Existence of minimizers for Kohn-Sham within the Local Spin Density Approximation

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Non-magnetic Hamiltonian for N-electrons:

$$H(v) = \underbrace{\sum_{i=1}^{N} -\frac{1}{2}\Delta_i}_{\text{kinetic energy}} + \underbrace{\sum_{1\le i<j\le N} |\mathbf{r}_i - \mathbf{r}_j|^{-1}}_{\text{interaction energy}} + \underbrace{\sum_{i=1}^{N} v(\mathbf{r}_i)}_{\text{external potential}} \quad .$$

$H(v)$ is linear and acts on the fermionic space $\bigwedge_{i=1}^{N} L^2(\mathbb{R}^3)$. Its domain is $\bigwedge_{i=1}^{N} H^1(\mathbb{R}^3)$:

$$\Psi \in \bigwedge_{i=1}^{N} H^1(\mathbb{R}^3) \Longrightarrow \begin{cases} \Psi(\mathbf{r}_{p(1)}, \mathbf{r}_{p(2)}, \dots, \mathbf{r}_{p(N)}) = \varepsilon(p)\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N). \\ \\ \displaystyle\sum_{i=1}^{N} \int_{\mathbb{R}^{3N}} |\nabla_i \Psi|^2 \mathrm{d}^3\mathbf{r}_1 \dots \mathrm{d}^3\mathbf{r}_N < \infty \end{cases}$$

Problem: Ψ lives in $\mathbb{R}^{3N}$.

"Curse of dimensionality" : impossible for a computer

For $\Psi \in \bigwedge_{i=1}^{N} H^1(\mathbb{R}^3)$, we can define

$$\Gamma_\Psi = |\Psi\rangle\,\langle\Psi| \quad \in \mathcal{S}\left(L^2(\mathbb{R}^{3N})\right)$$ the N-body density matrix

and we introduce

$$\mathcal{P}_N := \left\{\Gamma_\Psi, \quad \Psi \in H^1(\mathbb{R}^3), \quad \|\Psi\|_{L^2} = 1\right\}$$ the set of pure state N-body density matrices.

$\mathcal{P}_N$ is not convex. Its convex hull is

$$\mathcal{M}_N := \mathrm{CH}\left(\mathcal{P}_N\right)$$ the set of mixed state N-body density matrices.

Example: for N=1,

- $\mathcal{P}_1$ only contains rank-1 projectors.
- $\mathcal{M}_1$ is the set of operators Γ such that $0 \le \Gamma \le 1$ and $\mathrm{Tr}(\Gamma) = 1$.

$$\begin{pmatrix} 1 & 0 & \dots \\ 0 & 0 & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} \quad \text{versus} \quad \begin{pmatrix} n_1 & 0 & \dots \\ 0 & n_2 & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} \quad n_i \ge 0, \quad n_1 + n_2 + \ldots = 1.$$

One main object of interest is the ground state energy,

$$E(v) = \min_{\Psi \in \bigwedge H^1, \|\Psi\|_{L^2}=1} \langle \Psi | H(v) | \Psi \rangle,$$

or, equivalently,

$$E(v) = \min_{\Gamma \in \mathcal{P}_N} \mathrm{Tr}\left(H(v)\Gamma\right).$$

Because $H(v)$ is linear, and because $\mathcal{M}_N$ is the convex hull of $\mathcal{P}_N$, it holds

$$E(v) = \min_{\Gamma \in \mathcal{M}_N} \mathrm{Tr}\left(H(v)\Gamma\right).$$

With some calculations, it holds

$$\mathrm{Tr}\left(H(v)\Gamma\right) = \mathrm{Tr}\left(H_0\Gamma\right) + \int_{\mathbb{R}^3} v(\mathbf{r})\rho_\Gamma(\mathbf{r}) \, \mathrm{d}^3\mathbf{r}$$

with the electronic density

$$\rho_\Gamma(\mathbf{r}) := N \int_{\mathbb{R}^{3(N-1)}} \Gamma(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N; \mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N) \, \mathrm{d}^3\mathbf{r}_2 \ldots \mathrm{d}^3\mathbf{r}_N.$$

