Representability in non-collinear spin-polarized density functional theory

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Non-magnetic Hamiltonian for N-electrons:

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

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

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

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

$$\mathcal{P}_N := \{\Gamma_\Psi, \quad \Psi \in H^1(\mathbb{R}^3), \quad \|\Psi\|_{L^2} = 1\}$$ 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 orthogonal projector.
- $\mathcal{M}_1$ is the set of operators Γ such that $0 \leq \Gamma \leq 1$ and $\mathrm{Tr}(\Gamma) = 1$.

Usually, 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,

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

We will also be interested in the minimization problem

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

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 (here, X represents either $\mathcal{P}_N$ of $\mathcal{M}_N$):

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

$$= \min_{\rho \in \mathcal{I}_N(X)} \left\{ \int_{\mathbb{R}^3} v(\mathbf{r})\rho(\mathbf{r})\ \mathrm{d}^3\mathbf{r} + \min_{\Gamma \in X, \Gamma \to \rho} \left\{ \mathrm{Tr}\left(H_0\Gamma\right) \right\} \right\}$$

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

$$\mathcal{I}_N := \{\rho_\Gamma, \quad \Gamma \in X\}$$ set of representable electronic densities.

Introducing

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

The minimization problem into 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 $\mathcal{I}_N(X)$? N-representability problem

We are looking for the explicit form of

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

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:

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

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 the convex hull of $\mathcal{P}_N$
- Therefore, $\mathcal{I}_N(\mathcal{M}_N) = \rho(\mathcal{M}_N)$ is the convex hull of $\mathcal{I}_N(\mathcal{P}_N) = \rho(\mathcal{P}_N)$
- In particular, $\mathcal{I}_N$ is convex (not obvious)

Theorem (Harriman '81, Lieb '83)

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

Idea of the proof (Harriman).
If $\{\Phi_1, \ldots, \Phi_N\}$ are in H^1 and are L^2-orthonormal, then

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \det\left(\Phi_i(\mathbf{r}_j)\right)_{1 \leq i,j \leq N} \quad \text{satisfies} \quad \Psi \in \bigwedge_{i=1}^{N} H^1(\mathbb{R}^3) \quad \text{and} \quad \|\Psi\|_{L^2} = 1.$$

For this Ψ, we can calculate

$$\rho_\Psi(\mathbf{r}) = \sum_{i=1}^{N} |\Phi_i(\mathbf{r})|^2.$$

Inverse problem: for a given $\rho \in \mathcal{I}_N$, it is enough to take

$$\Phi_k(\mathbf{r}) := \sqrt{\frac{\rho(\mathbf{r})}{N}} \cdot \exp(2\pi i k\, f(\mathbf{r}))$$

where f is carefully chosen to ensure orthogonality.

We want to do the same work for the magnetic case

According to the Dirac equation, the Hamiltonian for N-electrons is

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

It is linear, and acts on the fermionic space $\bigwedge_{i=1}^{N} H^1(\mathbb{R}^3, \mathbb{C}^2)$:

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

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:

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

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:

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

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

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

This time, it holds

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

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:

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

With those notations, the usual electronic density is $\rho := \rho^{\uparrow\uparrow} + \rho^{\downarrow\downarrow}$.
We also introduce the matrix of spin-polarized electronic densities

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

We can then recast the above equation under the form

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

Similarly to standard DFT, we write:

$$E(v,\mathbf{B}) := \min_{\Gamma\in X} \operatorname{Tr}\left(H(v,\mathbf{B})\Gamma\right) = \min_{R\in\mathcal{J}_{\mathbf{N}}(X)} \left\{F(R) + (\mathcal{V}(v,\mathbf{B})|R)\right\}$$

with

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

and

$\mathcal{J}_N(X) := \{R_\Gamma, \Gamma \in X\}$ 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 $\mathcal{J}_N(X)$? N-representability problem

Remarks

- The representability of the R's is the same as the representability of $(\rho, \mathbf{m})$.
- In CDFT, we need the representability of $(\rho, \mathbf{j}_p)$. Lieb gave the answer to this question... 23 days ago!

We only have the answer for mixed states:

Theorem (DG)

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

- The $\sqrt{}$ is in the hermitian matrices sense
- Very beautiful 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, $\mathcal{C}_N$ is a convex set. This is not obvious,... I cannot prove it directly!

Some -useful- ideas of the proof

To check that some matrix R is indeed in $\mathcal{C}_N$, we use the following result.

