1D periodic Hartree–Fock as a proof-of-concept for regularised density-potential inversion

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Content

- Introduction to periodicity
- Periodic Hartree–Fock
- Moreau–Yosida regularisation
- Initial results

Spatial and periodic domains

- Spatial domain $\mathbb{R}^d, d \geq 1$.
- Periodic conditions in $p \leq d$.
- We are only going to look at the case when $p = d$.

Unit cell

- To define a unit cell, $\mathcal{C}$,
- we need a set primitive lattice vectors, $\{\boldsymbol{a}_i \mid \boldsymbol{a}_i \in \mathbb{R}^d\}$,

$$\mathcal{C} := \left\{ \sum_{i=1}^{d} \lambda_i \boldsymbol{a}_i \mid \lambda_i \in (0, 1] \right\} \tag{1}$$

- All physical quantity's repeat in the $\mathcal{C}$

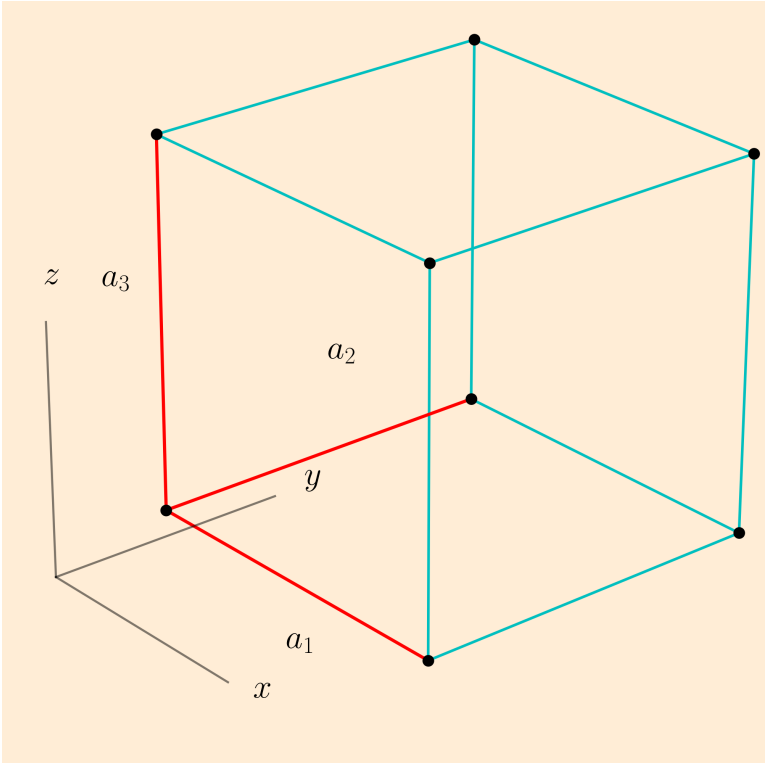


Figure 1: Unit cell

Crystal lattice

Definitions I

- The lattice vectors define a crystal lattice, of any size, by repeating the unit cell,

$$\Lambda := \left\{ \sum_{i=i}^{p} m_i \boldsymbol{a}_i \mid m_i \in \mathbb{Z} \right\} \tag{2}$$

- The Born–von Karman zone is a $N_1 \times \ldots \times N_p$ super cell

$$\Lambda_{\mathrm{BvK}} := \left\{ \sum_{i=1}^{p} N_i m_i \boldsymbol{a}_i \mid m_i \in \mathbb{Z} \right\} \subset \Lambda. \tag{3}$$

- Nonphysical quantities, such as the wave function, orbitals, repeat on the Born–von Karman lattice.