The density functional theory (DFT), such as presented by Levy (1979) and Lieb (1983), comes from the following calculations:

$$\begin{aligned}\min_{\Gamma\in\mathcal{M}_{\boldsymbol{N}}} \mathrm{Tr}\left(H(v)\Gamma\right) &= \min_{\Gamma\in\mathcal{M}_{\boldsymbol{N}}} \left\{\mathrm{Tr}\left(H_0\Gamma\right) + \int_{\mathbb{R}^3} v(\mathbf{r})\rho_\Gamma(\mathbf{r})\, \mathrm{d}^3\mathbf{r}\right\} \\ &= \min_{\rho\in\mathcal{I}_{\boldsymbol{N}}(\mathcal{M}_{\boldsymbol{N}})} \left\{\int_{\mathbb{R}^3} v(\mathbf{r})\rho(\mathbf{r})\, \mathrm{d}^3\mathbf{r} + \min_{\Gamma\in\mathcal{M}_{\boldsymbol{N}},\Gamma\to\rho} \left\{\mathrm{Tr}\left(H_0\Gamma\right)\right\}\right\}\end{aligned}$$

where the set $\mathcal{I}_N(\mathcal{M}_N)$ is defined by

$$\mathcal{I}_N := \left\{\rho_\Gamma, \quad \Gamma\in\mathcal{M}_N\right\}$$ set of N-representable electronic densities.

Introducing the universal functional

$$F(\rho) := \min_{\Gamma\in\boldsymbol{X},\Gamma\to\rho} \left\{\mathrm{Tr}\left(H_0\Gamma\right)\right\},$$

The minimization problem for the wave function can be recast into a minimization problem for the electronic density.

Questions:

- What is the functional F? (approximations: LDA, GGA,...)
- Do we have an explicit form of the set $\mathcal{I}_N(\mathcal{M}_N)$? N-representability problem

We are looking for the explicit form of

$$\mathcal{I}_N(\mathcal{M}_N) := \left\{ \rho_\Gamma, \Gamma \in \mathcal{M}_N \right\}.$$

Note that this problem is "Hamiltonian free": we do not suppose that Γ is the ground state of some Hamiltonian.

Historically, the DFT has been derived by Hohenberg and Kohn (1964). They considered:

$$\widetilde{\mathcal{I}_N}(\mathcal{M}_N) := \left\{ \rho_\Gamma, \Gamma \in \mathcal{M}_N, \exists\ v \text{ such that } \Gamma \text{ is the unique ground state of } H(v) \right\}.$$

Characterizing this set is the v-representability problem.

- it is much more difficult and useless
- when considering the magnetic case, the HK theory does no longer work

Theorem (Harriman '81, Lieb '83)

It holds $\mathcal{I}_N(\mathcal{P}_N) = \mathcal{I}_N(\mathcal{M}_N) := \mathcal{I}_N$, *with*

$$\mathcal{I}_N = \left\{ \rho \in L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3), \quad \rho \geq 0, \quad \int_{\mathbb{R}^3} \rho = N, \quad \sqrt{\rho} \in H^1(\mathbb{R}^3) \right\}.$$

Remarks:

- The map $\Gamma \to \rho_\Gamma$ is linear
- $\mathcal{M}_N$ is a convex set (it is the convex hull of $\mathcal{P}_N$)
- In particular, $\mathcal{I}_N$ is convex

We want to do the same work for the magnetic case

According to the Schrödinger-Pauli equation, the Hamiltonian for N-electrons is

$$H(v,\mathbf{A}) = \underbrace{\sum_{i=1}^{N} \frac{1}{2}\left(\sigma_i \cdot \left(-\mathrm{i}\nabla_i + \frac{1}{c}\mathbf{A}(\mathbf{r}_i)\right)\right)^2}_{\text{kinetic energy}} + \underbrace{\sum_{1\le i<j\le N} |\mathbf{r}_i - \mathbf{r}_j|^{-1}}_{\text{interaction energy}} + \underbrace{\sum_{i=1}^{N} v(\mathbf{r}_i)}_{\text{external potential}}$$

It is linear, and its form domain is $\bigwedge_{i=1}^{N} H^1(\mathbb{R}^3, \mathbb{C}^2)$:

$$\Psi \in \bigwedge_{i=1}^{N} H^1(\mathbb{R}^3,\mathbb{C}^2) \text{ has } 2^N \text{ components : } \begin{pmatrix} \Psi(\mathbf{r}_1,\uparrow,\mathbf{r}_2,\uparrow,\ldots,\mathbf{r}^N,\uparrow) \\ \Psi(\mathbf{r}_1,\uparrow,\mathbf{r}_2,\uparrow,\ldots,\mathbf{r}^N,\downarrow) \\ \vdots \\ \Psi(\mathbf{r}_1,\downarrow,\mathbf{r}_2,\downarrow,\ldots,\mathbf{r}^N,\downarrow) \end{pmatrix}$$

