Moreau-Yosida Regularization in Density-Functional Theory

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Introduction

$$\boxed{H = \underbrace{-\sum_{i=1}^{N} \Delta_{r_i}}_{T} + \underbrace{\frac{1}{2} \sum_{1 \leq i \neq j \leq N} w(r_i - r_j)}_{W} + \underbrace{\sum_{i=1}^{N} v(r_i)}_{V}}$$

- $H\psi = E\psi$
- $H = T + W + V = H_0 + V$
- $\psi = \psi(r_1, \ldots, r_N), \quad r_i \in \mathbb{R}^3$

Ground-state energy

$$H(v) = H_0 + V(v)$$

$$E = E(v)$$

$$E(v) = \inf \left\{ \langle \psi, H(v)\psi \rangle : \mathcal{W}_N \right\}$$

$$\mathcal{W}_N = \left\{ \psi \in \mathcal{L}(\mathbb{R}^{3N}) : \ \|\psi\|_{\mathcal{L}^2} = 1, \ K(\psi) < \infty \right\} \subset \mathcal{H}^1(\mathbb{R}^{3N})$$

Kinetic energy

$$K(\psi) = \int_{\mathbb{R}^{3N}} |\nabla \psi|^2$$

One-body particle density (Lieb, 1983)

$$\rho_\Psi(r) = N \int_{\mathbb{R}^{3(N-1)}} |\psi|^2, \tag{1}$$

$\psi \in \mathcal{W}_N \implies \rho_\Psi \in \mathcal{I}_N$

$$\mathcal{I}_N = \left\{ \rho \geq 0 : \ \sqrt{\rho} \in \mathcal{H}^1(\mathbb{R}^3), \ \|\rho\|_{\mathcal{L}^1} = N \right\} \subset L^1 \cap L^3 \tag{2}$$

Hohenberg–Kohn theorem (1964)

Mapping potentials v to densities ρ

Injective: for potentials in $L^p + L^\infty$, $p > 2$ (Garrigue, 2018)

$H(v) = H_0 + \sum_i v(r_i)$

Levy–Lieb functional

$$E(v) = \inf_{\rho} \left\{ \underbrace{\inf\{\langle \psi, H_0\psi\rangle : \rho_\psi = \rho\}}_{\tilde{F}(\rho)} + \int_{\mathbb{R}^3} v\rho \right\}$$

$$\boxed{\tilde{F}(\rho) = \inf \left\{ \langle \psi, H_0\psi\rangle : \psi \in \mathcal{W}_N,\ \rho_\psi = \rho \right\}}$$

- Ground-state energy

$$E(v) = \inf_{\rho} \left\{ \tilde{F}(\rho) + \int v\rho \right\} \tag{3}$$

- Lieb functional

$$F(\rho) = \sup_{v} \left\{ E(v) - \int v\rho \right\} \tag{4}$$

λ coupling constant:

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

Adiabatic connection

$\lambda \mapsto F^\lambda(\rho)$ concave function,

$$F^\lambda(\rho) = F^0(\rho) + \int_0^\lambda f^t(\rho)\mathrm{d}t, \qquad f^\lambda \in \overline{\partial} F^\lambda$$

Let $F^0 = T^0$ and D be the direct Coulomb (Hartree) term,

$$F^\lambda(\rho) = T^0(\rho) + \lambda D(\rho) + \underbrace{\int_0^\lambda (f^t(\rho) - D(\rho))\mathrm{d}t}_{\lambda E^\lambda_{\mathrm{xc}}(\rho)} \tag{5}$$

Exchange energy

A.L. et al 2024:

$$E_{\mathrm{x}}(\rho) = \lim_{\gamma\to\infty} \frac{1}{\gamma} E_{\mathrm{xc}}(\rho_\gamma) = \partial^+_\lambda F^\lambda(\rho)|_{\lambda=0} - D$$

Kohn–Sham (1965)

ρ ground-state density of $H(v_{\mathrm{ext}})$, find v_{KS} s.t.

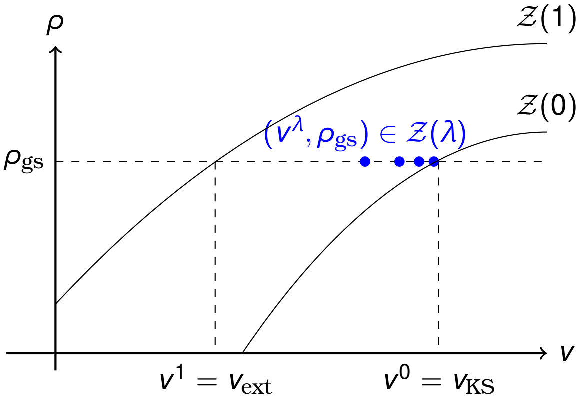
$$\rho = \mathrm{argmin}_{\rho'} \left\{ T^0(\rho') + \int v_{\mathrm{KS}}\, \rho' \right\}$$

$$\underline{\partial} T^0(\rho) + v_{\mathrm{KS}} \ni 0 \qquad \text{or} \qquad (-\Delta + v_{\mathrm{KS}})\, \varphi_j = e_j \varphi_j, \qquad \rho = \sum_j |\varphi_j|^2 \tag{6}$$

