Building Kohn-Sham potentials

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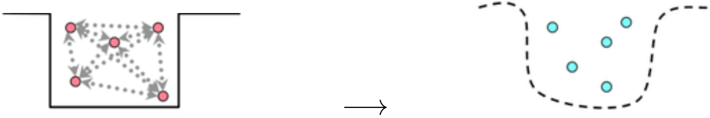
What is DFT

- Condensed matter, quantum chemistry, superconductivity, Bose-Einstein condensates, cold atoms, nuclear physics, dense plasmas, quantum and classical fluids, 2D materials
- Get rid of the complexity of interactions (DFT, DMFT, EOB)



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Framework

- Many-body Hamiltonian, potential v, interaction w (no spin)

$$H_N(v) = \sum_{i=1}^{N} -\Delta_{x_i} + \sum_{1\leqslant i<j\leqslant N} w(x_i - x_j) + \sum_{i=1}^{N} v(x_i)$$

- Ground and excited energies are

$$E_N^{(k)}(v) = \sup_{\substack{A\subset L^2_{\rm a}((\mathbb{R}^d)^N)\\ \dim_{\mathbb{C}} A=k}} \inf_{\substack{\Psi\in A^\perp\\ \int|\Psi|^2=1\\ \Psi\in H^1_{\rm a}((\mathbb{R}^d)^N)}} \langle\Psi, H_N(v)\Psi\rangle$$

with bound states $\Psi^{(k)}(v)$

- One-body density

$$\rho_\Psi(x) := N\int_{\mathbb{R}^{d(N-1)}} |\Psi|^2(x, x_2, \dots, x_N)\mathrm{d}x_2\cdots\mathrm{d}x_N$$

(Mostly practical) questions

DFT map: $v \mapsto \rho_{\Psi^{(0)}(v)} = \rho^{(0)}(v)$

Kohn-Sham (1965) : replace (v, w) by $(v_{\text{ks}}, 0)$ such that

$$\boxed{\rho^{(0)}_{w=0}(v_{ks}) = \rho^{(0)}(v)}$$

For the DFT map:

- What is the definition set ?
- Is it injective ?
- What is the image for $w = 0$ and for $w = |\cdot|^{-1}$, with pure and mixed states ? Is it dense, ie is every density ρ approximately invertible ?
- Is the inverse problem well-posed ?
- How to invert it algorithmically ?

The set of binding potentials

$$\mathcal{V}_{N,\partial}^{(0)} = \left\{ v \in L^p + L^\infty \;\middle|\; E_N^{(0)}(v) < \inf \sigma_{\text{ess}}(H_N(v)) \right\}$$

$$\mathcal{V}_N^{(0)} := \mathcal{V}_{N,\partial}^{(0)} \cap \left\{ v \mid \dim \left(H_N(v) - E_N^{(0)}(v) \right) = 1 \right\},$$

Theorem (Path-connectedness of the space of binding potentials)

$\cap_{i=1}^N \mathcal{V}_{i,\partial}^{(0)}$ *is path-connected*

- Conjecture : $\mathcal{V}_{i+1,\partial}^{(0)} \subset \mathcal{V}_{i,\partial}^{(0)}$. Would yield $\mathcal{V}_{N,\partial}^{(0)} = \cap_{i=1}^N \mathcal{V}_{i,\partial}^{(0)}$

Corollary (Path-connectedness of the set v-representable densities)

The set $\rho^{(0)} \left(\cap_{i=1}^N \mathcal{V}_{i,\partial}^{(0)} \right)$ *is path-connected*

- Is $\mathcal{V}_N^{(0)}$ path-connected ? Adiabatic equivalence ?

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Injectivity

Theorem (Hohenberg-Kohn, 1964)

Let $w, v_1, v_2 \in L^{p>\max(2,2d/3)}(\mathbb{R}^d) + L^\infty(\mathbb{R}^d)$. If there are two ground states Ψ_1 and Ψ_2 of $H_N(v_1)$ and $H_N(v_2)$, such that

$$\int_{\mathbb{R}^d} (v_1 - v_2)(\rho_{\Psi_1} - \rho_{\Psi_2}) = 0,$$

then $v_1 = v_2 + \frac{E_1 - E_2}{N}$.

