Regularization and density-potential inversion in density-functional theory

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MPI Hamburg seminar, November 2022

Acknowledgements

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Mathematical Modeling group OsloMet
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European Research Council
Established by the European Commission

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Acknowledgements

- Work part of ERC StG *REGAL–Regularized Density-Functional Analysis*
- Collaboration: M. Penz (Austria/Germany) and M.A. Csirik (Norway/Hungary)

- N interacting electrons:

$$T = \text{kinetic energy}, \qquad W = \text{two-particle interaction}$$
$$H = \underbrace{T + W}_{=:H_0} + V, \qquad V(r_1, \cdots, r_N) = \sum_{j=1}^{N} v(r_j)$$
$$E(v) = \inf\{\langle \psi, H\psi \rangle : \underbrace{\psi \in H^1(\mathbb{R}^{3N}), \|\psi\| = 1}_{=:\mathcal{W}_N}\},$$

- One-body (particle) density:

$$\rho_\psi(r) = N \int_{\mathbb{R}^{3(N-1)}} |\psi|^2, \qquad \psi \in \mathcal{W}_N \implies \rho_\psi \in L^1 \cap L^3 \tag{1}$$

Density functional theory II

- Using $H = H_0 + \sum_j v(r_j)$ and $\rho_\psi = N \int |\psi|^2$

$$\langle \psi, H\psi \rangle = \underbrace{\langle \psi, H_0\psi \rangle}_{\text{universal}} + \int_{\mathbb{R}^3} v\rho_\psi$$

- Ground-state energy via "constrained-search":

$$\begin{aligned} E(v) &= \inf_\psi \left\{ \langle \psi, H_0\psi \rangle + \int v\rho_\psi \mathrm{d}r \right\} \\ &= \inf_\rho \left\{ \underbrace{\inf\{\langle \psi, H_0\psi \rangle : \rho_\psi = \rho\}}_{\text{universal } \rho\text{-functional}} + \int v\rho \mathrm{d}r \right\} \end{aligned}$$

Densities

Γ density matrix

$$\Gamma = \sum_j f_j |\psi_j\rangle\langle\psi_j|, \quad f_j \in [0,1], \quad \sum_j f_j = N$$

$$\rho_\Gamma = \sum_j f_j \rho_{\psi_j}$$

- N-rep. density ρ: exists Γ such that $\rho = \rho_\Gamma$
- v-rep. density ρ: exists Γ such that $\rho = \rho_\Gamma$ and Γ is ground state
- In case Γ is a pure state, we may specify pure-state rep. (otherwise we use "ensemble").

Ensemble v-rep density are dense on the set of N-rep densities

Density Functionals

$$E(v) = \inf_{\rho} \left\{ \underbrace{\inf\{\langle \psi, H_0 \psi \rangle : \rho_\psi = \rho\}}_{\text{Levy–Lieb functional}} + \int v\rho \mathrm{d}r \right\}$$

Levy–Lieb functional

$$\tilde{F}(\rho) = \inf_{\psi : \rho_\psi = \rho} \{\langle \psi, H_0 \psi \rangle\}$$

is defined for N-rep. ρ, not convex.

$$E(v) = \inf_{\rho} \left\{ \tilde{F}(\rho) + \int v\rho \right\}$$

Lieb functional

$$F(\rho) = \sup_{v} \left\{ E(v) - \int v\rho \mathrm{d}r \right\}$$

is defined for N-rep. ρ, convex but **NOT** differentiable

Density functionals II

Lieb's constrained-search functional

$$F_{\mathrm{DM}}(\rho) = \inf_{\Gamma:\rho_\Gamma=\rho} \mathrm{tr}(\Gamma H_0)$$

Convex and defined for N-rep. densities

Theorem (Lieb 1983)