Lemma

$R := \begin{pmatrix} \rho^\uparrow & \sigma \\ \sigma^* & \rho^\downarrow \end{pmatrix}$ *is in* $\mathcal{C}_N$ *if and only if*

$$\begin{cases} \rho^{\uparrow/\downarrow} \geq 0, \quad \rho^\uparrow \rho^\downarrow - |\sigma|^2 \geq 0, \quad \int \rho^\uparrow + \int \rho^\downarrow = N, \\ \sqrt{\rho^{\uparrow/\downarrow}} \in H^1(\mathbb{R}^3), \quad \sigma, \sqrt{\det} \in W^{1,3/2}(\mathbb{R}^3), \\ |\nabla \sigma|^2 \rho^{-1} \in L^1(\mathbb{R}^3), \\ \left| \nabla \sqrt{\det(R)} \right|^2 \rho^{-1} \in L^1(\mathbb{R}^3). \end{cases}$$

- We will assume this lemma, and the fact that $\mathcal{J}_N(\mathcal{M}_N) \subset \mathcal{C}_N$.
- We now prove the converse, i.e. $\mathcal{C}_N \subset \mathcal{J}_N(\mathcal{M}_N)$.
- Recall that $\mathcal{J}_N(\mathcal{M}_N)$ is convex.

Lemma

If $R = \begin{pmatrix} \rho^\uparrow & \sigma \\ \sigma^* & \rho^\downarrow \end{pmatrix} \in \mathcal{C}_N$ *satisfies* $\det(R) = 0$ *and* $\rho^\uparrow \leq 2\rho^\downarrow$ *a.e., then* R *is pure state representable.*

Proof : similar to the original proof by Harriman.
Introduce $\Phi^\uparrow = \sigma / \sqrt{\rho^\downarrow}$, $\Phi^\downarrow = \sqrt{\rho^\downarrow}$ and

$$\Phi_k(\mathbf{r}) := \frac{1}{\sqrt{N}} \begin{pmatrix} \phi^\uparrow \\ \phi^\downarrow \end{pmatrix} . \exp(2\mathrm{i}\pi k f(\mathbf{r})),$$

where again, f is chosen to ensure orthogonality of $\{\Phi_1, \ldots, \Phi_N\}$.
It is easy to check that $\Gamma = |\Psi\rangle\langle\Psi|$ with $\Psi = (N!)^{1/2} \det(\phi_i(\mathbf{r}_j))$ satisfies $R_\Gamma = R$.

We check that $\Phi_k \in H^1(\mathbb{R}^3, \mathbb{C}^2)$. It is enough to check that $\phi^{\uparrow/\downarrow} \in H^1(\mathbb{R}^3)$.
Let us do for instance $\phi^\uparrow$:

$$|\nabla \phi^\uparrow|^2 = \left| \frac{\sqrt{\rho^\downarrow} \nabla \sigma - \sigma \nabla \sqrt{\rho^\downarrow}}{\rho^\downarrow} \right|^2$$

Then,

$$\begin{aligned}
|\nabla \phi^\uparrow|^2 &= \left| \frac{\sqrt{\rho^\downarrow}\nabla\sigma - \sigma\nabla\sqrt{\rho^\downarrow}}{\rho^\downarrow} \right|^2 && \text{(use } |a+b|^2 \leq 2|a|^2 + 2|b|^2\text{)} \\
&\leq 2\frac{|\nabla\sigma|^2}{\rho^\downarrow} + 2\frac{|\sigma|^2}{(\rho^\downarrow)^2}|\nabla\sqrt{\rho^\downarrow}|^2 && \text{(use } |\sigma|^2 = \rho^\uparrow\rho^\downarrow\text{)} \\
&\leq 2\frac{|\nabla\sigma|^2}{\rho}\frac{\rho^\uparrow+\rho^\downarrow}{\rho^\downarrow} + 2\frac{\rho^\uparrow}{\rho^\downarrow}|\nabla\sqrt{\rho^\downarrow}|^2 && \text{(use } \rho^\uparrow \leq 2\rho^\downarrow\text{)} \\
&\leq 6\frac{|\nabla\sigma|^2}{\rho} + 4|\nabla\sqrt{\rho^\downarrow}|^2 && \text{(use characterization of } \mathcal{C}_N\text{)} \\
&\in L^1(\mathbb{R}^3)
\end{aligned}$$

Remark:

- The condition $\rho^\uparrow \leq 2\rho^\downarrow$ is essential! I do not know whether we can remove this condition, and still ensure pure state representability...
- For the rest of the proof, we use the convexity of $\mathcal{J}_N(\mathcal{M}_N)$.

Lemma

If $R = \begin{pmatrix} \rho^\uparrow & \sigma \\ \sigma^* & \rho^\downarrow \end{pmatrix} \in \mathcal{C}_N$ *satisfies* $\det(R) = 0$ *a.e., then* R *is mixed state representable.*

Proof: space decomposition

Let $\chi \in \mathcal{C}^\infty(\mathbb{R})$ such that $\chi(x) = \begin{cases} 0 & \text{if} \quad x < \frac{1}{2}, \\ 1 & \text{if} \quad x > 2. \end{cases}$.

