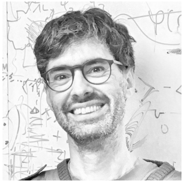
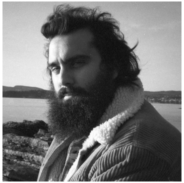
Mathematical and Theoretical Aspects of Density-Functional Theory

Vebjørn H. Bakkestuen
OSLO METROPOLITAN UNIVERSITY
STORBYUNIVERSITETET

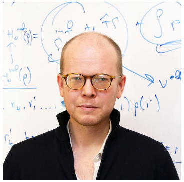
Acknowledgements

M. Herbst, M. Penz, M. Ruggenthaler, M. Csirik,
M. Lotfigolian, O. Bohle, V. Falmår, and A. Laestadius







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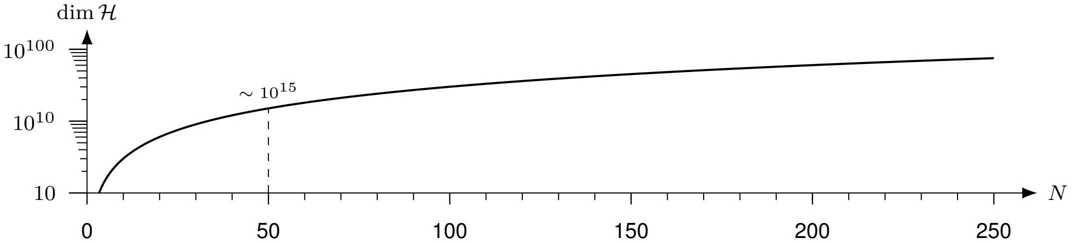
Outline

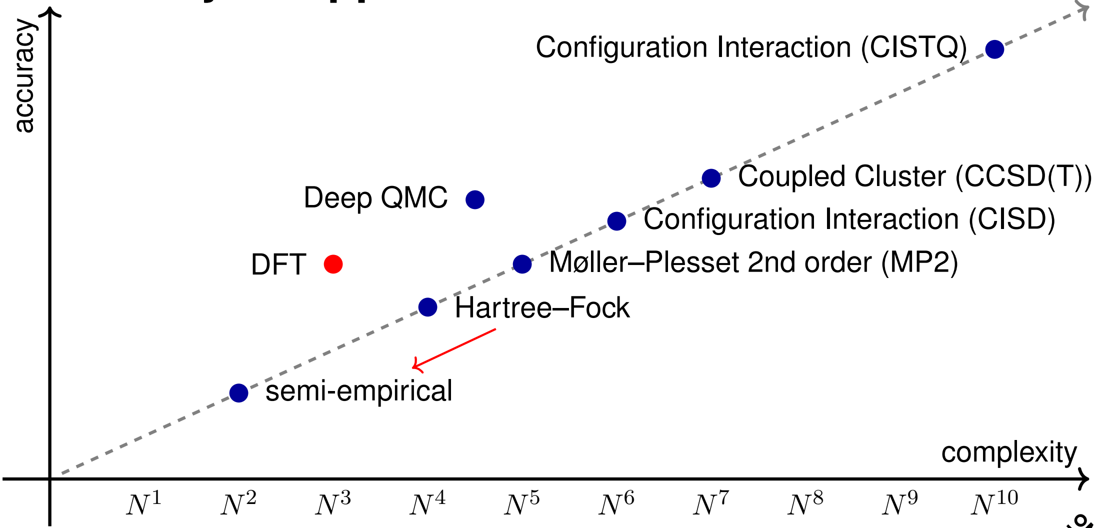
Electronic Structure Theory

$$\widehat{H} = -\frac{1}{2}\sum_{j=1}^{N} \nabla_{\mathbf{r}_j} + \sum_{j=1}^{N}\sum_{k>j}^{N} w(\mathbf{r}_j - \mathbf{r}_k) + \sum_{j=1}^{N} v(\mathbf{r}_j)$$

$$\widehat{H}\,|\psi\rangle = E\,|\psi\rangle\,, \qquad |\psi\rangle \in \mathcal{H} = \bigwedge_{n=1}^{N} \mathcal{H}_1$$