Crystal lattice

Visualise

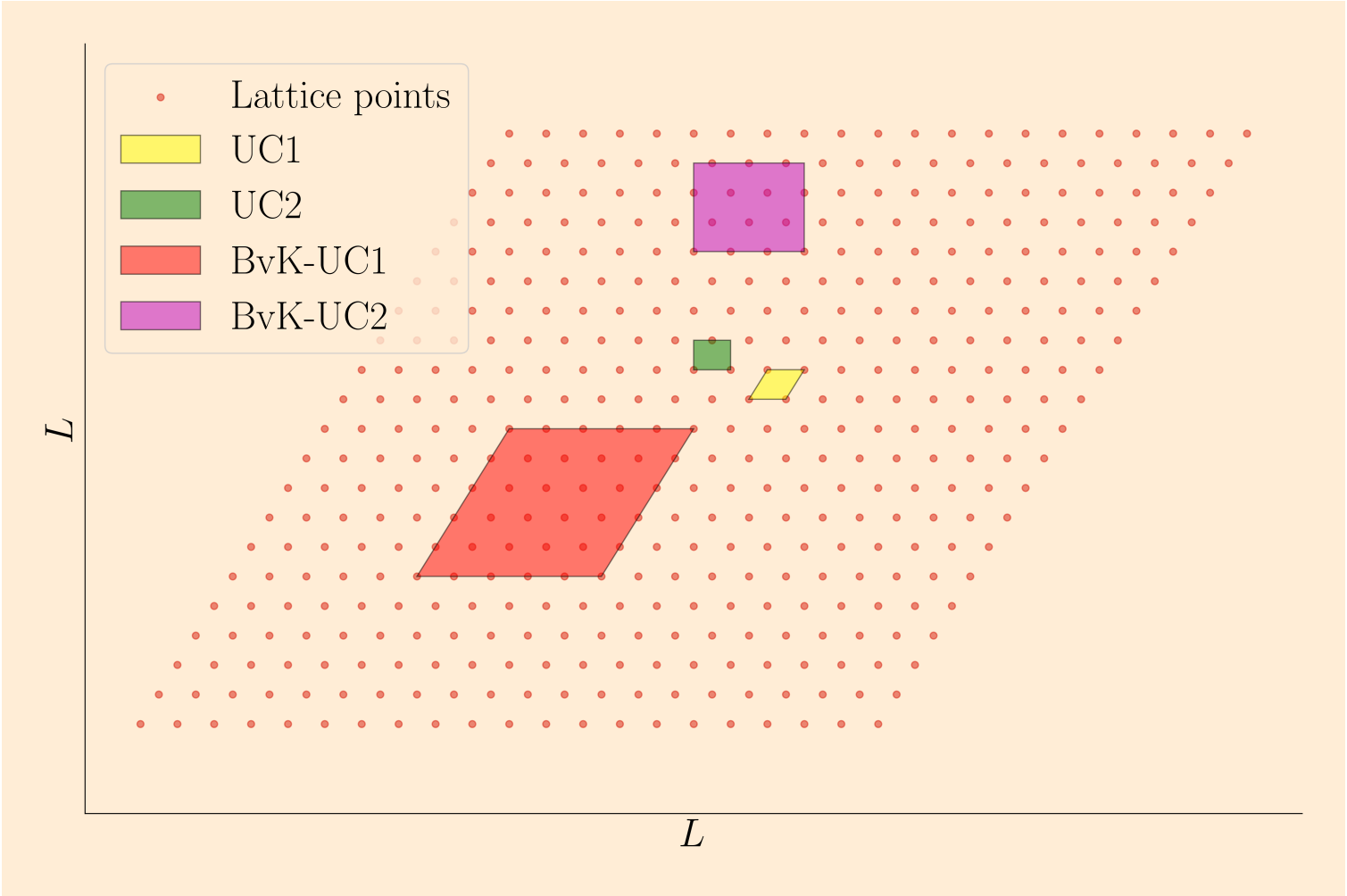


Figure 2

Reciprocal lattice

Definitions I

- Reciprocal lattice/dual lattice
- In order to define the dual lattice, we need a set of dual primitive vectors, $\{\boldsymbol{b}_i\}$.
- These must satisfy,

$$\boldsymbol{a}_i \cdot \boldsymbol{b}_j = 2\pi\delta_{i,j} \quad \text{equivalently} \quad \exp\{i\,\boldsymbol{b}_j \cdot \boldsymbol{a}_i\} = 1 \tag{4}$$

- Define the reciprocal lattice,

$$\Lambda^\star = \left\{ \sum_{i=1}^{p} m_i \boldsymbol{b}_i \mid m_i \in \mathbb{Z} \right\} \tag{5}$$

$$\Lambda^\star_{\mathrm{BvK}} = \left\{ \sum_{i=1}^{p} \frac{m_i}{N_i} \boldsymbol{b}_i \mid m_i \in \mathbb{Z} \right\} \tag{6}$$

