Mathematical Aspect of Density Functional Theory

Yukimi Goto

Faculty of Mathematics, Kyushu University
iTHEMS, RIKEN

Second Workshop on Fundamentals in Density Functional Theory
RIKEN Kobe Campus
February, 2024

Outline of the Talk

1. The Hohenberg–Kohn theory: The v-representation problem and mathematical problem of the original proof
2. In Levy–Lieb universal functional, the v-representation problem is settled
3. Other universal functionals: Lieb's functional and its grand-canonical version
4. Validity of Local Density Approximation in DFT

References:

- Lieb, *Density functionals for Coulomb systems*, 1983
- Lewin–Lieb–Seiringer, *Universal functionals in density functional theory*, 2020. *The local density approximation in DFT*, 2019 (include most of the talk)
- Helgaker–Teale, *Lieb variation principle in DFT*, 2022
- Lammert, *In search of the Hohenberg–Kohn theorem*, 2018

Density Functional Theory

Notation: $\boldsymbol{x} = (\boldsymbol{r}, \sigma)$, with $\boldsymbol{r} \in \mathbb{R}^d$ and $\sigma \in \{1, \ldots, q\}$. $q = 2$ for electrons. Write

$$\int d\boldsymbol{x} := \sum_{\sigma=1}^{q} \int_{\mathbb{R}^d} d\boldsymbol{r}$$

For N fermions $\psi(\boldsymbol{X}) = \psi(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N)$, we define single-particle density ρ_ψ by

$$\rho_\psi(\boldsymbol{r}) := N \sum_{\sigma_1, \ldots, \sigma_N = 1}^{q} \int_{\mathbb{R}^d} \cdots \int_{\mathbb{R}^d} |\psi(\boldsymbol{r}, \sigma_1, \boldsymbol{r}_2, \sigma_2, \ldots, \boldsymbol{r}_N, \sigma_N)|^2 \, d\boldsymbol{r}_2 \cdots d\boldsymbol{r}_N$$

The Hamiltonian we will consider is

$$H(v) := T + V + W,$$

$$T := -\sum_{j=1}^{N} \frac{\Delta_{\boldsymbol{r}_j}}{2}, \quad V = \sum_{j=1}^{N} v(\boldsymbol{r}_j), \quad W := \sum_{1 \le i < j \le N} w(\boldsymbol{r}_i - \boldsymbol{r}_j).$$

$$E_N(v) := \inf_{\langle \psi | \psi \rangle = 1} \langle \psi | H(v) | \psi \rangle = \text{Ground State Energy}$$

The Hohenberg–Kohn Theorem

Define $\mathcal{V}_N := \{v\colon H(v) \text{ has a ground state}\}$. ρ is v-representable $\Leftrightarrow$ ρ_ψ comes from a ground state ψ for $v \in \mathcal{V}_N$. Here

$$\mathcal{A}_N := \{\rho\colon v\text{-representable densities}\}$$

For $\rho \in \mathcal{A}_N$, define the Hohenberg–Kohn functional as

$$F_{\text{HK}}(\rho) := E_N(v) - \int_{\mathbb{R}^d} \rho_\psi(\boldsymbol{r}) v(\boldsymbol{r})\, d\boldsymbol{r}$$

Theorem 1 (Hohenberg–Kohn)

Assume $v_1, v_2 \in \mathcal{V}_N$ and there are two ground states ψ_1 and ψ_2 s.t. $\rho_{\psi_1} = \rho_{\psi_2}$. Then $v_1 = v_2 +$ constant, i.e., v is a unique functional of $\rho \in \mathcal{A}_N$. Moreover, the HK variational principle holds:

$$E_N(v) = \min\left\{F_{\text{HK}}(\rho) + \int v\rho\colon \rho \in \mathcal{A}_N\right\}$$

Original Proof of HK Theorem

Proof: "The proof proceeds by *reductio ad absurdum*" [Hohenberg–Kohn, 1964].
Assume $v_1 \neq v_2 +$ constant and $\rho_{\psi_1} = \rho_{\psi_2} = \rho$.
(A): "Now clearly ψ_1 cannot be equal to ψ_2 since they satisfy different Schödinger equations" [HK]. Also ψ_2 is not a ground state for $H(v_1)$.
Applying the Rayleigh-Ritz variational principle,

$$E_N(v_1) < \langle \psi_2 | H(v_1) | \psi_2 \rangle = E_N(v_2) + \int (v_1 - v_2)\rho.$$

Likewise $E_N(v_2) < E_N(v_1) + \int (v_2 - v_1)\rho$. These lead to the contradiction
$E_N(v_1) < E_N(v_1)$. □

Proof of (A): If $\psi_1 = \psi_2$,

$$(E_N(v_1) - E_N(v_2))\psi_1 = (H(v_1) - H(v_2))\psi_1 = (v_1 - v_2)\psi_1.$$

Hence if (B): ψ does not vanish almost everywhere, then $v_1 = v_2 + C$.
This contradicts the assumption. □
The condition (B) guaranteed by the unique continuation principle (UCP).

