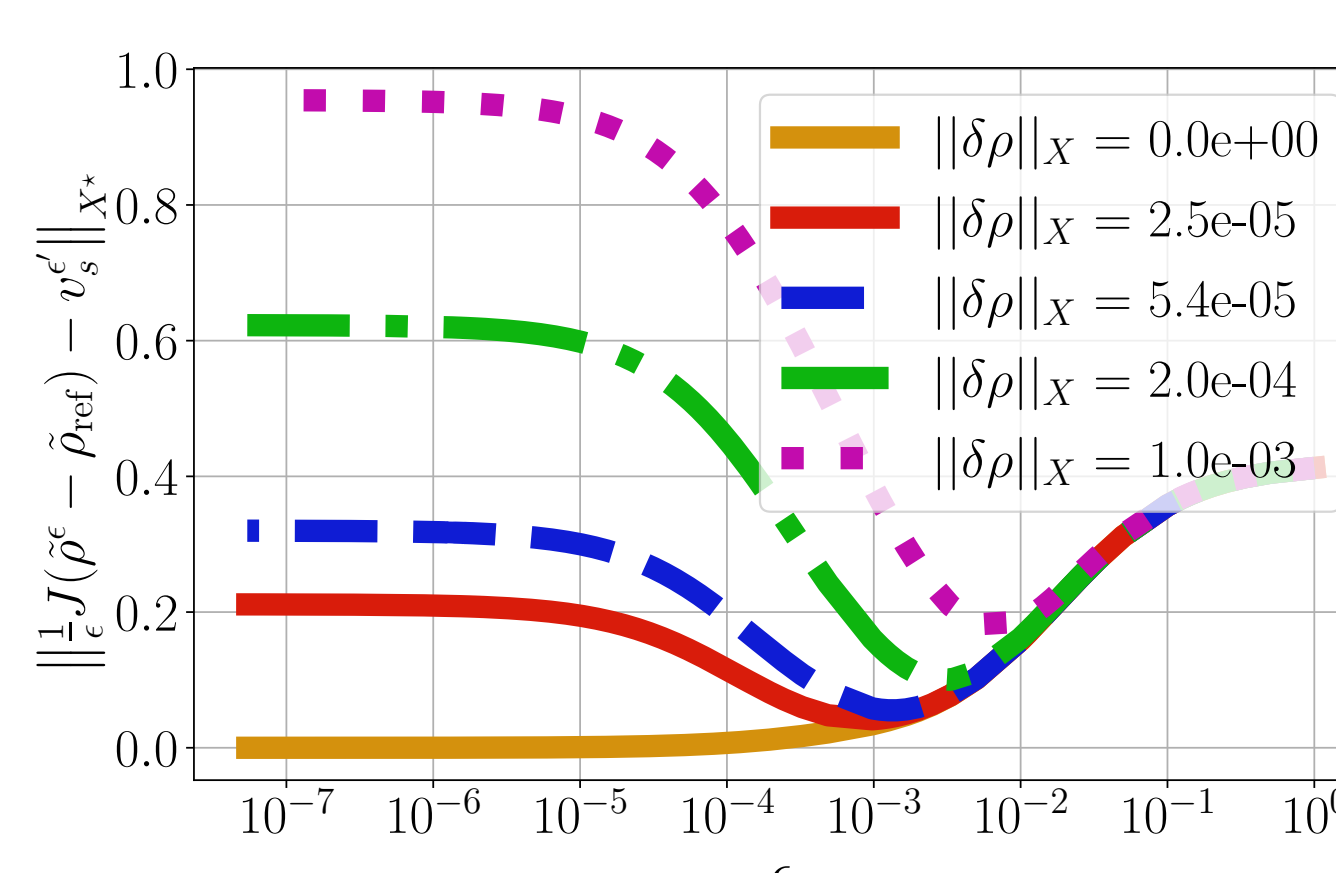
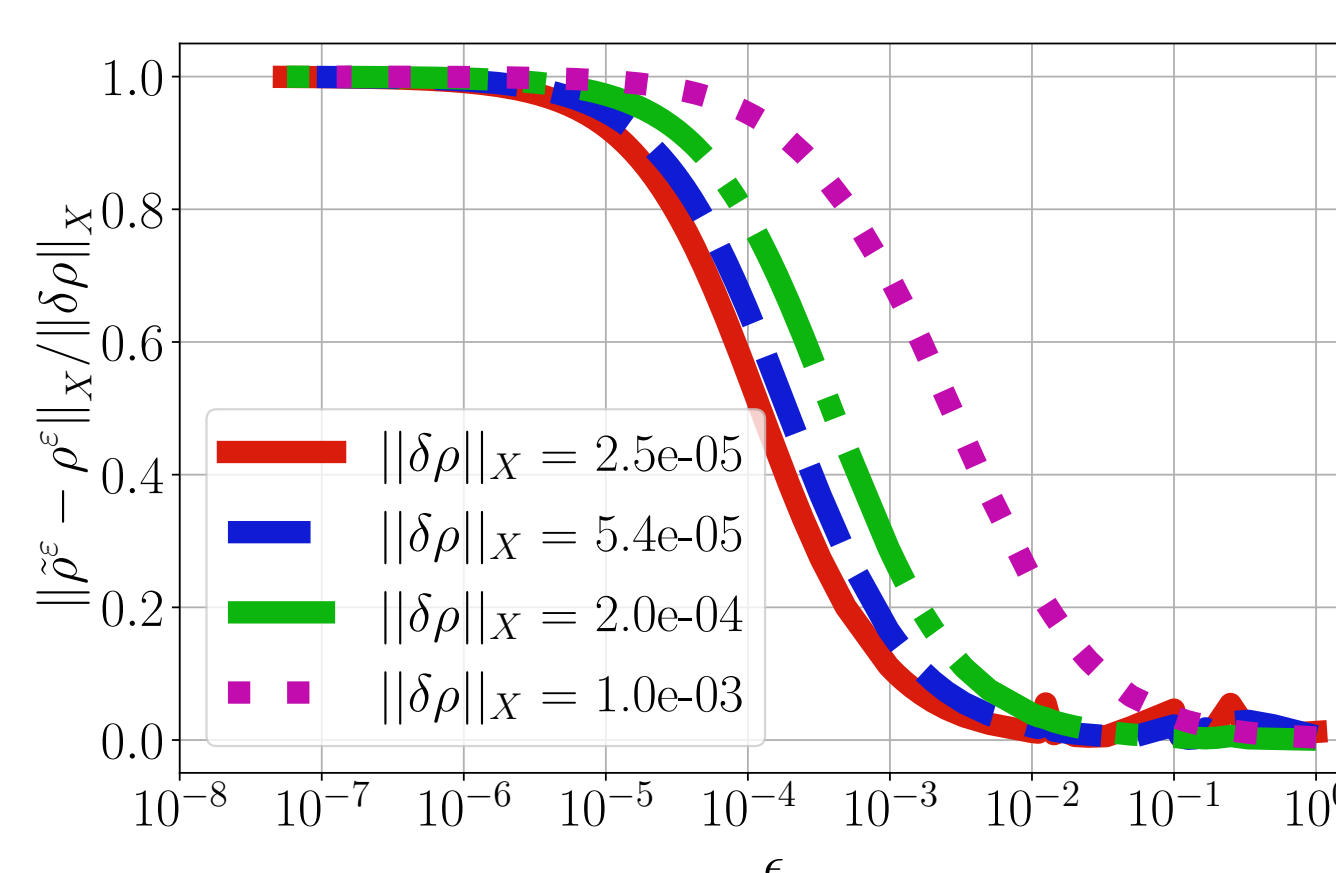
where  $\alpha, \xi \in \{0, 1\}$  and  $\sigma = 1/\varepsilon$ .