Hierarchy of Approximations



Adopted from https://github.com/janosh/diagrams

Density-Functional Theory

$$\widehat{H}^{\lambda}(v) = \widehat{T} + \lambda \widehat{W} + \widehat{V} = \widehat{H}_0^{\lambda} + \widehat{V}$$

$$E^{\lambda}(v) = \inf_{|\psi\rangle \in \mathcal{W}_N} \langle \psi | \widehat{H}^{\lambda}(v) | \psi \rangle = \inf_{|\psi\rangle \in \mathcal{W}_N} \left\{ \langle \psi | \widehat{H}_0^{\lambda} | \psi \rangle + \langle \psi | \widehat{V} | \psi \rangle \right\}$$

$$|\psi\rangle \longmapsto \rho \quad \Longrightarrow \quad \rho(\mathbf{r}) = N \int |\psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 \,\mathrm{d}\mathbf{r}_2 \dots \mathrm{d}\mathbf{r}_N$$

$$\begin{aligned} E^{\lambda}(v) &= \inf_{\rho} \left\{ \inf_{|\psi\rangle \mapsto \rho} \langle \psi | \widehat{H}_0^{\lambda} | \psi \rangle + \langle v, \rho \rangle \right\}, \\ &= \inf_{\rho} \left\{ F_{\mathrm{LL}}^{\lambda}(\rho) + \langle v, \rho \rangle \right\} \end{aligned} \qquad \langle v, \rho \rangle = \int v(\mathbf{r}) \rho(\mathbf{r}) \,\mathrm{d}\mathbf{r}$$

Universal Density Functionals

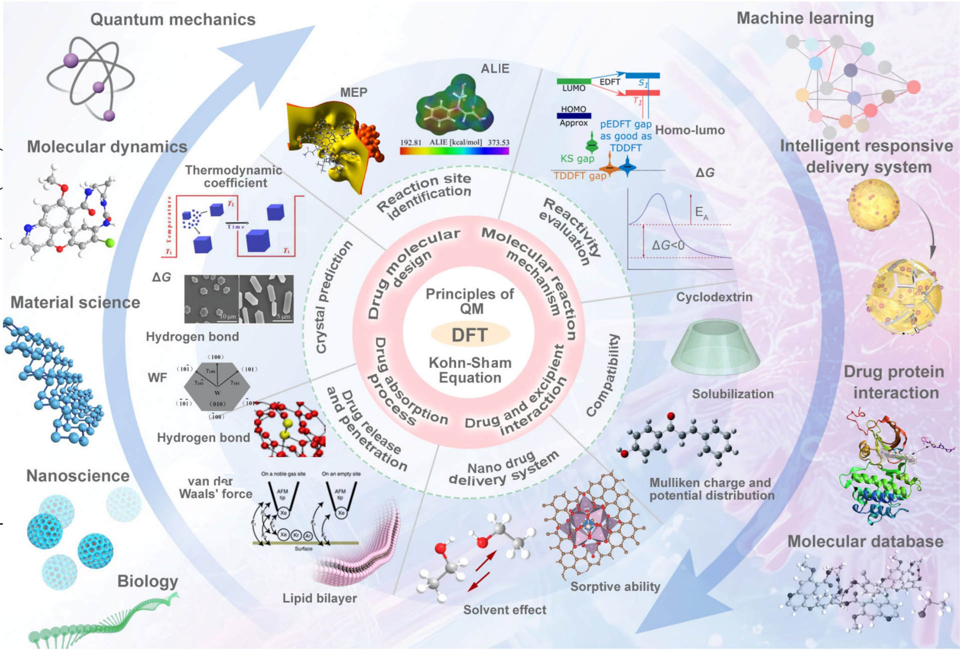
Space of densities X, potentials X^*

$$F^{\lambda}_{\mathrm{LL}}(\rho) = \inf_{|\psi\rangle \mapsto \rho} \langle \psi | \widehat{H}^{\lambda}_0 | \psi \rangle \qquad F^{\lambda}_{\mathrm{DM}}(\rho) = \inf_{\Gamma \mapsto \rho} \mathrm{Tr}\left[\widehat{H}^{\lambda}_0 \Gamma\right]$$