and still satisfies

$$\begin{cases} \Psi(\mathbf{r}_{p(1)},\alpha_{p(1)},\mathbf{r}_{p(2)},\alpha_{p(2)},\ldots,\mathbf{r}_{p(N)},\alpha_{p(N)}) = \varepsilon(p)\Psi(\mathbf{r}_1,\alpha_1,\mathbf{r}_2,\alpha_2,\ldots\mathbf{r}_N,\alpha_N) \\ \displaystyle\sum_{i=1}^{N} \sum_{\alpha_1,\ldots\alpha_N\in\{\uparrow,\downarrow\}} \int_{\mathbb{R}^{3N}} |\nabla_i\Psi(\mathbf{r}_1,\alpha_1,\ldots)|^2 \mathrm{d}^3\mathbf{r}_1\ldots\mathrm{d}^3\mathbf{r}_N < \infty \end{cases}$$

$\mathbf{A}$ is the magnetic potential vector (recall that $\mathbf{rot}(\mathbf{A}) = \mathbf{B}$ is the magnetic field), and σ_i contains the Pauli-matrices acting on the i-th spin.

New Hilbert space:

$$\mathcal{H} = L^2(\mathbb{R}^3, \mathbb{C}^2) := \left\{ \Phi = (\phi^\uparrow, \phi^\downarrow) \in L^2(\mathbb{R}^3), \quad \|\Phi\|_{\mathcal{H}} < \infty \right\}$$

with

$$\langle \Phi | \Psi \rangle_{\mathcal{H}} = \int_{\mathbb{R}^3} \left(\overline{\phi^\uparrow}(x)\psi^\uparrow(x) + \overline{\phi^\downarrow}(x)\psi^\downarrow(x) \right) \, \mathrm{d}^3 x.$$

For instance, the set of N-body pure states is now:

$$\mathcal{P}_N := \left\{ \Gamma = |\Psi\rangle \, \langle \Psi|, \quad \Psi \in \bigwedge_{i=1}^{N} H^1(\mathbb{R}^3, \mathbb{C}^2), \quad \|\Psi\|_{\mathcal{H}} = 1 \right\},$$

and the set of N-body mixed states $\mathcal{M}_N$ is again the convex hull of $\mathcal{P}_N$.

We want to minimize expression of the form

$$\min_{\Gamma \in \mathcal{M}_N} \mathrm{Tr}\left(H(v, \mathbf{A}) \Gamma \right).$$

This time, it holds

$$\mathrm{Tr}\left(H(v, \mathbf{A})\Gamma \right) = \mathrm{Tr}\left(H_0 \Gamma \right) \\ + \int \left(v(\mathbf{r}) + \frac{1}{2} \frac{|\mathbf{A}(\mathbf{r})|^2}{c^2} \right) \rho(\mathbf{r}) \mathrm{d}^3\mathbf{r} + \int_{\mathbb{R}^3} \mathbf{A}(\mathbf{r}) \cdot \mathbf{j}_p(\mathbf{r}) \, \mathrm{d}^3\mathbf{r} - \underbrace{\mu_B \int_{\mathbb{R}^3} \mathbf{B}(\mathbf{r}) \cdot \mathbf{m}(\mathbf{r}) \, \mathrm{d}^3\mathbf{r}}_{\text{Zeeman energy}}$$

where new objects have appeared:

- ρ is still the electronic density
- $\mathbf{j}_p$ is the paramagnetic current
- $\mathbf{m}$ is the spin density.

Recall that $\mathbf{A}$ and $\mathbf{B}$ satisfy $\mathbf{B} = \mathbf{rot}\ \mathbf{A}$. However, as $\mathbf{A}$ acts on the orbitals, whereas $\mathbf{B}$ acts on the spin, we usually study the two effects separately and choose:

- $\mathbf{A} = \mathbf{0}$ and $\mathbf{B} \neq \mathbf{0}$ for spin effects. Spin Density Functional Theory (SDFT).
- $\mathbf{A} \neq \mathbf{0}$ and $\mathbf{B} = \mathbf{0}$ for orbital effects. Current Density Functional Theory (CDFT).