- Gives a quantitative way to monitor convergence.



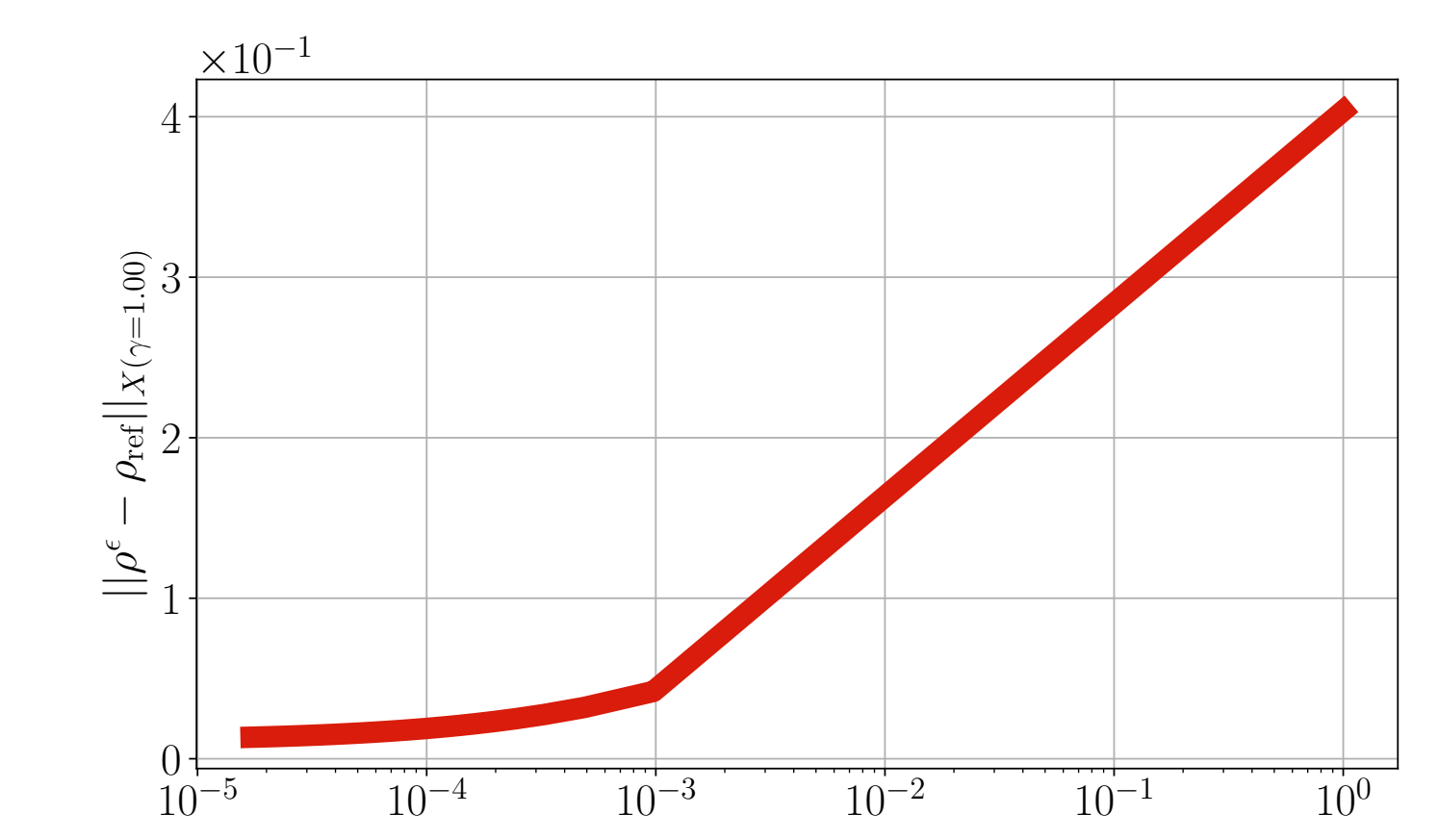
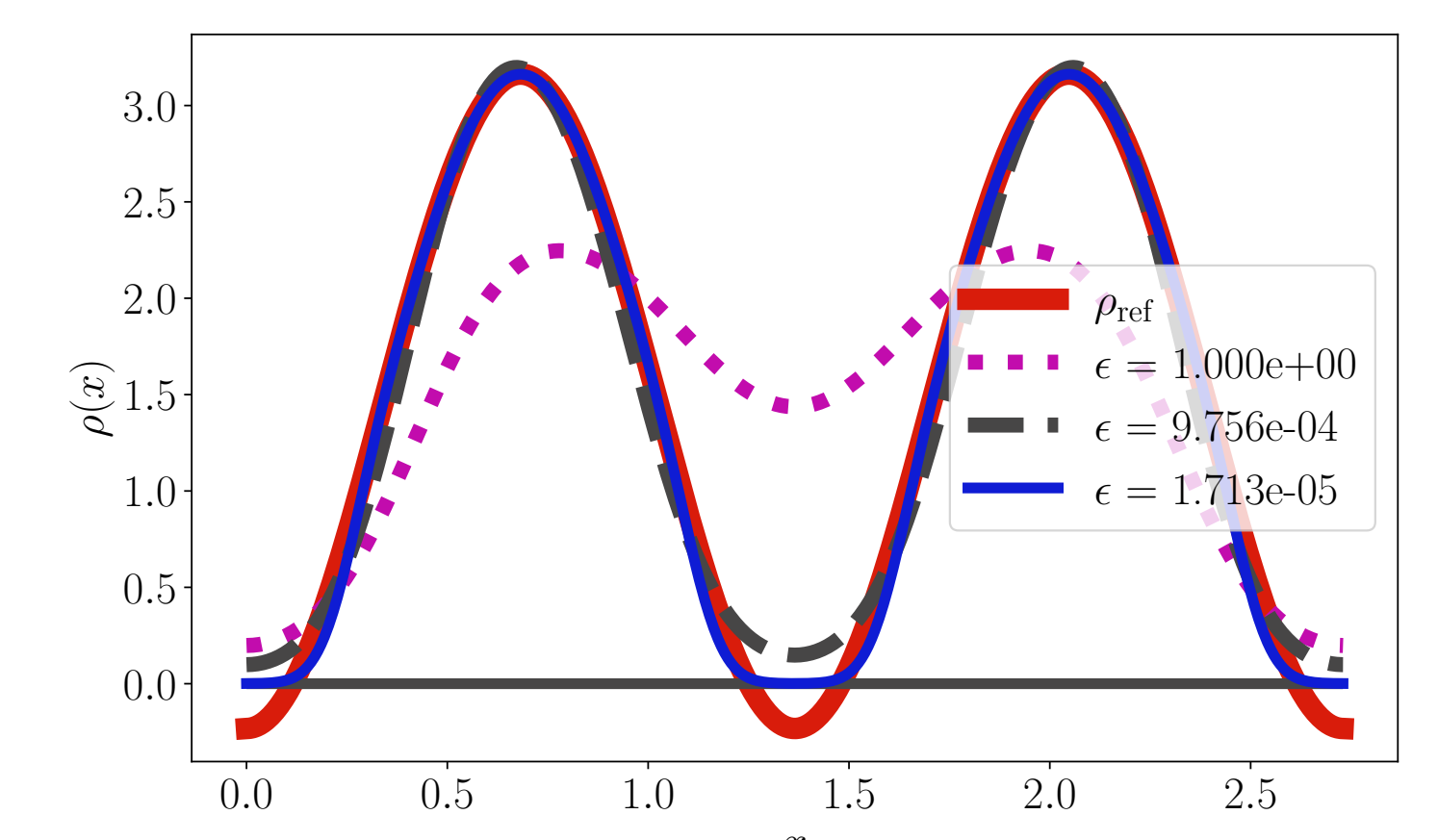
## Error Analysis

- Adding a perturbation,  $\delta\rho$ , to the reference density,  $\tilde{\rho}_{\text{ref}} = \rho_{\text{ref}} + \delta\rho$ , such that  $\delta\rho$  truncates  $\rho_{\text{ref}}$ .



## Non N-representable density

- Constructing a reference density that is not N-representable, specifically having negative regions in the unit cell.



## References

- (1) Zhao, Q. et al. *Phys. Rev. A* **1994**, 50, 2138.
- (2) Penz, M. et al. *Electron. Struct.* **2023**, 5, 014009.
- (3) Herbst, M. F. et al. *Phys. Rev. B* **2025**, 111, 205143.
- (4) Lieb, E. H. *Int. J. Quantum Chem.* **1983**, 24, 243–277.
- (5) Kvaal, S. et al. *J. Chem. Phys.* **2014**, 140, 18A518.