Reciprocal lattice

Visualise

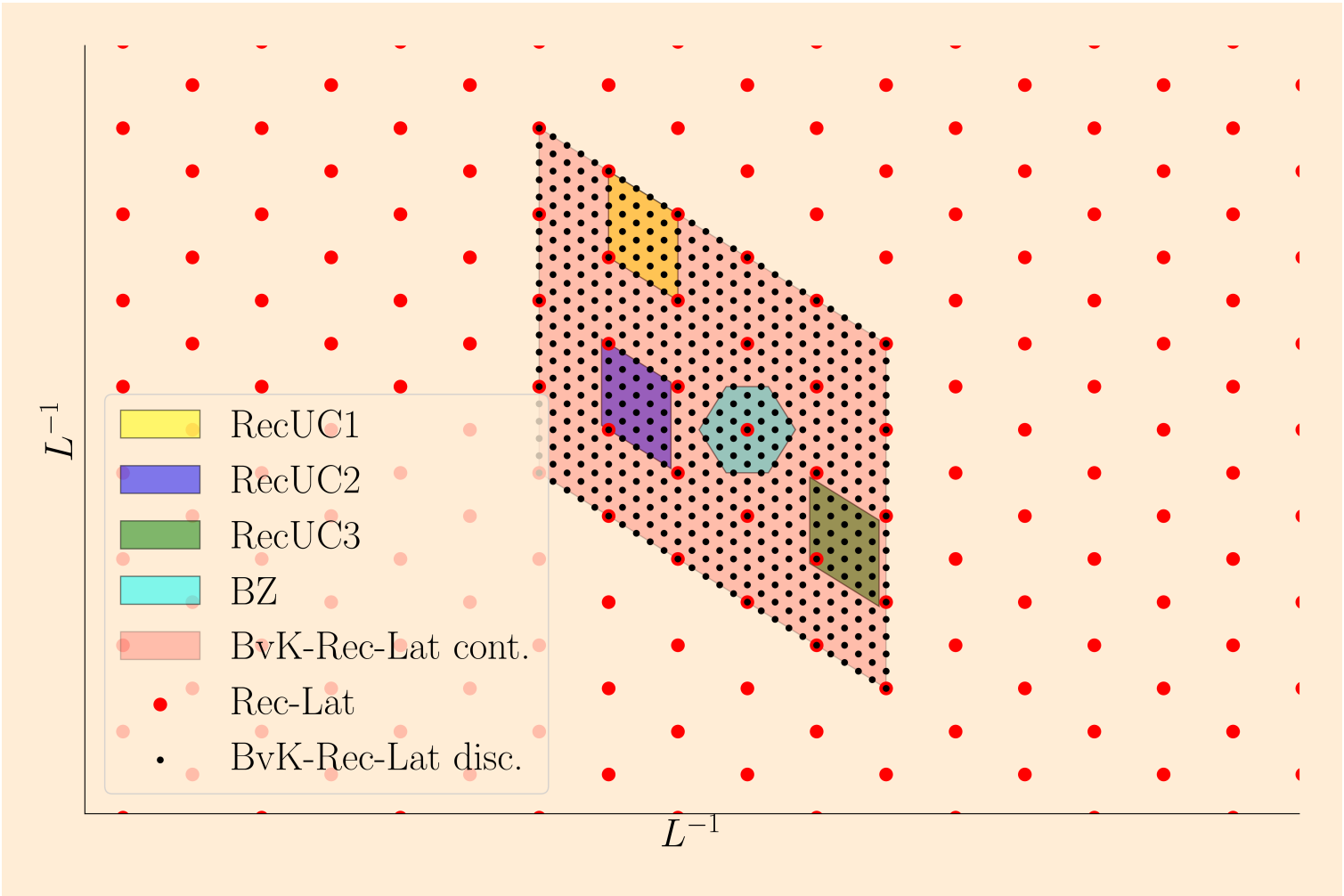


Figure 3: Visualise reciprocal space, with reciprocal unit cells and Born–von Karman

Brillouin Zone

- The 1^{st} Brillouin zone, $\mathcal{BZ}$, is defined as all points in reciprocal space that are closest to the origin than any other lattice site.

$$\mathcal{BZ} \coloneqq \{\boldsymbol{k} \in \mathbb{R}^d \;\big|\; |\boldsymbol{k}| \leq \min_{\boldsymbol{G}\in\Lambda^\star} |\boldsymbol{k}+\boldsymbol{G}|\}$$

Brillouin Zone

Visualise

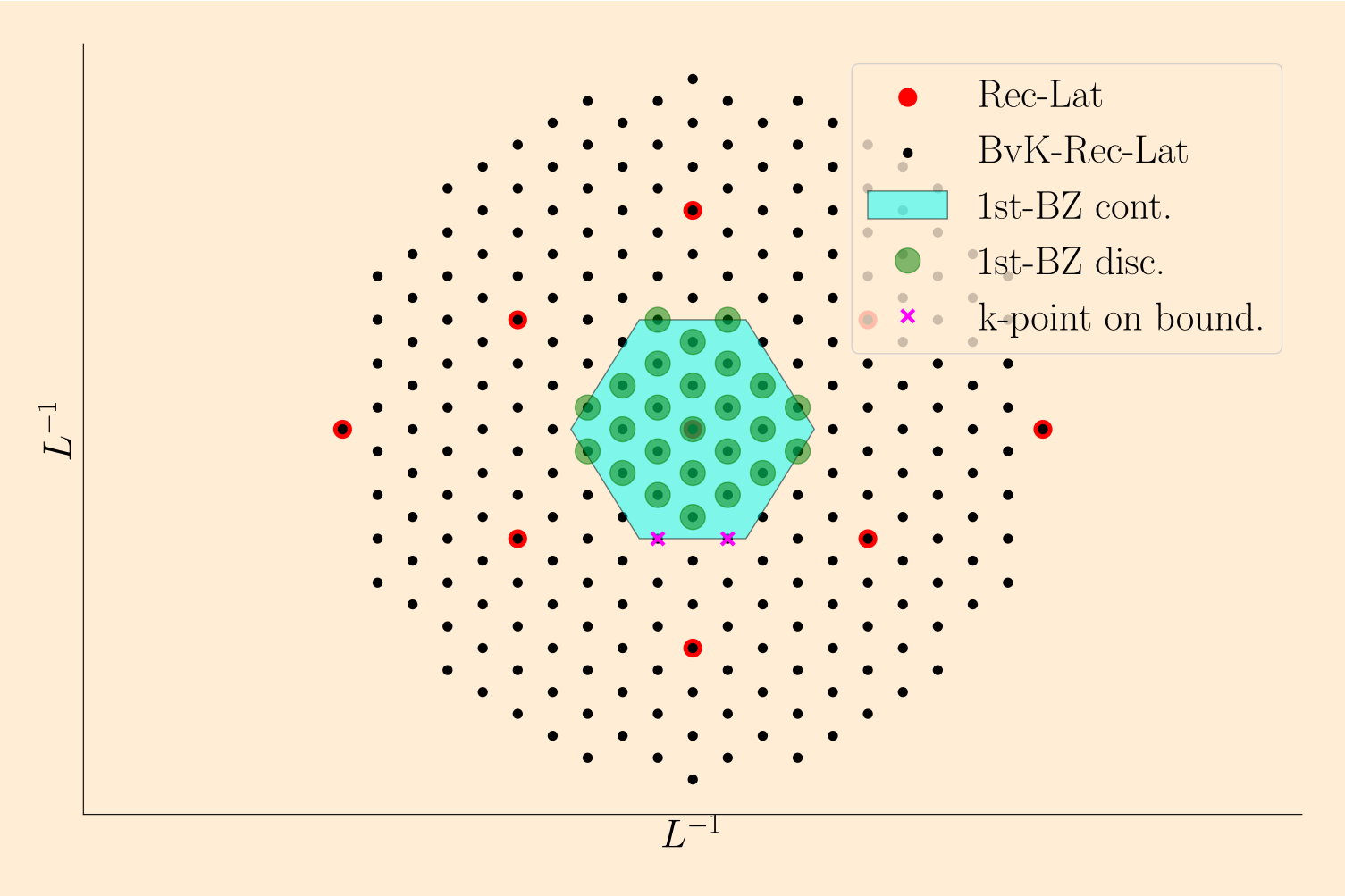


Figure 4

Periodic boundary conditions

PBC I

- We know from Blochs's theorem,
- if we put a particle in a periodic potential, $v(\boldsymbol{x}) = v(\boldsymbol{x} + \boldsymbol{a}_i)$
- we get that,

$$\psi_{\boldsymbol{k}}(\boldsymbol{x}) = e^{i\boldsymbol{k}\cdot\boldsymbol{x}} u_{\boldsymbol{k}}(\boldsymbol{x}), \qquad \boldsymbol{k} \in \mathcal{BZ} \tag{7}$$

- where $u_{\boldsymbol{k}}(\boldsymbol{x}) = u_{\boldsymbol{k}}(\boldsymbol{x} + \boldsymbol{a})$, is a periodic function.
- But, the wave function is periodic in the Born–von Karman lattice.

