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A repulsive multi-marginal transport model in quantum chemistry

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joined work with:

G.Buttazzo (Pisa), T. Champion (IMATH), L De Pascale (Firenze),

Papers in collaboration with Gianni:

- Integral representation and relaxation of convex local functionals on $BV(\Omega)$.
  Ann. Scuola Norm. Sup. Pisa Cl. Sci. (4) 20 (1993),
  (written during a 2 monthes invitation at SISSA in 1990)
- (with G.Alberti) The calibration method for the Mumford-Shah functional.
  C.R. Acad. Sci. Paris Sér. I Math (1999)
- (with G.Alberti) The calibration method for the Mumford-Shah functional and free-discontinuity problems
  Calc. Var. Partial Differential Equations (2003)

An asymptotic model in quantum chemistry, (P. Gori-Giorgi)

In the framework of *Strongly Correlated Electrons Density Functional Theory* (SCE-DFT), a very challenging issue is the asymptotic behavior as $\varepsilon \to 0$ of the infimum problem

$$\inf\{\varepsilon T(\rho) + C(\rho) - U(\rho) \ : \ \rho \in \mathcal{P}\} \qquad (1_\varepsilon)$$

where the parameter ε stands for the Planck constant and

- $\rho \in \mathcal{P}$ is a probability over $\mathbb{R}^d$ associated with the random distribution of N-electrons (given by $|\psi|^2$, $\psi \in L^2((\mathbb{R}^d)^N)$)
- $T(\rho)$ is the kinetic energy

$$T(\rho) = \int_{\mathbb{R}^d} |\nabla\sqrt{\rho}|^2 \, dx;$$

- $C(\rho)$ describes the electron-electron repulsive interaction;
- $U(\rho)$ is the potential term (created by M nuclei)

$$U(\rho) = \int_{\mathbb{R}^d} V(x)\rho \, dx;$$

The case $N = 1$, $V(x) = \frac{Z}{|x|}$ and $d = 3$

Then $C(\rho) \equiv 0$ and setting $\psi = \sqrt{\rho}$, (1_ε) becomes:

$$\inf\left\{ \int \left(\varepsilon\, |\nabla \psi|^2 - Z\frac{\psi^2}{|x|} \right) \ : \ \int \psi^2 = 1 \right\}$$

The negative minimum above is reached for ψ_ε solving

$$-\varepsilon \Delta \psi^\varepsilon - \frac{Z}{|x|}\psi^\varepsilon = \lambda_1^\varepsilon\, \psi^\varepsilon \quad \text{in } \mathbb{R}^3$$

Then the solution to (1_ε) reads $\rho_\varepsilon = \varepsilon^{-3}\rho_1(x/\varepsilon)$ where:

$$\rho_1(x) = \frac{Z^3}{8\pi}\exp^{-Z|x|} \text{ (Lieb)} \quad , \quad \lambda_1^\varepsilon = -\frac{Z^2}{4\varepsilon} \ = \min(1_\varepsilon).$$

Therefore

$$\rho_\varepsilon \overset{*}{\rightharpoonup} \delta_{X=0} \quad , \quad \varepsilon \ \min(1_\varepsilon) \to -\frac{Z^2}{4}$$

The case $C(\rho) \equiv 0$ and V associated with M-nuclei

Let $X_1, X_2, \ldots, X_M$ the position of M nuclei in $\mathbb{R}^3$ with charges $Z_1, Z_2, \ldots, Z_M$. The Coulomb potential reads:

$$V(x) = \sum_{k=1}^{M} \frac{Z_k}{|x - X_k|} \,.$$

By [bbcd18], the $\Gamma-$ limit of quadratic energies is local and:

$$\rho^\varepsilon \overset{*}{\rightharpoonup} \sum_{1}^{M} \alpha_k \delta_{X_k} \quad , \quad \varepsilon \min(1_\varepsilon) \sim -\frac{1}{4} \sum_k \alpha_k Z_k^2$$

Consequence: Minimizing with respect to the α_k's subject to $\sum \alpha_k = 1$, we see that ρ_ε concentrates on the nuclei with maximal mass (not physically reasonable !)