- Lieb (1964) remarked it relies on SUCP, L^p statement proved in G. (2019) using Carleman (1939), Hörmander (1963) and Koch-Tataru (2001). $v \mapsto \rho_{\Psi^{(0)}(v)}$ injective, hence bijective on its image
- Consequence: if v_{ks} exists, then it is unique

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Compactness of $v \mapsto \rho^{(0)}(v)$

Theorem (Main properties of $\Psi^{(0)}$)

- *$v \mapsto \Psi^{(k)}(v)$ is $\mathcal{C}^\infty$ from $\mathcal{V}_N^{(k)}$ to $H^1_{\rm p}$*
- *For $v \in \mathcal{V}_N^{(k)}$, $\mathrm{d}_v\Psi^{(k)} : L^{d/2} + L^\infty \to H^1 \cap \left\{\Psi^{(k)}(v)\right\}^\perp$*

$$\left(\mathrm{d}_v\Psi^{(k)}\right) u = -\left(H_N(v) - E_N^{(k)}(v)\right)_\perp^{-1}\left(\Sigma_{i=1}^N u(x_i)\right)\Psi^{(k)}(v),$$

$$\boxed{\mathrm{d}_v\Psi^{(k)} \text{ is compact}}$$

- *Let $\Lambda \subset \mathbb{R}^d$ be a bounded open set. Assume $v \in \mathcal{V}_N^{(0)}$, $\boxed{v_n \rightharpoonup v}$ and $v_n \mathbb{1}_{\mathbb{R}^d\setminus\Lambda} \to v\mathbb{1}_{\mathbb{R}^d\setminus\Lambda}$ in $L^{p+\epsilon} + L^\infty$. Then $E_N^{(0)}(v_n) \to E_N^{(0)}(v)$, $v_n \in \mathcal{V}_N^{(0)}$ for n large enough, and $\boxed{\Psi^{(0)}(v_n) \to \Psi^{(0)}(v)}$ in H^1*

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Inverse continuity

Proposition (Weak inverse continuity of Ψ)

Let $p > \max(2d/3, 2)$, $v, v_n \in \mathcal{V}^{(k)}_{N,\partial}$ *such that* $v_n - E^{(k)}_N(v_n)/N$ *is bounded in* $L^p + L^\infty$ *and* $\boxed{\Psi^{(k)}(v_n) \to \Psi^{(k)}(v)}$ *in* $H^2(\mathbb{R}^{dN})$. *Then* $\boxed{v_n \to v}$ *a.e. up to a subsequence.*

Ill-posedness of Kohn-Sham

Corollary (The set of v-rep densities is topologically small)

Consider that the system lives in a bounded open set $\Omega \subset \mathbb{R}^d$. Then $\boxed{v \mapsto \rho^{(0)}(v) \text{ is compact}}$, $(\rho^{(0)})^{-1}$ *is discontinuous, and* $\rho^{(0)}(\mathcal{V}_N^{(0)})$ *is a countable union of compact sets. Hence* $\rho^{(0)}(\mathcal{V}_N^{(0)})$ *has empty interior in* $W^{1,1} \cap \left\{ \int \cdot = N \right\}$.

For $v \in (\rho^{(0)})^{-1} \left(\rho^{(0)}(\mathcal{V}_N^{(0)}) \cap \rho_{w=0}^{(0)}(\mathcal{V}_{N,w=0}^{(0)}) \right)$, the Kohn-Sham potential

$$v_{\mathrm{ks}}(v) := (\rho_{w=0}^{(0)})^{-1} \circ \rho^{(0)}(v)$$

is ill-posed !