In this presentation, I will present SDFT ($\mathbf{A} = \mathbf{0}, \mathbf{B} \neq \mathbf{0}$):

$$\mathrm{Tr}\left(H(v, \mathbf{B})\Gamma\right) = \mathrm{Tr}\left(H_0\Gamma\right) + \int_{\mathbb{R}^3} v(\mathbf{r})\rho(\mathbf{r})\mathrm{d}^3\mathbf{r} - \mu_B \int_{\mathbb{R}^3} \mathbf{B}(\mathbf{r}) \cdot \mathbf{m}(\mathbf{r})\ \mathrm{d}^3\mathbf{r}.$$

For $\Gamma \in \mathcal{M}_N$, we can define the spin-polarized electronic densities: for $\alpha, \beta \in \{\uparrow, \downarrow\}^2$,

$$\rho_\Gamma^{\alpha\beta}(\mathbf{r}) := N \sum_{\alpha_2 \ldots \alpha_N \in \{\uparrow,\downarrow\}^{N-1}} \int_{\mathbb{R}^{3(N-1)}} \Gamma(\mathbf{r}\alpha, \mathbf{r}_2\alpha_2, \ldots, \mathbf{r}_N\alpha_N; \mathbf{r}\beta, \mathbf{r}_2\alpha_2, \ldots, \mathbf{r}_N\alpha_N)\ \mathrm{d}^3\mathbf{r}_2 \ldots \mathrm{d}^3\mathbf{r}_N.$$

We introduce the matrix of spin-polarized electronic densities

$$R_\Gamma(\mathbf{r}) = \begin{pmatrix} \rho^{\uparrow\uparrow}(\mathbf{r}) & \rho^{\uparrow\downarrow}(\mathbf{r}) \\ \rho^{\downarrow\uparrow}(\mathbf{r}) & \rho^{\downarrow\downarrow}(\mathbf{r}) \end{pmatrix}$$

With those notation,

- the usual electronic density is $\rho := \rho^{\uparrow\uparrow} + \rho^{\downarrow\downarrow}$
- the spin density is $\mathbf{m} = \mathrm{tr}_{\mathbb{C}^2}(\sigma \cdot R_\Gamma)$.

We can then recast the above equation under the form

$$\mathrm{Tr}\left(H(v, \mathbf{B})\Gamma\right) = \mathrm{Tr}\left(H_0\Gamma\right) + \int_{\mathbb{R}^3} \mathrm{tr}_{\mathbb{C}^2}\left(\underbrace{\begin{pmatrix} v - \mu_B \mathbf{B}_z & -\mu_B\mathbf{B}_x + \mathrm{i}\mu_B\mathbf{B}_y \\ -\mu_B\mathbf{B}_x - \mathrm{i}\mu_B\mathbf{B}_y & v + \mu_B\mathbf{B}_z \end{pmatrix}(\mathbf{r})}_{U}\ R_\Gamma(\mathbf{r}) \right)$$

Similarly to standard DFT, we write:

$$E(v, \mathbf{B}) := \min_{\Gamma \in \mathcal{M}_{\boldsymbol{N}}} \operatorname{Tr}\left(H(v, \mathbf{B})\Gamma\right) = \min_{R \in \mathcal{J}_{\boldsymbol{N}}(\mathcal{M}_{\boldsymbol{N}})} \left\{ F(R) + \int \operatorname{tr}_{\mathcal{C}^2}\left[UR\right] \right\}$$

with

$$F(R) := \inf_{\Gamma \in \mathcal{M}_{\boldsymbol{N}}, \Gamma \to R} \operatorname{Tr}\left(H_0 \Gamma\right)$$

and

$$\mathcal{J}_N(\mathcal{M}_N) := \left\{ R_\Gamma, \Gamma \in \mathcal{M}_N \right\}$$ set of representable spin-polarized electronic densities.

Problems

- We still do not know the functional F (approximations LSDA, GGA, ...)
- Can we have a characterization of the sets $\mathcal{J}_N(\mathcal{M}_N)$? N-representability problem

We only have the answer for mixed states:

Theorem (DG)

$$\mathcal{J}_N(\mathcal{M}_N) := \mathcal{J}_N = \Big\{ R \in \mathcal{M}_{2\times 2}\left(L^1(\mathbb{R}^3)\right), \quad R \textit{ is hermitian positive a.e.}, \\ \int_{\mathbb{R}^3} \mathrm{tr}_{\mathbb{C}^2}(R) = N, \quad \sqrt{R} \in \mathcal{M}_{2\times 2}\left(H^1(\mathbb{R}^3)\right) \Big\}.$$

- The $\sqrt{}$ is in the hermitian matrix sense
- Extension of the standard result:

Theorem (Harriman '81, Lieb '83)

$$\mathcal{I}_N = \left\{ \rho \in L^1(\mathbb{R}^3), \quad \rho \geq 0, \quad \int_{\mathbb{R}^3} \rho = N, \quad \sqrt{\rho} \in H^1(\mathbb{R}^3) \right\}.$$

Remark: In particular, $\mathcal{J}_N$ is a convex set.