[bbcd18] Dissociating limit in Density Functional Theory with Coulomb optimal transport cost in arXiv:1811.12085

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N -electrons (repulsive) interaction

It can be interpreted as a multi-marginal transport cost:

$$C(\rho)(= C_N(\rho)) = \inf \left\{ \int_{\mathbb{R}^{Nd}} c(x_1 \ldots, x_N)\, dP \ : \ P \in \Pi(\rho) \right\}$$

when

$$c(x_1 \ldots, x_N) = \sum_{1 \le i < j \le N} \frac{1}{|x_i - x_j|}$$

and $\Pi(\rho)$ is the family of transport plans

$$\Pi(\rho) = \left\{ P \in \mathcal{P}(\mathbb{R}^{Nd}) \ : \ \pi_i^{\#} P = \rho \text{ for all } i = 1, \ldots, N \right\}$$

being π_i the projections from $\mathbb{R}^{Nd}$ on the i-th factor $\mathbb{R}^d$ and $\pi_i^{\#}$ the push-forward operator

$$\pi_i^{\#} P(E) = P\left(\pi_i^{-1}(E)\right) \qquad \text{for all Borel sets } E \subset \mathbb{R}^d.$$

Basic facts about $C(\rho)$

- $C : \rho \in \mathcal{P}(\mathbb{R}^d) \to]0, +\infty]$ is convex weakly* l.s.c.
  But $\rho_n \overset{*}{\rightharpoonup} \rho$, $\sup_n C(\rho_n) < +\infty \not\Rightarrow \rho \in \mathcal{P}$
- $C(\rho) < +\infty$ whenever $\rho \in L^p(\mathbb{R}^d)$ for some $p > 1$, in particular if $T(\rho) < +\infty$ (since $\sqrt{\rho} \in W^{1,2} \Rightarrow \rho \in L^3$))
- $C(\rho) = +\infty$ if it exists x_0 such that $\rho(\{x_0\}) > \frac{1}{N}$.
- If $x_1, x_2, \ldots x_N$ are distincts, then ($P = \delta_{x_1} \otimes \delta_{x_2} \cdots \otimes \delta_{x_N}$)

$$C\left(\frac{1}{N}(\delta_{x_1} + \delta_{x_2} + \ldots \delta_{x_N})\right) = c(x_1, \ldots, x_N)$$

- For every x, there exists $\rho_n \overset{*}{\rightharpoonup} \frac{\delta_x}{N}$ and $C(\rho_n) \to 0$.
  (apply above with $x_1 = x$ and $\|x_i\| \to \infty$ for $2 \leq i \leq N$)
- $\frac{1}{N^2} C_N(\rho) \to C_\infty(\rho) := \int_{(\mathbb{R}^d)^2} \frac{\rho \otimes \rho}{|x-y|}$ as $N \to \infty$ (Choquet 1958)

- The asymptotic in (1_ε) in presence of the N-interactions term $C(\rho)(= C_N(\rho))$ is known for $N = 2$. In [bbcd18], the $\Gamma-$ limit of energies is derived:

$$\rho^\varepsilon \stackrel{*}{\rightharpoonup} \sum_1^M \alpha_k \delta_{x_k} \quad , \quad \varepsilon \min(1_\varepsilon) \sim \sum_k \alpha_k \, g(\alpha_k, Z_k)$$

where g is a suitable convex-concave function (not explicit !)