$$F^{\lambda}(\rho) = \sup_{v \in X^*} \left\{ E^{\lambda}(v) - \langle v, \rho \rangle \right\}$$

$$E^{\lambda}(v) = \inf_{\rho \in X} \left\{ F^{\lambda}(\rho) + \langle v, \rho \rangle \right\} = \inf_{\rho \in X} \left\{ F^{\lambda}_{\mathrm{DM}}(\rho) + \langle v, \rho \rangle \right\} = \inf_{\rho \in X} \left\{ F^{\lambda}_{\mathrm{LL}}(\rho) + \langle v, \rho \rangle \right\}$$

$$F^{\lambda}(\rho) \leq F^{\lambda}_{\mathrm{DM}}(\rho) \leq F^{\lambda}_{\mathrm{LL}}(\rho), \quad \forall \rho \in X$$



Adapted from Guan *et al.* *Int. J. Mol. Sci.* **26**, 3262 (2025).

Quantum Electrodynamical DFT

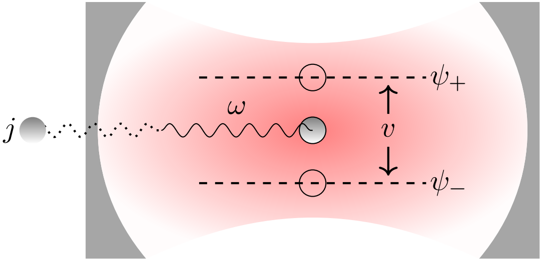
A Quantum Electrodynamical DFT

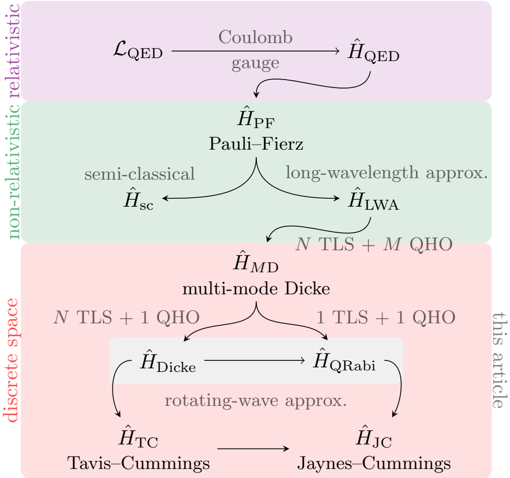
$$\widehat{H}_0^\lambda = \frac{1}{2}\widehat{p}^2 + \frac{\omega^2}{2}\widehat{q}^2 + \lambda g \widehat{\sigma}_z \widehat{q} - t\widehat{\sigma}_x$$

$$\widehat{H}^\lambda(v, j) = \widehat{H}_0^\lambda + v\widehat{\sigma}_z + j\widehat{q}$$

$$\sigma := \langle \psi | \widehat{\sigma}_z | \psi \rangle \in [-1, 1]$$

$$\xi := \langle \psi | \widehat{q} | \psi \rangle \in \mathbb{R}$$





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A Hohenberg–Kohn Theorem

Theorem (Hohenberg–Kohn)

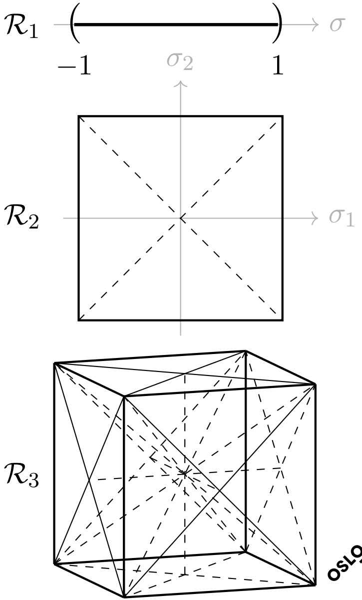
The density ρ uniquely determines the potential v, up to an additive constant.