$F_{\mathrm{DM}}(\rho) = F(\rho)$ *(convex and lsc)*

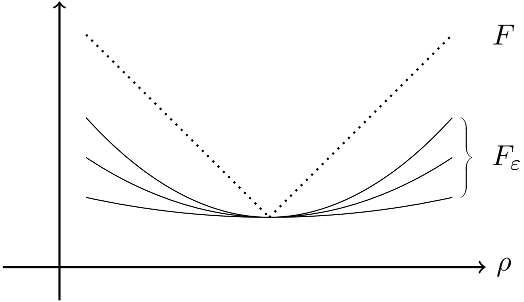
Hohenberg–Kohn variational principle:

$E(v) = \min_\rho \left\{F(\rho) + \int v\rho \, \mathrm{d}r\right\}$ $F(\rho)$ is highly irregular

Moreau–Yosida regularization:

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

$E^\varepsilon(v) = \min_\rho \left\{F^\varepsilon(\rho) + \int v\rho \, \mathrm{d}r\right\}$ $F^\varepsilon(\rho)$ is differentiable



Moreau–Yosida regularization II

- Suppose $\rho \in X, \quad v \in X^*$
- Let J be the duality mapping
- J maps elements from X to X^*
- Definition

$$J(\rho) = \{\xi \in X^* \mid \langle \xi, \rho \rangle = \|\rho\|_X^2 = \|\xi\|_{X^*}^2\}. \tag{2}$$

Moreau–Yosida regularization III

- Fixed choice of $\varepsilon > 0$ (reg. paramater)
- Moreau–Yosida regularization of a convex, lower semicontinuous functional $f : X \to \cup\{+\infty\}$
- Given by by the lower envelope of the parabola $\rho \mapsto \frac{1}{2\varepsilon}\|\rho\|_X^2$, tracing along the function

$$f^\varepsilon(\rho) = \inf_{\rho' \in X} \left\{ f(\rho') + \tfrac{1}{2\varepsilon}\|\rho - \rho'\|_X^2 \right\}. \tag{3}$$

- Infimum is attained at a unique point,
  proximal mapping $\Pi_f^\varepsilon : X \to X$ makes sense:

$$\rho^\varepsilon := \Pi_f^\varepsilon(\rho) = \mathrm{argmin}_{\rho' \in X} \left\{ f(\rho') + \tfrac{1}{2\varepsilon}\|\rho - \rho'\|_X^2 \right\}. \tag{4}$$

Moreau–Yosida regularization IV

- Proximal mapping Π_f^ε is singleton-valued (in particular nonempty) everywhere

  Moreover, $\boxed{\Pi_f^\varepsilon(\rho) \to \rho \text{ as } \varepsilon \to 0}$
- Derivative:

$$\nabla f^\varepsilon(\rho) = \frac{1}{\varepsilon} J(\rho - \Pi_f^\varepsilon(\rho))$$

- Subdifferential: For any $\rho, \rho_\varepsilon \in X$:

$$\rho^\varepsilon = \Pi_f^\varepsilon(\rho) \quad \iff \quad \nabla f^\varepsilon(\rho) \in \partial f(\rho_\varepsilon)$$

KS theory

- Given ρ_{gs} from $H = T + W + V_{\mathrm{ext}}$, i.e.,

$$(H + V_{\mathrm{ext}})\psi = E(v_{\mathrm{ext}})\psi, \qquad \rho_\psi = \rho_{\mathrm{gs}}$$

- Suppose that ρ_{gs} is both interacting and noninteracting v-rep., then by construction of the KS scheme,

$$\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{KS}}^{\rho_{\mathrm{gs}}}\right)\varphi_j = e_j\varphi_j, \qquad (T + V_{\mathrm{KS}})\Phi = E_{\mathrm{KS}}\Phi \tag{5}$$

and

$$\underbrace{\sum_j |\varphi_j|^2}_{\text{non-int}} = \rho_{\mathrm{gs}} = \underbrace{N\int_{\mathbb{R}^{3(N-1)}} |\psi|^2}_{\text{int.}}.$$

KS theory II

- In practice ρ_{gs} not known, only v_{ext}
- Define the Hartee potential

$$v_{\mathrm{H}}^{\rho}(r) = (\rho \star |\cdot|^{-1})(r) = \int \frac{\rho(r')}{|r - r'|} \mathrm{d}r',$$