- The case $N > 2$ is open (needs to relax $C(\rho)$)
- The situation gets much simpler if one assume that

$$V \in C_0(\mathbb{R}^d).$$

Then $\inf(1_\varepsilon)$ remains finite and by $\Gamma-$convergence, we get:

$$\inf(1_\varepsilon) \to \inf \left\{ C(\rho) - \int V \, d\rho \ : \ \rho \in \mathcal{P} \right\}$$

Main issues for: $\inf \left\{ C(\rho) - \int V \, d\rho \ : \ \rho \in \mathcal{P} \right\}$

Remark: we do not assume that V is confining (that is $\lim_{|x|\to\infty} V(x) = -\infty$)

- Existence of an optimal probability ρ ? (non existence means "ionization", [J.P. Solovej,Ann. of Math (2003)
- How to characterize the weak* limit of minimizing sequences in case of non existence ?
- Are they limit points ρ with fractional mass $\|\rho\| = \frac{k}{N}$? (k electrons among N remain at finite distance)

Outline

1. A non existence result.
2. Relaxed cost on $\mathcal{P}^-$ (sub-probabilities)
3. Dual formulation and Kantorovich potential
4. Mass quantization of optimal measures
5. Open problems and perspectives

T. Champion, G. Buttazzo, L. De Pascale, GB: Relaxed multi-marginal costs and quantization effects
(https://hal-univ-tln.archives-ouvertes.fr/hal-02352469)

I- A case of non existence

For every $V \in C_0(\mathbb{R}^d)$, we denote:

$$\alpha_N(V) = \inf \left\{ C_N(\rho) - \int V \, d\rho \ : \ \rho \in \mathcal{P} \right\}$$

Existence of an optimal probability is standard if V is a *confining* potential ($\lim_{|x| \to \infty} V(x) = -\infty$). The situation changes drastically when V is bounded from below.

Note that if $V \in C_0$, it is not restrictive to assume that $V \geq 0$.

Lemma 1 $\alpha_N(V) = \alpha_N(V^+) \leq -\frac{1}{N} \sup V^+$. In particular $\alpha_N(V) < 0$ for any non zero $V \geq 0$.

Proof: The first equality is deduced by duality techniques. For the second inequality, choose x_0 s.t. $V^+(x_0) = \max V^+$ and $\rho_n \stackrel{*}{\rightharpoonup} \frac{1}{N} \delta_{x_0}$ s.t. $C(\rho_n) \to 0$.

Proposition 2 Let $V \in C_0(\mathbb{R}^d; \mathbb{R}^+)$ with spt $V \subset B_R$. Then the infimum $\alpha_N(V)$ is not attained on $\mathcal{P}$ whenever

$$\max V \le \frac{N(N-1)}{2R}$$

Proof: In a first step we show that if $\rho \in \mathcal{P}$ is optimal, then spt $\rho \subset \overline{B_R}$. As a consequence the optimal transport plan associated with ρ is supported in $(\overline{B_R})^N$ where $c(x) \ge \frac{N(N-1)}{2}$. Thus, if $\max V \le \frac{N(N-1)}{2R}$, we find a contradiction with Lemma 1:

$$\alpha_N(V) = C(\rho) - \int V \, d\rho \ge \frac{N(N-1)}{2R} - \max V \ge 0$$

□

Consequence: existence of a loss of mass at infinity !

2- Relaxed cost on $\mathcal{P}^-$

For every $\rho \in \mathcal{P}^-$ (with mass $\|\rho\|$ in $[0,1]$), we need to characterize

$$\overline{C}(\rho) = \inf \left\{ \liminf_n C(\rho_n) \ : \ \rho_n \overset{*}{\rightharpoonup} \rho, \ \rho_n \in \mathcal{P} \right\}$$

We already know that $\overline{C}(\rho) = C(\rho)$ if $\rho \in \mathcal{P}$. A first guess would be that $\overline{C}(\rho) = C_N(\rho)$ for every $\rho \in \mathcal{P}^-$, being $C_N(\mu)$ the 1-homogneous extension:

$$\mathcal{C}_N(\mu) := \|\mu\| C\left(\frac{\mu}{\|\mu\|}\right) = \inf \left\{ \int_{\mathbb{R}^{Nd}} c(x_1 \dots, x_N)\, dP \ : \ P \in \Pi(\mu) \right\}$$

Indeed $\overline{C}(\rho) \le \mathcal{C}_N(\rho)$ but no converse inequality since:

$$\overline{C}(\rho) = 0 \iff \|\rho\| \ \le \ \frac{1}{N} \, .$$

Stratification formula for $\overline{C}(\rho)$

Set $\mathcal{C}_k(\rho) := \|\rho\| C_k(\frac{\rho}{\|\rho|}$ to denote the homogeneous version of the k-points interaction and $\mathcal{C}_1 \equiv 0$.