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

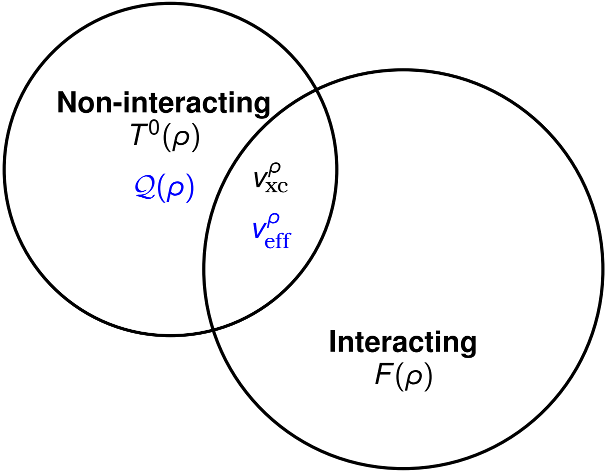
$$v_{\mathrm{H}} = \int |r - r'|^{-1} \rho(r') \mathrm{d}r' \tag{7}$$

$$\boxed{\mathcal{Z}(\lambda) = \left\{ (v, \rho) : \rho \text{ is a ground-state density of } \hat{H}^{\lambda}(v) \right\}}$$



$$v^0 = v^{\lambda} + \lambda v_{\mathrm{H}} + \lambda v_{\mathrm{xc}}^{\lambda} \tag{8}$$

Exchange-correlation = Nature's glue



Moreau–Yosida regularization

X reflexive, strictly convex (uniformly convex)

Convex, lower semicontinuous functional $f : X \to \mathbb{R} \cup \{+\infty\}$

$$f^\varepsilon(\rho) = \inf_{\rho' \in X} \left\{ f(\rho') + \frac{1}{2\varepsilon} \|\rho - \rho'\|_X^2 \right\}, \quad \varepsilon > 0 \tag{9}$$

Infimum is attained at a unique point

proximal mapping $\Pi_f^\varepsilon : X \to X$

$$\rho^\varepsilon := \Pi_f^\varepsilon(\rho) = \mathrm{argmin}_{\rho' \in X} \left\{ f(\rho') + \frac{1}{2\varepsilon} \|\rho - \rho'\|_X^2 \right\}. \tag{10}$$

$\rho^\varepsilon \to \rho$ as $\varepsilon \to 0+$

Exploiting the proximal point

$\mathcal{Q}$ convex, lsc

X, X^* uniformly convex

Duality map $J : X \to X^*$

$$\begin{aligned} &\inf_{\rho'} \left\{ \mathcal{Q}(\rho') + \frac{1}{2\varepsilon}\|\rho - \rho'\|^2 \right\} \\ &\underline{\partial}\mathcal{Q}(\rho^\varepsilon) + \underbrace{\frac{1}{\varepsilon}J(\rho^\varepsilon - \rho)}_{-\nabla Q^\varepsilon(\rho)} \ni 0 \end{aligned} \tag{11}$$

KS scheme $\quad \underline{\partial}Q(\rho) + v_{\mathrm{eff}} \ni 0 \quad$ and $\quad \rho^\varepsilon \to \rho, \;\; \varepsilon \to 0+$

$$v_{\mathrm{eff}} = \lim_{\varepsilon \to 0+} \frac{1}{\varepsilon} J(\rho^\varepsilon - \rho) \tag{12}$$

Density-potential inversion with MY reg

Theorem (Penz et al. (2023))

X, X^* uniformly convex, duality map $J : X \to X^*$

$\mathcal{Q}$ "KS density functional" to represent a model system

ρ ground-state density of interacting system

Suppose $\underline{\partial}\mathcal{Q}(\rho) \neq \emptyset$

We can then determine the missing effective potential thru

$$v_{\mathrm{eff}} = \lim_{\varepsilon \to 0+} \frac{1}{\varepsilon} J(\rho^{\varepsilon} - \rho) \tag{13}$$

Above convergence is strong and the limit is the min norm element in $-\underline{\partial}\mathcal{Q}(\rho)$

Examples

- For $X = H^{-1}(\Omega)$, $\Omega = \mathbb{R}^3$, then

$$\frac{1}{\varepsilon} J(\rho^{\varepsilon} - \rho) = \frac{1}{4\pi\varepsilon} \int_{\Omega} \frac{\rho^{\varepsilon}(r') - \rho(r')}{|r - r'|} e^{-\gamma|r-r'|} \mathrm{d}r' \tag{14}$$

- For $X = H^{-1}(\Omega)$, Ω bdd, then

$$\frac{1}{\varepsilon} J(\rho^{\varepsilon} - \rho) = \frac{1}{4\pi\varepsilon} \int_{\Omega} \frac{\rho^{\varepsilon}(r') - \rho(r')}{|r - r'|} \mathrm{d}r' + \text{corrector-term} \tag{15}$$

Thank you for your attention!

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