- Assumption: representability

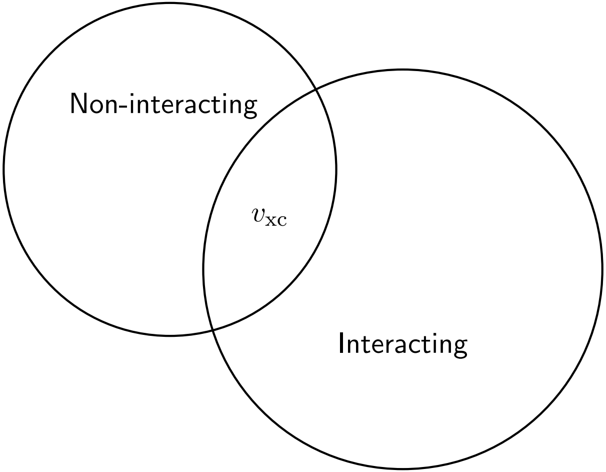
  We can then write

$$v_{\mathrm{KS}}^{\rho} = v_{\mathrm{ext}} + v_{\mathrm{H}}^{\rho} + v_{\mathrm{xc}}^{\rho}$$

  where v_{H}^{ρ} and v_{xc}^{ρ} are determined by the density ρ (the latter unknown)

$$\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{ext}} + v_{\mathrm{H}}^{\rho} + v_{\mathrm{xc}}^{\rho}\right)\varphi_j = e_j \varphi_j, \qquad \rho = \sum_{j=1}^{N} |\varphi_j|^2 \tag{6}$$

Exchange-correlation = Nature's glue



How can we determine v_{XC}, i.e., the KS potential given ρ_{gs}?

ZMP: Zhao–Morrison-Parr

- The ZMP method uses the constraint

$$\frac{\lambda}{2}\int\int \frac{(\rho(r)-\rho_{\mathrm{gs}}(r))(\rho(r')-\rho_{\mathrm{gs}}(r'))}{|r-r'|}\mathrm{d}r\mathrm{d}r'$$

- Lagrange multiplicator λ
- Given ρ_{gs}, the ZMP numerically allows to determine v_{xc} in the limit $\lambda \to \infty$ from KS-like eqs. ("ZMP eqs.")

ZMP II

$\boxed{\rho_{\text{gs}} \text{ is a ground-state of } H = T + W + V_{\text{ext}}}$

- $\rho^\lambda(r) = \sum_{j=1}^N |\varphi_j^\lambda(r)|^2$,

$$v^\lambda(r) = \lambda \int \frac{\rho^\lambda(r') - \rho_{\text{gs}}(r')}{|r - r'|} r', \qquad v_{\text{H}}^\lambda = (\rho^\lambda \star |\cdot|^{-1}),$$

where φ_j^λ satisfy the ZMP equations

$$\Big[-\frac{1}{2}\nabla^2 + v_{\text{ext}} + v_{\text{H}}^\lambda + v^\lambda \Big] \varphi_j^\lambda = e_j^\lambda \varphi_j^\lambda, \tag{7}$$

- Then, formally,

$$v_{\text{xc}}(r) = \lim_{\lambda\to\infty} (\lambda + 1) \int \frac{\rho^\lambda(r') - \rho_{\text{gs}}(r')}{|r - r'|} \mathrm{d}r'.$$

ZMP III (details: iteration at a given λ)

- The pair $(\rho^\lambda, v_{\mathrm{xc}}^\lambda)$ is determined self-consistently

$$v_{\mathrm{xc}}^\lambda(r) = (\lambda+1)\lim_{i\to\infty}\int \frac{\rho_i^\lambda(r') - \rho_{\mathrm{gs}}(r')}{|r-r'|}\mathrm{d}r'$$

- ρ_i is obtained from the orbitals being solutions of (7) with

$$v_i^\lambda(r) = \lambda \int \frac{\rho_{i-1}^\lambda(r') - \rho_{\mathrm{gs}}(r')}{|r-r'|}\mathrm{d}r',$$

