Pure-state N-representability in current-spin-density functional theory

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The set of admissible N-electron wave-functions (wave functions with finite kinetic energy) is the fermionic space

$$\mathcal{W}_N := \left\{ \Psi \in \bigwedge_{i=1}^{N} L^2(\mathbb{R}^3 \times \{\uparrow,\downarrow\}, \mathbb{C}),\ \|\nabla \Psi\|_{L^2} < \infty,\ \|\Psi\|_{L^2} = 1 \right\},$$

where $L^2(\mathbb{R}^3 \times \{\uparrow,\downarrow\}) = \left\{ \Phi = (\phi^\uparrow, \phi^\downarrow)^T,\ \|\Phi\|_{L^2}^2 := \int_{\mathbb{R}^3} |\phi^\uparrow|^2 + |\phi^\downarrow|^2 < \infty \right\}$.

For $\Psi \in \mathcal{W}_N$, the electronic density is

$$\rho_\Psi(\mathbf{r}) := N \sum_{(s_1,\cdots,s_N)\in\{\uparrow,\downarrow\}^N} \int_{\mathbb{R}^{3(N-1)}} |\Psi(\mathbf{r}, s_1, \mathbf{r}_2, s_2, \cdots, \mathbf{r}_n, s_N)|^2 \, \mathrm{d}^3\mathbf{r}_2 \cdots \mathrm{d}^3\mathbf{r}_N.$$

The N-representability problem (for pure-states) is

Is there a characterization of the set $I_N := \{\rho_\Psi, \Psi \in \mathcal{W}_N\}$?

Theorem (Gilbert[1], Harriman[2], Lieb[3])

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

Together with the constrained search by Levy[4]and Lieb[3],

$$E_N^0(v) := \inf_{\Psi \in \mathcal{W}_N} \langle \Psi | H(v) | \psi \rangle = \inf_{\rho \in \mathcal{I}_N} \left\{ F_{LL}(\rho) + \int_{\mathbb{R}^3} v\rho \right\}.$$

The first problem is linear, but very high-dimensional (curse of dimensionality), the second problem is low-dimensional (but with an unknown functional).

[1] T.L. Gilbert. Phys. Rev. B, 502, 1975.
[2] J.E. Harriman. Phys. Rev. A, 24,1981.
[3] E.H. Lieb. Int. J. Quantum Chem., 24, 1983.
[4] M. Levy, Proc. Natl. Acad. Sci. USA 76, 1979.

The N-representability problem with a magnetic field.

We consider a system under a magnetic vector potential $\mathbf{A}$. The Schrödinger-Pauli Hamiltonian reads in atomic unit

$$H(v, \mathbf{A}) := \sum_{k=1}^{N} \left(\frac{1}{2}(-\mathrm{i}\nabla + \mathbf{A}(\mathbf{r}_k))^2 + v(\mathbf{r}_k) \right) \mathbb{I}_2 - \frac{1}{2} \sum_{k=1}^{N} \mathbf{B}(\mathbf{r}_k) \cdot \sigma_k + \sum_{1 \le k < l \le N} \frac{1}{|\mathbf{r}_k - \mathbf{r}_l|} \mathbb{I}_2,$$

and it holds

$$\langle \Psi | H(v, \mathbf{A}) | \Psi \rangle = \langle \Psi | H(0, \mathbf{0}) | \Psi \rangle + \int_{\mathbb{R}^3} \mathrm{tr}_{\mathbb{C}_2} \left[U(v, \mathbf{A}) R_\Psi \right] + \int_{\mathbb{R}^3} \mathbf{A} \cdot \mathbf{j}_\Psi,$$

where

$$U(v, \mathbf{A}) := \frac{1}{2} \begin{pmatrix} 2v - B_z + |\mathbf{A}|^2 & -B_x + \mathrm{i} B_y \\ -B_x - \mathrm{i} B_y & 2v + B_z + |\mathbf{A}|^2 \end{pmatrix}.$$

Here, $\mathbf{B} = \mathbf{curl}(\mathbf{A})$ is the magnetic field.