Periodic boundary conditions

PBC II

- So in an infinite periodic lattice, Λ, we want the wave functions to have the periodicity of the Born–von Karman lattice,

$$\psi(\boldsymbol{x} + N_i \boldsymbol{a}_i) = \psi(\boldsymbol{x}) \tag{8}$$

$$\exp\{iN_i \boldsymbol{k} \cdot \boldsymbol{a}_i\} = 1, \tag{9}$$

hence,

$$\boldsymbol{k} = \sum_i \frac{m_i}{N_i} \boldsymbol{b}_i, \ m_i, N_i \in \mathbb{Z}. \tag{10}$$

Born–von Karman boundary conditions

How many states in the $\mathcal{BZ}$

- We see that the more unit cell we have in the super cell, the more states we have.

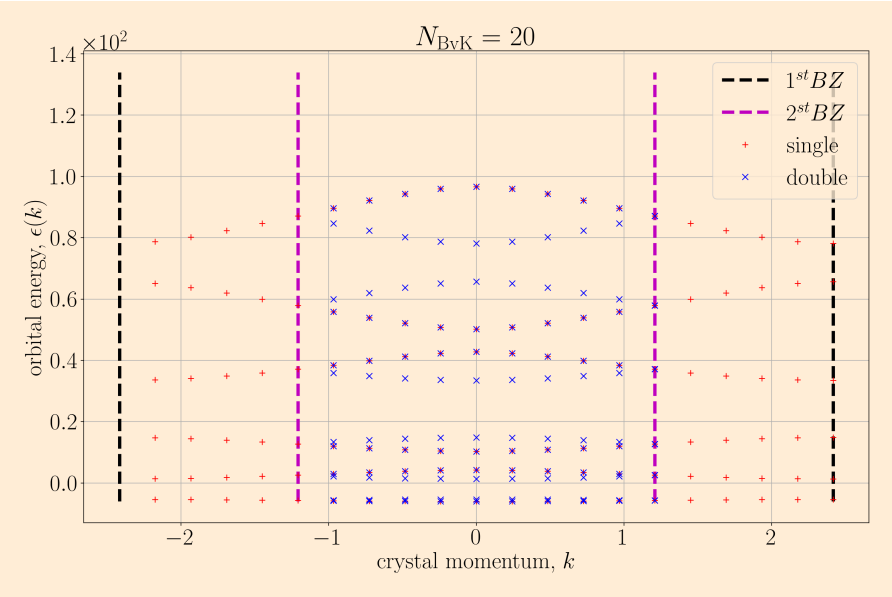


Figure 5

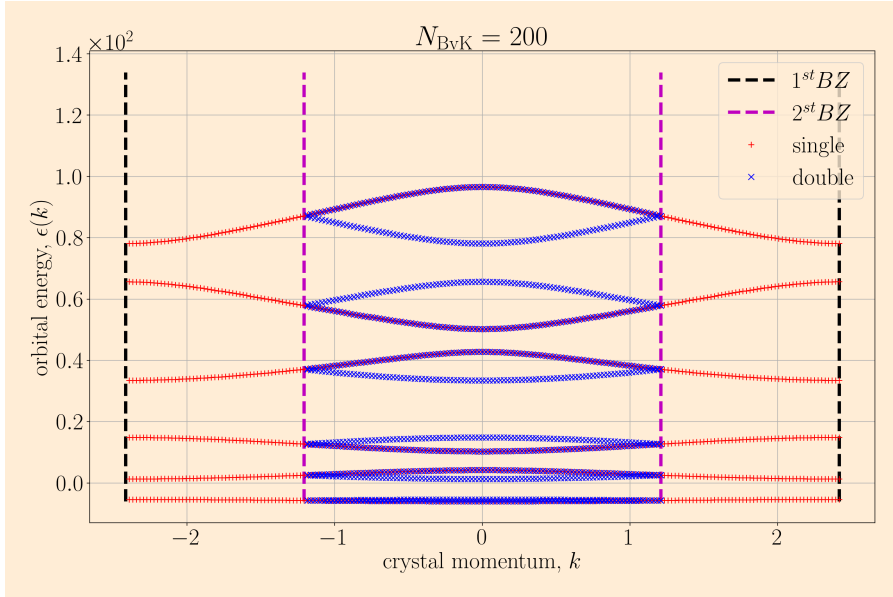


Figure 6

Density potential inversion

Background I

- Standard electronic structure problems deal with finding the ground-state density(wave-function) from an external potential, **Forward problem**.

- What we are interested in is the **Reverse problem**, given a ground-state density, what is the potential.