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Dual optimality

Target ρ: we search v such that $\rho_{\Psi^{(k)}(v)} = \rho$.

$$G_\rho^{(k)}(v) := E_N^{(k)}(v) - \int_{\mathbb{R}^d} v\rho$$

- Inverse problem solved for classical systems at $T > 0$ (Chayes Chayes Lieb 1984), quantum systems on lattices for $k = 0$ for mixed states (Chayes Chayes Ruskai 1985), approximate v-representability with mixed states for $k = 0$ (Lieb 1983)
- Gauge invariance

$$G_\rho^{(k)}(v + c) = G_\rho^{(k)}(v)$$

- Concave for $k = 0$
- The map $v \mapsto \rho_{\Psi^{(k)}(v)}$ is not differentiable on $\mathcal{V}_{N,\partial}^{(k)} \backslash \mathcal{V}_N^{(k)}$! Maximizing $G_\rho^{(k)}$ is a non-smooth optimization problem

Dual optimality

Theorem (Optimality in the dual problem)

Take $w \geqslant 0$, $\rho \in L^1(\mathbb{R}^d)$, $\rho \geqslant 0$, $\int \rho = N$, $\sqrt{\rho} \in H^1(\mathbb{R}^d)$, $v \in \mathcal{V}^{(k)}_{N,\partial}$.

i) The following assertions are equivalent

- *there is a* k^{th} *bound mixed state* Γ *of* v *such that* $\rho_\Gamma = \rho$
- v *is a local maximizer of* $G^{(k)}_\rho$
- v *is a global maximizer of* $G^{(k)}_\rho$

ii) If v *maximizes* $G^{(k)}_\rho$ *and*

- $\dim \operatorname{Ker}\left(H_N(v) - E^{(k)}_N(v)\right) \in \{1, 2\}$,
- *or* $d = 1$ *and* $w = 0$,

then v *has a* k^{th} *bound pure state* Ψ *such that* $\rho_\Psi = \rho$.

- Shows that to find v_{ks}, one indeed has to maximize $G^{(k)}_\rho$
- Absence of local maximas makes maximization comfortable
- To obtain v_{ks} for pure states, first obtain it for mixed states

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Local dual problem

$$ {}^{+}\delta_v G_\rho^{(k)}(u) = \max_{\substack{\Psi_0,\dots,\Psi_{M_k-k}\in\mathrm{Ker}\left(H_N(v)-E_N^{(k)}(v)\right)\\ \|\Psi_i\|=1,\Psi_i\perp\Psi_j\\ 0\leqslant i,j\leqslant M_k-k}} \min_{\substack{\Psi=\sum_{i=0}^{M_k-k}\lambda_i\Psi_i\\ \lambda_i\in\mathbb{C},\sum_i|\lambda_i|^2=1}} \int (\rho_\Psi - \rho)\, u $$

Proposition (Local dual problem)

Take $w \geqslant 0$, $v \in \mathcal{V}_{N,\partial}^{(k)}$. *We have*

$$ \sup_{\substack{u\in L^p+L^\infty\\ \|u\|_{L^p+L^\infty}=1}} {}^{+}\delta_v G^{(k)}(u) = \max_{\substack{Q\subset\mathrm{Ker}_{\mathbb{R}}(H_N(v)-E_N^{(k)}(v))\\ \dim_{\mathbb{R}} Q=M_k-k+1}} \min_{\substack{\Gamma\in\mathcal{S}(Q)\\ \Gamma\geqslant 0,\mathrm{Tr}\,\Gamma=1}} \|\rho_\Gamma - \rho\|_{L^{p'}}, $$

and the supremum is attained by $u^* = \left|\frac{\rho_{\Gamma^*}-\rho}{\|\rho_{\Gamma^*}-\rho\|_{L^{p'}}}\right|^{p'-1} \mathrm{sgn}(\rho_{\Gamma^*}-\rho)$, *where* Γ^* *is an optimizer of the right hand side.*

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Regularization

- $G_\rho^{(k)}(v) = E_N^{(k)}(v) - \int v\rho$ is not coercive in L^p ! Ex : $v \in L^1 \cap L^{p>1}$, $v \geqslant 0$, $v_n(x) := n^d v(nx)$, $\|v_n\|_{L^p}^p = n^{d(p-1)} \int v^p \to +\infty$ but $E_N^{(k)}(v_n) = 0$, and $\int v_n \rho \to \rho(0) \int v$ is bounded
- Dual : restriction to potentials $V = \sum_{i\in I} v_i \alpha_i$, $v \in (v_i)_{i\in I} \in \ell^\infty(I, \mathbb{R})$, $\alpha_i \in L^\infty(\Omega)$, $\sum_{i\in I} \alpha_i = \mathbb{1}_\Omega$, $r_i \in \mathbb{R}_+$, $r_i = \int \rho\alpha_i$, $\sum_{i\in I} r_i = N$

$$G_{r,\boldsymbol{\alpha}}^{(k)}(v) := E_N^{(k)}\left(\sum_{i\in I} v_i \alpha_i\right) - \sum_{i\in I} v_i r_i,$$