- Procedure is repeated for increasing values of λ: $\lambda\to\infty$ yields a potential $v_{\mathrm{xc}}^\lambda \to v_{\mathrm{xc}}$ that has the ground-state density ρ_{gs}

ZMP from MY regularization

- Choose space X, X^*
- Recall duality map $J : X \to X^*$
- Use "KS density functional"

$$f(\rho) := Q_{\mathrm{KS}}(\rho) = T(\rho) + \int v_{\mathrm{ext}}\rho\,\mathrm{d}r + \frac{1}{2}\int\int \frac{\rho(r)\rho(r')}{|r-r'|}\mathrm{d}r\mathrm{d}r'$$

- f chosen to that only "v_{xc} missing"

$$E_f(v^\varepsilon) = \underbrace{\inf_\rho (f(\rho) + \langle v^\varepsilon, \rho\rangle)}_{\text{“KS equations”}}$$

$v^\varepsilon =$ "ZMP v^λ"

ZMP from MY regularization II

- f is *not* differentiable
- Regularization: $f^\varepsilon(\rho) = \mathcal{Q}^\varepsilon_{\mathrm{KS}}(\rho)$

  Also: $\rho^\varepsilon_{\mathrm{gs}} \to \rho_{\mathrm{gs}}$
- "KS minimization"

$$E_f(v^\varepsilon) = \inf_\rho (f(\rho) + \langle v^\varepsilon, \rho\rangle)$$

- Computation of $v^\varepsilon \in -\underline{\partial} f(\rho^\varepsilon)$ is equivalent to $\rho^\varepsilon \in \overline{\partial} E_f(v^\varepsilon)$ by reciprocity relation of convex analysis:

$$-\nabla f^\varepsilon(\rho_{\mathrm{gs}}) = \frac{1}{\varepsilon} J(\rho^\varepsilon_{\mathrm{gs}} - \rho_{\mathrm{gs}}) \in -\underline{\partial} f(\rho^\varepsilon)$$

$$v^\varepsilon(\rho_{\mathrm{gs}}) = \frac{1}{\varepsilon} J(\rho^\varepsilon_{\mathrm{gs}} - \rho_{\mathrm{gs}}) \tag{8}$$

- Use "KS density functional"

$$f(\rho) := \mathcal{Q}_{\mathrm{KS}}(\rho) = T(\rho) + \int v_{\mathrm{ext}}\rho\,\mathrm{d}r + \frac{1}{2}\int\int \frac{\rho(r)\rho(r')}{|r-r'|}\mathrm{d}r\mathrm{d}r'$$

- To obtain ZMP, determine the proximal point ρ^ε and

$$v^\varepsilon := \frac{1}{\varepsilon}J(\rho^\varepsilon - \rho) \in -\underline{\partial} f(\rho^\varepsilon),$$

and let $\varepsilon \to 0$.

Conclusion II

- Solving $\rho^\varepsilon \in \overline{\partial} E_{f=\mathcal{Q}_{\mathrm{KS}}}(v^\varepsilon)$ for ρ^ε amounts to solving Kohn–Sham equations with v^ε in place of v_{xc}.

- Self-consistent scheme:
  - Given an iterate v_i^ε and ρ_i^ε
  - In the next step, we compute ρ_{i+1}^ε from $\rho_{i+1}^\varepsilon \in \overline{\partial} E_f(v_i^\varepsilon)$
  - update $v_{i+1}^\varepsilon := \frac{1}{\varepsilon} J(\rho_{i+1}^\varepsilon - \rho)$.

- For $X = H^{-1}(\Omega)$, Ω bdd, then $\varepsilon^{-1} J$ "almost" gives the ZMP,

$$\frac{1}{\varepsilon} J(\rho^\varepsilon - \rho) = \frac{1}{4\pi\varepsilon} \int_\Omega \frac{\rho^\varepsilon(r') - \rho(r')}{|r - r'|} \mathrm{d}r' + \text{corrector-term} \tag{9}$$

Thank you