- In DFT we can see this using Liebs formulation of DFT[1],

$$E(v) = \inf_{\rho \in X} \underbrace{\left\{ F_L^\lambda(\rho) + \langle \rho, v \rangle \right\}}_{\text{Convex}}, \quad F_L^\lambda(\rho) = \sup_{v \in X^\star} \underbrace{\left\{ E(v) - \langle v, \rho \rangle \right\}}_{\text{Concave}}$$

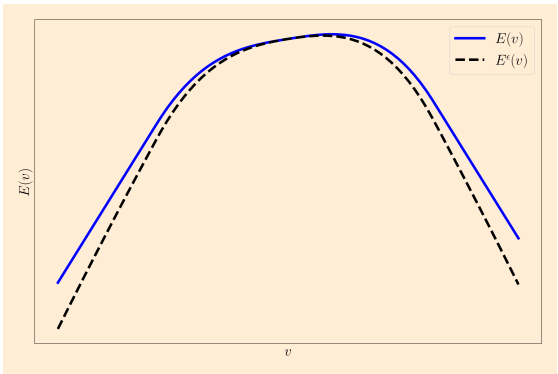
[1] Lieb, E. H. *International Journal of Quantum Chemistry* **1983**, *24*, 243–277.

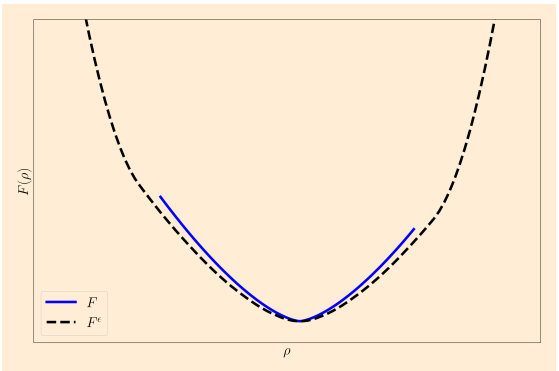
Moreau–Yosida regularisation

- Moreau–Yosida regularisation (MY) smothens out the functional[2] [3]

$$E^{\varepsilon}(v) = E(v) - \frac{1}{2}\varepsilon\|v\|^2 \tag{11}$$

$$F^{\varepsilon}(\sigma) = \inf_{\rho}\left(F(\rho) + \frac{1}{2\varepsilon}\|\rho - \sigma\|^2\right) \tag{12}$$





[2] Penz, M. et al. *Electron. Struct.* **2023**, *5*, 014009.

[3] Kvaal, S. et al. *The Journal of Chemical Physics* **2014**, *140*, 18A518.

Hartree–Fock

Slater Determinant

- Everything is represented as plane waves basis; orbitals, densitys and potentials.
- Orbitals that build up the Slater Determinant Φ, are periodic in the super cell,

$$\phi_{\boldsymbol{k},m}(\boldsymbol{x}) = e^{i\boldsymbol{k}\cdot\boldsymbol{x}} \sum_{\boldsymbol{G}\in\Lambda^\star} C_{\boldsymbol{G},m}(\boldsymbol{k}) e^{i\boldsymbol{G}\cdot\boldsymbol{x}}, \tag{13}$$

- where, $\boldsymbol{k} \in \Lambda^\star_{\mathrm{BvK}}$ and m is a band index
- where as densities and potentials are periodic in the unit cell

$$\rho(\boldsymbol{x}) = \sum_{\boldsymbol{G}\in\Lambda^\star} \hat{\rho}_{\boldsymbol{G}} e^{i\boldsymbol{G}\cdot\boldsymbol{x}} \qquad v(\boldsymbol{x}) = \sum_{\boldsymbol{G}\in\Lambda^\star} \hat{v}_{\boldsymbol{G}} e^{i\boldsymbol{G}\cdot\boldsymbol{x}}, \tag{14}$$

Density matrix

- Density matrix for a given $\boldsymbol{k} \in \Lambda^{\star}_{\mathrm{BvK}'}$

$$\mathcal{D}_{\boldsymbol{G},\boldsymbol{G}'}(\boldsymbol{k}) = \sum_m C_{\boldsymbol{G},m}(\boldsymbol{k}) C_{\boldsymbol{G}',m}(\boldsymbol{k})^* \tag{15}$$

- Block diagonal in $\boldsymbol{k}$,

$$\mathcal{D} = \begin{pmatrix} \mathcal{D}(\boldsymbol{k}_1) & \mathbf{0} & \dots & \mathbf{0} \\ \mathbf{0} & \mathcal{D}(\boldsymbol{k}_2) & \dots & \mathbf{0} \\ \vdots & \vdots & \ddots & \vdots \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathcal{D}(\boldsymbol{k}_{N_1 N_2 N_3}) \end{pmatrix}. \tag{16}$$

Hartree–Fock

Moreau–Yosida regularisation

- For a Hartree–Fock calculation we have,

$$\mathcal{E}'(\mathcal{D}) = \mathrm{tr}(\mathcal{D}h) + \lambda_{\mathrm{H}} J_{\mathrm{H}}(\rho_{\mathcal{D}}, \rho_{\mathcal{D}}) - \lambda_{\mathrm{X}} K(\mathcal{D}) \tag{17}$$

- Adding in MY,

$$\mathcal{E}(\mathcal{D}) = \mathrm{tr}(\mathcal{D}h) + \lambda_{\mathrm{H}} J_{\mathrm{H}}(\rho_{\mathcal{D}}, \rho_{\mathcal{D}}) - \lambda_{\mathrm{X}} K(\mathcal{D}) + \frac{1}{2\varepsilon} \|\rho_{\mathcal{D}} - \rho_{\mathrm{ref}}\|_{\mathrm{X}}^2 \tag{18}$$

$$v_{\mathrm{eff}} = \lim_{\varepsilon \to 0+} \frac{1}{2\varepsilon} (\rho^{\varepsilon} - \rho_{\mathrm{ref}}) \tag{19}$$

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[4] Herbst, M. F. et al. Kohn-Sham inversion with mathematical guarantees, 2024.

[5] Zhao, Q. et al. *Phys. Rev. A* **1994**, *50*, 2138.