Theorem (Strong HK)

Any $(\boldsymbol{\sigma}, \boldsymbol{\xi}) \in \mathcal{R}_N \times \mathbb{R}^M$ that is the density pair of a ground state uniquely determines an external pair $(\mathbf{v}, \mathbf{j}) \in \mathbb{R}^{N+M}$. That is, the mapping

$$\mathbb{R}^N \times \mathbb{R}^M \ni (\mathbf{v}, \mathbf{j}) \longmapsto (\boldsymbol{\sigma}, \boldsymbol{\xi}) \in \mathcal{R}_N \times \mathbb{R}^M$$

is an injection.



Bakkestuen *et al. J. Stat. Phys.* **192**, 61 (2025)
Hohenberg and Kohn, *Phys. Rev.* **136**, B864 (1964).

The Constrained-Search Functional

$$E^\lambda(v,j) = \inf_{|\psi\rangle \in Q_0} \langle\psi|\widehat{H}^\lambda(v,j)|\psi\rangle = \inf_{(\sigma,\xi)\in[-1,1]\times\mathbb{R}} \left[F^\lambda_{\mathrm{LL}}(\sigma,\xi) + v\sigma + j\xi\right]$$

$$F^\lambda_{\mathrm{LL}}(\sigma,\xi) = \inf_{|\psi\rangle\in\mathcal{M}_{\sigma,\xi}} \langle\psi|\widehat{H}^\lambda_0|\psi\rangle$$

Theorem

For every density pair $(\sigma,\xi)\in(-1,1)\times\mathbb{R}$ there exists a unique real-valued and strictly positive optimiser $|\psi\rangle\in\mathcal{M}_{\sigma,\xi}$ of $F_{\mathrm{LL}}(\sigma,\xi)$ that is the (non-degenerate) ground-state solution of $\widehat{H}^\lambda(v,j)\,|\psi\rangle = E^\lambda(v,j)\,|\psi\rangle$

unique pure-state v-representability for $(\sigma,\xi)\in(-1,1)\times\mathbb{R}$

$$F^\lambda_{\mathrm{LL}}(\sigma,\xi) = F^\lambda_{\mathrm{DM}}(\sigma,\xi) = F^\lambda(\sigma,\xi) \qquad \forall(\sigma,\xi)\in(-1,1)\times\mathbb{R}$$

The Adiabatic Connection Functional

$$g\,\langle\psi^\lambda|\widehat{\sigma}_z\widehat{q}|\psi^\lambda\rangle \in \overline{\partial}_\lambda F^\lambda(\sigma,\xi)$$

$$\begin{aligned}F^\lambda(\sigma,\xi) &= F^0(\sigma,\xi) + \int_0^\lambda g\,\langle\psi^\mu|\widehat{\sigma}_z\widehat{q}|\psi^\mu\rangle\,\mathrm{d}\mu \\ &= \frac{\omega}{2} - t\sqrt{1-\sigma^2} + \frac{\omega^2}{2}\xi^2 + \underbrace{\lambda g\sigma\xi}_{\lambda D(\sigma,\xi)} - \frac{\lambda^2 g^2}{2\omega^2}(1-\sigma^2) - \frac{4t}{\omega^2}\int_0^\lambda\int_{\mathbb{R}} {\varphi_+^\mu}'\varphi_-^\mu\,\mathrm{d}q\,\mathrm{d}\mu\end{aligned}$$

$\varphi_\pm^\lambda(q)$ the optimisers of $F^\lambda(\sigma,0)$ $\qquad D(\sigma,\xi) \sim E_{\mathrm{H}}(\rho)$

Standard DFT:

$$F^\lambda(\rho) = T(\rho) + \lambda E_{\mathrm{H}}(\rho) + \int_0^\lambda \Big(\mathrm{Tr}\Big[\widehat{W}\Gamma^\mu\Big] - E_{\mathrm{H}}(\rho)\Big)\,\mathrm{d}\mu$$

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Kohn–Sham Inversion

The Inverse Kohn–Sham Problem

Interacting electrons

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

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 inverse problem: Given a $\rho_{\text{gs}}(\mathbf{r})$, what is $v_{\text{xc}}(\mathbf{r})$?