We introduced the following Ψ-dependent quantities:

- The spin-polarized density 2×2 matrix R_Ψ, defined by

$$R_\Psi = \begin{pmatrix} \rho_\Psi^{\uparrow\uparrow} & \rho_\Psi^{\uparrow\downarrow} \\ \rho_\Psi^{\downarrow\uparrow} & \rho_\Psi^{\downarrow\downarrow} \end{pmatrix}$$

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

$$\rho_\Psi^{\alpha\beta}(\mathbf{r}) := N \sum_{\vec{s} \in \{\uparrow,\downarrow\}^{N-1}} \int_{\mathbb{R}^{3(N-1)}} \overline{\Psi(\mathbf{r}, \alpha, \vec{\mathbf{z}}, \vec{s})} \Psi(\mathbf{r}, \beta, \vec{\mathbf{z}}, \vec{s}) \, \mathrm{d}^{3(N-1)} \vec{\mathbf{z}}.$$

Note that R_Ψ is an hermitian function-valued 2×2 matrix, and it holds

$$\mathrm{tr}_{\mathbb{C}^2}[U(v, \mathbf{A}) R_\Psi] = \left(v + \frac{|\mathbf{A}|^2}{2} \right) \rho - \frac{1}{2} \mathbf{B} \cdot \mathbf{m},$$

where ρ is the total electronic density, and $\mathbf{m}$ is the spin angular momentum density.
Remark: R contains exactly the same information as the pair $(\rho, \mathbf{m})$.

- The paramagnetic current $\mathbf{j}_\Psi$ is the vector-valued function

$$\mathbf{j}(\mathbf{r}) = \mathrm{Im} \left(N \sum_{\vec{s} \in \{\uparrow,\downarrow\}^{(N)}} \int_{\mathbb{R}^{3(N-1)}} \overline{\Psi(\mathbf{r}, \vec{\mathbf{z}}, \vec{s})} \, \nabla_{\mathbf{r}'} \Psi(\mathbf{r}', \vec{\mathbf{z}}, \vec{s}) \Big|_{\mathbf{r}'=\mathbf{r}} \mathrm{d}^{3(N-1)} \vec{\mathbf{z}} \right).$$

We apply the constrained-search, and obtain

$$E_N^0(v, \mathbf{A}) = \inf_{\Psi \in \mathcal{W}_N} \langle \Psi | H(v, \mathbf{A}) | \Psi = \inf_{(R, \mathbf{j}) \in \mathcal{K}_N} \left\{ F(R, \mathbf{j}) + \int_{\mathbb{R}^3} \mathrm{tr}_{\mathbb{C}^2} \left[U(v, \mathbf{A}) R \right] + \mathbf{A} \cdot \mathbf{j} \right\},$$

which leads to the current-spin-density functional theory (CSDFT).

The N-representability problem (for pure-state) is

Is there a characterization of the CSDFT-set $\mathcal{K}_N := \{(R_\Psi, \mathbf{j}_\Psi),\ \Psi \in \mathcal{W}_N\}$?

Remark:

- If we neglect the spin-effects (*i.e.* the Zeeman term $\mathbf{B} \cdot \mathbf{m}$), this energy depends only on the pair $(\rho, \mathbf{j})$. This leads to the current-DFT (CDFT).
- If we neglect the orbital term (*i.e.* $\mathbf{A} \cdot \mathbf{j}$), this energy depends only on R. This leads to the non-collinear spin-DFT (SDFT).

$\Longrightarrow$ Is there a characterization of the SDFT-set $\mathcal{J}_N := \{R_\Psi,\ \Psi \in \mathcal{W}_N\}$?

Slater determinants:
A special case of wave functions are the Slater determinants of N orthonormal functions $\left\{\Phi_k = (\phi_k^\uparrow, \phi_k^\downarrow)^T\right\}_{1\le k\le N}$:

$$\mathscr{S}[\Phi_1, \cdots, \Phi_N] := \frac{1}{\sqrt{N!}} \det\left(\Phi_i(\mathbf{r}_j)\right)_{1\le i,j\le N}.$$

For such a wave-function, the previous quantities have a very special form, namely

$$R = \sum_{k=1}^N \begin{pmatrix} |\phi_k^\uparrow|^2 & \phi_k^\uparrow \overline{\phi_k^\downarrow} \\ \overline{\phi_k^\uparrow}\phi_k^\downarrow & |\phi_k^\downarrow|^2 \end{pmatrix}, \quad \rho = \sum_{k=1}^N |\phi_k^\uparrow|^2 + |\phi_k^\downarrow|^2 \quad \text{and} \quad \mathbf{j} = \sum_{k=1}^N \mathrm{Im}\left(\overline{\phi_k^\uparrow}\nabla\phi_k^\uparrow + \overline{\phi_k^\downarrow}\nabla\phi_k^\downarrow\right)$$