Implementation in 1d

- Our code is a periodic HF code.
- the two electron interaction operator used the Yukawa interaction

$$w(x, x') = e^{-\gamma|x-x'|}, \gamma > 0 \tag{20}$$

Preliminary results

External potential

- In the next two example systems the external potential is represented as a well centered in the middle of unit cell

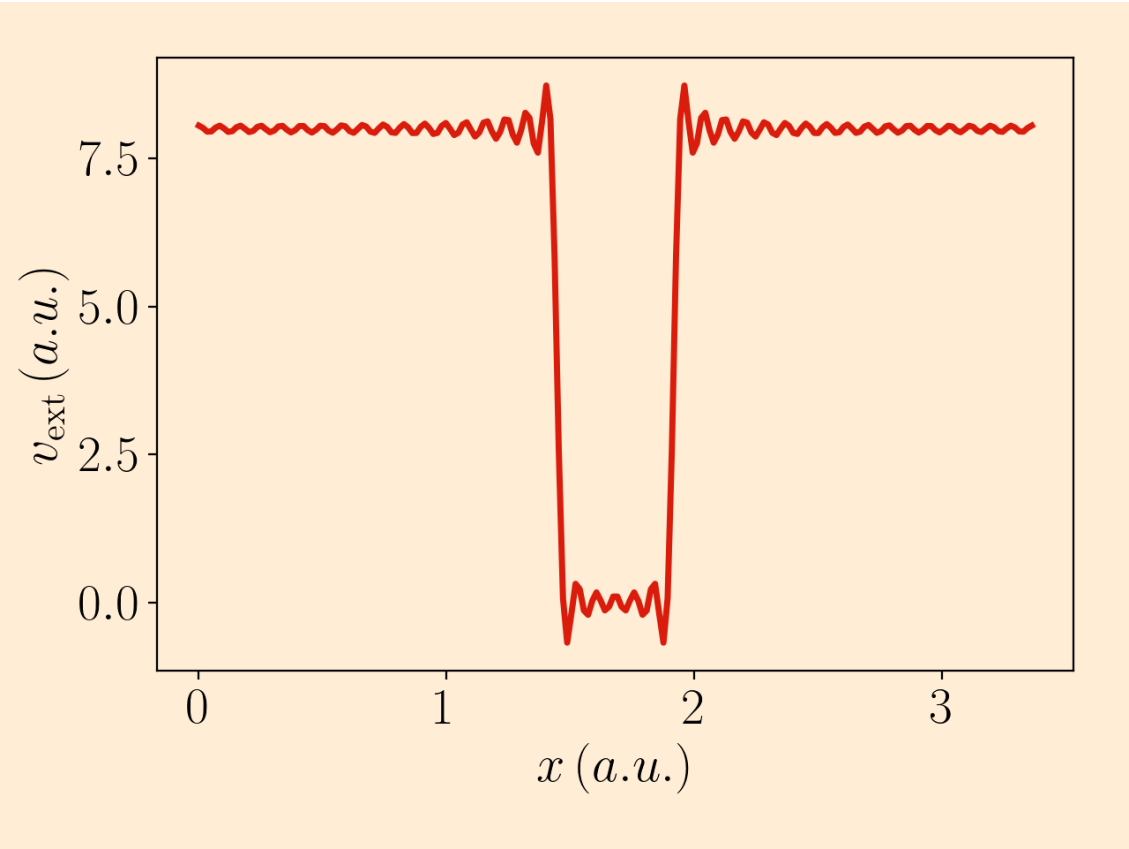

Figure 7: External potential

Preliminary results

System I

- Rerfrence density, ρ_{ref}, is generated from a HF calculation
- Turn off Exchange, λ_{X},
- From first expection this looks rather good!