Local Spin Density Approximation (LSDA)

Recall that, in SDFT, we want to find:

$$E_N := \min_{\Gamma \in \mathcal{M}_N} \mathrm{Tr}\left(H(v, \mathbf{B})\Gamma\right) = \min_{R \in \mathcal{J}_N} \left\{ F(R) + \int \mathrm{tr}_{\mathcal{C}^2}\left[UR\right] \right\}$$

with

$$F(R) := \inf_{\Gamma \in X, \Gamma \to R} \mathrm{Tr}\left(H_0 \Gamma\right).$$

Approximation of F?

For $\Gamma \in \mathcal{M}_N$, introduce the 1-body density matrix

$$\gamma(\mathbf{r}, \mathbf{r}') = \begin{pmatrix} \gamma^{\uparrow\uparrow} & \gamma^{\uparrow\downarrow} \\ \gamma^{\downarrow\uparrow} & \gamma^{\downarrow\downarrow} \end{pmatrix} (\mathbf{r}, \mathbf{r}')$$

with, for $\alpha, \beta \in \{\uparrow, \downarrow\}^2$,

$$\gamma_\Gamma^{\alpha\beta}(\mathbf{r}, \mathbf{r}') := N \sum_{\alpha_2 \ldots \alpha_N \in \{\uparrow,\downarrow\}^{N-1}} \int_{\mathbb{R}^{3(N-1)}} \Gamma(\mathbf{r}\alpha, \mathbf{r}_2\alpha_2, \ldots, \mathbf{r}_N\alpha_N; \mathbf{r}'\beta, \mathbf{r}_2\alpha_2, \ldots, \mathbf{r}_N\alpha_N)\, \mathrm{d}^3\mathbf{r}_2 \ldots \mathrm{d}^3\mathbf{r}_N.$$

Remarks

- It holds $R_\Gamma(\mathbf{r}) = \gamma_\Gamma(\mathbf{r}, \mathbf{r})$.
- The set $\mathcal{A}_N := \{\gamma_\Gamma, \Gamma \in \mathcal{M}_N\}$ is (Coleman 1963)

$$\mathcal{A}_N = \left\{ \gamma \in \mathcal{S}(L^2(\mathbb{R}^3, \mathbb{C}^2)), \quad 0 \le \gamma \le 1, \quad \mathrm{Tr}(\gamma) = N, \right.$$
$$\left. \mathrm{Tr}(-\Delta\gamma) := \mathrm{Tr}(-\Delta\gamma^{\uparrow\uparrow}) + \mathrm{Tr}(-\Delta\gamma^{\downarrow\downarrow}) < \infty \right\}.$$

Following Kohn and Sham (1965), we split $F(R)$ in three parts:

$$F(R) = T^{\mathrm{KS}}(R) + J(R) + E_{\mathrm{xc}}(R).$$

- $T^{\mathrm{KS}}(R)$ is the Kohn-Sham kinetic energy:

$$T^{\mathrm{KS}}(R) := \inf_{\gamma \in \mathcal{A}_{\boldsymbol{N}}, \gamma \to R} \left\{ \frac{1}{2} \mathrm{Tr}(-\Delta \gamma) \right\}$$

- $J(R)$ is the Hartree energy:

$$J(R) := \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{r} \, \mathrm{d}\mathbf{r}'$$

- $E_{\mathrm{xc}}(R)$ is the exchange correlation term: $E_{\mathrm{xc}}(R) := F(R) - T^{\mathrm{KS}}(R) - J(R)$.

How to choose $E_{\mathrm{xc}}(R)$?

Local Spin Density Approximation (von Barth and Hedin 1972):
If for an unpolarized model, a local density approximation (LDA) functional is used

$$E^{\mathrm{LDA}}(\rho) = \int g(\rho),$$

then the following ansatz can be used for a polarized model,

$$E_{\mathrm{xc}}(R) \approx E_{\mathrm{xc}}^{\mathrm{LSDA}}(R) := \frac{1}{2}\left(\int g(2\rho^+) + \int g(2\rho^-)\right).$$

where ρ^+ and ρ^- are the two eigenvalues of R.

Remarks

- This ansatz is exact for the exchange energy.
- Depends only on the eigenvalues $\Longrightarrow$ invariance under local spin-rotations.
- We recover the unpolarized case: $\rho^+ = \rho^- = \rho/2$.