Mathematical Problem of Hohenberg–Kohn Theorem

HK approach is not satisfactory from a mathematical point of view since:

- $\mathcal{A}_N$ and $\mathcal{V}_N$ are unknown sets (v-representability problem)
- The proof requires $v_1\psi = v_2\psi$ implies $v_1 = v_2$ (unique continuation principle)

Denote $|A| :=$ the volume (Lebesgue measure) of set A.

Definition (Unique Continuation Principle)

The potential v and w satisfy the unique continuation principle (UCP) if $H(v)\psi = 0$ for some ψ and $|\{\psi = 0\}| > 0$, then $\psi \equiv 0$.

Notation: $L^p := \{f : \int_{\mathbb{R}^d} f(x)^p dx < \infty\}$ and $f \in L^p + L^\infty$ if $f = g + h$ with $g \in L^p$ and h is bounded.

Theorem 2 (UCP for L^p potential [Garrigue, 2018])

Any v, w s.t. and $v, w \in L^p + L^\infty$ with $p > \max(2, 2d/3)$ satisfy UCP.

E.g. Coulomb Hamiltonian satisfies UCP. (proved in 2018!)

Hohenberg–Kohn Theorem via UCP

Theorem 3 (New HK Theorem)

Assume v_i, $w \in L^p + L^\infty$ and (v_i, w) satisfy UCP. If there are G.S. ψ_i s.t. $\rho_{\psi_1} = \rho_{\psi_2}$, then $v_1 = v_2 +$ constant.

Proof.

$$\begin{aligned} \langle\psi_1|H(v_1)|\psi_1\rangle = \langle\psi_1|H(v_2)|\psi_1\rangle + \int \rho_{\psi_1}(v_1 - v_2) &\geq \langle\psi_2|H(v_2)|\psi_2\rangle + \int \rho_{\psi_1}(v_1 - v_2) \\ &\geq \langle\psi_1|H(v_1)|\psi_1\rangle \end{aligned}$$

Hence ψ_1 is a g.s. for $H(v_2)$ and

$$(H(v_1) - H(v_2))\psi_1 = \sum_{j=1}^{N}(v_1(\boldsymbol{r}_j) - v_2(\boldsymbol{r}_j))\psi_1 = 0.$$

UCP implies $|\{\psi_1 = 0\}| = 0$, so that for a.e. $\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N$

$$\sum_j (v_1(\boldsymbol{r}_j) - v_2(\boldsymbol{r}_j)) = 0, \quad \therefore v_1 = v_2 + C. \quad (C = (E(v_1) - E(v_2))/N) \quad \square$$

Summary of HK Theorem via UCP

- Usually, HK theorem has the v-representablity problem.
- The proof relies on the unique continuation principle.
- For many-body Coulomb potential, UCP was proved for the first time in 2018

Consider $w \in L^p + L^\infty$. Define the new set of v-representable densities:

$$\mathcal{R}_w := \{\rho_\psi \colon \psi \text{ ground state of } H(v) \text{ for some } (v, w) \text{ satisfying UCP}\}$$

Then HK theorem says that any $\rho \in \mathcal{R}_w$ arises from a unique potential v.
However, the set $\mathcal{R}_w$ is still essentially unknown.
It is an important problem to determine how large $\mathcal{R}_w$ is.
In other words, to generalize UCP to more general potentials v.
Mathematically, the Levy–Lieb universal functional is more accessible.