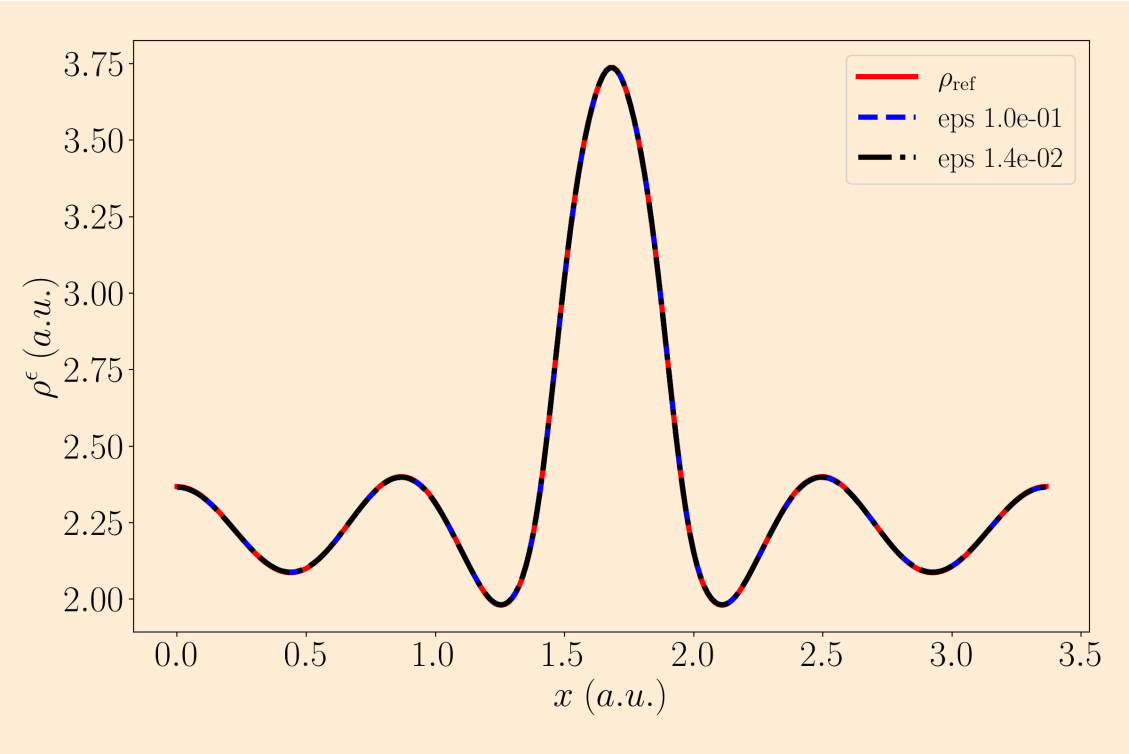

Figure 8: Density

Preliminary results

System I

- When looking at the error difference and error norm, we are $\approx 10^{-3}$ off,