Theorem 3 For every $\rho \in \mathcal{P}^-$ it holds

$$\overline{C}(\rho) = \inf \left\{ \sum_{k=1}^{N} \mathcal{C}_k(\rho_k) \ : \ \rho_k \in \mathcal{P}^-, \ \sum_{k=1}^{N} \frac{k}{N} \rho_k = \rho, \ \sum_{k=1}^{N} \|\rho_k\| \leq 1 \right\}.$$

- Infimum achieved if $0 < \overline{C}(\rho) < +\infty$ and $\sum_{k=1}^{N} \|\rho_k\| = 1$.
- Case of fractional masses: a useful inequality (by taking $\rho_k = \frac{N}{k}\rho$ and $\rho_l = 0$ if $l \neq k$)

$$\|\rho\| = \frac{k}{N} \ \Rightarrow \ \overline{C}(\rho) \leq \frac{N}{k} \mathcal{C}_k(\rho)$$

- If $\frac{k}{N} < \|\rho\| < \frac{k+1}{N}$, it seems numerically that only k and $k+1$ are involved in an optimal decomposition ?? (may be untrue !)

Sketch of the proof

- In a first step, we associate to $\rho \in \mathcal{P}^-$ a probalility $\tilde{\rho}$ on $X = \mathbb{R}^d \cup \{\omega\}$ the the Alexandrov's compactification of $\mathbb{R}^d$ defined by $\tilde{\rho} = \rho + (1 - \|\rho\|)\delta_\omega$. Then, if $\tilde{c}$ denotes the natural l.s.c. extension of the Coulomb cost to X^N,

$$\overline{C}(\rho) = \tilde{C}(\tilde{\rho}) := \min \left\{ \int_{X^N} \tilde{c}\, d\tilde{P} \ :\ \tilde{P} \in \mathcal{P}(X^N),\ \tilde{P} \in \Pi(\tilde{\rho}) \right\}.$$

- Let $\tilde{P} \in \mathcal{P}(X^N)$ be an optimal symmetric plan for $\tilde{C}(\tilde{\rho})$ and set

$$\tilde{\mu}_k := \pi_1^\# \left(\tilde{P} \llcorner \left(\mathbb{R}^{kd} \times \{\omega\}^{N-k} \right) \right)$$

Then the stratification formula holds with ρ_k given by

$$\rho_k := \binom{N}{k} \tilde{\mu}_k \llcorner \mathbb{R}^d$$

3- Dual formulation and Kantorovich potential

Duality: Let $\rho \in \mathcal{P}^-(\mathbb{R}^d)$ and $\tilde{\rho} = \rho + (1 - \|\rho\|)\delta_\omega \in \mathcal{P}(X)$. It is natural to use the duality between $\mathcal{M}(X)$ and $C_0(\mathbb{R}^d) \oplus \mathbb{R}$ the set of continuous potentials u **with a constant value** u_∞ at infinity:

$$< u, \tilde{\rho} >= \int_X u \, d\tilde{\rho} = \int_{\mathbb{R}^d} u \, d\rho + (1 - \|\rho\|) u_\infty \ .$$

Theorem 4 Let $\mathcal{A}$ be the class of admissible functions defined by

$$\mathcal{A} = \left\{ u \in C_0 \oplus \mathbb{R} \ : \ \frac{1}{N} \sum_{i=1}^{N} u(x_i) \leq c(x_1, \ldots, x_N) \quad \forall x_i \in (\mathbb{R}^d)^N \right\}.$$

Then $\quad \overline{C}(\rho) = \sup \left\{ \int u \, d\rho + (1 - \|\rho\|) u_\infty \ : \ u \in \mathcal{A} \right\}$.