The Levy–Lieb Universal Functional

Consider $d \geq 3$ and $v, w \in L^{d/2} + L^{\infty}$. Levy–Lieb gave the following two-step minimization:

$$E_N(v) = \inf \left\{ F_{\mathrm{LL}}[\rho] + \int_{\mathbb{R}^d} v(\boldsymbol{r})\rho(\boldsymbol{r})\, d\boldsymbol{r} : \ \int \rho = N \right\}$$

$$F_{\mathrm{LL}}[\rho] = \inf_{\substack{\langle\psi|\psi\rangle = 1, \\ \rho_\psi = \rho}} \left\{ \frac{1}{2} \sum_{j=1}^{N} \int |\nabla_j \psi(\boldsymbol{X})|^2 \, d\boldsymbol{X} + \sum_{1 \leq j < k \leq N} \int |\psi(\boldsymbol{X})|^2 w(\boldsymbol{r}_j - \boldsymbol{r}_k)\, d\boldsymbol{X} \right\}$$

$F_{\mathrm{LL}}[\rho]$ is independent of v, so it is a universal functional of ρ.
This requires to identify the N-representable densities. Note

Theorem 4 (Hoffmann-Ostenhof Inequality)

$$\sum_{j=1}^{N} \int |\nabla_j \psi(\boldsymbol{X})|^2 \, d\boldsymbol{X} \geq \int_{\mathbb{R}^d} |\nabla \sqrt{\rho_\psi}(\boldsymbol{r})|^2 \, d\boldsymbol{r}.$$

This will give the optimal restriction $\sqrt{\rho} \in H^1 := \{ f \in L^2 : \nabla f \in L^2 \}$.

Theorem 5 (Representablity of the one-particle density)

Assume $\sqrt{\rho} \in H^1$ *and* $\int \rho = N$. *Then there is* $\psi \in H^1$ *s.t.* $\rho = \rho_\psi$.

Proof: For $q \geq N$ (e.g. He), just take

$$\psi(\boldsymbol{X}) = \prod_{j=1}^{N} \sqrt{\frac{\rho(\boldsymbol{r}_j)}{N}} \frac{\det(\delta_j(\sigma_k))_{1\leq j,k\leq N}}{\sqrt{N!}}$$

For $q < N$, take a Slater determinant

$$\psi(\boldsymbol{X}) = \frac{\det(\varphi_j(\boldsymbol{x}_k))_{1\leq j,k\leq N}}{\sqrt{N!}}, \quad \varphi_j(x) = \sqrt{\frac{\rho(\boldsymbol{r})}{N}} \exp(i\theta_j(\boldsymbol{r}))\delta_0(\sigma)$$

where θ_j are chosen to φ_j orthonormal, e.g. (not so good for computation)

$$\theta_j(\boldsymbol{r}) = \frac{2ij\pi}{N} \int_{-\infty}^{r_1} dt \int_{\mathbb{R}^{d-1}} \rho(t, \boldsymbol{r}')d\boldsymbol{r}'. \quad \square$$

v-representablity for Levy–Lieb Functional

Collectively, the set of N-representable densities $\mathcal{I}_N$ is

$$\mathcal{I}_N = \{\rho \in L^1 \cap L^3 \colon \rho \geq 0, \int \rho = N, \nabla\sqrt{\rho} \in H^1\}$$

Then for $v, w \in L^{d/2} + L^\infty$, we have

$$E_N(v) = \inf_{\rho \in \mathcal{I}_N} \left\{ F_{\mathrm{LL}}[\rho] + \int_{\mathbb{R}^d} v(\boldsymbol{r})\rho(\boldsymbol{r})\, d\boldsymbol{r} \right\}, \quad F_{\mathrm{LL}}[\rho] = \inf_{\substack{\langle\psi|\psi\rangle=1,\\ \rho_\psi=\rho}} (\cdots)$$

Since $\mathcal{I}_N$ is explicitly known, v-representablity problem has been settled.
Note

$$\underbrace{\mathcal{A}_N}_{\text{not convex set}} \subset \underbrace{\mathcal{I}_N}_{\text{convex set}} \subset \underbrace{L^1 \cap L^3}_{\text{vector space}} .$$

Since $v \mapsto E_N(v)$ is concave, we can see $E_N(v)$ is the Legendre transform of F_{LL} on $\mathcal{I}_N$
Remark: The harmonic oscillator potential is not in $L^{d/2} + L^\infty$.