Coercivity

Theorem (Existence of the dual potential)

When I is finite $G^{(k)}_{r,\boldsymbol{\alpha}}$ is coercive and there exists a maximizer v. If $\Omega \subset \mathbb{R}^d$ is bounded, there is a k^{th} excited N-particle ground mixed state Γ_v of $H_N\left(\sum_{i\in I} v_i\alpha_i\right)$ such that $\int \alpha_i \rho_{\Gamma_v} = r_i$.

- We can represent ρ by taking $(r_\rho)_i := \int \rho\alpha_i$ and finer sequences of weights $\boldsymbol{\alpha}_n$
- **Constructive v-representability with mixed states**
  For a given k, ρ, $\epsilon > 0$, there exists a potential v and Γ_v with $\operatorname{Ran}\Gamma_v \subset \operatorname{Ker}\left(H_N(v) - E^{(k)}_N(v)\right)$ such that $\|\rho_{\Gamma_v} - \rho\|_{L^1\cap L^q} \leqslant \epsilon$. The state can be chosen to be **pure** when $d = 1$ and $w = 0$.

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Numerical inversion, $w = 0$

- Consider the Hamiltonian **without interaction**

$$H_N^{w=0}(v) := \sum_{i=1}^{N} \big(-\Delta_i + v(x_i) \big).$$

- Let φ_i be the first eigenfunctions of $-\Delta + v$. Eigenfunctions of $H_N^{w=0}(v)$ are

$$\bigwedge_{i \in S} \varphi_i^v,$$

where $S \subset \mathbb{N}$ depends on k and v. $S = \{1, \dots, N\}$ for $k = 0$.

- Consider a target density $\rho \geqslant 0$ with $\int \rho = N$ and we search v such that

$$\sum_{i \in S} |\varphi_i^v|^2 = \rho.$$

- Inversion for $(d, k) = (1, 0)$ done in Wu, Yang 2003 and others

“Gradient” ascent

First idea, minimize $J(v) := \int_{\mathbb{R}^d} \left(\rho_{\Psi^{(k)}(v)} - \rho\right)^2$. Problem : J is not differentiable, its directional derivative is involved.
Second idea, maximize $G_\rho^{(k)}$

- Grid discretization $\mathbb{Z}^d$
- Consider a target $\rho \geqslant 0$, $\int \rho = N$
- Start from Bohm's potential $v_0 = \frac{\Delta\sqrt{\rho}}{\sqrt{\rho}}$
- Iterate $v_{n+1} = v_n + \alpha u^*$, where u^* is the steepest ascent direction $^+\delta_v G_\rho^{(k)}(u^*) = \max_{\|u\|=1} {}^+\delta_v G_\rho^{(k)}(u) > 0$
- Line search for α ; temperature to take degeneracies into account in a continuous way
- Convergence criterion: $\left\|\rho^{(k)}(v_n) - \rho\right\|_{L^1} / N \leqslant \epsilon$

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$d = 1$

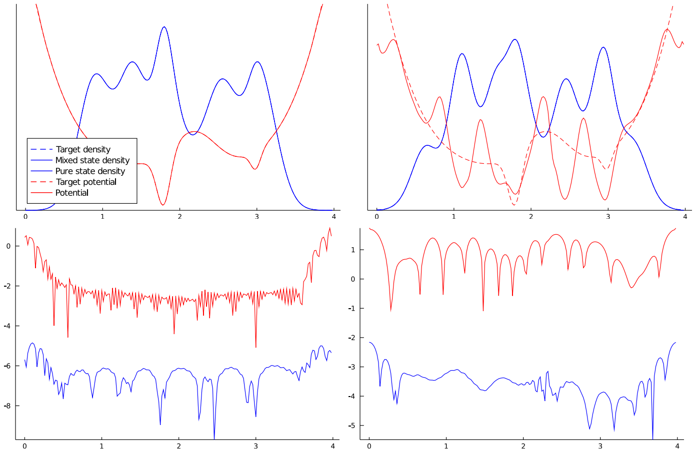

Figure: Plot for $d = 1$, $N = 5$, $k = 0$ on the left, $k = 3$ on the right, $\log_{10}|\rho_n - \rho|$, $\log_{10}|v_n - v|$