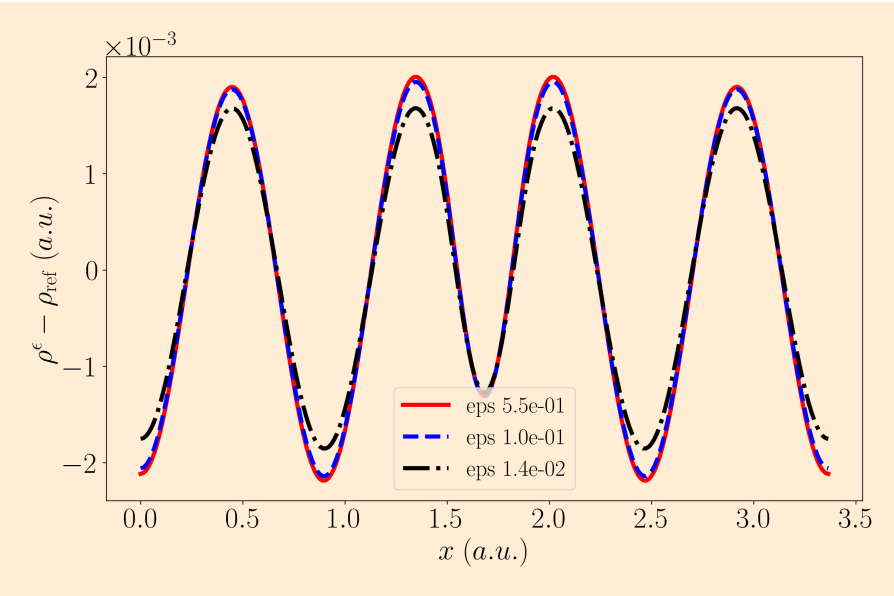

Figure 9: Proximal point error

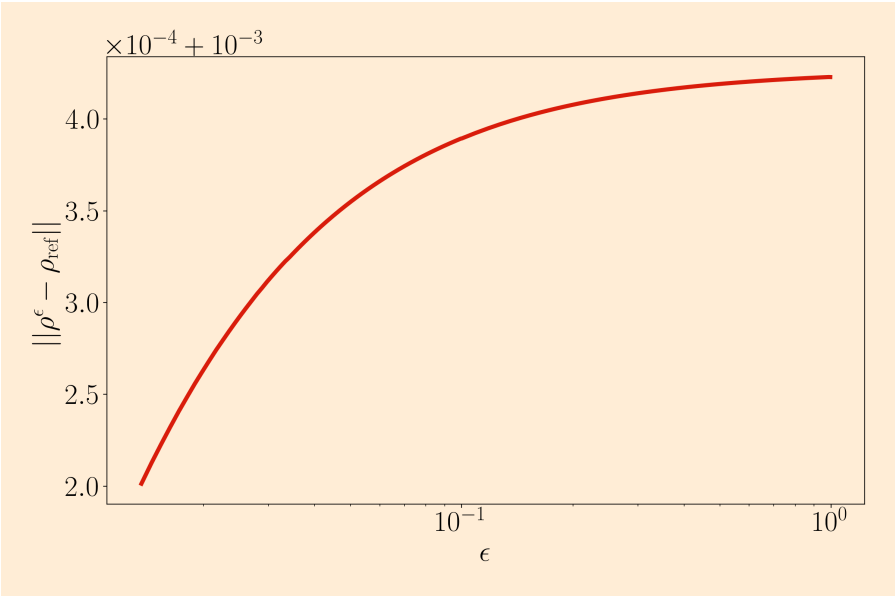

Figure 10: Epsilon sequence norm error

Preliminary results

System II

- Refrence density, ρ_{ref}, from non-interacting system.
- Turn off v_{ext},

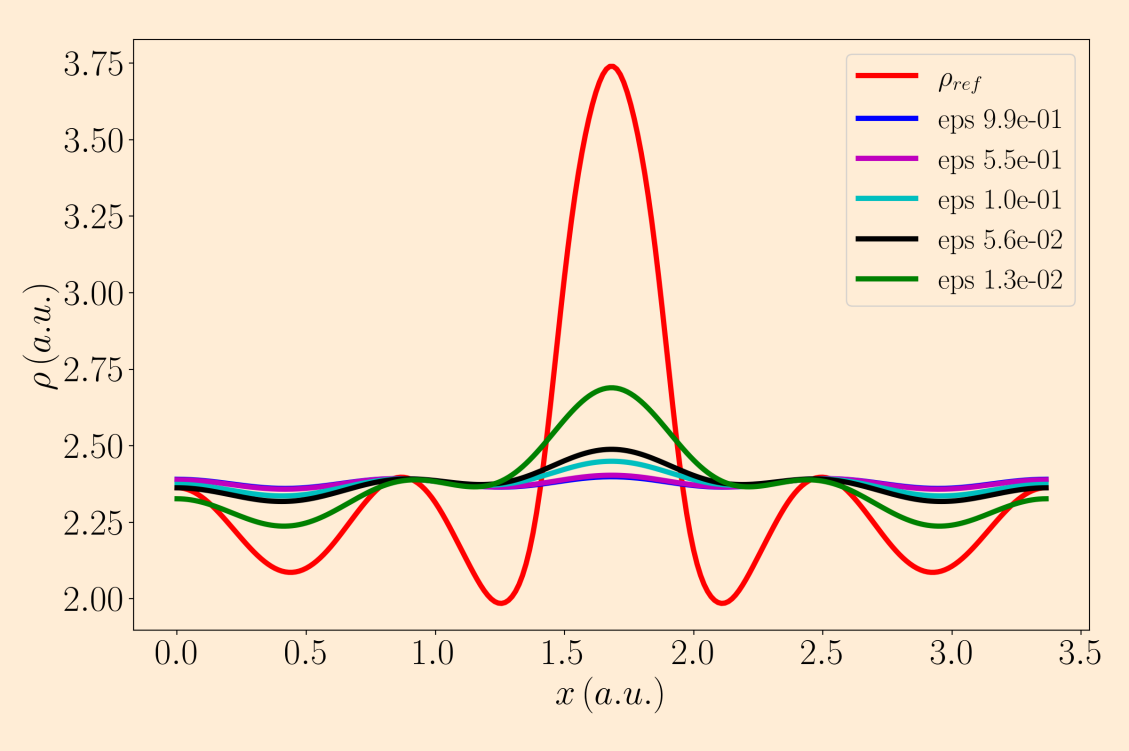

Figure 11: Density

Results

System II

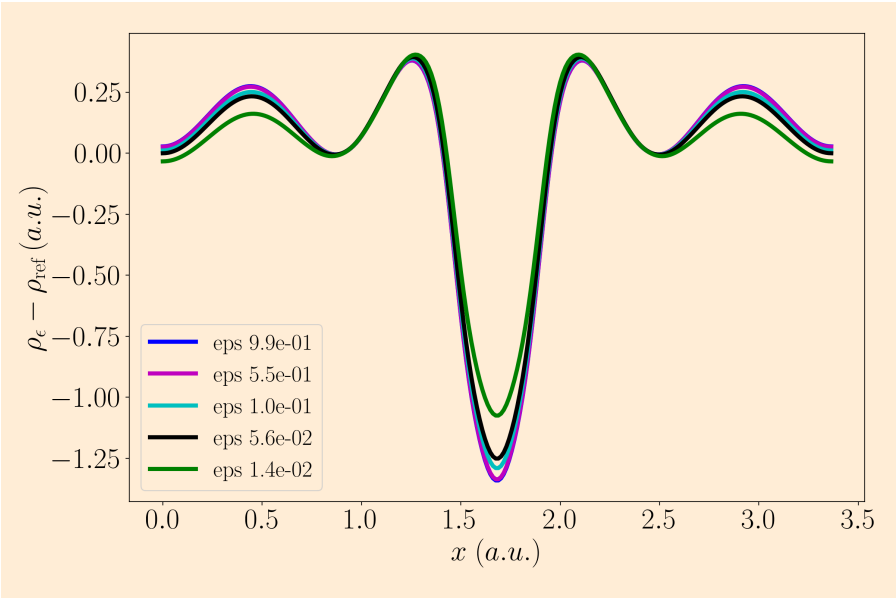

Figure 12: Proximal point error

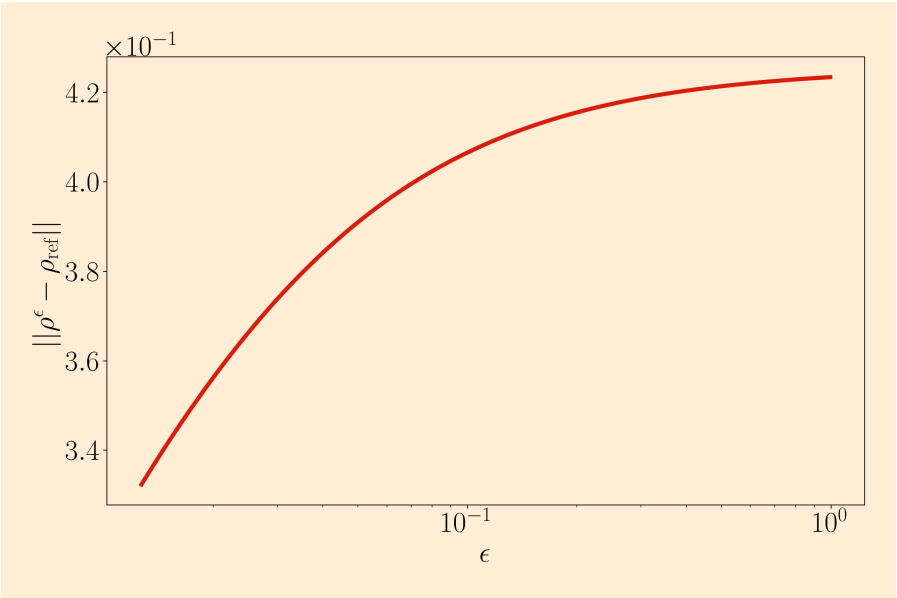

Figure 13: Epsilon sequence norm error

Future development

- Need to improve the SCF procedure
- Adding temperature to help convergence (pseudo regularisation)
- Go to post HF methods to see if we can effective potential for missing correlation

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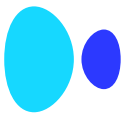

Hylleraas

CompSci

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