Lieb's Universal Functional

However, F_{LL} is not convex. We use the convex hull

$$F_{\mathrm{L}} := \mathrm{Conv}_{\mathcal{I}_N}(F_{\mathrm{LL}}) := \sup\{f(\rho) \colon f \text{ convex, } f(\rho') \leq F_{\mathrm{LL}}[\rho'], \forall \rho' \in \mathcal{I}_N\},$$

which is the Legendre transform of $E_N(v)$.
Let Γ be a mixed state obeying

$$\Gamma = \sum_j \alpha_j \left|\psi_j\right\rangle \left\langle\psi_j\right|, \quad \alpha_j \geq 0, \quad \sum_j \alpha_j = 1$$

and $\rho_\Gamma := \sum_j \alpha_j \rho_{\psi_j}$. Then we can write

$$F_{\mathrm{L}}[\rho] = \inf\left\{\mathrm{Tr}\left(\Gamma H(v=0)\right) : \Gamma \geq 0, \mathrm{Tr}(\Gamma) = 1, \ \rho_\Gamma = \rho\right\}$$

Theorem 6 (Variational Principle for F_{L} and F_{LL})

For $\rho \in \mathcal{I}_N$, the infima of F_{L} and F_{LL} are attained, i.e., $\inf = \min$.

Duality Between F_{L} and $E_N(v)$

Explicitly,

$$F_L[\rho] = \min\left\{\sum_j \alpha_j F_{\mathrm{LL}} : \rho = \sum_j \alpha_j \rho_j,\ \sum_j \alpha_j = 1,\ \rho \in \mathcal{I}_N\right\}$$

$$\begin{aligned} E_N(v) &= \inf\left\{\mathrm{Tr}\left(\Gamma H(v)\right) : \Gamma \geq 0, \mathrm{Tr}(\Gamma) = 1,\ \rho_\Gamma = \rho\right\} \\ &= \inf_{\rho \in \mathcal{I}_N}\left\{F_{\mathrm{L}}[\rho] + \int_{\mathbb{R}^d} v(\boldsymbol{r})\rho(\boldsymbol{r})\, d\boldsymbol{r}\right\}. \end{aligned}$$

Then we have the duality principle

$$\begin{aligned} F_{\mathrm{L}}[\rho] &:= \sup\left\{E_N(v) - \int_{\mathbb{R}^d} v(\boldsymbol{r})\rho(\boldsymbol{r})\, d\boldsymbol{r} : v \in L^{d/2} + L^\infty\right\} \\ &= \sup\left\{-\int_{\mathbb{R}^d} v(\boldsymbol{r})\rho(\boldsymbol{r})\, d\boldsymbol{r} : v \in L^{d/2} + L^\infty,\ H(v) \geq 0\right\}. \end{aligned}$$

In this sense, F_{L} is more natural than F_{LL}. However, this supremum is not attained for most densities (e.g. for v with UCP and ρ vanishes on a set).

Grand-Canonical Universal Functional

The grand-canonical (GC) universal functional is

$$F_{\mathrm{GC}}[\rho] := \inf\left\{\sum_{n\geq 1} \mathrm{Tr}\left(H(0)\Gamma_n\right) : \sum_{n\geq 1} \mathrm{Tr}(\Gamma_n) \leq 1, \sum_{n\geq 1} \rho_{\Gamma_n} = \rho\right\}$$

Then the infimum is attained and we have

$$\begin{aligned} F_{\mathrm{GC}}[\rho] &= \min\left\{\sum_j \alpha_j F_{\mathrm{L}}[\rho_j] \colon \rho = \sum_j \alpha_j \rho_j, \sum_j \alpha_j = 1, \rho_j \in \mathcal{I}_j\right\} \\ &= \min\left\{\sum_j \beta_j F_{\mathrm{LL}}[\rho_j] \colon \rho = \sum_j \beta_j \rho_j, \sum_j \beta_j = 1, \int \rho_j \in \mathbb{N}\right\} \end{aligned}$$

Hence the GC functional is also a convex hull of F_{LL}.
For F_{GC}, ρ_j have an arbitrary number of particles.

Duality of F_{GC}

The Legendre transform of F_{GC} is

$$E_\lambda^{\mathrm{GC}}(v) := \inf_{\rho \in \mathcal{I}_\lambda} \left\{ F_{\mathrm{GC}}[\rho] + \int v\rho \right\} = \inf_{\substack{\sum_n \alpha_n = 1 \\ \sum_n n\alpha_n = \lambda}} \sum_n \alpha_n E_n(v)$$

For $\lambda = N \in \mathbb{N}$, we have $E_N^{\mathrm{GC}}(v) \leq E_N(v)$. If $n \mapsto E_n(v)$ is convex, i.e.,

$$E_n(v) - E_{n-1}(v) \leq E_{n+1}(v) - E_n(v), \quad n \geq 1$$

then $E_N^{\mathrm{GC}}(v) = E_N(v)$ holds true.
Such a convexity for the Coulomb potential is still open.