Is a well-posed? Do the eigenvalues of R have good properties?

$$E_{\mathrm{xc}}^{\mathrm{LSDA}}(R) = \frac{1}{2}\int g(2\rho^+) + g(2\rho^-)$$

Lemma

If R is such that $\sqrt{R} \in H^1(\mathbb{R}^3)$, then $\sqrt{\rho^{+/-}} \in H^1(\mathbb{R}^3) \hookrightarrow L^1(\mathbb{R}^3) \bigcap L^6(\mathbb{R}^3)$.

In particular, if g is a good function for the unpolarized case, then g is also a good function for the polarized case.

Examples

- $X\alpha$-functional: $g(\rho) = -C_X\rho^{4/3}$.
- Homogeneous Electron Gas: $g(\rho) = g^{\mathrm{HEG}}(\rho)$.
- ...

Usually, g satisfies the following conditions:

$$(*) \quad \begin{cases} g(0) = 0 \\ g' \leq 0 \\ \exists\, 0 < \beta^- \leq \beta^+ < \dfrac{2}{3}, \quad \sup\limits_{\rho\in\mathbb{R}^+} \dfrac{|g'(\rho)|}{\rho^{\beta^-} + \rho^{\beta^+}} < \infty \\ \exists\, 1 \leq \alpha < \dfrac{3}{2}, \quad \limsup\limits_{\rho\to 0^+} \dfrac{g(\rho)}{\rho^\alpha} < 0. \end{cases}$$

Finally, we recast the problem into 1-body density matrices:

$$E_N^{\mathrm{LSDA}} := \inf_{\gamma \in \mathcal{A}_N} \left\{ \frac{1}{2}\mathrm{Tr}(-\Delta\gamma) + \int \mathrm{tr}_{\mathcal{C}^2}\left[UR\right] + J(R) + \frac{1}{2}\left(\int g(2\rho^+) + \int g(2\rho^-) \right) \right\},$$

with

$$\int \mathrm{tr}_{\mathcal{C}^2}\left[UR\right] = \int V\rho - \mu_B \int \mathbf{B}\cdot\mathbf{m}$$

and

$$\mathrm{Tr}(-\Delta\gamma) = \mathrm{Tr}(-\Delta\gamma^{\uparrow\uparrow}) + \mathrm{Tr}(-\Delta\gamma^{\downarrow\downarrow}).$$

Objects	spin-unpolarized	spin-polarized
Hilbert space	$L^2(\mathbb{R}^3,\mathbb{C})$	$L^2(\mathbb{R}^3,\mathbb{C}^2)$
1-boby density matrix	$\gamma(\mathbf{r},\mathbf{r}')$ complex	$\gamma(\mathbf{r},\mathbf{r}')$ hermitian 2×2 matrix
Density	$\rho(\mathbf{r})$ real	$R(\mathbf{r})$ hermitian 2×2 matrix
Condition for the density	$\rho \geq 0, \quad \sqrt{\rho}\in H^1$	$R \geq 0, \quad \sqrt{R}\in H^1$
Magnetic contribution	none	$-\mu_B \int \mathbf{B}\cdot\mathbf{m}$ (Zeeman term)
xc energy in the L(S)DA	$\int g(\rho)$	$\frac{1}{2}\int g(2\rho^+) + g(2\rho^-)$

Let

$$\mathcal{E}^{\mathrm{LSDA}}(\gamma) := \frac{1}{2}\mathrm{Tr}(-\Delta\gamma) + \int \mathrm{tr}_{\mathcal{C}^2}[UR] + J(R) + \frac{1}{2}\left(\int g(2\rho^+) + \int g(2\rho^-)\right).$$

Collinear SDFT

$$E_N^{\text{collinear}} = \inf\left\{\mathcal{E}(\gamma), \quad \gamma \in \mathcal{A}_N, \quad \gamma^{\uparrow\downarrow} = \gamma^{\downarrow\uparrow} = 0\right\}.$$

Then, $\{\rho^+, \rho^-\} = \{\rho^{\uparrow\uparrow}, \rho^{\downarrow\downarrow}\}$, and

$$\int \mathrm{tr}_{\mathbb{C}^2}[UR] = \int V\rho - \mu_B \int B_z \rho\zeta, \text{ where } \quad \zeta = \frac{\rho^{\uparrow\uparrow} - \rho^{\downarrow\downarrow}}{\rho^{\uparrow\uparrow} + \rho^{\downarrow\downarrow}}$$ is the relative spin polarization.