For practical computations

In Theorem 4, the class $\mathcal{A}$ of admissible u can be relaxed to

$$\mathcal{B} := \left\{ u \in \mathcal{S}(X) \ : \ \frac{1}{N}\sum_{i=1}^{N} u(x_i) \le c(x_1,\dots,x_N) \quad \tilde{\rho}^{N\otimes} \text{ a.e. } x \in X^N \right\}$$

being $\mathcal{S}(X)$ the l.s.c. functions $X \to \mathbb{R} \cup \{+\infty\}$.
Thus, in case of a discrete measure ρ, we are reduced to a finite number of constraints. For instance if $\rho = \sum_{i=1}^{3} \alpha_i \delta_{a_i}$ where $|a_i - a_j| = 1$ for $i \neq j$ and $\|\rho\| = \sum \alpha_i < 1$, then we have to solve an elementary LP problem

$$\overline{C}(\rho) = \sup \left\{ \begin{array}{ll} \displaystyle\sum_{i=1}^{3} \alpha_i\, y_i + (1 - \sum_j \alpha_j)\, y_4 \ : & \frac{y_1+y_2+y_3}{3} \le 3 \\ y_k + 2y_4 \le 0, \ \ k \in \{1,2,3\}, & \frac{y_k+y_l+y_4}{3} \le 1, k < l \end{array} \right\}$$

where $y_i = u(a_i)$ for $i \in \{1,2,3\}$ and $y_4 = u(\omega)$.

Existence of a Kantorovich potential

In the case $\|\rho\| = 1$, existence of a Lipschitz dual potential appeared in [bcd16] under a non concentration assumption. For every $\rho \in \mathcal{P}^-$, we define

$$K(\rho) = \sup \left\{ \rho(\{x\}) \ : \ x \in \mathbb{R}^d \right\}.$$

After a technical and long proof, we extend [bcd16] as follows:

Theorem 5 Let $\rho \in \mathcal{P}^-$ such that $K(\rho) < \frac{1}{N}$. Then $\overline{C}(\rho)$ is finite and there exists an optimal Lipchitz potential $u \in C_0(\mathbb{R}^d) \oplus \mathbb{R}$. Any other optimal potential $\tilde{u}$ satisfies $\tilde{u} = u \quad \tilde{\rho}$ - a.e.

Remark If (ρ_n) is a sequence in $\mathcal{P}^-$ such that $\sup_n K(\rho_n) < \frac{1}{N}$, then the Lipschitz constant of the associated potentials u_n is uniformly bounded. This happens in particular if $T(\rho_n) = \int |\nabla \sqrt{\rho_n}|^2 \leq C$.

4- Mass quantization of optimal measures

Let V be a given potential in $C_0(\mathbb{R}^d)$ and $N \geq 2$. We focus on the relaxed problem associated with

$$\alpha_N(V) = \inf \left\{ C(\rho) - \int V \, d\rho \ : \ \rho \in \mathcal{P} \right\}$$
$$= \min \left\{ \overline{C}(\rho) - \int V \, d\rho \ : \ \rho \in \mathcal{P}^- \right\}$$

As $\mathcal{P}^-$ is compact for the weak* convergence, solutions to latter problem always exist. As they might be non unique, we consider the minimal mass among them

$$\mathcal{I}_N(V) := \min \left\{ \|\rho\| \ : \ \overline{C}(\rho) - \int V \, d\rho = \alpha_N(V) \right\}$$

($\mathcal{I}_N(v) = 1$ means that all minimizers are probabilities solving the non relaxed problem)

Quantization statement

Theorem 5. Let $V \in C_0(\mathbb{R}^d; \mathbb{R}^+)$ be such that $\sup V > 0$. Then

$$\mathcal{I}_N(V) \in \left\{ \frac{k}{N} \ : \ 1 \le k \le N \right\} .$$

The proof relies on primal-dual optimality conditions. Let us introduce, for $1 \le k \le N$:

$$M_k(V) \ = \sup_{x \in (\mathbb{R}^d)^N} \left\{ \frac{1}{k} \sum_{i=1}^{k} V(x_i) - c_k(x_1, x_2, \dots, x_k) \right\}$$

The definition of $M_k(V)$ extends to unbounded potentials. In particular if $V(x) \to -\infty$ as $|x| \to \infty$, the supremum is attained on $(\mathbb{R}^d)^k$.