Theorem 7 (Lewin–Lieb–Seiringer '21)

For any $\sqrt{\rho} \in H^1$ *there are* $\sqrt{\rho_n} \in H^1$ *s.t.* $\int \rho_n \in \mathbb{N}$ *and* $F_{\mathrm{GC}}[\rho] = \lim_{n\to\infty} F_{\mathrm{L}}[\rho_n]$

The Kohn–Sham Theory

The Kohn–Sham (KS) theory provides a good representation of the kinetic energy T_N:

$$T_S[\rho] := \min\left\{\langle\psi|T_N|\psi\rangle : \psi \text{ is a Slater determinant}, \rho_\psi = \rho\right\}, \quad T_N := -\sum_{j=1}^{N} \frac{\Delta_{\boldsymbol{r}_j}}{2}.$$

Then we have for $\Phi = (\varphi_1, \ldots, \varphi_N)$

$$\begin{aligned} E_N(v) = \inf_{\varphi_j:\text{ONS}} \Bigg\{ & \frac{1}{2}\sum_{j=1}^{N} \int |\nabla\varphi_j(\boldsymbol{x})|^2 \, d\boldsymbol{x} + \int_{\mathbb{R}^d} v(\boldsymbol{r})\rho_\Phi(\boldsymbol{r})\, d\boldsymbol{r} \\ & + \frac{1}{2}\iint d\boldsymbol{r}d\boldsymbol{r}' w(\boldsymbol{r}-\boldsymbol{r}')\rho_\Phi(\boldsymbol{r})\rho_\Phi(\boldsymbol{r}') + E_{\text{xc}}[\rho_\Phi] \Bigg\}, \end{aligned}$$

$$E_{\text{xc}}[\rho] := F_{\text{LL}}[\rho] - T_S[\rho] - \frac{1}{2}\iint d\boldsymbol{r}d\boldsymbol{r}' w(\boldsymbol{r}-\boldsymbol{r}')\rho_\Phi(\boldsymbol{r})\rho_\Phi(\boldsymbol{r}').$$

In principle, the exchange term $E_{\text{xc}}[\rho]$ requires to study both $F_{\text{LL}}[\rho]$ and $T_S[\rho]$.

The Local Density Approximation

From now on, we consider $w(\boldsymbol{r}) = |\boldsymbol{r}|^{-1}$ in $d = 3$ and

$$F_{\mathrm{L,LL,GC}}[\rho] \approx \underbrace{\frac{1}{2}\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\,d\boldsymbol{r}d\boldsymbol{r}'}_{\text{non local}} + \underbrace{\int_{\mathbb{R}^3} f(\rho(\boldsymbol{r}))\,d\boldsymbol{r}}_{\text{local}} =: D[\rho] + E_{\mathrm{LDA}}[\rho].$$

Theorem 8 (Validity of LDA, Lewin–Lieb–Seiringer '20)

There is a $C = C(q) > 0$ s.t. for any $\varepsilon > 0$ and ρ

$$\begin{aligned}&|F_{\mathrm{GC}}[\rho] - D[\rho] - E_{\mathrm{LDA}}[\rho]|\\ &\leq \varepsilon\int(\rho+\rho^2) + C\left(1+\frac{1}{\varepsilon}\right)\int_{\mathbb{R}^3}|\nabla\sqrt{\rho}(\boldsymbol{r})|^2 d\boldsymbol{r} + \frac{C}{\varepsilon}\int_{\mathbb{R}^3}|\nabla\sqrt{\rho}(\boldsymbol{r})|^4 d\boldsymbol{r}.\end{aligned}$$

with f like $\quad f(\rho) = \begin{cases} c_1\rho^{4/3} + o(\rho^{4/3}) & (\rho\to 0+)\\ c_2\rho^{5/3} - c_3\rho^{4/3} + o(\rho^{4/3}) & (\rho\to\infty)\end{cases}$

Remark on Theorem

- It is expected that same result for F_{LL} and F_{L}
- Error term is not optimal.
- Maybe it should only involve $\rho^{5/3}, \rho^{4/3}, |\nabla\sqrt{\rho}|^2, |\nabla\rho^{1/3}|^2$ or $|\nabla\rho|$.
- For $\rho_N(\boldsymbol{r}) = \rho(N^{-1/3}\boldsymbol{r})$ we obtain

$$F_{\mathrm{GC}}[\rho_N] = N^{5/3}D[\rho] + NE_{\mathrm{LDA}}[f] + O\left(N^{\frac{11}{12}}\right)$$

- Extended to short-range potentials [Mietzsch '20].