Uniqueness

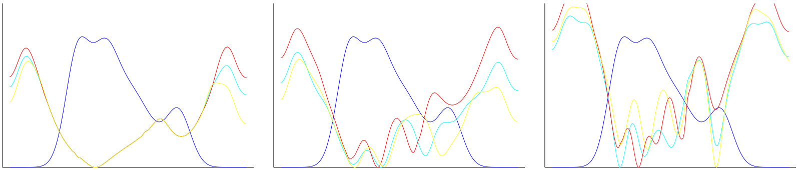

Figure: $d = 1$, $N = 3$, $k = 0$ left, $k = 1$ middle, $k = 5$ right. Densities in blue, inverse potentials in other colors

$d = 2$

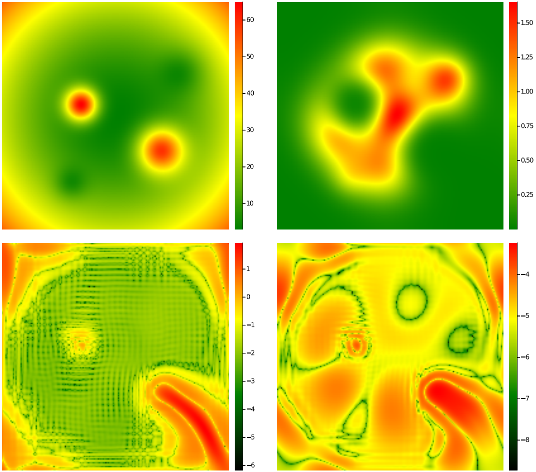

Figure: $d = 2$, $N = 5$, $k = 0$; v, $\rho_{\Psi^{(0)}(v)}$, $\log_{10} |v_n - v|$, $\log_{10} \left|\rho_n - \rho_{\Psi^{(0)}(v)}\right|$

$d = 3$

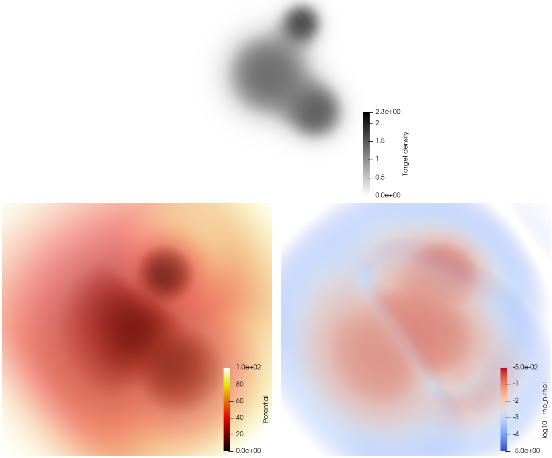

Figure: $d = 3,\ N = 4,\ k = 1\ ;\ \rho,\ v_n,\ \log_{10}|\rho_n - \rho|$

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What we learn from simulations

- Confirms Gaudoin and Burke (2004), no uniqueness for $k \geqslant 1$
- Degeneracies are generic, except for $(d, k, w) = (1, 0, 0)$. Need to be considered, otherwise the algorithm blocks.
  Perturbations of ρ do not lift degeneracies
- Approximate v-representability with pure states for $d = 1$ and $d = 2$ (theoretically proved for $d = 1$, verified in simulations ; for $d = 2$, remarked in simulations)
- Non approximate v-representability with pure states in $d = 3$ (implied by continuity of Levy and Levy-Lieb functionals, which is conjectured ; verified in simulations)

Thank you !