Systems of points with Coulomb interactions.

If V is *confining* , $M_N(V)$ is related to a hudge litterature about the systems of points interactions theory (see for instance Choquet 1958 and the recent papers by Serfaty-Leblé, Serfaty-Petrache and references therein, M. Lewin).

$$-M_N(-N^2V) = \inf\left\{\mathcal{H}_N(x_1, x_2, \ldots, x_N) : x_i \in \mathbb{R}^d\right\}$$

where $\mathcal{H}_N$ is of the form

$$\mathcal{H}_N(x_1, x_2, \ldots, x_N) = \sum_{1\leq<i<j} \ell(|x_i - x_j|) + N\sum_{i=1}^{N} V(x_i).$$

In such a setting, the asymptotic limit as $N \to \infty$ is one of the main point of interest of the mathematical physics community.

Useful properties of functionals $M_k : C_0 \mapsto \mathbb{R}^+$

i) The functional $M_k(V)$ is convex, 1-Lipschitz on C_0 and

$$\lim_{t\to+\infty} \frac{M_k(tV)}{t} = M_1(V) = \sup V \ .$$

ii) For every $V \in C_0$ and $N \in \mathbb{N}^*$, we have:

$$M_1(\frac{V}{N}) \leq \cdots \leq M_k\left(\frac{kV}{N}\right) \leq M_{k+1}\left(\frac{(k+1)V}{N}\right) \leq \cdots \leq M_N(V).$$

iii) For every $\rho \in \mathcal{P}^-$, we have

$$\overline{C}(\rho) = \sup_{V\in C_0} \left\{ \int V \, d\rho - M_N(V) \right\}$$

In particular $\alpha_N(V) = -M_N(V) \leq -\frac{1}{N} \sup V$ and $\partial M_N(V)$ is the set of minimizers.

iv) For every $k \in \mathbb{N}^*$, $\rho \in \mathcal{P}^-$ and $V \in C_0$, it holds

$$M_k(V) = M_k(V_+) \ , \ \mathcal{C}_k(\rho) = \sup_{V\in C_0} \left\{ \int V \, d\rho - \|\rho\| M_k(V) \right\}$$

Optimality conditions

Theorem 6. Let $\rho \in \mathcal{P}^-$ and $V \in C_0(\mathbb{R}^d;\mathbb{R}^+)$ be s.t. $\sup V > 0$. Let $\{\rho_k\}$ be an admissible decomposition of ρ i.e.:

$$\rho = \sum_{k=1}^{N} \frac{k}{N}\rho_k \quad , \quad \sum_{k=1}^{N} \|\rho_k\| \leq 1.$$

Then $\{\rho_k\}$ is optimal for $\overline{C}(\rho)$ and V is an optimal potential for ρ iff the following conditions hold:

i) $\displaystyle\sum_{k=1}^{N} \|\rho_k\| = 1,$

ii) For all k, $\displaystyle\mathcal{C}_k(\rho_k) - \int \frac{kV}{N} d\rho_k = -M_k(\frac{kV}{N})$

iii) $M_k(\frac{k\,V}{N}) = M_N(V)$ holds whenever $\|\rho_k\| > 0$.

Additional comments

- As noticed in Sec 1, we have $\alpha_N(V) \leq -\frac{1}{N} \sup V < 0$. Thus an optimal ρ satisfies $\|\rho\| \geq \frac{1}{N}$ (otherwise $\overline{C}(\rho) - \int V d\rho = -\int V d\rho > -\frac{1}{N} \sup V$)
- By the monotonicity property of the M_k's, the equality in iii) holds whenever it exists $l \leq k$ such that $\|\rho_l\| > 0$.
- Let $\overline{k}$ denote the integer part of $N\|\rho\|$. Then $N\|\rho\| = \sum_{k=1}^N k\|\rho_k\|$ and $\sum_{k=1}^N \|\rho_k\| = 1$ imply the existence of two integers $l_- \leq \overline{k} \leq l_+$ such that $\|\rho_{l_\pm}\| > 0$. Accordingly by iii):