The Kinetic Energy Functional

Consider

$$T[\rho] := \min\left\{\langle\psi|T_N|\psi\rangle \,:\, \langle\psi|\psi\rangle = 1,\, \rho_\psi = \rho\right\} = F_{\mathrm{LL}}^{w=0}[\rho].$$

For one-particle density matrix with kernel γ_ψ

$$\gamma_\psi(\boldsymbol{x},\boldsymbol{y}) = N\int \psi(\boldsymbol{x},\boldsymbol{X})\overline{\psi(\boldsymbol{y},\boldsymbol{X})}\,d\boldsymbol{X}, \quad \rho_{\gamma_\psi}(\boldsymbol{x}) := \gamma_\psi(\boldsymbol{x},\boldsymbol{x})$$

we have $\langle\psi|T_N|\psi\rangle = \mathrm{Tr}\left[\left(\frac{-\Delta}{2}\right)\gamma_\psi\right]$. The set of N-representable density matrix is

$$\mathcal{RD}_N := \left\{\gamma = \gamma^\dagger : 0 \le \gamma \le 1,\, \mathrm{Tr}\,(-\Delta\gamma) < \infty,\, \mathrm{Tr}(\gamma) = N\right\},$$

$$T_{\mathrm{GC}}[\rho] := \min\left\{\mathrm{Tr}\left[\left(\frac{-\Delta}{2}\right)\gamma\right] : 0 \le \gamma = \gamma^\dagger \le 1,\, \mathrm{Tr}(-\Delta\gamma) < \infty,\, \rho_\gamma = \rho\right\}$$

Note $\int\rho \in \mathbb{R}$, and, if $\int\rho \in \mathbb{N}$, then $T_{\mathrm{GC}}[\rho] = F_L^0[\rho]$.
Also $T_{\mathrm{GC}}[\rho] \le T[\rho] \le T_{\mathrm{S}}[\rho]$ holds, and $E_{\mathrm{xc}}[\rho] = F_{\mathrm{L}}[\rho] - T_{\mathrm{GC}}[\rho] - D[\rho]$.

The Extended Kohn–Sham Model

Finally, we define the extended Kohn–Sham model as

$$E_N^{\mathrm{EKS}}(v) := \inf_{\gamma \in \mathcal{RD}_N} \left\{ \mathrm{Tr}\left(-\frac{1}{2}\Delta\gamma\right) + \int \rho_\gamma v + D[\rho_\gamma] + E_{\mathrm{xc}}(\rho_\gamma) \right\}$$

Then $E_N^{\mathrm{EKS}}(v) = E_N(v)$. Consider the Kohn–Sham LDA as

$$E_\lambda^{\mathrm{KSLDA}}(v) := \inf_{\gamma \in \mathcal{RD}_\lambda} \left\{ \mathrm{Tr}\left(-\frac{1}{2}\Delta\gamma\right) + \int \rho_\gamma v + D[\rho_\gamma] + E_{\mathrm{LDA}}(\rho_\gamma) \right\}, \quad \lambda \in \mathbb{R}.$$

Theorem 9 (Anantharaman–Cancés, '09)

For Coulomb system, if $\lambda \le Z =$ total nuclear charge, $E_\lambda^{\mathrm{KSLDA}}(v)$ has a minimizer γ_0 obeying the Kohn–Sham equation

$$\left(-\frac{\Delta}{2} + v + \rho_{\gamma_0} * |\boldsymbol{r}|^{-1} + f'(\rho_{\gamma_0})\right)\varphi_i = e_i\varphi_i.$$

Summary

- The Hohenberg–Kohn Theory is not satisfactory from a mathematical point of view
- Indeed, v-representability problem exists
- Mathematically, HK theory needs the unique continuation principle which is not yet completely understood
- The Levy–Lieb functional is a universal functional of densities, and v-representability problem is settled, but not convex.
- The convex hull of LL functional are Lieb's universal functional and grand-canonical functional
- For GC functional, the local density approximation is justified in a sense.
- There are some mathematical results for Kohn–Sham theory (e.g. Goto 2022, etc)

Thank you for coming to my talk