Ingredients

The *duality mapping* $J : X \to X^*$

The guiding functional $\mathcal{F}(\rho) = T(\rho) + E_{\mathrm{H}}(\rho) + \int v_{\mathrm{ext}}(\mathbf{r})\rho(\mathbf{r})\,\mathrm{d}\mathbf{r}$

Minimise $\mathcal{E}(\rho;\rho_{\mathrm{gs}}) = \mathcal{F}(\rho) + \frac{1}{2\varepsilon}\|\rho - \rho_{\mathrm{gs}}\|_X^2$

$$\rho^\varepsilon(\mathbf{r}) = \operatorname*{prox}_{\varepsilon\mathcal{F}}(\rho_{\mathrm{gs}})(\mathbf{r}) \qquad v_{\mathrm{xc}}^\varepsilon(\mathbf{r}) = \frac{1}{\varepsilon}J(\rho^\varepsilon - \rho_{\mathrm{gs}})(\mathbf{r})$$

$$v_{\mathrm{xc}}(\mathbf{r}) = \lim_{\varepsilon\to 0^+} v_{\mathrm{xc}}^\varepsilon(\mathbf{r}) = \lim_{\varepsilon\to 0^+}\frac{1}{\varepsilon}J(\rho^\varepsilon - \rho_{\mathrm{gs}})(\mathbf{r})$$

Penz *et al.* *Electron. Struct.* **5**, 014009 (2023)
Herbst, Bakkestuen, Laestadius *Phys. Rev. B* **111**, 205143 (2025)
Bakkestuen *et al.* In preparation (2026)

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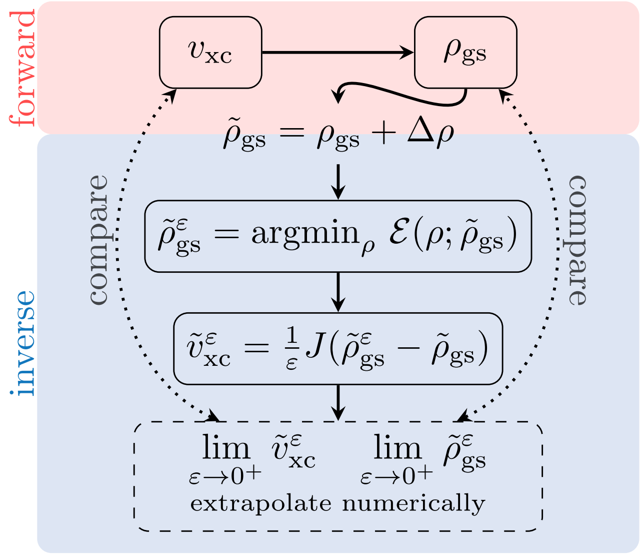
The Inversion Algorithm



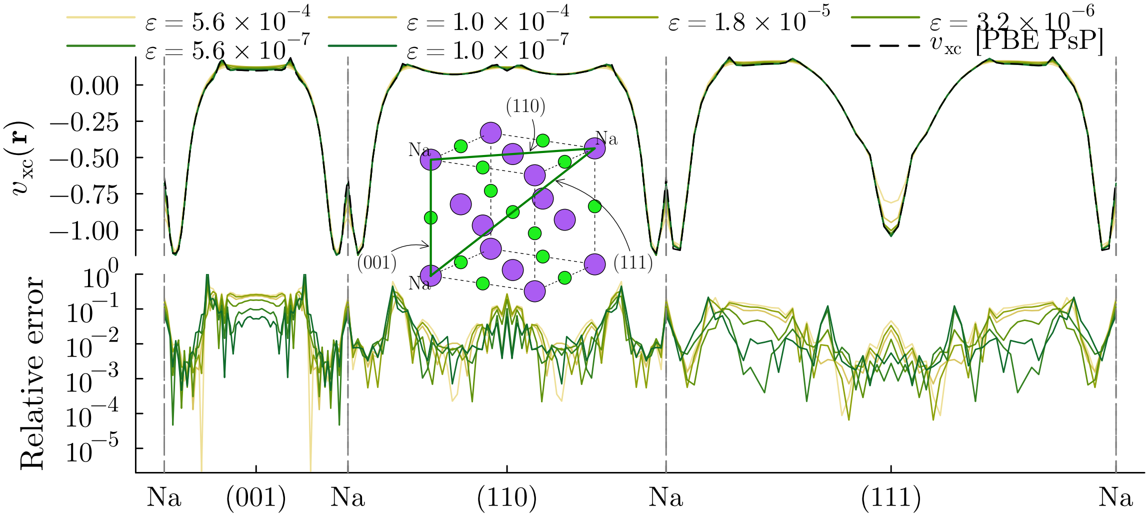
Planewave KS-DFT:

$$\Phi = (\varphi_1, \ldots, \varphi_N)$$

Minimise $\quad \mathcal{E}(\Phi;\, \rho_{\text{gs}})$

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

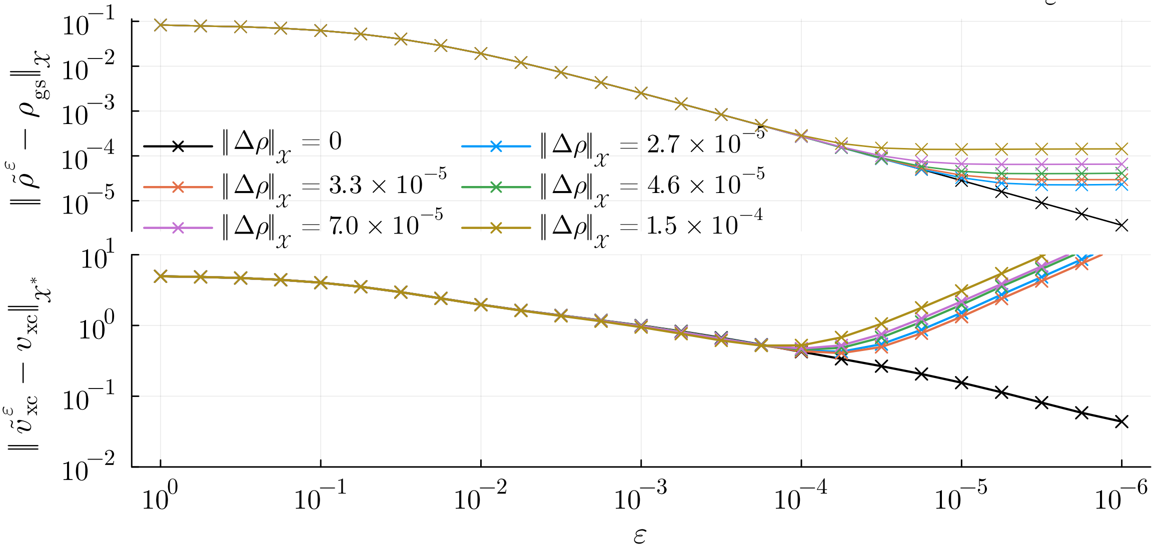
Sodium Chloride (NaCl)



Implementation: github.com/vebjorhb/MY-periodic-inversion

Bulk Silicon

$$\widetilde{\rho}_{\mathrm{gs}} = \rho_{\mathrm{gs}} + \Delta\rho \qquad \|v_{\mathrm{xc}} - \widetilde{v}^{\varepsilon}_{\mathrm{xc}}\|_{X^*} \le \|v_{\mathrm{xc}} - v^{\varepsilon}_{\mathrm{xc}}\|_{X^*} + \frac{1}{\varepsilon}\|\Delta\rho\|_X$$



Summary and Outlook

QEDFT for the Quantum Rabi model

- Quantitative HK theorem
- v-representability, differentiability, and $F^\lambda = F^\lambda_{\mathrm{DM}} = F^\lambda_{\mathrm{LL}}$ (QRabi)
- Adiabatic connection functional
- Illustrates central ideas in DFT without approximations

$\longrightarrow$ generalisations $\longrightarrow$ Pauli–Fierz Hamiltonian

Kohn–Sham Inversion

- Mathematically rigorous inversion scheme
- Offers error estimates
- Practical use case of Moreau–Yosida regularisation

$\longrightarrow$ More efficient implementation

$\longrightarrow$ Densities from accurate sources

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Thank you for your attention!

Vebjørn H. Bakkestuen
OSLO METROPOLITAN UNIVERSITY
STORBYUNIVERSITETET

✉: vebjorn.bakkestuen@oslomet.no