$$M_k(\frac{k\,V}{N}) = M_N(V) \quad \text{for all } k > N\|\rho\| - 1.$$

A quantitative criterium for existence in $\mathcal{P}$

Corollary 7. Assume that the potential V satisfies the condition

$$M_N(V) > M_{N-1}\Big(\frac{N-1}{N}V\Big). \qquad (*)$$

Then the supremum defining $M_N(V)$ is achieved in $(\mathbb{R}^d)^N$ and all optimal ρ satisfy $\|\rho\| = 1$.

Remarks:

- Recall that $M_N(V) \geq M_{N-1}\Big(\frac{N-1}{N}V\Big)$ is always true.
- If $\sup V > 0$, condition (*) is satisfied for *large* V (i.e. by tV for $t >> 1$).
- If ρ is optimal and equality holds in (*), we do not know if $\|\rho\| < 1$ except if $\partial M_N(V) = \{\rho\}$
  ($\partial M_N(V) =$ the set of optimal ρ associated with V)

Proof and consequence of Corollary 7

If an optimal ρ satisfies $\|\rho\| < 1$, then $\bar{k}$ the integer part of $N\|\rho\|$ is not larger than $N-1$. This implies that $M_N(V) = M_{N-1}\left(\frac{N-1}{N}V\right)$ in contradiction with (*). For the first statement we consider a maximal N-uplet $x \in X^N$ ($X = \mathbb{R} \cup \{\omega\}$). If the supremum is not reached on $(\mathbb{R}^d)^N$, this means that $x_i = \omega$ for at most one index i and in this case we would have again $M_N(V) = M_{N-1}\left(\frac{N-1}{N}\right)V$.

□

Corollary 8 Let V be a potential $V \in C_0^+$ such that:

$$\beta := \limsup_{|x| \to +\infty} |x| V(x) > 0.$$

Then all optimal ρ are in $\mathcal{P}$ provided $\beta > N(N-1)$.

Proof of Theorem 5 (quantization)

We introduce

$$\bar{k} := \max\left\{k \in \{1,2,\dots,N\} \ : \ M_k\Big(\frac{k}{N}\,V\Big) > M_{k-1}\Big(\frac{k-1}{N}\,V\Big)\right\}$$

With the convention $M_0 = 0$ and since $M_1(\frac{V}{N}) = \frac{1}{N}\sup V > 0$, $\bar{k}$ is well defined. As $M_{\bar{k}}(\frac{\bar{k}}{N}V) > M_{k-1}(\frac{\bar{k}-1}{N}V)$, we apply Corollary 7 considering instead of $C = C_N$ the $\bar{k}$-multimarginal energy C_k and choosing $\bar{k}V/N$ as a potential. We infer the existence of an optimal proba $\rho_{\bar{k}}$ such that

$$C_{\bar{k}}(\rho_{\bar{k}}) - \int V\,d\rho_{\bar{k}} = -M_{\bar{k}}\Big(\frac{\bar{k}V}{N}\Big)$$

Then $\rho := \frac{\bar{k}}{N}\rho_{\bar{k}}$ has a mass $\frac{\bar{k}}{N}$ and satisfies

$$\overline{C}(\rho) - \int V\,d\rho \le C_{\bar{k}}(\rho_{\bar{k}}) - \int \frac{\bar{k}V}{N}\,d\rho_{\bar{k}} = -M_{\bar{k}}\Big(\frac{\bar{k}V}{N}\Big) = -M_N(V).$$

Thus $\mathcal{I}_N(V) \le \frac{\bar{k}}{N}$.

Let us prove now the opposite inequality. Let ρ optimal and let $\{\rho_k\}$ be an optimal decomposition for ρ according to rhe stratification formula

$$\rho = \sum_{k=1}^{N} \frac{k}{N} \rho_k.$$

By using the monotonicity property of the M_k's and the definition of $\bar{k}$, we infer that $M_k\big(\frac{k}{N} V\big) < M_N(V)$ for every $k \leq \bar{k} - 1$, thus by the optimality condition iii) of Theorem 6, it holds $\rho_k = 0$ for $k \leq \bar{k} - 1$.