Mixed-states:
It is possible to extend the notion of R, ρ and $\mathbf{j}$ to mixed-states. We will say that a spin-density matrix R is mixed-state representable (and similarly for ρ and $\mathbf{j}$) if R can be written as a convex combination of pure-state representable spin-density matrices:

$$R = \sum_{k=1}^\infty \lambda_k R_k, \quad 0 \le \lambda_k \le 1, \quad \sum_{k=1}^\infty \lambda_k = 1, \quad \text{and} \quad R_k \quad \text{pure-state representable.}$$

Results (previous and new).

Representability for SDFT (in the pure-state case, and in the mixed-state case):

Theorem (DG 2013[1])

- *A spin-density matrix R is mixed-state representable iff*

$$R \in \mathcal{J}_N := \left\{ R \in \mathcal{M}_{2\times 2}(L^1(\mathbb{R}^3)),\ R \geq 0,\ \int_{\mathbb{R}^3} \mathrm{tr}_{\mathbb{C}^2}[R] = N,\ \sqrt{R} \in \mathcal{M}_{2\times 2}(H^1(\mathbb{R}^3, \mathbb{C})) \right\}.$$

If $N \geq 2$, it is also pure-state representable (by a Slater determinant).

- ***Case*** $N = 1$
A spin-density matrix R is (pure-state) representable by a single orbital iff

$$R \in \mathcal{J}_1 \quad \text{and} \quad \det R \equiv 0.$$

- The $\sqrt{}$ is in the hermitian matrices sense
- It is a natural extension of the previous result for ρ:

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

[1] D. Gontier. Phys. Rev. Lett. 111, 2013.

In the Local Spin-Density Approximation (LSDA) introduced by von Barth and Hedin[1], we write

$$E_{\mathrm{xc}}(R) \approx E_{\mathrm{xc}}^{\mathrm{LSDA}}(\rho^{+}, \rho^{-}) := \frac{1}{2}\left[E_{\mathrm{xc}}^{\mathrm{LDA}}(2\rho^{+}) + E_{\mathrm{xc}}^{\mathrm{LDA}}(2\rho^{-})\right] \quad (1)$$

where $\rho^{+/-}$ are the two eigenvalues of the 2×2 matrix R, and $E_{\mathrm{xc}}^{\mathrm{LDA}}$ is the standard exchange-correlation functional in the non-polarized case.

Lemma (DG 2013)

If $R \in \mathcal{J}_N$, then its eigenvalues $\rho^{+,-}$ satisfy

$$\rho^{+,-} \in L^1(\mathbb{R}^3), \quad \rho^{+,-} \geq 0, \quad \sqrt{\rho^{+/-}} \in H^1(\mathbb{R}^3).$$

(the converse is false).

Remark: $E_{\mathrm{xc}}^{\mathrm{LSDA}}$ is well-defined if $E_{\mathrm{xc}}^{\mathrm{LDA}}$ is well-defined.

[1] U. von Barth and L. Hedin. J. Phys. C 5, 1972.

Previous results for representability in CDFT

Theorem (Tellgren, Kvall, Helgaker, 2014[1])

The pair $(\rho, \mathbf{j})$ *is mixed-state representable whenever*

$$\rho \in \mathcal{I}_N, \quad \frac{|\mathbf{j}|^2}{\rho} \in L^1(\mathbb{R}^3) \quad \textit{and} \quad (1 + |\cdot|^2)\rho|\nabla(\rho^{-1}\mathbf{j})|^2 \in L^1(\mathbb{R}^3) \quad \textit{(mild condition).}$$

Theorem (Lieb, Schrader, 2013[2])

The pair $(\rho, \mathbf{j})$ *is pure-state representable (by a Slater determinant) whenever*

$$\rho \in \mathcal{I}_N, \quad \frac{|\mathbf{j}|^2}{\rho} \in L^1(\mathbb{R}^3) \quad \textit{with} \quad N \geq 4 \textit{ and other mild conditions}^3.$$

Remark: The conditions $\rho \in \mathcal{I}_N$ and $|\mathbf{j}|^2/\rho \in L^1(\mathbb{R}^3)$ are also necessary conditions.