Unpolarized DFT

$$E_N^{\text{unpolarized}} = \inf\left\{\mathcal{E}(\gamma), \quad \gamma \in \mathcal{A}_N, \quad \gamma^{\uparrow\downarrow} = \gamma^{\downarrow\uparrow} = 0, \quad \gamma^{\uparrow\uparrow} = \gamma^{\downarrow\downarrow}\right\}.$$

Then, $\rho^+ = \rho^- = \rho/2$, and

$$\int \mathrm{tr}_{\mathbb{C}^2}[UR] = \int V\rho.$$

$$E_N^{\mathrm{LSDA}} := \inf_{\gamma \in \mathcal{A}_N} \left\{ \frac{1}{2}\mathrm{Tr}(-\Delta\gamma) + \int \mathrm{tr}_{\mathcal{C}^2}[UR] + J(R) + \frac{1}{2}\left(\int g(2\rho^+) + \int g(2\rho^-) \right) \right\}.$$

Question:

Does a minimizer exist? (not obvious, this a non-convex problem due to the g term).

For the unpolarized case $(\rho^+ = \rho^-)$

Theorem (Anantharaman, Cancès, 2009)

If the functional g satisfies the conditions $(*)$, and if the electronic potential has the form

$$V(\mathbf{r}) = -\sum_{k \le M} \frac{z_k}{|\mathbf{r} - \mathbf{r}_k|}, \quad z_k \in \mathbb{N}^*, \quad \sum_{k \in M} z_k = Z,$$

then, for $N \le Z$, the problem $E_N^{unpolarized}$ admits a minimizer.

For the polarized case

Theorem (DG)

Under the same conditions, and if $\mathbf{B} \in L^{3/2+\epsilon} + L^\infty$ is a magnetic field that vanishes at infinity, then, for $N \le Z$, the problem E_N^{LSDA} admits a minimizer.

The proof relies on concentration-compacity techniques (Lions 1984).

For $\lambda \in \mathbb{R}^+$, introduce

$$\mathcal{A}_\lambda = \{\gamma \in \mathcal{S}(L^2(\mathbb{R}^3, \mathbb{C}^2)), \quad 0 \le \gamma \le 1, \quad \mathrm{Tr}(\gamma) = \lambda, \quad \mathrm{Tr}(-\Delta\gamma) < \infty\},$$

the minimization problem for λ

$$E_\lambda^{\mathrm{LSDA}} := \inf_{\gamma \in \mathcal{A}_\lambda} \left\{ \frac{1}{2}\mathrm{Tr}(-\Delta\gamma) + \int \mathrm{tr}_{\mathcal{C}^2}[UR] + J(R) + \frac{1}{2}\left(\int g(2\rho^+) + \int g(2\rho^-) \right) \right\},$$

and the problem at infinity for λ

$$E_\lambda^{\mathrm{LSDA},\infty} = \inf_{\gamma \in \mathcal{A}_\lambda} \left\{ \frac{1}{2}\mathrm{Tr}(-\Delta\gamma) + J(R) + \frac{1}{2}\left(\int g(2\rho^+) + \int g(2\rho^-) \right) \right\}.$$

Lemma (Binding inequality)

For all $0 \le \mu \le \lambda$, it holds $E_\lambda^{\mathrm{LSDA}} \le E_\mu^{\mathrm{LSDA}} + E_{\lambda-\mu}^{\mathrm{LSDA},\infty}$.

- This lemma tells that electrons are not leaking away ($\approx$ compactness)
- Allows to prove the convergence of the minimizing sequences.

Lemma

For all $0 \leq \mu \leq \lambda$, it holds $E_\lambda^{\mathrm{LSDA}} \leq E_\mu^{\mathrm{LSDA}} + E_{\lambda-\mu}^{\mathrm{LSDA},\infty}$.

Proof (for the potential part):

Let $\gamma \in \mathcal{A}_\mu$, and $\gamma^\infty \in \mathcal{A}_{\lambda-\mu}$. Let $\gamma_0 = \gamma + \gamma^\infty \in \mathcal{A}_\lambda$. Then,

$$\mathrm{tr}_{\mathbb{C}^2}\left[U\gamma_0\right] = \mathrm{tr}_{\mathbb{C}^2}\left[U\gamma\right] + \mathrm{tr}_{\mathbb{C}^2}\left[U\gamma^\infty\right] = \mathrm{tr}_{\mathbb{C}^2}\left[U\gamma\right] + \overbrace{V\rho^\infty}^{<0} - \overbrace{\mu_B \mathbf{B}\cdot\mathbf{m}^\infty}^{\textit{sign?}}.$$