Recalling that $\sum_k \|\rho_k\| = 1$ (by optimality condition i)), we have

$$\|\rho\| = \sum_{k=\bar{k}}^{N} \frac{k}{N} \|\rho_k\| \geq \frac{\bar{k}}{N} \sum_{k=\bar{k}}^{N} \|\rho_k\| \geq \frac{\bar{k}}{N},$$

hence $\mathcal{I}_N(V) \geq \bar{k}/N$. □

Back to the Strongly Correlated Electrons Density Functional Theory (SCE-DFT) with

$$\inf \{\varepsilon T(\rho) + C(\rho) - U(\rho) \ : \ \rho \in \mathcal{P}\} \qquad (1_\varepsilon)$$

Setting $\rho = u^2$ and using dual representation of $\overline{C}$, we are led (after relaxation) to

$$\min_{\int u^2 \leq 1} \sup_{\varphi \in C_0} \int \left(\varepsilon |\nabla u|^2 + (\varphi - V)u^2\right) - M_N(\varphi)$$

Dual problem for Kantorovich potentials

By compactness (with respect to $u \in L^2$), we may switch inf and sup to obtain a dual problem:

$$\sup_{\varphi \in C_0} \inf_{\int u^2 \leq 1} \int \left(\varepsilon \left|\nabla u\right|^2 + (\varphi - V)u^2\right) - M_N(\varphi)$$

Computing the minimum with respect to u, we deduce the dual problem in term of

$$\lambda_1^\varepsilon(\varphi - V) = \text{ ground state energy level of } -\varepsilon\Delta + (\varphi - V)$$

$$\sup_{\varphi \in C_0} \left\{-(\lambda_1^\varepsilon(\varphi - V))^- - M_N(\varphi)\right\}.$$

Saddle points formulation

By the existence of a Kantorovich potential for $\rho = \sqrt{u^2}$, we deduce the existence of a saddle point for the convex-concave problem

$$\min_{u \in \mathcal{U}} \max_{\varphi \in \mathcal{K}} \int \left(\varepsilon |\nabla u|^2 + (\varphi - V)u^2\right) - M_N(\varphi)$$

where:

- $\mathcal{U} = \{u \in L^2(\mathbb{R}^d) : \int |u|^2 \, dx \leq 1\}$.
- $\mathcal{K}$ is an equi-Lipschiz subset of $C_0(\mathbb{R}^d)$.

Seems to be worth for motivating numerical studies.

Remark $u = 0$ cannot be optimal (since $\inf(1_\varepsilon) < 0$). Thus potentials φ such that $\lambda_1^\varepsilon(\varphi - V) > 0$ are ruled out. Moreover an optimal u such that $\int u^2 < 1$ (ionization) is possible only if

$$\lambda_1^\varepsilon(\varphi - V)) = 0 \qquad \text{(bottom of essential spectrum)}$$

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Open problems

- Let C be the N-multimarginal cost and ρ a probability with finite support such that $C(\rho) < +\infty$. Then the function

$$\varphi : t \in [0,1] \mapsto \overline{C}(t\rho)$$

is convex continous and vanishes on $[0, \frac{1}{N}]$. It seems that in addition φ is piecewise affine and that the jump set of the slope is contained in $\left\{ \frac{k}{N} \ : \ 1 \leq k \leq N-1 \right\}$

- If $\|\rho\| = \frac{k}{N}$, do we have $\overline{C}(\rho) = C_k(\frac{N}{k}\rho)$? It seems that counterexamples exist , M.Lewin -S Di Marino-L. Nenna in progress
- Given potential $V \in C_0$, does the semi-classical procedure ($\varepsilon \to 0$) selects a particular minimizer ? Same question in case of a Coulomb's type potential.

Thanks and . . .

Happy Birthday Gianni !