[1] E.I. Tellgren, S. Kvaal, and T. Helgaker. Phys. Rev. A, 89, 2014.

[2] E.H. Lieb and R. Schrader. Phys. Rev. A, 88, 2013.

[3] Namely, if $\mathbf{w} = \mathbf{curl}(\mathbf{j}/\rho)$,

$$\sup_{\mathbf{r}\in\mathbb{R}^3} (1 + (r_1)^2)^{(1+\delta)/2}(1 + (r_2)^2)^{(1+\delta)/2}(1 + (r_3)^2)^{(1+\delta)/2} (|\mathbf{w}(\mathbf{r})| + |\nabla \mathbf{w}(\mathbf{r})|) < \infty$$

Representability for CSDFT, for $N = 1$

Lemma (DG)

A necessary condition for a pair $(R, \mathbf{j})$ to be pure-state representable by a single orbital (having smooth enough global phases) is[1]

$$R \in \mathcal{J}_1 \quad \textit{with} \quad \det(R) \equiv 0 \quad \textit{and} \quad \textbf{\textit{curl}} \left(\frac{\mathbf{j}}{\rho} - \frac{\mathrm{Im}\,(\overline{\rho^{\uparrow\downarrow}} \nabla \rho^{\uparrow\downarrow})}{\rho \rho^{\downarrow\downarrow}} \right) = \mathbf{0}$$

Remark: We recover the traditional curl-free condition in the unpolarized case, which amounts to setting $\rho^{\uparrow\downarrow} = 0$: a necessary condition for a pair $(\rho, \mathbf{j})$ to be pure-state representable by a single orbital (having a smooth enough global phase) is

$$\rho \in \mathcal{I}_1 \quad \text{and} \quad \mathbf{curl} \left(\frac{\mathbf{j}}{\rho} \right) = \mathbf{0}.$$

[1] Recall that

$$R = \begin{pmatrix} \rho^{\uparrow\uparrow} & \rho^{\uparrow\downarrow} \\ \rho^{\downarrow\uparrow} & \rho^{\downarrow\downarrow} \end{pmatrix}$$

Representability for CSDFT, for $N \geq 12$

Theorem (DG)

A pair $(R, \mathbf{j})$ is pure-state representable (by a Slater determinant) whenever

$$R \in \mathcal{J}_N, \quad \frac{|\mathbf{j}|^2}{\rho} \in L^1(\mathbb{R}^3), \quad \textit{with} \quad N \geq 12 \textit{ and the same previous mild conditions}$$

Remark 1: To prove the result, we decompose R into 3 well-behaved matrices $R = R_1 + R_2 + R_3$, and we apply on each R_k the Lieb and Schrader result (which holds for $N \geq 4$). Hence the result for $N \geq 3 \times 4 = 12$.

Remark 2: We believe that the result also holds for some $N < 12$ but we do not have a proof of this fact.

Corollary

A pair $(R, \mathbf{j})$ is mixed-state representable whenever

$$R \in \mathcal{J}_N, \quad \frac{|\mathbf{j}|^2}{\rho} \in L^1(\mathbb{R}^3), \quad \textit{with} \quad N \in \mathbb{N}^* \textit{ and the same previous mild conditions}$$

Summary:

- We gave necessary and sufficient conditions for pure-state N-representability in SDFT.
- We gave sufficient conditions for pure-state N-representability in CSDFT when $N \geq 12$.
- When $N = 1$, there is a non-trivial interplay between the spin-density R and the paramagnetic current $\mathbf{j}$, namely

$$\mathbf{curl}\left(\frac{\mathbf{j}}{\rho} - \frac{\mathrm{Im}\,(\overline{\rho^{\uparrow\downarrow}}\nabla\rho^{\uparrow\downarrow})}{\rho\rho^{\downarrow\downarrow}}\right) = \mathbf{0}.$$

Comments and future work:

- Our results use the so-called Lazarev-Lieb orthogonalization process[1]. In particular, we were not able to bound the kinetic energy of the representing Slater determinants.
- We leave the question $N < 12$ open.

Thank you for your attention!

[1] E.H. Lieb and O. Lazarev. Indiana Univ. Math. Jour., 2014.