In order to control the sign of the last term, we introduce the flip transform.

$$\text{If} \quad \gamma^\infty = \begin{pmatrix} \gamma^{\uparrow\uparrow,\infty} & \gamma^{\uparrow\downarrow,\infty} \\ \gamma^{\downarrow\uparrow,\infty} & \gamma^{\downarrow\downarrow,\infty} \end{pmatrix}, \quad \text{then} \quad \widetilde{\gamma^\infty}(\mathbf{r},\mathbf{r}') = \begin{pmatrix} \gamma^{\downarrow\downarrow,\infty} & -\gamma^{\uparrow\downarrow,\infty} \\ -\gamma^{\downarrow\uparrow,\infty} & \gamma^{\uparrow\uparrow,\infty} \end{pmatrix}(\mathbf{r}',\mathbf{r}).$$

Lemma

$\widetilde{\gamma^\infty} \in \mathcal{A}_{\lambda-\mu}$, and it holds $\widetilde{\rho^\infty} = \rho^\infty$, $\widetilde{\mathbf{m}^\infty} = -\mathbf{m}^\infty$.

Introducing $\gamma_0^\sharp = \gamma + \widetilde{\gamma^\infty} \in \mathcal{A}_\lambda$, we get

$$\mathrm{tr}_{\mathbb{C}^2}\left[U\gamma_0\right] + \mathrm{tr}_{\mathbb{C}^2}\left[U\gamma_0^\sharp\right] = 2\mathrm{tr}_{\mathbb{C}^2}\left[U\gamma\right] + 2V\rho^\infty < 2\mathrm{tr}_{\mathbb{C}^2}\left[U\gamma\right].$$

Therefore, one of two real numbers $\mathrm{tr}_{\mathbb{C}^2}\left[U\gamma_0\right]$ or $\mathrm{tr}_{\mathbb{C}^2}\left[U\gamma_0^\sharp\right]$ is strictly less than $\mathrm{tr}_{\mathbb{C}^2}\left[U\gamma\right]$.

We also get the Euler-Lagrange equation.

Theorem

If γ_0 is a minimizer for $E_\lambda^{\mathrm{LSDA}}$, then γ_0 satisfies the Euler-Lagrange equation

$$\gamma_0 = \mathbb{1}(H_{\gamma_0} < \varepsilon_F) + \delta \quad \textit{with} \quad \delta \subset \mathit{Ker}(H_{\gamma_0} - \varepsilon_F),$$

where ε_F is the Fermi energy, and

$$\begin{aligned} H_{\gamma_0} = & \left(-\frac{1}{2}\Delta + \rho_0 \star |\cdot|^{-1}\right)\mathbb{1}_2 + U + \\ & + \frac{g'(\rho_0^+)}{2}\left[\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} + \frac{1}{\sqrt{(\rho_0^{\uparrow\uparrow}-\rho_0^{\downarrow\downarrow})^2 + 4|\rho_0^{\uparrow\downarrow}|^2}}\begin{pmatrix}\rho_0^{\uparrow\uparrow}-\rho_0^{\downarrow\downarrow} & 2\rho_0^{\uparrow\downarrow}\\ 2\rho_0^{\downarrow\uparrow} & \rho_0^{\downarrow\downarrow}-\rho_0^{\uparrow\uparrow}\end{pmatrix}\right] \\ & + \frac{g'(\rho_0^-)}{2}\left[\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} - \frac{1}{\sqrt{(\rho_0^{\uparrow\uparrow}-\rho_0^{\downarrow\downarrow})^2 + 4|\rho_0^{\uparrow\downarrow}|^2}}\begin{pmatrix}\rho_0^{\uparrow\uparrow}-\rho_0^{\downarrow\downarrow} & 2\rho_0^{\uparrow\downarrow}\\ 2\rho_0^{\downarrow\uparrow} & \rho_0^{\downarrow\downarrow}-\rho_0^{\uparrow\uparrow}\end{pmatrix}\right]. \end{aligned}$$

It holds $\sigma_{ess}(H_{\gamma_0}) = [0, +\infty[$. Moreover, if $0 < \lambda < Z$, then

- *H_{γ_0} has infinitely many negative eigenvalues*
- *every eigenvector corresponding to such an eigenvalue is exponentially decreasing.*

Conclusion

- We extended the representability result in the non-collinear spin-polarized case.
- We proved the existence of minimizers for SDFT within the LSDA.

Future work

- Prove the existence of minimizers with other xc functionals (GGA,...).
- Numerical questions.

Thank you for your attention