Introduce

$$\tilde{R}_1 = \chi^2\left(\frac{\rho^\uparrow}{\rho^\downarrow}\right) R \quad \text{and} \quad \tilde{R}_2 = \left(1 - \chi^2\left(\frac{\rho^\uparrow}{\rho^\downarrow}\right)\right) R.$$

Let $t = N^{-1} \int \mathrm{tr}_{\mathbb{C}^2}(\tilde{R}_1(\mathbf{x}))\, \mathrm{d}^3\mathbf{x} \in [0,1]$, and finally $R_1 = t^{-1}\tilde{R}_1$ and $R_2 = (1-t)^{-1}\tilde{R}_2$. Then,

$$R = tR_1 + (1-t)R_2,$$

and R_1, R_2 satisfy the hypothesis of the previous lemma, so are pure-state representable.

$$R_1 \in \mathcal{J}_N(\mathcal{M}_N), \quad R_2 \in \mathcal{J}_N(\mathcal{M}_N) \quad \text{and} \quad \mathcal{J}_N(\mathcal{M}_N) \text{ is convex} \Longrightarrow R \in \mathcal{J}_N(\mathcal{M}_N)$$

Lemma

If $R = \begin{pmatrix} \rho^\uparrow & \sigma \\ \sigma^* & \rho^\downarrow \end{pmatrix} \in \mathcal{C}_N$*, then* R *is mixed state representable.*

Proof: rank-1 decomposition

Let us note

$$\sqrt{R} = \begin{pmatrix} r^\uparrow & s \\ s^* & r^\downarrow \end{pmatrix} \quad \text{so that} \quad R = \begin{pmatrix} (r^\uparrow)^2 + |s|^2 & s(r^\uparrow + r^\downarrow) \\ s^*(r^\uparrow + r^\downarrow) & (r^\downarrow)^2 + |s|^2 \end{pmatrix}$$

We introduce this time

$$\tilde{R}_1 = \begin{pmatrix} (r^\uparrow)^2 & sr^\uparrow \\ s^* r^\uparrow & |s|^2 \end{pmatrix} \quad \text{and} \quad \tilde{R}_2 = \begin{pmatrix} |s|^2 & sr^\downarrow \\ s^* r^\downarrow & (r^\downarrow)^2 \end{pmatrix}.$$

Let $t = N^{-1} \int \mathrm{tr}_{\mathbb{C}^2}(\tilde{R}_1(\mathbf{x}))\, \mathrm{d}^3\mathbf{x} \in [0,1]$, and finally $R_1 = t^{-1}\tilde{R}_1$ and $R_2 = (1-t)^{-1}\tilde{R}_2$. Then,

$$R = tR_1 + (1-t)R_2.$$

Because $R \in \mathcal{C}_N$, then $r^\uparrow, r^\downarrow$ and s are in $H^1(\mathbb{R}^3)$. Moreover, $\det(R_{1,2}) = 0$ a.e., so that $R_{1,2}$ satisfy the conditions of the previous lemma, and therefore are representable.
We conclude as before.

One application of this result

In the polarized case, we write

$$F(R) := \min_{\Gamma \in X, \Gamma \to R} \mathrm{Tr}\,(H_0 \Gamma) = E_K^{HF}(R) + \int_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho(\mathbf{x})\rho(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} \mathrm{d}^3\mathbf{x}\, \mathrm{d}^3\mathbf{y} + E_{xc}(R)$$

and find approximations for $E_{xc}(R)$.

Local approximation: E_{xc} is a local functional.
In particular, if $U(\mathbf{r})$ is a field of unitary matrices, it holds

$$E_{xc}(R) = E_{xc}(U^* R U).$$

Therefore,

$$E_{xc}(R) = \tilde{E}_{xc}(\rho^+, \rho^-)$$

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

What is the functional space for (ρ^+, ρ^-) ?

Lemma

If $R \in \mathcal{J}_N(\mathcal{M}_N)$, then $\sqrt{\rho^{+/-}} \in H^1(\mathbb{R}^3)$.

Proof

- $\sqrt{\rho^{+/-}}$ are the eigenvalues of $\sqrt{R} := \begin{pmatrix} r^\uparrow & s \\ s^* & r^\downarrow \end{pmatrix} \in \mathcal{M}_{2\times 2}\left(H^1(\mathbb{R}^3)\right)$.
- $\sqrt{\rho^{+/-}}$ are the roots of $x \mapsto x^2 - (r^\uparrow + r^\downarrow)x + (r^\uparrow r^\downarrow - |s|^2)$.
- The discriminant is $\Delta := (r^\uparrow + r^\downarrow)^2 - 4(r^\uparrow r^\downarrow - |s|^2) = (r^\uparrow - r^\downarrow)^2 + 4|s|^2$
- The functional $\|\nabla\sqrt{\cdot}\|_{L^2}^2$ is convex, so $\sqrt{\Delta} \in H^1(\mathbb{R}^3)$.
- Finally, $\rho^{+/-} := \dfrac{r^\uparrow + r^\downarrow \pm \sqrt{\Delta}}{2} \in H^1(\mathbb{R}^3)$.

Conclusion

- We have extended the representability result in the non-collinear spin-polarized case
- The result only holds in the mixed state setting

Future work

- With the recent work of Lieb in CDFT, we can probably find the representability conditions in CSDFT: representability of $(\rho, \mathbf{j}, \mathbf{m})$
- Study mathematically some models used in physics (well-posedness of LSDA...)
- Study some non-collinear spin effects (magnons, frustrated solid)

THANK YOU FOR YOUR ATTENTION